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The Trimerization of Aldehydes.

George Neal Grammer
Louisiana State University and Agricultural & Mechanical College

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THE TRIMERIZATION OF ALDEHYDES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

George Neal Grammer
B. S., Northwestern State College of Louisiana, 1952
M. S., Louisiana State University, 1954
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The spontaneous polymerization of phenylacetaldehyde. - It is known that phenylacetaldehyde, if allowed to stand for a period of several months, gradually becomes increasingly viscous and finally deposits a crystalline substance which has a molecular weight corresponding to that of a trimer of phenylacetaldehyde. It has been assumed that this behavior is due to polymerization processes. Since neither the structure of the crystalline substance nor the nature of the polymerization process has been established, the need for further experimental study to explain the so-called spontaneous polymerization of phenylacetaldehyde initiated this investigation.

The crystalline trimer, m.p. 114.5-115°, was obtained by allowing freshly distilled phenylacetaldehyde to stand at room temperature for eight to ten months. It was found, however, that the rate of formation of this substance was greatly accelerated by the presence of a catalytic amount of alcoholic potassium hydroxide, so that satisfactory yields were obtained within five to seven days. The trimer yielded a mono-acetate and a mono-benzoate, and its infrared spectrum showed characteristic bands for hydroxyl and ether absorption. Its formation by a base-catalyzed process suggested that an aldol condensation had produced phenylacetaldol, which then combined with another molecule of phenylacetaldehyde to yield a cyclic sesquiacetal, 2,4-dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane. The proposed structure was confirmed by reducing the trimer with zinc and hydrochloric acid to yield a cyclic acetal, 2,4-dibenzyl-5-phenyl-1,3-dioxane, which was also prepared for comparison by condensing 2,4-diphenyl-1,3-butenediol with phenylacetaldehyde dimethylacetal. The trimer, upon treatment with lithium aluminum hydride or by catalytic hydrogenation, yielded β-phenylethyl alcohol and 2,4-diphenyl-1,3-butenediol, the reduction product of phenylacetaldol. Distillation of the trimer at reduced pressures yielded nearly the theoretical
quantities of phenylacetaldehyde and either phenylacetaldol or its dehydration product, \( \alpha, \gamma \)-diphenylcrotonaldehyde.

The viscous oil obtained as a result of the polymerization of phenylacetaldehyde gave an infrared spectrum which was almost identical with that of a saturated solution of the trimer in freshly distilled phenylacetaldehyde. These results suggested that polymerization resulted principally in an equilibrium mixture of phenylacetaldehyde, phenylacetaldol, and \( 2,4 \)-dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane.

The base-catalyzed trimerization of aliphatic aldehydes. It is known that isobutyraldehyde undergoes a base-catalyzed reaction to form a trimer, which has been assigned the structure, \( 2,4 \)-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane. The present results confirm this structure conclusively.

The trimer of isobutyraldehyde was converted into \( 2,4 \)-diisopropyl-5,5-dimethyl-6-chloro-1,3-dioxane. This chloride was reduced to a cyclic acetal, \( 2,4 \)-diisopropyl-5,5-dimethyl-1,3-dioxane, which was prepared independently by the condensation of isobutyraldehyde with \( 2,2,4 \)-trimethyl-1,3-pentanediol.

The trimers of octanal, nonanal, decanal, undecanal and lauraldehyde were prepared for the first time by the base-catalyzed trimerization process. Molecular weights, analyses and infrared spectroscopic data supported the sesquiacetal-type structure. The unstable hexanal trimer was isolated in the form of its acetate.

Vinyl acetate reacted with the trimers of acetaldehyde, butyraldehyde and isobutyraldehyde to yield the corresponding acetates. The pyrolysis of acetates such as \( 2,4 \)-dimethyl-6-acetoxy-1,3-dioxane seemed to offer a possible means of obtaining a series of new compounds having a 1,3-dioxene-type structure. \( 2,4 \)-Dimethyl-6-acetoxy-1,3-dioxane was subjected to such
treatment, but gave only acetic acid, acetaldehyde and crotonaldehyde.
Similarly, 2,4'-diethyl-5-methyl-6-acetoxy-1,3-dioxane suffered extensive
decomposition and yielded acetic acid, propionaldehyde and 2-methyl-2-pentenal.

The acid-catalyzed trimerization of aliphatic normal aldehydes. -
Aliphatic aldehydes undergo an acid-catalyzed reaction to yield trimers
which have a 2,4,6-trialkyl-1,3,5-trioxane structure. A table showing the
physical constants of all aliphatic normal aldehydes possessing from one to
eighteen carbon atoms, and their corresponding trimers, has been carefully
prepared. Two of these trimers (para-n-valeraldehyde and para-n-hexanal),
as well as the melting points of four aldehydes (hexanal, octanal, nonanal,
decanal), have not been reported in the literature.
Phenylacetaldehyde, when carefully purified, is a colorless, mobile liquid, which has definite physical properties and its chemical behavior towards most reagents is that predicted for a typical aldehyde. Upon standing for several weeks, however, its physical characteristics undergo a noticeable and gradual change, which may be followed by determining at intervals of time either its vapor pressure, refractive index, density, or infrared spectrum. Over a longer period of time, and apparently by a spontaneous process, phenylacetaldehyde yields an increasingly viscous oil, from which a crystalline substance is continuously separating. It has been assumed that such behavior is due to polymerization processes. The stabilization of phenylacetaldehyde against polymerization has been a problem of much concern to manufacturers and users of this substance, and this investigation has been directed towards the identification of the crystalline substance and the nature of the viscous oil resulting from the so-called spontaneous polymerization of phenylacetaldehyde.

Measurements\textsuperscript{1,2} involving rates of change in physical properties appear to have been of little value in determining the nature of this polymerization process. Such data is normally more valuable after the products from such a process are known. Stobbe and Lippold\textsuperscript{1} and later Treibs and Krumbholz\textsuperscript{3} have obtained by various methods a number of viscous oils and resins by treating phenylacetaldehyde with alkali. These substances have been analyzed for

\textsuperscript{1} H. Stobbe and A. Lippold, J. prakt. Chem., \textit{90}, 277 (1914).
\textsuperscript{3} W. Treibs and K. Krumbholz, Ber., \textit{85}, 1116 (1952).
carbon and hydrogen and their average molecular weight determined, but efforts to identify them have failed, and suggestions as to the structure of these substances are not convincing. Pound observed that a very old sample of phenylacetaldehyde contained a crystalline substance which melted at 104°, and had a molecular weight corresponding to that of a trimer, but no further investigation was made of this product.

In this investigation, it has been observed that phenylacetaldehyde, upon storage for a period of 8 to 10 months, becomes very viscous and there is deposited a crystalline substance, which may be collected by filtration and recrystallized from a mixture of benzene and petroleum ether to yield a well-defined crystalline product melting at 114.5-115°. The yields vary from 20 to 30%, depending upon the length of time of storage. The filtrate, however, continues slowly to yield these crystals, and if they are removed periodically, yields higher than 50% may be obtained at the end of 12 to 14 months. Since the rate of formation of this substance was found to be catalyzed by bases, a number of basic catalysts in varying quantities were added to highly purified samples of phenylacetaldehyde and allowed to stand at various temperatures for several weeks. From these experiments there was developed one successful method of synthesis, which gave the desired product in a reasonable length of time. It was found that alcoholic potassium hydroxide at a concentration of 0.03% in phenylacetaldehyde increases the rate of formation of this substance about fiftyfold, so that yields of 25 to 30% may be obtained within 5 to 7 days. Much larger yields may be obtained over a longer period of time. The concentration of the catalyst is very critical. If much lower concentrations of the base are used, the rate of the reaction is substantially reduced, resulting in weeks rather than days for a profitable yield of product, and higher concentrations cause the
reaction to become very exothermic, as apparently progressive condensations take place, yielding only viscous, discolored oils. Moderate variation of the temperature does not affect appreciably the rate of this process. Manifestly, this polymer is not identical with the paraldehyde-type trimer, 2,4,6-tribenzyl-s-trioctane (Ia), m.p. 155-156°, obtained by Stobbe and Lippold\(^1\) from phenylacetaldehyde by an acid-catalyzed process.

The carbon-hydrogen analysis and molecular weight of the crystalline substance, m.p. 114.5-115°, require that the structure correspond to that of a trimer of phenylacetaldehyde. It yields a mono-acetate and a mono-benzoate, and its infrared spectrum shows strong absorption bands at 2.98 and 8.74 μ, suggesting structural features such as a hydroxyl group and an ether linkage. The formation of this substance from phenylacetaldehyde by a base-catalyzed process suggests that an aldol condensation may have taken place to yield phenylacetaldol (II), which then combined with another molecule of phenylacetaldehyde to yield the sesquiacetal (I). A cyclic compound of this type would be, in fact, the cyclic acetal of phenylacetaldehyde and the hemiacetal of phenylacetaldol. Sesquiacetals of this type have been obtained as liquids by a number of workers\(^4\) from acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde.

The proposed structure (I) for the trimer of phenylacetaldehyde was confirmed by reducing the trimer to 2,4-dibenzyl-5-phenyl-1,3-dioxane (IV), which was shown to be identical with the 1,3-dioxane obtained by treating 2,4-diphenyl-1,3-butanediol (V) with phenylacetaldehyde dimethylacetal.

\(^{(4)}\) E. Spath, R. Lorenz and E. Freund, Ber., 76, 57, 1196 (1943); E. Hanschke, Ber., 76, 180 (1943); R. H. Saunders, N. J. Murray et al., J. Am. Chem. Soc., 66, 1309, 1714 (1943); 66, 206 (1944).

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Reduction of the sesquiacetal (I) with zinc and hydrochloric acid gave the 1,3-dioxane (IV), whereas with lithium aluminum hydride or by catalytic hydrogenation, there was obtained \( p \)-phenylethyl alcohol and also a crystalline substance, which was identified as 2,4-diphenyl-1,3-butanediol (V), the reduction product of phenylacetaldol, by comparing it with an authentic sample of V obtained by an independent method. \( p \)-Hydroxy-\( \alpha, \gamma \)-diphenylbutyric acid (VII) was synthesized by treating phenylacetalddehyde with the Ivanoff reagent (VI), and also by a second method which involved the reduction and subsequent hydrolysis of ethyl \( \alpha, \gamma \)-diphenylacetoacetate (VIII) according to the procedure of Davies and Morris. The reduction of the hydroxy acid (VII) with lithium aluminum hydride yielded 2,4-diphenyl-1,3-butanediol (V), which was identical with the product obtained by reduction of the trimer of phenylacetalddehyde (I) with lithium aluminum hydride, or by catalytic hydrogenation. An attempt was made to obtain V by the direct reduction of VIII with lithium aluminum hydride, but there was obtained a substance, m.p. 134.5-135°, whose carbon-hydrogen analysis, molecular weight and infrared spectrum suggested the diastereoisomer of 2,4-diphenyl-1,3-butanediol (V), m.p. 98.5-99°, but no such relationship was established.

Thermal decomposition of the sesquiacetal (I) in a closed system at pressures ranging from 5 to 20 microns, and with the still at 120° and the receiver at -75°, gave in a short time a distillate, which was obtained in a yield of 31% by weight, and identified as phenylacetalddehyde. The residue, a viscous, sticky liquid, presumably consisted of almost pure phenylacetaldol,


which slowly reverted, however, to monomeric phenylacetaldehyde if the distillation was given unlimited time. Distillation of I at 0.5 mm. or at higher pressures yielded phenylacetaldehyde, water and \( \alpha \beta \)-diphenylcrotonaldehyde (III), which is the dehydration product of phenylacetaldol (II).

While the isolation and identification of these decomposition products seem to furnish ample evidence for the existence of phenylacetaldol, this work was unduly complicated because none of the usual, serviceable methods of purification appear to be applicable to this substance. It undergoes, apparently, either a reversal of the aldol condensation, or dehydration, or both, when heated, so that distillation methods are not useful, and efforts to crystallize this substance seem futile. Its viscosity is such that it does not permit the determination of many physical constants by the usual methods. The residue obtained from the distillation of I may be regarded as phenylacetaldol (II), since it yields, when mixed with an equivalent quantity of phenylacetaldehyde, the sesquiacetal (I).

It has been shown that phenylacetaldehyde polymerizes spontaneously to yield a crystalline trimer (I) and a viscous oil, which apparently is saturated with the trimer, but the concentration of the trimer in this oil is not known. A saturated solution of the trimer in pure phenylacetaldehyde, however, was found to contain about 25% of the trimer at 25°C, and gave an infrared spectrum identical, except for very small differences in the region of 10 to 12 microns, with the spectrum of the viscous oil obtained from a sample of phenylacetaldehyde, which had been stored for six months and had deposited crystals of I. These results suggest that polymerization of phenylacetaldehyde results principally in an equilibrium mixture of phenylacetaldehyde, phenylacetaldol (II), and 2,4-dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane (I), and that the equilibrium favors I sufficiently to prevent further aldol condensation.
EXPERIMENTAL

Spontaneous polymerization of phenylacetaldehyde. A sample of phenylacetaldehyde (Givaudan-Delawanna, Inc.), b.p. 81-83° (12 mm.), n^D 1.5220, upon storage at room temperature and in diffused light, became only slightly discolored, but increasingly viscous, and after 8 to 10 months began to deposit slowly a crystalline substance, which was separated from the viscous liquid by filtration. Although somewhat slower, decantation also was found to be a satisfactory method of separation. The crystals were then washed with 100 ml. of an equal mixture of benzene and low-boiling petroleum ether. From 200 g. of phenylacetaldehyde there was obtained 36 g. of this crystalline substance, m.p. 111-113°. Upon standing for 2 months longer the filtrate yielded an additional 12 g. of crystals, making a total of 48 g., or a yield of 24%. After recrystallization from a mixture of benzene and petroleum ether, and once from methyl alcohol, the product melted at 114.5-115°, and gave a molecular weight corresponding to that of a trimer of phenylacetaldehyde. The infrared spectrum showed characteristic bands for hydroxyl at 2.98 μ and for ether at 8.74 μ, but no carbonyl band.

Anal. Calcd. for (C₆H₅O)₃: C, 79.97; H, 6.71; OH, 4.72; mol. wt., 360.4. Found: C, 79.74, 80.15; H, 6.70, 6.95; OH, 4.96; mol. wt. (benzene), 354, 362, 350, 362; (nitrobenzene), 366, 360, 364.

The acetate crystallized from a mixture of benzene and petroleum ether and melted at 125-125.5°. Infrared maxima 5.61, 8.24, 8.75 μ.


(7) Melting points are corrected and boiling points are uncorrected. Microanalyses were determined by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. Infrared spectra were recorded on a Perkin-Elmer Model 21 Infrared Spectrophotometer.
The benzoate melted at 158.5-159° after recrystallization from a benzene-petroleum ether mixture.

**Anal.** Calcd. for C₃₁H₂₈O₄: C, 80.15; H, 6.08. Found: C, 80.74; H, 6.41.

2,4-Dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane (I). Phenylacetaldehyde was purified through the bisulfite compound. Distillation in a nitrogen atmosphere through a 9-inch vacuum-jacketed, packed column gave a fraction, b.p. 96.5-97° (25 mm.), n°D 1.5218, which was taken as the pure aldehyde.

To 100 g. (0.835 mole) of pure phenylacetaldehyde was added dropwise 0.3 g. of a 10% alcoholic potassium hydroxide solution with intermittent shaking during a period of 30 minutes. Upon standing for 24 hours at 55° the liquid became viscous, and after 4 days a small quantity of crystals had formed. The quantity increased steadily until at the end of 7 days the whole sample appeared to have solidified. A mixture of benzene and petroleum ether was added to facilitate filtration. After recrystallization from a mixture of benzene and petroleum ether, and then from methyl alcohol, there was obtained 27.5 g. (27.5%) of the trimer (I), m.p. 114.2-115°, which showed no depression in melting point when mixed with the trimer which had formed spontaneously, and apparently with no catalyst present.

2,4-Dibenzyl-5-phenyl-1,3-dioxane (IV). The trimer gave a reduction product, procedure A, which was identical with an authentic sample of IV obtained by procedure B.

**A. By reduction of I.** Hydrogen chloride was passed into a stirred mixture of 1.5 g. (0.0042 mole) of the trimer, 15 ml. of glacial acetic acid, and 3.0 g. of amalgamated zinc dust for 1 hour at a rate sufficient to maintain a temperature of 40-45°. The reaction mixture was stirred for
an additional 45 minutes at room temperature, and was then diluted with ether and filtered into 75 ml. of water. The aqueous phase was extracted several times with ether and the combined ether extracts were washed with 5% sodium carbonate solution and then with water. The ether solution was dried over magnesium sulfate and the solvent removed by evaporation to yield an oil which solidified upon cooling. Recrystallization of the product from methyl alcohol gave 0.50 g. (35%) of colorless crystals, m.p. 100-101°. The infrared spectrum showed an ether band at 8.84 μ, but no hydroxyl band near 3.0 μ.

Anal. Calcd. for C_{24}H_{24}O_{2}: C, 83.69; H, 7.02. Found: C, 83.60; H, 7.04.

In a subsequent reaction using 2.0 g. of the trimer, the anhydrous hydrogen chloride was replaced by 5 ml. of concentrated hydrochloric acid and the reaction mixture was refluxed for 30 minutes. The yield of product, m.p. 100-101°, was 0.3 g.

It was shown that the reduction product does not survive completely when drastic hydrolysis and alcoholysis conditions are imposed during the reduction process. A homogeneous solution consisting of 8.5 g. (0.024 mole) of the trimer, 25 ml. of concentrated hydrochloric acid, and 20 ml. of ethyl alcohol was stirred and refluxed with 30 g. of activated zinc dust for 6 hours, during which time two 10-ml. portions of hydrochloric acid were added. The reaction mixture was rectified as above and yielded two distinct crystalline products, one of which dissolved in hot ligroin and gave, upon cooling, 1.2 g. of the reduction product, m.p. 100-101°. The remaining substance was recrystallized from a mixture of benzene and ligroin to yield 2.5 g. of small needles, m.p. 98.5-99°, identified later as 2,4-diphenyl-1,3-butanediol (V).

**B. By condensation of V with phenylacetaldehyde dimethylacetal.**

An independent method for the preparation of IV was developed. A solution
of 1.0 g. (0.0041 mole) of 2,4-diphenyl-1,3-butanediol (V), 0.76 g. (0.0046 mole) of phenylacetaldehyde dimethylacetal, b.p. 220-220.7°C, nD25 1.5001, and a small crystal of benzenesulfonic acid in 30 ml. of dry benzene was heated in a 50-ml. distilling flask so that slow distillation occurred. After 45 minutes the distilling flask contained approximately 10 ml. of solution, which was washed with 5% sodium carbonate solution and then with water, and was dried over magnesium sulfate and concentrated under reduced pressure to yield 1.26 g. (89%) of IV, m.p. 99-100.6°C. Recrystallization from ligroin and then from methyl alcohol raised the melting point to 100-101°C. A mixture of this compound and IV obtained in procedure A showed no depression in melting point.

2,4-Diphenyl-1,3-butanediol (V). The trimer gave a reduction product, procedures A and B, which was identical with an authentic sample of V, obtained by procedure C.

A. By reduction of the trimer with lithium aluminum hydride. To a stirred suspension of 3.5 g. (0.092 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether was added dropwise a solution of 10.0 g. (0.0278 mole) of the trimer in 75 ml. of ether. The excess hydride was destroyed cautiously with water and the precipitated alumina was dissolved with cold 10% sulfuric acid. The ether solution was washed with water, dried over anhydrous sodium sulfate, and concentrated to yield 6.17 g. of a crystalline substance, m.p. 92-96°C, and a filtrate which was distilled to give 2.01 g. (60%) of β-phenylethyl alcohol, b.p. 219-221°C, α-naphthylurethan, m.p. 117.5°C, mixed m.p. 117.5°C. The residue (0.71 g.) from the distillation was triturated with ligroin and yielded an additional 0.42 g. of crystals, m.p. 96-97.3°C. The combined crystalline fractions were recrystallized from a
mixture of benzene and ligroin to yield 6.22 g. (93%) of a product, m.p. 98.5-99°, later identified as V. The infrared spectrum showed hydroxyl bands at 2.96 μ and 9.33 μ, but no absorption in the 8.0-9.0 μ region.

Anal. Calcd. for C₁₆H₁₈O₂: C, 79.31; H, 7.49; OH, 14.04; mol. wt., 242.3. Found: C, 79.20, 79.28, 79.50, 79.27; H, 7.49, 7.44, 7.54, 7.64; OH, 14.2; mol. wt. (Rast), 244.

The dibenzoate, after recrystallization from methyl alcohol, melted at 107-107.5°.

Anal. Calcd. for C₃₀H₂₆O₄: C, 79.98; H, 5.82. Found: C, 79.84; H, 5.87.

B. By reduction of the trimer with catalytic hydrogen. A solution of 2.2 g. (0.0061 mole) of the trimer and 0.15 g. of glacial acetic acid in 10 ml. of isopropyl alcohol was shaken with 1.0 g. of Raney nickel for 12 hours at a maximum temperature of 80° under a hydrogen pressure of 3 atmospheres. The solution was freed of catalyst and concentrated under reduced pressure. The residue was dissolved in ether, washed with water, dried over sodium sulfate, and concentrated to yield a solid, which was recrystallized from a benzene-ligroin mixture to give 0.81 g. (55%) of reduction product, m.p. 98-99°.

C. By reduction of β-hydroxy-ω-γ-diphenylbutyric acid (VII) with lithium aluminum hydride. An authentic specimen of V was prepared by an independent method. To a suspension of 1.5 g. (0.04 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether was added dropwise a solution of 2.50 g. (0.0098 mole) of VII in 40 ml. of pure dioxane. The mixture was stirred for 1 hour, the excess hydride was destroyed cautiously with water, and the phases were clarified with cold 10% sulfuric acid. The upper layer was washed with 5% sodium carbonate solution and then with water, and was dried over sodium sulfate and concentrated to an oil which solidified upon
cooling. Recrystallization from a mixture of benzene and ligroin yielded 2.03 g. (87%) of small needles, m.p. 98.5-99°, identical with V obtained in procedures A and B. The 2,4-diphenyl-1,3-butanediol dibenzoate, m.p. 107-107.5°, was identical with the dibenzoate obtained in procedure A.

**β-Hydroxy-α,γ-diphenylbutyric acid (VII).** A. By the reaction between phenylacetaldehyde and the Ivanoff reagent (VI).5 Isopropyl bromide (1.0 g.) was added to 4.8 g. (0.20 atom) of magnesium turnings under 10 ml. of anhydrous ether. When the reaction started, 18.2 g. (0.115 mole) of dry, pulverized sodium phenylacetate and 14.0 ml. of ether were added immediately, followed by the dropwise addition of 23.6 g. (total, 24.6 g., 0.20 mole) of isopropyl bromide dissolved in 50 ml. of ether. The mixture was refluxed for 1.5 hours until the evolution of propane ceased, then an ethereal solution of 13.8 g. (0.115 mole) of freshly distilled phenylacetaldehyde, b.p. 81-82° (12 mm.), was added dropwise, and the mixture was refluxed for an additional 3 hours and hydrolyzed with iced hydrochloric acid. The product solidified and was collected by filtration, then was washed with cold ether to remove any phenylacetic acid. There was obtained 14.5 g. (49%) of VII, which crystallized as needles, m.p. 207-207.5°, from methyl alcohol.

Calcd. for C_{16}H_{18}O_3: neut. equiv., 256.3. Found: neut. equiv., 256.

B. By the reduction and subsequent hydrolysis of ethyl α,γ-diphenylacetooacetate (VIII). Two molecules of ethyl phenylacetate were condensed according to the method of Conant and Blatt8 to yield VIII (71%), melting at 78-78.5° (lit. 78° m.p. 78°). This ester was converted into β-hydroxy-α,γ-diphenylbutyric acid (VII) according to the procedure of Davies and Morris6 by the catalytic hydrogenation of VIII to yield, as an intermediate,

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ethyl β-hydroxy-α,β-diphenylbutyrate, which was hydrolyzed without purification. From 3.5 g. (0.012 mole) of VIII there was obtained 1.4 g. of product, m.p. 207-207.5° (lit.6 m.p. 210°), which was identical with VII obtained in procedure A.

Reduction of VIII with lithium aluminum hydride. This reaction was carried out by the procedure described previously for the reduction of I with lithium aluminum hydride. From 13.0 g. (0.046 mole) of VIII and a 50% excess of lithium aluminum hydride there was obtained 7.3 g. of a white, fluffy crystalline product which was recrystallized from a benzene-petroleum ether mixture and melted at 134.5-135°. Infrared maximum (-OH) 2.93 μ.

Anal. Calcd. for C_{16}H_{18}O_2: C, 79.31; H, 7.49; mol. wt., 242.3.
Found: C, 78.95, 79.05; H, 7.37, 7.18; mol. wt. (Rast), 258.

Thermal decomposition of the sesquiacetal (I). Two 15-ml. round-bottomed flasks (still and receiver) were connected to the ends of a short inverted U-tube, which was provided in the center with an outlet to permit evacuation. After adding 10.0 g. (0.0278 mole) of I to the still of this distilling apparatus, both the still and receiver were immersed in a Dry Ice-acetone bath. The system was evacuated to 10 microns, sealed off, and the temperature of the still was elevated gradually. When the temperature reached 115°, the melting point of I, there was much evidence of decomposition. The still was heated to 120° and maintained at that temperature for 1 hour, after which the decomposition was no longer noticeable. There was obtained 6.52 g. (98%) of a waxy residue (assumed to be phenylacetaldo1) and 3.10 g. (93%) of distillate, which was identified as phenylacetaldehyde, b.p. 82.5-83.5° (13 mm.), n^25D 1.5227. When the distillation was conducted as above and continued for 24 hours, it was found that I almost completely
detrimerized to yield monomeric phenylacetaldehyde. There was no evidence of water as one of the decomposition products.

Distillation of I at higher pressures resulted in more extensive decomposition. From 10.0 g. of I, the following fractions were obtained: (1), 4.6 g., b.p. 95-96° (25 mm.); (2), 0.8 g., b.p. 45-145° (0.55 mm.); (3), 2.8 g., b.p. 145-146° (0.55 mm.); (4), 1.3 g., above 146° (0.55 mm.).

Fraction 1, which was identified as phenylacetaldehyde, contained drops of water. Fraction 3 solidified upon cooling to yield a crystalline substance, which was purified by recrystallization from methyl alcohol and was identified as α,γ-diphenylcrotonaldehyde (III), m.p. 39.5-40° (lit.3 m.p. 39°), nD^20 1.5938. The infrared spectrum showed strong absorption bands at 5.91, 6.11, and 6.24 μ.

Anal. Calcd. for C_{16}H_{14}O: C, 86.45; H, 6.35. Found: C, 86.47; H, 6.41.

The solubility of I in phenylacetaldehyde was determined by adding it as a fine powder to freshly distilled phenylacetaldehyde at 25° until no more dissolved after inoculation with a crystal. The trimer (I) was soluble to the extent of 1.66 g. in 5.0 g. of phenylacetaldehyde, or 25% by weight. The infrared spectrum of the saturated solution showed the bands (0.025-mm. cell): 2.89 m, 3.27 m, 3.42 m, 3.52 m, 3.64 m, 5.78 s, 6.21 m, 6.28 w, 6.67 s, 6.85 s, 7.08 m, 7.12 m, 8.47 m, 8.86 s, 9.26 s, 9.70 s, 10.63 m, 10.95 m, 11.47 w, 13.32 s, and 14.20-14.36 s microns.

In comparison, the spectrum of the viscous oil obtained from a sample of phenylacetaldehyde, which had been stored for 6 months and had deposited crystals of I, showed only slight irregularities beyond 10 microns. Absorption bands (same cell): 2.89 m, 3.27 m, 3.42 m, 3.52 m, 3.64 m, 5.78 s, 6.21 m, 6.28 w, 6.67 s, 6.85 s, 7.08 m, 7.12 m, 8.47 m, 8.86 s, 9.27 s, 9.70 s, 10.62 s, 10.95 m, 11.49 w, 13.33 s, and 14.20-14.36 s microns.
Distillation of the polymeric oil. The viscous oil (130 g.), obtained from the polymerization of phenylacetaldehyde, was distilled to yield the following fractions: (1), 97.0 g., b.p. 69-75° (1.5 mm.); (2), 5.3 g., b.p. 70-156° (0.8 mm.); (3), 23.3 g., b.p. 156-158° (0.8 mm.); (4), 4.4 g., above 158° (0.8 mm.).

Fraction 1 contained drops of water, and was identified as phenylacetaldehyde. Fraction 3 was refractionated to yield 20 g. of a pale-yellow liquid, b.p. 145-146° (0.5 mm.), which solidified upon cooling to give crystals, m.p. 36.5-38°. After recrystallization from a mixture of benzene and petroleum ether, the product melted at 39.5-40° and was identified as III.
THE BASE-CATALYZED TRIMERIZATION OF ALIPHATIC ALDEHYDES

A study of the literature reveals that acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde yield trimolecular condensation products under conditions suitable for aldol addition.

The reported yields of acetaldol range from 50 to 60%, but invariably fall below 66% by weight. This observation led to the prediction that acetaldehyde and acetaldol might form an addition product which would decompose upon distillation to yield equal molecular quantities of the aldehyde and aldol. This idea would explain the limited yields of acetaldol reported, and would require the maximum yield of acetaldol to be no more than 66.67% by weight.

Shilov\(^2\) condensed acetaldehyde in the presence of 2.5% sodium hydroxide solution. A sesquiacetal structure (I) was arbitrarily assigned to the product, but no evidence was presented in support of this structure.

\[
\begin{align*}
\text{CH}_3\text{-CH-CH}_2\text{-CH-OH} \\
\begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \\
\text{O} \\
\begin{array}{c}
\text{CH}_3
\end{array}
\end{align*}
\]

\(2,4\text{-Dimethyl-6-hydroxy-1,3-dioxane}\)

Saunders and coworkers\(^3\) condensed acetaldehyde in an effort to obtain acetaldol, but the Raman spectrum of the product showed no carboxyl band.

\(\text{(1) H. Hibbert, J. Am. Chem. Soc., 27, 1760 (1915).}\)

\(\text{(2) E. A. Shilov, J. Applied Chem. (U. S. S. R.), 8, 93 (1935).}\)

A later communication\(^4\) stated that the product actually obtained should be represented by the structure, 2,4-dimethyl-6-hydroxy-1,3-dioxane (I). This product was obtained\(^5\) also by heating acetaldehyde in a sealed tube with paraldol, the dimer of acetalaldol.

Confirmatory evidence for the structure (I) was presented by Hanschke,\(^6\) who hydrogenated 2,4-dimethyl-6-acetoxys-1,3-dioxane (Ia) and obtained the reduction product, 2,4-dimethyl-1,3-dioxane (Ib), which was found to be identical with the 1,3-dioxane resulting from the reaction between acetalddehyde and 1,3-butanediol.

\[
\begin{align*}
\text{CH}_3\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}=\text{O} & \quad \text{H}_2 \quad \text{Pd} \quad \text{CH}_3\text{CH}-\text{CH}_2\text{CH}_2\text{OH} \\
\text{Ia} & \quad \text{Ib}
\end{align*}
\]

The condensation of propionaldehyde under conditions suitable for aldol addition results in the formation of a trimeric product which has been assigned the structure, 2,4-diethyl-5-methyl-6-hydroxy-1,3-dioxane (II). Spath, Lorenz and Freund\(^7\) prepared this compound by using a saturated solution of potassium carbonate as the catalyst. The product yielded an acetate upon treatment with acetic anhydride. When II was distilled in the presence of a small amount of adipic acid, propionaldehyde and propionaldol were obtained in equal molecular quantities.

(5) E. Spath, R. Lorenz and E. Freund, Ber., 76, 57 (1943).
(6) E. Hanschke, Ber., 76, 180 (1943).
(7) E. Spath, R. Lorenz and E. Freund, Ber., 76, 1196 (1943).
2,4-Diethyl-5-methyl-6-hydroxy-1,3-dioxane (II) was obtained also by Saunders, et al. during an attempt to obtain propionaldol. The lack of carbonyl absorption bands in the Raman spectrum of the product gave additional evidence for the assigned structure (II).

In 1943, Spath, Lorenz and Freund obtained from butyraldehyde an unstable aldol condensation product which yielded butyraldol and butyraldehyde upon distillation, but gave a stable acetate (IIIA). The structure, 2,4-dipropyl-5-ethyl-6-hydroxy-1,3-dioxane (III) was assigned to the crude condensation product of butyraldehyde.

In the same year it was reported that freshly distilled butyraldol exhibited a carbonyl Raman absorption band which was of a temporary nature and disappeared completely within two weeks. This product yielded IIIa upon acetylation.

It has been observed that isobutyraldehyde reacts in the presence of an alkaline catalyst to form a trimer. This substance gave approximately
equal molecular quantities of the phenylhydrazones of isobutyraldehyde and isobutyraldol when treated with phenylhydrazine; yielded isobutyraldehyde and isobutyraldol when distilled with an acid catalyst; and gave a monoacetate (IVa). The trimer of isobutyraldehyde was assigned the structure, 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane (IV).

\[
3 (\text{CH}_3)_2\text{CH}-\text{CH}=\text{O} \xrightarrow{\text{OH}^-} (\text{CH}_3)_2\text{CH}-\text{CH}-\text{C}=\text{O} \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} (\text{CH}_3)_2\text{CH}-\text{CH}-\text{C}=\text{O}+\text{CH}_3\text{COCH}_3
\]

IV

IVa

Similar results were reported by Saunders, et al., who prepared also the methyl ether of IV. In addition, the ethyl ether has been obtained.

The previous work dealing with the base-catalyzed trimerization of aldehydes shows that only the structure of the acetaldehyde trimer (I) has been confirmed in a classical sense. The unequivocal structural proof of such compounds, and their acetates, depends upon the establishment of a structure similar to that of 2,4-dimethyl-1,3-dioxane (Ib). The trimers (II, III, and IV) obtained from propionaldehyde, butyraldehyde and isobutyraldehyde have been characterized on the basis of their derivatives and decomposition products, and it is surprising that hydrogenation methods similar to those employed by Hanschke have not been investigated as a possible means of establishing more definitely the structures of these trimers.


Consequently, efforts were made during the present investigation to reduce catalytically the acetates (IIa, IIIa, IVa) obtained from the trimers of propionaldehyde, butyraldehyde and isobutyraldehyde, but these experiments were not successful. In each case the starting material was recovered unchanged. It was found, however, that the desired result could be obtained for the trimer of isobutyraldehyde by using a different method. The assigned structure (IV) was confirmed by the results of the reaction sequence shown below.

\[ \text{CH}_3 \text{CH}_3 \]
\[ (\text{CH}_3)_2\text{CH-CH-C-C}=\text{OH} \]
\[ \text{CH}_3 \]
\[ (\text{CH}_3)_2\text{CH-CH-CH}_2\text{OH} \]
\[ \text{CH}(\text{CH}_3)_2 \]

\[ \text{IV} \]
\[ \text{IVb} \]

The sesquiacetal (IV), upon treatment with hydrogen chloride, yielded 2,4-diisopropyl-5,5-dimethyl-6-chloro-1,3-dioxane (IVb). The reduction of IVb with lithium aluminum hydride gave 2,4-diisopropyl-5,5-dimethyl-1,3-dioxane (IVc), which was shown to be identical with the 1,3-dioxane obtained by condensing 2,2,4-trimethyl-1,3-pentanediol (V) with isobutyraldehyde.

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These results established the identity of IVc and therefore confirmed the structure (IV) of the trimer of isobutyraldehyde. 2,4-Diisopropyl-5,5-dimethyl-6-chloro-1,3-dioxane (IVb) is the first derivative of this type to be obtained from an aldehyde trimer.

The reduction of either IV or its acetate (IVa) did not give the same product that was obtained from the chloride (IVb), but yielded a mixture of isobutyl alcohol and 2,2,4-trimethyl-1,3-pentanediol (V), the reduction product of isobutyraldol.

Under conditions suitable for aldol addition, isobutyraldehyde reacts with benzaldehyde to form a substituted 1,3-dioxane. In 1899, Stritar\textsuperscript{10} treated a mixture of these two aldehydes with a saturated potassium carbonate solution, but did not assign a structure to the product. Many years later, the compound was identified\textsuperscript{11} as 2-isopropyl-4-phenyl-5,5-dimethyl-6-hydroxy-1,3-dioxane (VI, R = phenyl).

\[
\begin{align*}
R-\text{CH}=O + (\text{CH}_3)_2\text{CH}-\text{CH}=O & \overset{\text{OH}}{\longrightarrow} R-\text{CH}-\text{CH}=O \overset{\text{CH}_3}{\longrightarrow} R-\text{CH}-\text{CH}=O \overset{(\text{CH}_3)_2\text{CH}=\text{CH}=\text{O}}{\longrightarrow} R-\text{CH}-\text{CH}=O \overset{\text{CH}_3}{\longrightarrow} R-\text{CH}-\text{CH}=O \\
\text{OH} \quad \text{CH}_3 & \quad \text{OH} \quad \text{CH}_3 & \quad \text{OH} \quad \text{CH}_3 & \quad \text{OH} \quad \text{CH}_3 & \quad \text{OH} \quad \text{CH}_3
\end{align*}
\]

VI

In this investigation isobutyraldehyde was condensed with cumaldehyde and also with p-tert-butylbenzaldehyde, and similar results were observed. The products were obtained as white, crystalline solids, and their carbon-hydrogen analyses, molecular weights and infrared spectra were in harmony.

\textsuperscript{10} M. J. Stritar, Monatsh., 20, 617 (1899).

\textsuperscript{11} E. Spath, R. Lorenz and E. Altmann, Ber., 76, 513 (1943).
with the structures, 2-isopropyl-4-(p-isopropylphenyl)-5,5-dimethyl-6-hydroxy-1,3-dioxane (VI, \( R = p\)-isopropylphenyl) and 2-isopropyl-4-(p-tert-butylphenyl)-5,5-dimethyl-6-hydroxy-1,3-dioxane (VI, \( R = p\)-tert-butylphenyl).

The base-catalyzed trimerization of aliphatic aldehydes has been described only for acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde. It was of interest in this investigation to obtain a more representative series of aldehyde trimers. Consequently, compounds of this type have been prepared from a number of aliphatic normal aldehydes for the first time. Considerable difficulty was encountered in the purification of these products. Both the liquid and solid compounds were unstable when heated, so that distillation techniques could not be employed. Crystallization methods were also complicated by the presence of the monomeric aldehyde, which could be removed only by repeated washing of the low melting crystalline product with the appropriate solvent. Because of these difficulties, the trimers of valeraldehyde, hexanal and heptanal were not obtained. Of these three compounds, the undistilled condensation product obtained from hexanal was converted into the acetate (VII), which distilled without decomposition.

\[
3 \text{C}_5\text{H}_11\text{-CH}=\text{O} \underset{\text{OH}^-}{\overset{\text{(CH}_3\text{CO})_2\text{O}}{\longrightarrow}} \text{C}_5\text{H}_11\text{-CH}-\text{CH}-\text{CH}-\text{OH} \longrightarrow \text{C}_5\text{H}_11\text{-CH}-\text{CH}-\text{CH}-\text{COOH}_3
\]

VII

The infrared spectrum of 2,4-dipentyl-5-butyl-6-acetoxy-1,3-dioxane (VII) was found to coincide closely with that of 2,4-diethyl-5-methyl-6-acetoxy-1,3-dioxane (IIa).
Octanal, nonanal, decanal, undecanal and lauraldehyde each yielded a crystalline solid from the base-catalyzed trimerization process. The carbon-hydrogen analysis and molecular weight required each of these substances to be a trimer of the corresponding aldehyde. Convincing evidence for the sesquiacetal structures (VIII) was furnished by the infrared spectra which were obtained by using potassium bromide pellets of the compounds. The spectrograms were almost identical throughout the absorbing region, except for small differences in the intensities of some of the peaks. These differences were doubtless caused by unequal concentrations among the KBr pellets.

\[
\begin{align*}
\text{R} & \quad \text{RCH}_2\text{CHCHCH}_2\text{OH} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{CHCH}_2\text{R}
\end{align*}
\]

VIII

The most helpful bands for identification of compounds of this type are those attributed to hydroxyl and ether absorption. The spectra of these
trimers exhibit strong bands in the ranges of 2.92-2.96 and 8.68-8.70 μ, which are in harmony with the assigned -OH and C-O-C absorption maxima, respectively. Significantly, the spectra exhibit no peak which can be attributed to carbonyl absorption, so that the sesquiacetal structures for the trimers are supported. The features of the spectrograms are recorded below, and may be compared with the infrared spectrum of 2,4-dimethyl-6-hydroxy-1,3-dioxane (I), the trimer of acetaldehyde.

<table>
<thead>
<tr>
<th>Comparison of Spectra (Wavelength in μ) of Sesquiacetals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>2.90 s</td>
</tr>
<tr>
<td>3.36 m</td>
</tr>
<tr>
<td>6.90 m</td>
</tr>
<tr>
<td>7.05 m</td>
</tr>
<tr>
<td>7.22 m</td>
</tr>
<tr>
<td>7.48 m</td>
</tr>
<tr>
<td>8.49 w</td>
</tr>
<tr>
<td>8.72 s</td>
</tr>
<tr>
<td>9.10 s</td>
</tr>
<tr>
<td>10.48 m</td>
</tr>
<tr>
<td>11.10 m</td>
</tr>
<tr>
<td>11.76 w</td>
</tr>
<tr>
<td>11.94 w</td>
</tr>
<tr>
<td>13.15 w</td>
</tr>
</tbody>
</table>
The use of vinyl acetate as an acetylation agent for sesquiacetals such as 2,4-dimethyl-6-hydroxy-1,3-dioxane (I) was investigated during this work.

Marvel, et al.\(^\text{12}\) obtained 2,4-dimethyl-6-acetoxy-1,3-dioxane (Ia) from a sodium-catalyzed reaction between acetaldehyde and vinyl acetate. This compound was thought to have formed by the condensation of two moles of acetaldehyde with one mole of vinyl acetate, and resembled a product normally obtained in a Prins reaction using, however, an acid catalyst.

\[
2 \text{CH}_3\text{CHO} + \text{CH}_2=\text{CH-COCOOCH}_3 \rightarrow \text{CH}_3\text{CH}2\text{CH}2\text{CH-COCOOCH}_3
\]

More recently, Herrmann and Haehnel\(^\text{13}\) prepared a compound, C\(_8\)H\(_{14}\)O\(_4\), of unknown structure by adding aqueous sodium hydroxide to a cold mixture of vinyl acetate and water. In a similar manner, Uelzmann\(^\text{14}\) obtained 2,4-dimethyl-6-propionoxy-1,3-dioxane, the propionate of I, and suggested that the product prepared by Herrmann and Haehnel might correspond to Ia.

In the present study the alkaline hydrolysis of vinyl acetate was performed by the method\(^\text{13}\) mentioned above, and the expected product (Ia) was obtained. Since an enol acetate upon hydrolysis yields the corresponding aldehyde, the formation of Ia may be explained by (1) alkaline hydrolysis


\(\text{(13) W. O. Herrmann and W. Haehnel, German Patent 844,441 (July 21, 1952).}\)

\(\text{(14) H. Uelzmann, Ber., 87, 1162 (1954).}\)
of vinyl acetate to yield sodium acetate and acetaldehyde, (2) the base-catalyzed trimerization of acetaldehyde to produce 2,4-dimethyl-6-hydroxy-1,3-dioxane (I), and (3) the acetylation of I with vinyl acetate to yield the final product. It would appear that this process and the sodium-catalyzed reaction between acetaldehyde and vinyl acetate proceed by the same mechanism.

In support of this idea, it was shown that vinyl acetate may function as an acetylating agent for the trimers (I and III) of acetaldehyde and butyraldehyde. Acetaldehyde was condensed by using powdered sodium hydroxide as the catalyst, and there was obtained 2,4-dimethyl-6-hydroxy-1,3-dioxane (I). When vinyl acetate was added to the condensation product, there was obtained Ia, the same compound which resulted from the use of metallic sodium as the catalyst. Similarly, the undistilled condensation product of butyraldehyde was treated with vinyl acetate and yielded 2,4-dipropyl-5-ethyl-6-acetoxy-1,3-dioxane (IIa).

It was reported previously that no reaction resulted between vinyl acetate and either propionaldehyde, butyraldehyde or isobutyraldehyde when sodium was used as the catalyst. On the contrary, it was found during the present investigation that metallic sodium initiated a reaction between isobutyraldehyde and vinyl acetate, and the product was identified as 2,4-diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane (IVA). This result further illustrated the role of vinyl acetate as an acetylating agent, and clearly established that the aldehyde did not react with the alkene linkage of vinyl acetate. Otherwise, a different compound, 2,4-diisopropyl-6-acetoxy-1,3-dioxane (having two carbon atoms less than IVa), should have been obtained. The effectiveness of sodium may be explained by assuming that water is present to furnish the hydroxyl ion required for the base-catalyzed
trimerization process, since it is very difficult to remove the last traces of water from the lower members of the aldehyde series.

\[
\begin{align*}
\text{CH}_3\text{CH} & \quad \text{CH}_2\text{=CHOCH}_3 \\
\text{CH} & \quad \text{CH}_2\text{=COCH}_3 + \text{CH}_2\text{=CH-OH}
\end{align*}
\]

(IV) \quad \text{IVa}

**Pyrolysis of Ia and IIa**

Herrmann and Haehnel\(^{15}\) reported that their new compound, C\(_8\)H\(_{14}\)O\(_4\), upon distillation in the presence of an equivalent amount of an organic acid such as adipic acid, yielded a substance (C\(_6\)H\(_{10}\)O\(_2\)) which was assigned the structure of acetaldehyde divinylacetal, CH\(_2\)CH(OC=CH\(_2\))\(_2\).

The compound, C\(_8\)H\(_{14}\)O\(_4\), was identified during the present investigation as 2,4-dimethyl-6-acetoxy-1,3-dioxane (Ia), and it was not obvious how acetaldehyde divinylacetal could be produced by heating this substance with adipic acid. It was suspected that such a decomposition might result in the elimination of acetic acid, but that under anhydrous conditions the 1,3-dioxane ring might survive. The reaction product in this case would be 2,4-dimethyl-1,3-diox-5-ene (Ic), which has the same molecular formula as acetaldehyde divinylacetal. This idea seemed very attractive, because the 1,3-dioxenes represent a class of compounds whose preparation might be accomplished by the pyrolysis of acetates such as Ia. The only known member of

\(^{15}\) W. O. Herrmann and W. Haehnel, German Patent 846,848 (August 18, 1952).
this class of compounds is 2-phenyl-1,3-dioxene, which was prepared, however, by a method different from the one proposed above.

Unfortunately, the investigation of the decomposition products of Ia did not yield either the expected product (Ic) or the reported acetal. Instead, the products isolated were acetaldehyde, acetic acid, and crotonaldehyde, so that the structure of the reported product could not be disputed. If Ic was formed at all as an intermediate, it was very unstable in the presence of hot acid solution and decomposed to yield the observed products.

![Chemical structure of Ia and Ic]

Similar results were obtained from the pyrolysis of 2,4-diethyl-5-methyl-6-acetoxy-1,3-dioxane (IIa). The products were identified as propion-aldehyde, acetic acid and 2-methyl-2-pentenal, resulting from complete decomposition of the dioxane ring. The same products were observed when IIa was heated alone or with adipic acid at the decomposition temperature.

![Chemical structure of IIa]

(16) H. O. L. Fischer, L. Ahlstrom and H. Richter, Ber., 64, 611 (1931).
**EXPERIMENTAL**

2,4-Diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane (IV). Three molecules of isobutyraldehyde were condensed by the base-catalyzed trimerization process.

A. **By using aqueous potassium hydroxide solution.** The procedure of Saunders, Murray and Cleveland was followed, except for the omission of dibutylamine and the use of an extended reaction period.

To a stirred solution of 246 g. (3.42 moles) of freshly distilled isobutyraldehyde, b.p. 64-65°C, in 250 ml. of ether was added 100 g. of a 10% potassium hydroxide solution at such a rate that the temperature was maintained below 5°C. The reaction mixture was stirred for an additional 12 hours at 0°C, after which time the separated ether layer was washed with water until neutral, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield a clear, viscous oil. Distillation yielded 228 g. (93%) of IV, b.p. 82-85°C (0.5 mm.), n\(^\text{D}^{25}\) 1.4468 (lit.\(^8\) b.p. 110-111°C (8 mm.), n\(^\text{D}^{25}\) 1.4461; and\(^7\) b.p. 95°C (0.8 mm.), n\(^\text{D}^{20}\) 1.4437). The infrared spectrum showed a hydroxyl band at 2.90 μ and an ether band in the range of 8.70-9.20 μ.

B. **By using alcoholic potassium hydroxide solution.** To 160 g. (2.22 moles) of freshly distilled isobutyraldehyde was added 0.30 g. of potassium hydroxide dissolved in 2.70 g. of methyl alcohol. The reaction flask was stoppered and was shaken intermittently. After standing for 6 days at room temperature the clear, viscous liquid which had formed was diluted with ether, washed thoroughly with water, dried over sodium sulfate, and concentrated

---

(17) Microanalyses were determined by Weiler and Strauss Microanalytical Laboratories, Oxford, England.
under reduced pressure. Fractionation in a nitrogen atmosphere through a 9-inch vacuum-jacketed column gave 125 g. (78%) of pure distillate, b.p. 83-84° (1 mm.), n^25D 1.4459. The infrared spectrum was identical with that of IV obtained in procedure A.

2,4-Diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane (IVa). To 100 g. (0.463 mole) of IV was added 100 g. of anhydrous pyridine and 100 g. of acetic anhydride. After 24 hours the lower-boiling components were removed under reduced pressure and the remaining oil was distilled to yield 110 g. (92%) of IVa, b.p. 87-89° (1.6 mm.), n^25D 1.4353 (lit. b.p. 93-93.5° (0.9 mm.), n^20D 1.4381; and b.p. 93.5° (2 mm.), n^25D 1.4355).

Attempted hydrogenation of IVa. Several attempts were made to reduce IVa catalytically. Glacial acetic acid was used as the solvent, with either palladium black, palladium-on-carbon, or Raney nickel as the catalyst. Temperatures varying from 25° to 60° were employed and a hydrogen pressure of 3 atmospheres was used. In no case was there any detectable hydrogen uptake, and IVa was recovered unchanged.

Attempted hydrogenation of IIIa and of IIIa was performed by the method described above, and the same result was obtained. The preparations of IIIa and IIIa are described later.

2,4-Diisopropyl-5,5-dimethyl-6-chloro-1,3-dioxane (IVb). Hydrogen chloride was bubbled into a chilled solution consisting of 50.0 g. (0.232 mole) of 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane (IV), b.p. 83-84° (1 mm.), and 25.0 g. of benzene. After slightly more than the calculated amount of HCl was absorbed, the water which had formed was removed and the
remaining solution was dried over anhydrous calcium chloride. The benzene
and excess HCl were removed under reduced pressure and the residue was
distilled to yield 40.2 g. (75%) of a colorless liquid, b.p. 88-90° (3 mm.).
Fractionation in a nitrogen atmosphere through a 9-inch vacuum-jacketed,
packed column afforded 36.0 g. of IVb, b.p. 89-90° (3 mm.), n^25D 1.4510,
d^25 0.9982, MRD 63.24 (calcd. 63.57). Infrared maxima 3.38, 6.80, 8.80,
13.71 μ.

Anal. Calcd. for C_{12}H_{23}O_{2}Cl: C, 61.37; H, 9.87. Found: C, 61.20;
H, 9.45.

2,2,4-Trimethyl-1,3-pentanediol (V). The reduction of IV and IVa
(procedures A and B) gave the same product, which was identical with an
authentic specimen of V.

A. By reduction of IV with lithium aluminum hydride. To a suspension
of 4.0 g. (0.105 mole) of lithium aluminum hydride in 50 ml. of anhydrous
ether was added dropwise a solution of 10.0 g. (0.046 mole) of IV in 30 ml.
of ether. The mixture was stirred for 0.5 hour, the excess hydride was
destroyed cautiously with water, and the precipitated alumina was dissolved
with cold 10% sulfuric acid. The ether solution was washed with water, dried
over anhydrous magnesium sulfate, and concentrated to yield an oil which
solidified upon cooling. Recrystallization from petroleum ether gave 5.09 g.
(75%) of a crystalline product, m.p. 52.5-53.5°. There was no depression in
melting point when this substance was mixed with an authentic sample of V.

B. By reduction of IVa with lithium aluminum hydride. To a slurry of
6.0 g. (0.158 mole) of lithium aluminum hydride in 30 ml. of anhydrous ether
was added, over a period of 1 hour, a solution of 25.8 g. (0.10 mole) of IVa
in 25 ml. of ether. The excess reducing agent was decomposed with water and
the inorganic precipitate was dissolved with cold 10% sulfuric acid. The ether solution was dried over magnesium sulfate and concentrated to give an oil, which was heated at 130-140° in a small distilling flask until no more distillate was obtained. Redistillation yielded 0.52 g. of isobutyl alcohol, b.p. 109-113°, n\textsuperscript{25D} 1.3938 (lit.\textsuperscript{18} b.p. 106-108°, n\textsuperscript{19.6} 1.3963). The residue from the previous distillation was triturated with cold petroleum ether and yielded 10.6 g. (73%) of a crystalline product, m.p. 51-52°. Recrystallization from petroleum ether raised the melting point to 52.2-53°. This product was identical with V obtained in procedure A.

2,4-Diisopropyl-5,5-dimethyl-1,3-dioxane (IVc). The reduction of IVb gave a product (procedure A) which was shown to be identical with an authentic sample of IVc obtained by procedure B.

A. By reduction of IVb. To a suspension of 5.0 g. (0.132 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether was added dropwise a solution of 33.5 g. (0.143 mole) of 2,4-diisopropyl-5,5-dimethyl-6-chloro-1,3-dioxane (IVb) in 50 ml. of ether. After the vigorous reaction was complete, the excess hydride was destroyed cautiously with water, and the precipitated alumina was dissolved with cold 10% sulfuric acid. The upper layer was separated and the aqueous phase was extracted three times with ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated under diminished pressure. Distillation of the remaining liquid through a 6-inch vacuum-jacketed column gave 23.8 g. (83%) of product, b.p. 103-105° (29 mm.), n\textsuperscript{25D} 1.4305. Refractionation in a nitrogen atmosphere through a 9-inch vacuum-jacketed, packed

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column yielded 21.0 g. of pure distillate, b.p. 103-103.5° (30 mm.), n$_{25}^D$
1.4302, d$_4^{25}$ 0.8847, MRP 58.49 (calcd. 58.70). The infrared spectrum showed
a broad ether absorption band in the range of 8.95-9.10 μ.

Anal. Calcd. for C$_{12}$H$_{24}$O$_2$: C, 71.95; H, 12.08. Found: C, 72.01; H, 11.58.

B. By condensation of V with isobutyraldehyde. This procedure was
patterned after the one used by Blicke and Anderson$^{19}$ in preparing a number
of similar 1,3-dioxanes.

A mixture of 73 g. (0.50 mole) of 2,2,4-trimethyl-1,3-pentanediol (V)
and 40.0 g. (0.556 mole) of freshly distilled isobutyraldehyde, b.p. 64-65°,
was heated on the steam bath until solution occurred, after which 2.0 ml.
of 85% phosphoric acid was added and the mixture was heated for 2 hours.
After standing for 5 hours at room temperature, the aqueous phase was with­
drawn and the remaining liquid was diluted with ether, washed thoroughly with
water, dried over anhydrous magnesium sulfate, and the solvent was removed
under reduced pressure. Distillation of the residue gave 80.0 g. (80%) of
a water-white liquid, b.p. 103-107° (31 mm.). Redistillation in a nitrogen
atmosphere through a 9-inch vacuum-jacketed, packed column yielded a center
fraction of 58.5 g., b.p. 104-105° (31 mm.), n$_{25}^D$ 1.4305, d$_4^{25}$ 0.8854, MRP
58.48 (calcd. 58.70). The infrared spectrum was superimposable upon that of
IVc obtained in procedure A.

2-Isopropyl-4-(p-isoproplyphenyl)-5,5-dimethyl-6-hydroxy-1,3-dioxane
(VI, R = p-isoproplyphenyl). This compound was prepared according to the

$^{19}$ F. F. Blicke and F. E. Anderson, J. Am. Chem. Soc., 74, 1733
(1952).
procedure used by Spath, Lorenz and Altmann\textsuperscript{11} for the condensation of benzaldehyde with isobutyraldehyde.

A mixture composed of 21.6 g. (0.30 mole) of freshly distilled isobutyraldehyde, 22.2 g. (0.15 mole) of cumaldehyde and 50 ml. of saturated potassium carbonate solution was stirred at 27\textdegree{} for 36 hours, after which a white, semisolid mass had formed. The product was dissolved in ether, washed with water until neutral, dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation. The residue, upon cooling, yielded a crystalline mass which was dissolved in warm methyl alcohol, and water was added carefully in order to induce crystallization. There was obtained 12.0 g. (27\%) of a white, crystalline product which, after a second recrystallization from methyl alcohol, melted at 98.7-99.3\textdegree{}. The infrared spectrum exhibited strong hydroxyl and ether absorption bands at 2.94 \mu{} and 8.92 \mu{}, respectively, but no carbonyl band.

\textit{Anal.} Calcd. for C\textsubscript{18}H\textsubscript{28}O\textsubscript{3}: C, 73.93; H, 9.65; mol. wt., 292.4.

Found: C, 74.10; H, 9.31; mol. wt. (benzene), 293.

\textbf{2-Isopropyl-4-(p-tert-butylphenyl)-5,5-dimethyl-6-hydroxy-1,3-dioxane (VI, R = p-tert-butylphenyl).} The procedure\textsuperscript{11} was essentially the same as that described above.

A mixture of 21.6 g. (0.30 mole) of freshly distilled isobutyraldehyde, 24.3 g. (0.15 mole) of p-tert-butylbenzaldehyde and 50 ml. of saturated potassium carbonate solution was stirred vigorously at 27\textdegree{} for 20 hours, after which time a white solid had formed. The reaction mixture was stirred for an additional 4 hours, diluted with water, and the product was collected by filtration. The crystalline solid was then dissolved in ether and washed thoroughly with water to remove the last traces of the catalyst. The dried
ether solution was concentrated by evaporation to yield a crystalline product. Recrystallization from a mixture of benzene and petroleum ether gave 37.9 g. (83%) of crystals, m.p. 107.3-108°. The infrared spectrum showed characteristic bands for hydroxyl at 2.93 μ and ether at 8.96 μ, but no carbonyl band.


2,4-Dipentyl-5-buty1-6-acetoxy-1,3-dioxane (VII). To 140 g. (1.40 moles) of hexanal, b.p. 128-130° (lit. b.p. 128°), was added 0.70 g. of potassium hydroxide dissolved in 6.30 g. of absolute methyl alcohol. The solution was shaken intermittently and was allowed to stand at room temperature for 10 days. The resulting clear, viscous liquid was diluted with ether, washed with water until neutral, dried over anhydrous sodium sulfate, and the ether and unreacted hexanal were removed under reduced pressure at a maximum temperature of 45°. An attempt was made to purify 20 g. of the residue by distillation at 0.1 mm., but extensive decomposition resulted, as evidenced by an abundance of white clouds of vapor and a steady increase in pressure, and by the collection of water in the cold trap. To 107 g. of the remaining condensation product was added 100 g. of pyridine and 100 g. of acetic anhydride. The lower-boiling components were removed under reduced pressure after 12 hours, and the residual oil was fractionated in a nitrogen atmosphere through a 9-inch vacuum-jacketed column to yield 49.5 g. (41%, based on the undistilled trimer) of distillate, b.p. 132.5-135° (0.2 mm.), which upon re fractionation gave 47.3 g. of VII, b.p. 128-130° (0.12 mm.),

(20) P. Sabatier and A. Mailhe, Compt. rend., 158, 986 (1914).
n^2D 1.4450, d^2 0.9344, M.R.D 97.55 (calcd. 97.30). Infrared maxima 5.68, 8.15, 8.60, 8.94 μ.

Anal. Calcd. for C_{20}H_{38}O_{4}: C, 70.13; H, 11.18. Found: C, 69.70; H, 10.81.

2,4-Dibenzyl-5-hexyl-6-hydroxy-1,3-dioxane (VIII, R = C_6H_5). The base-catalyzed trimerization of octanal was accomplished by using a saturated solution of potassium carbonate as the catalyst.

A mixture composed of 26.0 g. (0.203 mole) of octanal, b.p. 65-67° (11 mm.) (lit. b.p. 60-61° (9 mm.)), and 30 ml. of saturated potassium carbonate solution was shaken for 72 hours at 25°. To the semisolid mass which had formed was added 15 ml. of water, and shaking was continued for an additional 4 hours. The product was dissolved in ether, washed with water until neutral, dried over anhydrous magnesium sulfate, and the solution was concentrated by evaporation to yield an oil which crystallized slowly upon cooling. The product was triturated with cold methyl alcohol and collected on a cold funnel by filtration. The crystals were dissolved in warm methyl alcohol and allowed to recrystallize very slowly. In this manner, the product was obtained in the form of slender needles (10.5 g., 40%) which, after four subsequent recrystallizations, melted at 58.5-59°. The infrared spectrum showed strong -OH and C-O-C absorption bands at 2.96 and 8.68 μ, respectively, but no C=O band.

Anal. Calcd. for (C_8H_{16}O)_3: C, 74.94; H, 12.58; mol. wt., 384.6. Found: C, 75.21, 75.39; H, 12.31, 12.42; mol. wt. (benzene), 393.

(21) This catalyst was used by Spath, et al. (reference 7) for the trimerization of lower members of the aldehyde series.

(22) F. W. Semmler, Ber., 42, 1161 (1909).
2,4-Dietyl-5-heptyl-6-hydroxy-1,3-dioxane (VIII, \( R = \text{C}_7\text{H}_{15} \)). A mixture of 28.0 g. (0.197 mole) of freshly distilled nonanal, b.p. 79-81\(^\circ\) (12 mm.) (lit.\(^\text{23}\) b.p. 80-82\(^\circ\) (13 mm.)), and 30 ml. of saturated potassium carbonate\(^\text{21}\) solution was shaken for 4 days at room temperature. There had formed a viscous, slightly discolored oil, but there was no evidence of crystal formation. The oil was dissolved in ether, washed thoroughly with water, dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation. The residue failed to solidify at room temperature, but yielded a crystalline mass after being cooled in an iced water-bath for 12 hours. The product was triturated with cold methyl alcohol in order to free the crystals from adhering oil, and filtration yielded 5.0 g. (18\%) of slender needles. It was necessary during recrystallization from methyl alcohol to control the temperature very carefully to prevent the formation of a soft, solid mass instead of needles. After four such recrystallizations from methyl alcohol, the product melted at 53.5-54.5\(^\circ\). This compound was readily soluble in such solvents as carbon tetrachloride, benzene, petroleum ether, chloroform and acetone. The infrared spectrum exhibited bands for hydroxyl at 2.92 and for ether at 8.68 \( \mu \), but no carbonyl band.

Anal. Calcd. for \( (\text{C}_7\text{H}_{18}\text{O})_3 \): C, 75.99; H, 12.76; mol. wt., 426.7.
Found: C, 75.79, 75.74; H, 12.33, 12.36; mol. wt. (benzene), 422, 421.

2,4-Dinonyl-5-octyl-6-hydroxy-1,3-dioxane (VIII, \( R = \text{C}_8\text{H}_{17} \)). A mixture of 25.0 g. (0.16 mole) of freshly distilled decanal, b.p. 91-93\(^\circ\) (10 mm.) (lit.\(^\text{24}\) b.p. 92\(^\circ\) (10 mm.)), and 30 ml. of saturated potassium carbonate\(^\text{21}\)

\(^{(23)} \) H. Walbaum and K. Stephen, Ber., 22, 2303 (1900).
solution was shaken for 24 hours at 25°. The white, solid mass which had formed was collected by filtration, dissolved in ether, and the remaining catalyst was removed by washing repeatedly with water. The dried ether solution was concentrated by evaporation to yield a viscous oil which slowly formed a crystalline mass. The adhering oil was removed by triturating the crystals with cold methyl alcohol and filtering, and there was obtained 14.2 g. (57%) of white needles. This product was recrystallized very slowly from methyl alcohol to prevent the formation of an oil, and this process was continued until the melting point reached the constant value of 57.5-58°. The infrared spectrum showed characteristic bands for hydroxyl at 2.96 and for ether at 3.69 μ, but no carbonyl band.

**Anal.** Calcd. for (C_{10}H_{20}O)_{3}: C, 76.86; H, 12.90; mol. wt., 468.8. Found: C, 76.58, 76.77; H, 12.89, 12.85; mol. wt. (benzene), 461, 474.

2,4-Didecyl-5-nonyl-6-hydroxy-1,3-dioxane (VIII, R = C_{9}H_{19}). This compound was prepared by shaking a mixture of 16.5 g. (0.097 mole) of freshly distilled undecanal, b.p. 93-95° (6 mm.) (lit.25 b.p. 116-117° (18 mm.)), and 20 ml. of saturated potassium carbonate solution for 30 hours at room temperature. The solid reaction product was collected by filtration, dissolved in ether, and washed with water until neutral. The dried ether solution was concentrated by evaporation to give a viscous oil which slowly crystallized upon cooling, but the product was contaminated with unreacted aldehyde. The adhering oil was removed with difficulty by triturating the crystals with cold methyl alcohol, filtering, and washing with several portions of cold methyl alcohol. There was obtained 10.4 g. (63%) of this

substance, which was recrystallized very slowly from methyl alcohol until the melting point reached the constant value of 52.6-53°. Recrystallization from cold petroleum ether did not cause an elevation in melting point. The infrared spectrum showed absorption bands for hydroxyl at 2.95 and for ether at 8.68 μ, but no carbonyl band.

*Anal.* Calcd. for (C_{11}H_{22}O)\textsubscript{3}: C, 77.58; H, 13.02; mol. wt., 510.9.

Found: C, 77.17, 76.99; H, 12.66, 12.69; mol. wt. (benzene), 503, 498.

2,4-Diundecyl-5-decyl-6-hydroxy-1,3-dioxane (VIII, R = C_{10}H_{21}). A mixture of 25.0 g. (0.136 mole) of freshly distilled laurialdehyde, b.p. 103-104° (4 mm.) (lit.\textsuperscript{26} b.p. 103-104° (4 mm.)), and 30 ml. of a saturated potassium carbonate\textsuperscript{21} solution was shaken at 25° for 24 hours. There had formed a hard, white solid product, which was broken into lumps and collected by filtration, and washed with water to remove most of the catalyst. It was then dissolved in ether, washed with water until neutral, dried over anhydrous magnesium sulfate, and the ether was removed by evaporation. The residue soon formed a crystalline mass, which was recrystallized from a mixture of acetone and methyl alcohol to yield 16.8 g. (67%) of soft, white crystals, m.p. 63-64°. After three subsequent recrystallizations, the product melted at 65.5-66°. The infrared spectrum showed characteristic bands for hydroxyl at 2.96 and for ether at 8.70 μ, but no carbonyl band.

*Anal.* Calcd. for (C_{12}H_{24}O)\textsubscript{3}: C, 78.19; H, 13.13; mol. wt., 552.9.

Found: C, 78.29, 78.31; H, 13.01, 13.06; mol. wt. (benzene), 543, 560.

The Use of Vinyl Acetate as an Acetylating Agent

2,4-Dimethyl-6-acetoxy-1,3-dioxane (Ia). The alkaline hydrolysis of vinyl acetate gave a product, procedure A, which was identical with Ia obtained by procedures B and C.

A. The procedure of Herrmann and Haehnel\(^\text{13}\) was used. To a stirred mixture of 207 g. (2.41 moles) of freshly distilled vinyl acetate, b.p. 73°, and 100 g. of water was added a solution of 72.0 g. (1.8 moles) of sodium hydroxide in 240 g. of water. The temperature was not allowed to exceed 10°. The reaction mixture was stirred for 0.5 hour, after which the upper layer was diluted with petroleum ether and dried over anhydrous magnesium sulfate. Removal of the low-boiling materials under reduced pressure, followed by distillation of the remaining oil yielded 100 g. of liquid, b.p. 88-91° (12 mm.). After two fractionations in a nitrogen atmosphere through a 6-inch vacuum-jacketed, packed column, there was obtained 93.4 g. (67%) of pure distillate, b.p. 86-88° (10.5 mm.), \(n^\text{D} 1.4280\) (for \(\text{C}_9\text{H}_{14}\text{O}_4\), lit.\(^\text{13}\) b.p. 92-100° (22-14 mm.)).

B. The procedure of Marvel, et al.\(^\text{12}\) was followed, but no ethyl alcohol was added after the reaction was complete. To 142.4 g. (3.24 moles) of cold, freshly distilled acetaldehyde was added six 4-mm. cubes of metallic sodium, which reacted vigorously for about 20 minutes, during which time the temperature was not allowed to exceed 45°. After an additional 30 minutes the clear, viscous reaction product had cooled to room temperature. The unreacted sodium was removed and 186 g. (2.16 moles) of freshly distilled vinyl acetate, b.p. 73°, was added. The temperature was maintained below 50° by cooling externally. After 24 hours the white, flocculent precipitate which had formed was removed by filtration, the unreacted acetaldehyde and
vinyl acetate were removed under reduced pressure, and the residue was distilled to yield 143.2 g. (76%) of colorless liquid, b.p. 81.5-89° (10 mm.). Fractionation through a 9-inch vacuum-jacketed, packed column gave 112.0 g. (60%) of Ia, b.p. 86.5-88° (10.5 mm.), n²D 1.4289 (lit.¹² b.p. 74-75° (6 mm.), n²D 1.4310; and b.p. 85-86° (11 mm.), n²D 1.4308; and b.p. 86° (10 mm.), n²D 1.4301; and b.p. 85.5° (10 mm.), n²D 1.4278).

C. This experiment was performed in exactly the same manner as described in procedure B, except that metallic sodium was replaced by powdered sodium hydroxide. From 112 g. (2.55 moles) of acetaldehyde, 0.61 g. of powdered sodium hydroxide and 146 g. of vinyl acetate, there was obtained 101 g. (68%) of a colorless oil, b.p. 62-70° (2 mm.), which upon fractionation gave 66.7 g. of Ia, b.p. 85-86°, n²D 1.4288.

2,4-Dimethyl-6-hydroxy-1,3-dioxane (I). In a 200-ml. round-bottomed flask, fitted with an efficient reflux condenser, was placed 56.0 g. (1.27 moles) of freshly distilled acetaldehyde which was cooled to 5°, and then 0.3 g. of powdered sodium hydroxide was added. A vigorous reaction began when the cooling bath was removed, and the solution warmed to 35-40°. When the product had cooled to room temperature, it was dissolved in 100 ml. of ether, washed thoroughly with water, dried over anhydrous sodium sulfate, and the ether and unreacted acetaldehyde were removed under reduced pressure. The residual oil was fractionated in a nitrogen atmosphere through a 9-inch vacuum-jacketed, packed column to yield 20.0 g. (36%) of I, b.p. 76-77° (5 mm.), n²D 1.4380 (lit.⁷ b.p. 68-70° (2 mm.), n²D 1.4407; and n²D 1.4380).

2,4-Dipropyl-5-ethyl-6-acetoxy-1,3-dioxane (IIIa). Three molecules of butyraldehyde, b.p. 75-77°, were condensed according to the procedure of

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Saunders, et al., 3 by using a 10% potassium hydroxide solution as the catalyst. The unreacted butyraldehyde was removed from the product by heating at 40° under reduced pressure. To 70.0 g. (0.324 mole) of this undistilled trimer (III), n\textsubscript{D} 1.4487 (lit. 7 n\textsubscript{D} 1.4495), was added 0.5 ml. of a 10% alcoholic potassium hydroxide solution and 43.0 g. (0.50 mole) of vinyl acetate, b.p. 73°. The reaction flask was stoppered and its contents were maintained at a temperature below 50° by external cooling until the reaction subsided. After 2 days, the flocculent precipitate which had formed was removed by filtration and the lower-boiling components were removed under reduced pressure. Distillation of the residue yielded 65.4 g. (78%) of a colorless oil, b.p. 99-110° (1.5 mm.), with the major fraction distilling at 108° (1.5 mm.). Fractionation through a 9-inch vacuum-jacketed, packed column gave the pure acetate (IIIa), b.p. 115-116° (3 mm.), n\textsubscript{D} 1.4378 (lit. 4 b.p. 114° (3 mm.), n\textsubscript{D} 1.4378; and 7 b.p. 105-106° (1 mm.), n\textsubscript{D} 1.4405).

No reaction resulted between butyraldehyde and vinyl acetate in the presence of a catalytic amount of metallic sodium.

2,4-Diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane (IVA). This reaction was performed according to the method of Marvel, Harmon and Riddle, 12 who condensed acetaldehyde with vinyl acetate and reported, however, that isobutyraldehyde would not react under the conditions used.

Freshly distilled isobutyraldehyde (72.0 g., 1.0 mole), b.p. 64-65°, was cooled to 0° and four 4-mm. cubes of sodium were added. The cooling bath was removed and a vigorous reaction ensued and lasted for 15-20 minutes, during which time the temperature was not allowed to exceed 45°. After the unreacted sodium was removed, the contents of the reaction flask were cooled
externally, and 43.0 g. (0.50 mole) of vinyl acetate, b.p. 73°, was added. The stoppered flask was shaken, and the reaction mixture warmed spontaneously to 40-45°. When room temperature was reached the white, flocculent precipitate which had formed was dissolved by the addition of 25 ml. of absolute ethyl alcohol. On the following day the unreacted isobutyaldehyde, vinyl acetate, and the ethyl alcohol were removed under reduced pressure. The remaining oil yielded 68.0 g. (79%) of a clear distillate, b.p. 82-91° (1.4 mm.). Fractionation in a nitrogen atmosphere through a 9-inch vacuum-jacketed column gave 60.3 g. of IVa, b.p. 85-87° (1.4 mm.), nD 1.4356, d425 0.9719, which was identical with IVa prepared by another method (page 30).

Pyrolysis of Ia and IIa

Thermal decomposition of 2,4-dimethyl-6-acetoxy-1,3-dioxane (Ia) in the presence of adipic acid. The procedure of Herrmann and Haehnel was used in an attempt to isolate a stable 1,3-dioxene (Ic).

A mixture of 46.7 g. (0.268 mole) of Ia, b.p. 86-88° (10.5 mm.), and 19.6 g. (0.134 mole) of dry, pulverized adipic acid was heated in a distilling apparatus at 125° until solution occurred. As the bath temperature was elevated gradually, a low-boiling fraction (30-60°) distilled slowly and finally, the vapor temperature reached a high value of 115°. The last traces of volatile material were obtained by heating under reduced pressure (25 mm.). There was obtained a total of 44.9 g. of distillate, which upon refractionation yielded 10.1 g. (85.6%) of acetaldehyde, b.p. 20-24°, and a second fraction, b.p. 102-115°. The acetic acid was removed from the last fraction by washing with 10% sodium carbonate solution. The organic layer was dried over anhydrous potassium carbonate and distilled to yield 6.2 g. (33%) of
crotonaldehyde, b.p. 102-106°, which was further identified by means of its semicarbazone, m.p. 198-198.5°.

2,4-Diethyl-5-methyl-6-acetoxy-1,3-dioxane (IIa). This compound was prepared by the procedure of Saunders and Murray,⁴ except that no dibutylamine was added.

To a stirred solution of 220 g. (3.8 moles) of freshly distilled propionaldehyde, b.p. 49-50°, and 260 ml. of ether was added slowly 150 g. of 10% potassium hydroxide solution. The temperature was maintained below 5°. The ether layer was washed with cold water until neutral, dried over anhydrous sodium sulfate, and the lower-boiling components were removed under reduced pressure. To the remaining oil was added an acetylation mixture of 250 g. of pyridine and 250 g. of acetic anhydride. After 12 hours this solution was concentrated under reduced pressure, and the residual oil was distilled to yield 127 g. (46%, based on propionaldehyde) of a colorless liquid, b.p. 100-107° (7 mm.), n^20_D 1.4333. Fractionation of this material through a 9-inch vacuum-jacketed, packed column gave 119 g. of IIa, b.p. 103.8-104° (6 mm.), n^25_D 1.4330 (lit.⁴ b.p. 100° (7 mm.), n^25_D 1.4328; and⁷ b.p. 85-85.5° (1.4 mm.), n^20_D 1.4355).

Thermal decomposition of IIa. A. By heating with adipic acid. The procedure¹⁵ was essentially the same as that used for the decomposition of Ia.

Adipic acid (20.3 g., 0.139 mole) was dissolved in 60.0 g. (0.278 mole) of IIa by heating the mixture at 125-130° for 45 minutes. The temperature of the bath was elevated to 155° and propionaldehyde, b.p. 48-50°, began to distill. A second fraction, b.p. 115-130°, was collected, and the last traces of volatile material were collected by heating under reduced pressure.
The entire distillate consisted of 54.2 g., and there remained a residue of 25.8 g. Fractionation of the distillate yielded 13.4 g. (83%) of propionaldehyde, b.p. 48-51°, and 39.4 g. of a second fraction boiling at 117-136°. The acetic acid was removed from the second fraction by washing with 10% sodium carbonate solution, and the remaining organic phase was washed with water and dried over anhydrous potassium carbonate. Distillation of this liquid yielded 18.2 g. (67%) of 2-methyl-2-pentenal, b.p. 135-137°, n^25_D 1.4454 (lit. 27 b.p. 134-136°, n_D 1.4465).

R. By heat only. The procedure was the same as that described above, except that no adipic acid was used.

2,4-Diethyl-5-methyl-6-acetoxy-1,3-dioxane (40.4 g., 0.192 mole) was heated in a distilling apparatus at 170-180° so that fractional distillation occurred slowly. The temperature of the bath was elevated to 280° in order to obtain the last traces of volatile material, but the vapor temperature did not exceed 135°. The distillate was refractionated to yield 9.0 g. (81%) of propionaldehyde, b.p. 48-51°, and 26.6 g. of material boiling at 115-135°. After removal of the acetic acid by washing with 10% sodium carbonate solution and with water, distillation of the remaining liquid gave 11.4 g. (61%) of 2-methyl-2-pentenal, b.p. 135.5-138.5°, n^25_D 1.4466. Infrared maxima 5.90, 6.06 μ.

THE ACID-CATALYZED TRIMERIZATION OF ALIPHATIC NORMAL ALDEHYDES

It has been shown that a number of aldehydes undergo a base-catalyzed reaction to form 1,3-dioxanes (m-dioxanes). The acid catalyzed reaction, however, yields 1,3,5-trioxanes (s-trioxanes). It is now more than 100 years since Fehling\(^3\) discovered paraldehyde in 1838, and it is surprising to find that the trimerization of even some of the lower members of the aliphatic aldehyde series has not been reported.

<table>
<thead>
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<th>Year reported</th>
<th>Trimer of monomeric aldehyde</th>
<th>Reference, literature</th>
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<tr>
<td>1884</td>
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<td>C(_{11})</td>
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<tr>
<td>1904</td>
<td>C(_{17})</td>
<td>14</td>
</tr>
<tr>
<td>1905</td>
<td>C(<em>{13}), C(</em>{14}), C(<em>{15}), C(</em>{16})</td>
<td>13</td>
</tr>
<tr>
<td>1907</td>
<td>C(_{10})</td>
<td>10</td>
</tr>
<tr>
<td>1912</td>
<td>C(_4), C(_7)</td>
<td>6</td>
</tr>
<tr>
<td>1925</td>
<td>C(_{18})</td>
<td>15</td>
</tr>
<tr>
<td>1930</td>
<td>C(_{12})</td>
<td>12</td>
</tr>
<tr>
<td>1938</td>
<td>C(_9)</td>
<td>9</td>
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<tr>
<td>1951</td>
<td>C(_8)</td>
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</table>

The 1,3,5-trioxanes have been of interest in this laboratory for a number of years. In order to complete the above series of aldehyde trimers, para-n-valeraldehyde and para-n-hexanal were prepared\(^7\) and characterized for the first time. In addition, the melting points of four aldehydes (hexanal, octanal, nonenal, and decanal) have not been reported in the literature.
Consequently, the lacking physical constants have been determined and are recorded in Table I, which includes all aliphatic normal aldehydes and their trimers from formaldehyde to stearaldehyde (C\textsubscript{1} to C\textsubscript{18}) and serves as a convenient reference for such information.

**TABLE I**

The physical constants in this table were selected from original sources in the literature. The melting points marked with an asterisk were not found recorded in the literature, and were determined in this laboratory.

<table>
<thead>
<tr>
<th>Aliphatic normal aldehydes</th>
<th>2,4,6-Trialkyl-1,3,5-trioxanes</th>
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*(1) L. Pratesi, Gazz. chim. ital, 14, 140 (1884).*

*This laboratory, unpublished results, J. L. E. Erickson, C. R. Campbell, and G. N. Grammer.

(1) L. Pratesi, Gazz. chim. ital, 14, 140 (1884).

In addition to the trimers of valeraldehyde and hexanal, the following aldehyde trimers were prepared, and their molecular weights and melting points were redetermined.

**Trimers of Aldehydes**

- Butyraldehyde, m.p. -12.4°. Orndorff\(^4\) reported m.p. below -20°.
- Octanal, m.p. 30.3°. Wakayama\(^8\) reported m.p. 33.5-34°.
- Nonanal, m.p. 33.5°. King\(^9\) reported m.p. 33.5°.
- Decanal, m.p. 43.8°. Bagard\(^10\) reported m.p. 43°.
- Lauraldehyde, m.p. 58.3°. Mannich and Nadelmann\(^12\) reported m.p. 57°.

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(5) This Laboratory, m.p. was redetermined, and compared with values reported in the literature.
(5a) This Laboratory, m.p. was determined, since none was recorded in the literature.
(7) This Laboratory, compound was prepared, since it was not reported in the literature; anal., mol. wt., m.p. and b.p. were determined.
The polymerization of aliphatic aldehydes to yield trimers of the 2,4,6-trialkly-1,3,5-trioxane type may be catalyzed by such proton acids as sulfuric acid, benzenesulfonic acid, hydrochloric acid, phosphoric acid, and by a number of protonoid (proton-like) acids, such as boron fluoride, aluminum chloride, ferric chloride, zinc chloride, etc. All of the above catalysts proved to be very effective. The mechanism of this acid-catalyzed process may be formulated as follows:

\[
\begin{align*}
RCH=O & \quad \xleftarrow{\text{HB}} \quad RCH=O^+ \quad \xrightarrow{\text{B}} \quad RCH=O-H \quad \xrightarrow{\text{O}} \quad R-CH-OH \quad \xrightarrow{\text{RCH}=O} \\
RCH-OH & \quad \xrightarrow{\text{O}} \quad RCH=OH \quad \xrightarrow{\text{B}} \quad RCH=O-H \quad \xrightarrow{\text{O}} \quad RCH=O
\end{align*}
\]

The reaction is completely reversible, and the aldehyde may be regenerated by heating the trimer in the presence of an acid catalyst.

EXPERIMENTAL

Preparation of aldehyde trimers. About 20 g. of monomeric aldehyde was placed in an Erlenmeyer flask and treated with a catalyst. One drop of concentrated sulfuric acid or an equivalent quantity of boron fluoride-etherate or benzenesulfonic acid proved to be particularly effective.

(1) In the polymerization of butyraldehyde, valeraldehyde, hexanal and octanal, the aldehyde and catalyst were allowed to stand for 24 hours with intermittent shaking. The resulting product was washed with 10% sodium bicarbonate solution and then with water, and dried over calcium chloride. The liquid was fractionated in a distillation apparatus, and after removal of the monomeric aldehyde, the trimer was collected. In the case of octanal, the trimer was not distilled. Instead, it was taken up in acetone and purified by recrystallization from that solvent. The yields of purified products were 50-60%, but no attempt was made to recover all of the product to insure high yields.

(2) The polymerization of nonanal, decanal and lauraldehyde was carried out by adding the catalyst to the aldehyde and allowing the mixture to stand for a short time. It was then cooled slightly, if necessary, to cause crystallization of the trimer, which was then purified by recrystallization from acetone, or from a mixture of acetone and alcohol. The yields were almost quantitative.

**Butyraldehyde trimer.** - M.p. -12.4°, b.p. 84-88° (5 mm.).

**Anal.** Calcd. for (C₄H₇O)₃: C, 66.63; H, 11.18; mol. wt., 216.3.

**Found:** C, 66.48; H, 11.34; mol. wt. (benzene), 210, 219.
Valeraldehyde trimer. - M.p. -8.8°, b.p. 126-128° (4 mm.).
Anal. Calcd. for (C₅H₁₀O)₃: C, 69.72; H, 11.70; mol. wt., 258.4.
Found: C, 69.63; H, 11.82; mol. wt. (benzene), 259, 254, 241.

Hexanal trimer. - M.p. -5.2°, b.p. 153-156° (5 mm.).
Anal. Calcd. for (C₆H₁₂O)₃: C, 71.95; H, 12.08; mol. wt., 300.5.
Found: C, 71.81; H, 12.24; mol. wt. (benzene), 298, 294, 300.

Octanal trimer. - M.p. 30.3°.
Calcd. for (C₈H₁₆O)₃: mol. wt., 384.6.
Found: mol. wt. (benzene), 375, 377, 383.

Nonanal trimer. - M.p. 33.5°.

Decanal trimer. - M.p. 43.8°.
Calcd. for (C₁₀H₂₀O)₃: mol. wt., 468.8.
Found: mol. wt. (benzene), 459, 462, 463.

Lauraldehyde trimer. - M.p. 58.3°.
Calcd. for (C₁₂H₂₄O)₃: mol. wt., 552.9.
Found: mol. wt. (benzene), 549, 544, 569.
Phenylacetaldehyde polymerizes slowly to yield a crystalline substance, which has been identified as a cyclic sesquiacetal, 2,4-dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane. A method for the synthesis of this compound has been developed.

The trimer obtained from isobutyraldehyde by the base-catalyzed trimerization reaction has been shown to have the structure, 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane. The trimers of five aliphatic normal aldehydes have been prepared for the first time.

Vinyl acetate serves as an acetylating agent for the sesquiacetals obtained from acetaldehyde, butyraldehyde and isobutyraldehyde. There is no evidence that any of these aldehydes react with the alkene linkage of vinyl acetate in a reaction which is catalyzed by bases. Pyrolysis of the acetates, obtained from the trimers of acetaldehyde and propionaldehyde, yielded mixtures consisting of the monomeric aldehyde, an unsaturated aldehyde, and acetic acid.

Aliphatic aldehydes undergo an acid-catalyzed reaction to yield 1,3,5-trioxanes. A table has been prepared to show the physical constants of all aliphatic normal aldehydes and their trimers from formaldehyde to stearaldehyde. Two of these trimers, as well as the melting points of four aldehydes, have not been reported in the literature.
SELECTED BIBLIOGRAPHY

ANNOTATED AND ALPHABETIZED ACCORDING TO AUTHORS

THE POLYMERIZATION OF PHENYLACETALDEHYDE
Conant, J. B. and Blatt, A. H.
The Action of the Grignard Reagent on Highly Branched Carbonyl Compounds.

"Three-tenths of a mole (49.2 g.) of phenylacetic ester was added to a theoretical 0.5 mole of isopropylmagnesium bromide chilled in an ice-bath. There was a steady evolution of saturated gas and the separation of a light gray magnesium compound. After standing overnight the reaction mixture was decomposed and the ether layer on evaporation gave 39.5 g. of crude diphenylacetoacetic ester; yield, 94%. The crude ester melted at 72-75°. After it was triturated in a mortar with cold alcohol, filtered and dried, it melted at 78°. This product may be recrystallized from alcohol with only slight loss."

Davies, J. S. H. and Morris, D. S.
Derivatives of Indene and of Butyric Acid.

Ethyl α,γ-diphenylacetoacetate (28.2 g.) was hydrogenated in ethyl alcohol at atmospheric pressure and a maximum temperature of 50-60° in the presence of Raney nickel; one molecular proportion of hydrogen was absorbed. Removal of the catalyst and solvent, followed by hydrolysis of the residue by refluxing it for 4 hours with 6.5 g. of potassium hydroxide in 50% aqueous alcohol, gave a mixture of 3.8 g. of a neutral substance, believed to be phenylethyl alcohol, and 13.5 g. of β-hydroxy-α,γ-diphenylbutyric acid, which formed needles, m.p. 210°, from aqueous methyl alcohol. Calcd. for C_{16}H_{16}O_{3}: C, 75.0; H, 6.3; neut. equiv., 256. Found: C, 75.1; H, 6.6; neut. equiv., 254.

The ethyl ester was prepared by refluxing 10.5 g. of the hydroxy acid for 4 hours in saturated ethyl alcoholic HCl. There was obtained 9.5 g. of product, b.p. 158-160° (1 mm.), which slowly solidified and melted at 61-62°. Calcd. for C_{18}H_{20}O_{3}: C, 76.1; H, 7.0. Found: C, 76.3; H, 7.3.

All attempts to dehydrate the acid or ester were unsuccessful.

Enklaar, C. J.
Phenylacetaldehyde.

A sample of phenylacetaldehyde was kept in the dark for 6 months, and polymerized to the extent of nearly 50% during this time. After being stored at 0-5° for a month longer, a quantity of crystals, m.p. 33-34°, had separated from the liquid. This solid was assumed to be a monomeric form. It formed a p-nitrophenylhydrazone, the analysis of which did not afford useful results.
Franke, A. and Sigmund, F.

The Effect of Ultraviolet Rays on Aldehydes.


When exposed to ultraviolet light certain aldehydes, such as heptanal, isobutyraldehyde and propionaldehyde, lose carbon monoxide. The behavior of phenylacetaldehyde under these conditions was studied. Phenylacetaldehyde was prepared by the dry distillation of a mixture of the calcium salts of phenylacetic acid and formic acid. The aldehyde boiled at 204-208°. A 1.4 g. sample of this aldehyde was placed in a small tube which was connected to a gas burette containing water, and was exposed to the radiation of a quartz mercury lamp for a period of 16 hours. The distance of the sample from the lamp was varied from 40 mm. to 2 mm., and the temperature was varied from 30° to 100°. In no case was the slightest evolution of gas detected.

Ivanoff, D. and Nicoloff, N. I.

Syntheses with Magnesium Halide Derivatives of Sodium Phenylacetate. I. Preparation of $\beta$-Hydroxy Aryl Aliphatic Acids (Substituted $\beta$-Lactic Acids).


Aldehydes reacted with C6H5CH(MgCl)CO2Na (I) to give $\alpha$-phenyl-$\beta$-lactic acids. Sodium phenylacetate was converted into I by means of isopropyl chloride and, after refluxing until the evolution of propane had ceased, an ethereal solution of the aldehyde was added. After hydrolysis, the acid was separated by treating the ethereal solution with dilute alkali, acidifying, and then extracting with ether.

Butyraldehyde, isobutyraldehyde and heptanal yielded, respectively: 2-phenyl-3-hydroxyhexanoic acid, m.p. 155-156°; a mixture of two isomers of 4-methyl-2-phenyl-3-hydroxypentanoic acid, obtained as colorless prisms, m.p. 139-140° (64%), and colorless needles, m.p. 171-172° (13%); and 2-phenyl-3-hydroxypropanoic acid, m.p. 107-108°. Benzaldehyde, p-chlorobenzaldehyde, anisaldehyde and piperonal gave, respectively: 60% of 2,3-diphenyl-3-hydroxypropanoic acid, m.p. 175°; 40% of 2-phenyl-3-p-chlorophenyl-3-hydroxypropanoic acid, m.p. 138-139.5°; 95.8% of 2-phenyl-3-methoxyphenyl-3-hydroxypropanoic acid, m.p. 136.5°; and 23% of 2-phenyl-3-piperonyl-3-hydroxypropanoic acid, m.p. 166-167°. Cinnamaldehyde and furfural yielded, respectively, 75% of 2,5-diphenyl-3-hydroxy-4-pentenoic acid, m.p. 136-137°, and 2-phenyl-3-furyl-3-hydroxypropanoic acid, m.p. 175° (dec.).

Meerwein, H.

1,5-Dialdehydes and 1,5-Diketones. Conversion to $\delta$-Lactones.


$\alpha$-Phenylcinnamaldehyde was prepared by shaking a mixture of 12 g. of phenylacetaldehyde, 10.6 g. of benzaldehyde, 800 ml. of water, and 10 ml. of 8% potassium hydroxide solution for 2 days. An oil was
obtained which distilled at 195-200° (17 mm.), and after crystallization from alcohol, melted at 94°. Calcd. for C15H12O: C, 86.5; H, 5.81. Found: C, 85.95; H, 5.96.

Muller, A.
Polymerization of Phenylacetaldehyde.

Phenylacetaldehyde, stored in a white glass bottle, polymerized to the extent of approximately 25% when exposed to diffused autumn sunlight for 30 days, while a sample stored in a brown glass bottle under identical conditions polymerized to the extent of about 6%. The degree of polymerization was reversed when the samples were stored in diffused summer sunlight. Polymerization was followed by density, refractive index, and determination of aldehyde content by the hydroxylamine method.

"It is at once evident that the polymerization of phenylacetaldehyde and allied aldehydes represents a very complicated problem and requires further explanation."

Muller, A.
Constitution of the Phenylacetaldehyde Trimer.

The trimer of phenylacetaldehyde was prepared by dissolving the monomer in carbon tetrachloride and storing the solution in a brown bottle in diffused light for 4 days. The trimer melted at 155-156°, and was assumed to have the triphenylparaldehyde structure since it was unaffected by acetic acid or formic acid. Ultraviolet spectra were given for both phenylacetaldehyde and the trimer.

Pound, J. R.
Phenylacetaldehyde and its Polymerization.

The acidities of samples of phenylacetaldehyde were determined by titration with carbonate-free alkali. It was found that phenylacetaldehyde did not oxidize appreciably on exposure to air.

A sample of phenylacetaldehyde in a dark cupboard became viscous, and small crystals appeared in the body of the liquid after 17 months. Some crystals had formed above the liquid some months previous. The refractive index, density and viscosity of the sample increased with age. The results showed that the density increased linearly with time and that, in general, there was a linear relationship between refractive index and time. The rate of formation of the crystalline polymer was
approximately three to four times faster at 30° than at 15°.

Two lots of the crystalline polymer were obtained by extracting an old stock sample of phenylacetaldehyde with alcohol and filtering. After washing the product with alcohol, it was found to melt sharply at 104°. This substance dissolved as a trimer of phenylacetaldehyde in benzene, ethylene bromide, benzophenone, acetophenone, cyclohexanol and paraldehyde, but dissolved as a hexamer in bromoform. Calcld. for (C_7H_7O)_n: C, 80.0; H, 6.72. Found: C, 79.75, 80.0; H, 6.67, 6.71.

Rassow, B. and Burmeister, F.
β-Phenyl-α-chlorolactic Acid and Phenylacetaldehyde.

Phenylacetaldehyde in contact with the air became discolored and resinous, and formed after several weeks a transparent, waxy product, most of which dissolved in ether, but left behind a quantity of well-developed crystals, m.p. 148°. Calcld. for C_7H_7O: C, 78.50; H, 6.54. Found: C, 78.27, 78.42; H, 6.63, 6.41. This substance could not be obtained in sufficient quantity for identification.

Spath, E.
An α-Hydroxy Lactone from Phenylacetaldehyde.

α,γ-Diphenyl-β-hydroxybutyraldehyde cyanohydrin was prepared by mixing 10 g. of phenylacetaldehyde and 60 ml. of 80% alcohol with 20 g. of potassium cyanide in 35 ml. of water. The mixture became colored and after a time deposited crystals, which were stirred with 50% alcohol and washed with water. The white residue (6.9 g.) melted at 144-146° (dec.). The mother liquor contained an amorphous condensation product which boiled at 260-280° (0.1 mm.) and whose analysis corresponded to the formula, C_32H_50O_3. The cyanohydrin was converted into alpha-hydroxy-beta-phenyl-gamma-benzylbutyrolactone, m.p. 114-115°, by warming 10 g. of this substance with 40 ml. of 96% alcohol and 30 ml. of concentrated hydrochloric acid. The lactone yielded an acetate as an oil, and a benzoate, m.p. 126-127°. Both the acetate and benzoate regenerated the lactone when acidified. The lactone was unchanged when heated with methyl alcohol which was saturated with HCl.

Stobbe, H. and Lippold, A.
The Photochemistry of Phenylacetaldehyde. Formation of Triphenylparaldehyde and other Polymers.

Polymerization of phenylacetaldehyde in the presence of acids.
A mixture of 23% sulfuric acid and phenylacetaldehyde was converted after
several days into colorless crystals which, after recrystallization from alcohol, melted at 155-156°. Calcd. for (CgHgO)o: C, 80.00; H, 6.67; mol. wt., 360. Found: C, 80.27, 79.93; H, 6.88, 6.76; mol. wt., 341, 363, 336, 512, 443, 410, 389.

This trimer was easily soluble in benzene, chloroform, and acetone; difficultly soluble in alcohol, ether, and glacial acetic acid; and practically insoluble in water. It did not react with ammoniacal silver nitrate, Fuchsin reagent or potassium hydroxide, and gave no oxime. A trimeric structure analogous to that of paraaldehyde was proposed.

At 0.01 mm. the trimer distilled at 150-160° without decomposition; at 13 mm, it distilled at 240-250° with slight decomposition; and at atmospheric pressure it decomposed to yield 98.5% of the monomer, which distilled at 199-222°. When the trimer was heated in a higher-boiling solvent, partial depolymerization occurred.

At room temperature as well as at -80°, phenylacetaldehyde formed a resin when treated with concentrated sulfuric acid. With 23% hydrochloric acid, the aldehyde yielded a viscous oil which solidified after 2 days. This product was non-crystalline and was described as an amorphous polymer, which regenerated phenylacetaldehyde upon being heated. Phenylacetaldehyde formed a sticky, fibrous mass when treated with hydrogen chloride, but was not affected appreciably by formic acid.

**Polymerization of phenylacetaldehyde with alkali.** Upon treatment with cold 10% potassium hydroxide solution, phenylacetaldehyde was instantly converted into a yellow, amorphous mass which did not crystallize from alcohol, ether, chloroform, benzene or light petroleum. This product exhibited a molecular weight, in acetic acid, which corresponded to that of a dimer of phenylacetaldehyde. The resin melted at about 50°, and decomposed rapidly when heated at 80-90° to yield the monomeric aldehyde.

**Polymerization of phenylacetaldehyde in the dark and in ultraviolet light without a catalyst.** Phenylacetaldehyde samples were placed in a thermostat which was maintained at 21°; the thermostat and sample containers were constructed of glass which would allow light of wavelengths up to 280 mp to pass. The absorption range of 0.001 N phenylacetaldehyde in ethanol and of 1 N phenylacetaldehyde in ethanol extended to 290 mp and 330 mp, respectively, so that the radiation used was sufficient. Duplicate samples were placed in the thermostat, except that one was covered completely with a black cloth, and the other was exposed to the radiation. The aldehyde was exposed daily for several hours to the radiation of a mercury vapor lamp. After several months, the original thin oil in both flasks was changed into a heavy, viscous oil, which was not uniform. After 98 days the aldehyde solution contained 50% of the viscous oil, which was analyzed. Calcd. for (CgHgO)5; C, 80.00; H, 6.67; mol. wt., 600. Found: C, 78.86, 79.40; H, 6.94, 6.85; mol. wt. (acetic acid), 613, 598.

This work indicated the formation of a pentamer, but whether the
product actually had this formula remained unsettled, since the elemental analysis did not indicate whether the product was a mixture of substances or not. It was stated with certainty, however, that phenylacetaldehyde formed a polymer, without the aid of a catalyst, which had a molecular weight higher than those of the polymers formed in the presence of acidic or basic catalysts. The trimer, m.p. 155-156°, did not crystallize from the viscous oil upon seeding, and the refractive index of this oil was much higher than that of a solution of the trimer in phenylacetaldehyde.

In order to follow more closely the above polymerization process, the refractive indices of two samples of phenylacetaldehyde were measured daily. Both samples were kept at 21°, and one was exposed periodically to the radiation of a lamp. It was found that polymerization proceeded continuously in the dark without interruption. For the irradiated sample, the value of the refractive index remained unchanged during the radiation period, but increased between intervals of radiation. Thus the polymerization was apparently checked in the light and proceeded only in darkness. Further, it was concluded that polymerization proceeded rapidly during darkness, and that depolymerization occurred slowly during radiation. A comparison of the refractive indices of the two samples showed that the one which was irradiated periodically polymerized to a greater extent, and it was concluded that light acted indirectly as an accelerator to the polymerization process, but that the actual polymerization proceeded during the period of darkness following the irradiation.

The effect of heat was studied by sealing 1 ml. of phenylacetaldehyde in a tube and heating at 100° with the exclusion of light. The refractive index rose very rapidly and reached a value in 25 minutes which had previously required 20 days under the influence of ultraviolet light.

The trimer, m.p. 155-156°, of phenylacetaldehyde was obtained by exposing the monomer daily for periods of 5 to 10 minutes to the rays of refracted, diffused sunlight. This product was identical with that obtained by the action of 23% sulfuric acid on phenylacetaldehyde.

Stoermer, R. and Biesenbach, T.
The Cleavage of Carbon Monoxide and Carbon Dioxide from α-Phenoxy-β-phenylpropionic Acid.
Ber., 38, 1958-69 (1905).

The heating of phenylacetaldehyde at 190° in the presence of 16% alcoholic potassium hydroxide resulted in the formation of three crystalline substances and an oil. One of the crystalline products, m.p. 170-171°, corresponded in analysis to 1,3,5-triphenylbenzene. The filtrate obtained from this product was distilled to yield an oil, b.p. 157-160°, which was described as 1,3-diphenyltetramethylene. This oil, upon acidification with hydrochloric acid, yielded two crystalline products, m.p. 176° and m.p. 96°, which were not studied further.

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Stoermer, R. and Thier, C.
The Constitution of the so-called Diphenyl Cyclobutane.

Phenylacetaldehyde (10 g.) was heated on a steam bath for 2 hours with a solution of 5 g. of potassium hydroxide in 35 ml. of alcohol. The resulting dark yellow solution was extracted with ether, washed with water, and the solvent was removed. Distillation of the remaining oil yielded 5.8 g. (68%) of 1,3-diphenylpropene, b.p. 178-179° (14 mm.), which solidified when cooled and melted at 15-16°. The alkaline wash solution from this preparation contained products of a complex nature. Three crystalline substances which melted at 108-109°, 133°, and 165°, respectively, were isolated and assumed to be isomeric lactones.

Treibs, W. and Krumbholz, K.
Some Aldol and Condensation Reactions of Phenylacetaldehyde.

A sample of phenylacetaldehyde became viscous after several months and was subjected to exhaustive steam distillation. There remained a hard, brittle product which softened at 45-50°, and whose molecular weight corresponded to that of phenylacetaldehyde. Calcd. for C_{16}H_{16}O_{2}: mol. wt., 240.3. Found: mol. wt., 253.2, 261.3.

This product was kept for 20 hours in 88% formic acid at 20°, and yielded an oil which, upon fractional distillation, gave 30% of 2,4-diphenylcrotonaldehyde, b.p. 208-210° (16 mm.). Upon redistillation, this product formed crystals, m.p. 39°, and gave a semicarbazone, m.p. 170°. Calcd. for C_{16}H_{14}O: C, 86.46; H, 6.35; mol. wt., 222.3. Found: C, 86.02; H, 6.73; mol. wt., 227.3, 220.5.

2,4-Diphenylcrotonaldehyde was also prepared by adding 160 g. of phenylacetaldehyde to a mixture of 0.28 g. of acetic acid and 0.4 g. of piperidine in a little ethyl alcohol. After 12 hours the mixture was heated to gentle boiling under nitrogen for 2 to 3 hours and fractionated. The product, m.p. 39°, was obtained in 35% yield.

5-Hydroxy-2,4,6-triphenyl-2-hexenal, m.p. 196°, was obtained by adding 2 Normal alcoholic potassium hydroxide solution to 60 g. of phenylacetaldehyde dissolved in 100 ml. of ethyl alcohol, and allowing this mixture to stand for 2 days. Calcd. for C_{24}H_{22}O_{4}: C, 84.18; H, 6.49; mol. wt., 342.4. Found: C, 84.39; H, 6.48; mol. wt., 354.7, 338.5.

The liquid from which the above product, m.p. 196°, was obtained gave a resin which softened at 50-60°, and which corresponded in molecular weight to 3,5,7-trihydroxy-2,4,6,8-tetraphenylloctanal. Calcd. for C_{32}H_{20}O_{4}: mol. wt., 480.6. Found: mol. wt., 509.8; equiv. wt., 152.4 (based on active hydrogen).
By treating 15 g. of 3,5,7-trihydroxy-2,4,6,8-tetraphenyloctanal with 60 ml. of 88% formic acid and fractionating, there was obtained an oil, b.p. 208-210°, which crystallized from alcohol and melted at 94°. This substance formed a semicarbazone, m.p. 198°, and was assumed to be a stereoisomer of 2,4-diphenylcrotonaldehyde, because of its analysis and molecular weight. Calcd. for C_{16}H_{14}O: C, 86.46; H, 6.35; mol. wt., 222.3. Found: C, 86.65; H, 6.18; mol. wt., 204.7.

Young, D. C., Assignor to the Dow Chemical Company.
Method for Stabilizing and Purifying Phenylacetaldehyde.

Phenylacetaldehyde is converted to the trimer, m.p. 154-156°, by the action of hydrogen fluoride, boron trifluoride, and compounds which generate either of these agents. The monomeric aldehyde is regenerated by rapid distillation of the trimer at atmospheric pressure. Decomposition of the trimer begins slightly above 154-156°, and the aldehyde distils at 195-197°.

The conversion of phenylacetaldehyde to the trimer may be conducted in such solvents as benzene, chlorobenzene, carbon tetrachloride, petroleum, and naphtha, but a solvent is not necessary.

In a typical experiment, 180 g. of anhydrous HF was added to 18 pounds of 80% phenylacetaldehyde under continuous stirring. After 2 hours, an additional 80 g. of HF was added and stirring was continued for an additional 1.5 hours. The HF was neutralized with potassium carbonate, and the thick mixture was thinned with methyl alcohol and filtered, then washed with methyl alcohol and dried. There was obtained a 78% yield of the trimer, m.p. 154-156°.

The pure trimer (77 g.) was heated rapidly at atmospheric pressure so that phenylacetaldehyde was flash distilled. The pot temperature rose to 290° toward the end of the distillation, and the vapor temperature remained near 195-197°. The yield of phenylacetaldehyde was 92%, based on the trimer.
SELECTED BIBLIOGRAPHY

ANNOTATED AND ALPHABETIZED ACCORDING TO AUTHORS

THE TRIMERIZATION OF ALIPHATIC ALDEHYDES
Ethyl orthoformate (45.0 g., 0.31 mole) was caused to react with 48.1 g. (0.222 mole) of the trimer, b.p. 80° (1 mm.), n\text{D}^{20} 1.4487, of isobutyraldehyde. There was obtained 42.0 g. (78%) of colorless liquid, b.p. 61° (1.5 mm.), n\text{D}^{20} 1.4321, d\text{D}^{20} 0.9162. This material did not react with metallic sodium, potassium permanganate or bromine in carbon tetrachloride solution. Fehling and Tollens tests were also negative. On long standing, the liquid produced a weak color with fuchsin reagent. Infrared analysis indicated that oxygen was present only in the form of ether linkages. Calcd. for C\textsubscript{14}H\textsubscript{28}O\textsubscript{3}: C, 68.82; H, 11.53; ethoxy, 18.40; mol. wt., 244; M\text{R}D, 69.60. Found: C, 68.97; H, 11.56; ethoxy, 18.59; mol. wt., 238; M\text{R}D, 69.23.

These properties are those to be expected of 2,4-diisopropyl-5,5-dimethyl-6-ethoxy-1,3-dioxane.

Freshly distilled propionaldol (58.1 g., 0.5 mole) was caused to react with an excess of ethyl orthoformate. Distillation of the product gave two distinct fractions and a residue which was discarded. There was obtained 12.0 g. of the lower boiling fraction, b.p. 86° (14 mm.), n\text{D}^{20} 1.4253, d\text{D}^{20} 0.9230. These data, together with the correct elemental and ethoxy analyses, molecular weight, and molecular refractivity, led to the conclusion that the compound was 2,4-diethyl-5-methyl-6-ethoxy-1,3-dioxane.

Under the influence of a trace of concentrated sulfuric acid, caproaldehyde polymerizes with evolution of heat. The polymer is a liquid at ordinary temperatures, but solidifies to a white, crystalline mass from a chilled chloroform solution.

The monomeric aldehyde is regenerated in part by distilling the polymer at reduced pressure.
Bagard, P.
A Method of Preparing Acyclic Aldehydes. II.

Nonanal polymerizes easily under the influence of sulfuric acid to give a product, which is a liquid at ordinary temperatures. Decanal polymerizes very readily when treated with a halogen or a proton acid. The product is a solid melting at 43°, and is fairly soluble in petroleum ether.

Blaise, E. and Guerin, G.
Undecyl Aldehyde.

Undecyl aldehyde, obtained by the oxidation of α-hydroxylauric acid, polymerized to form a solid which melted at 47-48°. The reaction was catalyzed with a few drops of sulfuric acid. The polymer was re-crystallized from ether, washed with sodium bisulfite solution, and any liquid was removed by distillation to leave a residue of pure polymer. Calcd. for (C_{11}H_{22}O)_{n}; mol. wt., 510. Found: mol. wt. (benzene), 468.44.

Fehling, H.
Two Isomeric Aldehyde Compounds.
Ann., 27, 319-22 (1838).

A quantity of crystals formed in a sample of acetaldehyde which had been kept at about 0° for several weeks. Upon slight warming, the greater part of the crystalline mass melted. The remaining crystals were found to sublime without melting when heated to 120°. There was only a very small amount of this latter substance, which gave the same analysis as acetaldehyde. Calcd. for (C_{2}H_{4}O)n; C, 54.53; H, 9.15. Found: C, 54.51; H, 9.05.

Fischer, H. O. L., Ahlstrom, L. and Richter, H.

2-p-Toluenesulfonyl-1,3-benzalglycerin. – 1,3-Benzalglycerin (20.5 g.) was dissolved in 6 ml. of dry pyridine and mixed with 21.6 g. of p-toluenesulfonyl chloride. After 12 hours the separated pyridine hydrochloride was dissolved in water by rapid stirring, and the crystalline mass which immediately formed was washed with water under suction. The substance was recrystallized from hot alcohol and yielded 33 g. (86.7%) of product, m.p. 125°. Calcd. for C_{17}H_{18}O_{5}: C, 61.08; H, 5.39; S, 9.58. Found: C, 61.16; H, 5.57; S, 9.67.
Benzal Compound of 1,3-Propenediol. - 2-p-Toluenesulfonyl-1,3-benzalglycerin (20 g.) is heated with the calculated amount of technical, pulverized alkali in a 750-ml. distilling flask at about 1 mm. One heats first for 0.5 hour at 110°; by slowly heating further, there occurs at about 125° a sudden gas evolution, and the unsaturated product, as well as an abundance of water (which obviously comes from the alkali), distils over. The thermometer shows a high temperature of 97° and the pressure increases to 20 mm. The distillate is caught in a cold receiver, and the yield of crude material is 4.8 g. The fraction boiling at 70-90° is redistilled and yields a water-white, unstable oil, b.p. 72-75° (0.1 mm.), nD20 1.5408, d19.8 1.126, MRd 45.24 (calcd. 45.40).

Calcd. for C10H10O2: C, 74.10; H, 6.2. Found: C, 74.32, 74.2; H, 6.07, 6.17.

Franke, A. and Wozelka, H.
The Polymerization of Aldehydes of the CnH2nO Series.

Butyraldehyde is polymerized in the cold upon treatment with anhydrous hydrogen chloride, yielding parabutyraldehyde, (C4H8O)3, in 80% yield. The product boils at 105-108° (12 mm.) and does not solidify when cooled to -20°. It is easily depolymerized by heating with a trace of hydrogen chloride.

In the same manner, paraheptanal, m.p. 20°, b.p. 200-203° (12 mm.), and paraisovaleraldehyde, m.p. -5°, b.p. 122-124° (12 mm.), are prepared in yields of 75% and 60%, respectively.

Molecular weights are reported for these trimers.

Hanschke, E.
A Compound from Aldol and Acetaldehyde.

It was shown that acetalaldol and acetaldehyde condense to form a cyclic hemiacetal.

A condensation product of acetaldehyde, consisting of approximately 51% acetalaldol and 47% acetaldehyde, reacted with acetic anhydride in pyridine to yield an acetate, b.p. 85-86° (11 mm.), which analyzed for 2,4-dimethyl-6-acetoxy-1,3-dioxane. Calcd. for C9H14O4: C, 55.15; H, 8.05; mol. wt., 174. Found: C, 54.91, 55.09; H, 7.83, 7.91; mol. wt., 168.

The corresponding benzoate, m.p. 90-91°, was prepared by reacting the crude condensation product with benzoyl chloride in pyridine. Calcd. for C13H16O4: C, 66.10; H, 6.71. Found: C, 66.32, 66.46; H, 6.84, 6.96.
2,4-Dimethyl-6-acetoxy-1,3-dioxane was hydrogenated in glacial acetic acid with palladium black as the catalyst. The reduction product was identified as acetaldehyde-butanediol-1,3-acetal by comparing the boiling point and refractive index with those values of the product which resulted from the reaction between acetaldehyde and 1,3-butanediol.

Herrmann, W. O. and Haehnel, W.
Preparation of an Organic Compound from Vinyl Acetate.

The treatment of vinyl acetate with alkali hydroxide below 15° results in the formation of a new compound, in addition to sodium acetate. For 1 mole of vinyl acetate used, 0.6-0.8 mole of alkali is favorable. Further, for 1 mole of vinyl acetate, 7-10 moles of water should be used. The product has the formula, C₈H₁₀O₂, has a density of 1.08, is colorless and somewhat viscous, and boils at 92-100° (22-14 mm.).

In the presence of water, the compound yields one mole of acetic acid, one mole of acetaldehyde, and one mole of crotonaldehyde. In the presence of small amounts of concentrated sulfuric acid, the compound reacts with n-butyl alcohol to yield n-butyl acetate, acetaldehyde dibutylacetal, and crotonaldehyde dibutylacetal. Yellow mercuric oxide reacts with the compound to yield white, crystalline mercuric acetate. Because of its ability to split off aldehyde, the compound shows a high reactivity toward organic bases, and yields bisulfite compounds.

"Vinyl acetate (1036 g.) was emulsified with 500 g. of water in a stirring vessel. To this emulsion was added dropwise, over a period of 1.75 hours, a solution of 360 g. of sodium hydroxide in 1200 g. of water. Continuous stirring was applied and the temperature was maintained by exterior cooling at 0-10°. After the addition was complete, the mixture was stirred for another 0.5 hour. There appeared two phases, and the upper one was separated. The remaining vinyl acetate in this phase was distilled at normal pressure by heating at 85°. The remaining compound distilled between 92-100° (22-14 mm.), and gave a yield of 493 g. of pure product. Sodium acetate is obtained as a by-product, and can be obtained from the water phase."

Herrmann, W. O. and Haehnel, W.
Preparation of Acetaldehyde Divinylacetel.

The compound, C₈H₁₀O₂, prepared by treating vinyl acetate with sodium hydroxide below 15°, exhibits the two components, acetic acid and C₆H₁₀O₂. The acetic acid in C₈H₁₀O₂ can be replaced by heating the compound with other organic acids in the manner:

\[
\text{Acid I} + \text{C}_{6}\text{H}_{10}\text{O}_{2} \rightarrow \text{Acid II} \rightarrow \text{Acid II} + \text{C}_{6}\text{H}_{10}\text{O}_{2} + \text{Acid I}
\]

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Acid I refers to a monobasic lower fatty acid, especially acetic acid, compounded with $\text{C}_6\text{H}_{10}\text{O}_2$ to give one molecule. Acid II is another free organic acid. This reaction can also be carried out if Acid II is a dibasic acid which is soluble in Acid I+$\text{C}_6\text{H}_{10}\text{O}_2$. In this case, however, the compounds represented by Acid II+$\text{C}_6\text{H}_{10}\text{O}_2$ do not distill. At elevated temperatures, cleavage occurs according to the following equation:

$$\text{Acid II} + \text{C}_6\text{H}_{10}\text{O}_2 \rightarrow \text{Acid II} \rightarrow \text{Acid II} \rightarrow \text{C}_6\text{H}_{10}\text{O}_2$$

The dibasic acid is regenerated and remains in the reaction flask while the compound, $\text{C}_6\text{H}_{10}\text{O}_2$, distils off. This product is a colorless liquid, b.p. 105° (720 mm.), $d_{20}^0$ 0.943, which has been assigned the structure of acetaldehyde divinylacetal.

"Adipic acid (109 g.) was dissolved in 261 g. of the compound, $\text{C}_8\text{H}_{14}\text{O}_4$, by warming, and the solution was further heated to about 170° and distilled at 12-17 mm. The distillate consisted of 257 g. of liquid, of which 84 g. was acetic acid and 173 g. was crude acetaldehyde divinylacetal. The crude product was purified by neutralizing the acetic acid with sodium carbonate solution, shaking with sodium hydroxide, drying over metallic sodium, and fractionating. The fraction distilling at 104-107° was analyzed. Calcd. for $\text{C}_6\text{H}_{10}\text{O}_2$: C, 63.2; H, 8.8. Found: C, 63.0; H, 8.7."

The same product was obtained when sebacic acid was used. In this case, the reaction mixture was heated only to 120° before the product was distilled, and the yield of acetaldehyde divinylacetal was not given.

Hibbert, H.
Use of Iodine as a Dehydrating and Condensing Agent.

Investigation of the different fractions obtained upon distillation of acetaldol, crotonaldehyde, or paraldol suggested the idea that crotonaldehyde and acetaldehyde might form a compound which would decompose into these two components upon repeated distillations.

With this in mind it seemed reasonable that acetaldol and acetaldehyde might also form an addition compound. Such a compound was expected to exist because distillation of the product, obtained by the alkaline-catalyzed condensation of acetaldehyde to a product thought to be acetaldol, generally gave yields of approximately 66% acetaldol and 33% acetaldehyde. The observed products would arise from the decomposition of the predicted addition compound when it was heated or distilled.
King, G.
The Oxidation of the 9,10-Dihydroxystearic Acids with Periodic Acid.

Nonaldehyde was prepared by the oxidation of 9,10-dihydroxystearic acid with periodic acid at 50-55°C. A fraction of 3.37 g. of the aldehyde, b.p. 85-90°C (20 mm.), was collected and steam distilled. After standing for 48 hours, the non-volatile residue from the steam distillation crystallized when alcohol was added and yielded 1.1 g. of colorless needles, m.p. 33.5°C. This compound was the trimer of nonanal, and was depolymerized by slow distillation in the presence of 30% sulfuric acid solution. Calcd. for (C9H18O)3: C, 76.0; H, 12.7; mol. wt., 426. Found: C, 75.9; H, 12.6; mol. wt. (Rast), 464.

Lacey, R. N. and Cooper, L. E. (to British Industrial Solvents, Ltd.).
Alcohols.

A process for the hydrogenation of 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane to produce isobutyl alcohol and 2,2,4-trimethyl-1,3-pentanediol is presented.

Crude 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane (282 parts) and 50% Raney nickel paste (50 parts) in isopropyl alcohol and acetic acid (5 parts) are agitated for 8 hours with hydrogen at 50-80°C. Hydrogen (4.5 parts) is absorbed and distillation of the product gives 80% of 2,2,4-trimethyl-1,3-pentanediol, b.p. 122°C (20 mm.), m.p. 32-33°C. After recrystallization from aqueous ethyl alcohol, the product melts at 51°C.

When the hydrogenation is performed without acetic acid, the crude starting material is previously dried over calcium chloride. In this case, 71% of 2,2,4-trimethyl-1,3-pentanediol and 43% of isobutyl alcohol are obtained.

LeSueur, H. R.
The Action of Heat on α-Hydroxycarboxylic Acids. I. α-Hydroxystearic Acid.

Margaraldehyde, m.p. 35-36°C, b.p. 203-204°C (26 mm.), was prepared by the thermal decomposition of α-hydroxystearic acid. After standing for a period of six weeks, the aldehyde had formed a polymeride, m.p. 77-78°C. The trimeric structure was indicated by molecular weight measurement. Calcd. for C51H102O3: mol. wt., 762. Found: mol. wt., 813.

When the polymeride was heated at 245-250°C for a short time, it was reconverted into margaraldehyde.
LeSueur, H. R.
The Action of Heat on $\alpha$-Hydroxycarboxylic Acids. II. $\alpha$-Hydroxymargaric Acid, $\alpha$-Hydroxypalmitic Acid, $\alpha$-Hydroxypentadecylic Acid, and $\alpha$-Hydroxymyristic Acid.

Pure specimens of tridecanal, myristaldehyde, pentadecanal, and pelmataldehyde each yielded solid compounds after being stored for a period of three to six weeks. The products were recrystallized from ether until the melting points remained constant, and were shown to be trimeric compounds by elemental analysis and molecular weight determination. They exhibited the following melting points: ($C_{13}H_{26}O_3$), m.p. 61.5°; ($C_{14}H_{28}O_3$), m.p. 65.5°; ($C_{15}H_{30}O_3$), m.p. 69-70°; and ($C_{16}H_{32}O_3$), m.p. 73°.

The trimers were reconverted almost quantitatively into the monomeric aldehydes by slow distillation at reduced pressure.

Mannich, C. and Nadelmann, A. H.
Hydrogenation of Liquid Acid Anhydrides.

A polymer of lauraldehyde was prepared by the catalytic hydrogenation of lauric anhydride in the presence of hydrochloric acid. This compound melted at 57° and boiled at 238-242° (0.1 mm.). The same polymer was formed rapidly when lauraldehyde was allowed to stand exposed to the atmosphere. Small amounts of mineral acids hastened the formation of the polymer. Calcd. for ($C_{12}H_{24}O_n$): C, 78.18; H, 13.13. Found: C, 78.0; H, 13.0.

The polymer was stable when heated, steam distilled, or warmed with dilute or concentrated sulfuric acid. It was depolymerized to lauraldehyde by distillation at high vacuum in the presence of a little phosphorus pentoxide.

Marvel, C. S., Harmon, J. and Riddle, E. H.
The Condensation of Acetaldehyde and Vinyl Acetate.

A cyclic acetal, 2,4-dimethyl-6-acetoxy-1,3-dioxane, was prepared by the sodium-catalyzed reaction between acetaldehyde and vinyl acetate.

A mixture of 11 g. (0.25 mole) of acetaldehyde and a 4-mm. cube of sodium was allowed to react for 15 minutes, after which the unreacted sodium was removed and 22 g. (0.25 mole) of vinyl acetate was added. The mixture was clarified by the addition of 25 ml. of ethyl alcohol. After 2 days the unchanged reactants and ethyl alcohol were removed by distillation. The residue yielded 12 g. of product, b.p. 70-77° (6 mm.).
Redistillation yielded 10 g. (46%) of the acetal, b.p. 74-75° (6 mm.), n^20D 1.4310, d^20 1.0655, M_R 42.28 (calcd. 41.88). Calcd. for C_8H_14O_4:
C, 55.2; H, 8.05; mol. wt., 174. Found: C, 55.21; H, 8.16; mol. wt., 178, 181, 173.

The acetal was hydrolyzed to yield acetaldehyde, acetaldol, and acetic acid.

No reaction of propionaldehyde, butyraldehyde, isobutyraldehyde, or benzaldehyde was obtained under similar conditions. No reaction was effected between acetaldehyde and vinyl acetate when alcoholic potassium hydroxide, zinc chloride, barium hydroxide, sodium ethoxide, magnesium methoxide, sodium phenoxide, sodium carbonate, acetic acid, stannic chloride, or p-toluenesulfonic acid or hydrogen chloride in benzene were used as catalysts.

Orndorff, W. R.
Parapropionic and Metapropionic Aldehydes.
Am. Chem. J., 12, 353 (1890).

Hydrogen chloride was passed into propionaldehyde which was cooled in an ice-salt bath. Parapropionic aldehyde was readily formed, along with a little metapropionic aldehyde. The two forms were separated and the parapropionic aldehyde was fractionally distilled to yield a colorless liquid, b.p. 169-171°, m.p. -20°. By heating the trimer with sulfuric acid or hydrogen chloride, the monomer was regenerated. Calcd. for (C_3H_6O)_3: mol. wt., 174. Found: mol. wt., 170, 170, 172, 172, 173.

Pascal, P. and Dupuy.
Physical Chemistry Studies on Mixtures of Water, Acetaldehyde, and Paraldehyde.

A study was conducted on the equilibrium of the acetaldehyde-paraldehyde reaction in the presence of sulfuric acid. The paraldehyde used in these experiments was highly purified by recrystallization and melted at 12.4°.

Pratesi, L.
Trioxymethylene.
Gazz. chim. ital., 14, 140 (1884).

Trioxymethylene (trioxane), m.p. 61°, b.p. 115°, was prepared by heating polyoxymethylene in a sealed tube with a trace of sulfuric acid at 115°. The product sublimed at ordinary temperatures. Calcd. for (CH_2O)_3: C, 40.00; H, 6.67. Found: C, 39.62, 39.74; H, 6.64, 6.69.
Saunders, R. H., Murray, M. J., Cleveland, F. F. and Komarewsky, V. I.  

It was suggested that the β-hydroxyaldehyde formulas may not be entirely correct representations for aldols.

The Raman spectrum of freshly prepared and distilled acetaldol shows no indication of either carboxyl or ethylenic absorption peaks. The gradual thickening of acetaldol cannot be due to the disappearance of a carboxyl group, and any aldol formula containing this feature must be incorrect or is truly representative only for a short time.

Similarly, there was never any discernible carboxyl group in propionaldol, even after a year. The Raman spectrum of the aged, viscous material was identical with that of a fresh sample.

The spectrum of butyraldol showed a carboxyl functional group which disappeared gradually, and after two weeks there was no trace of this group.

The aldols were prepared by cooling equal volumes of ether and the aldehyde to 0-5°, and then adding 2 drops of dibutylamine. To this stirred solution was added a 10% potassium hydroxide solution at such a rate that the temperature was maintained at 5-10°. When the temperature no longer tended to rise upon adding more alkali, the reaction was assumed to be complete. The ether solution was neutralized with 5% sulfuric acid, dried over sodium sulfate, and the aldol was distilled at reduced pressure.

Saunders, R. H., Murray, M. J. and Cleveland, F. F.  
The Aldol Condensation. II. The Reaction of Isobutyraldehyde with its Aldol.  

"Experimental work with the aldols is complicated by the fact that even such ordinary treatment as distillation may either eliminate water to produce the unsaturated compound or dealdolize the material to the simple aldehyde. To obviate part of this difficulty the present work has been confined to 2,2,4,4-tetramethylaldol (isobutyraldol) which, because of the two methyl groups in the alpha position, has practically no tendency to eliminate water during distillation.

According to the literature, the action of potassium hydroxide on isobutyraldehyde at or below room temperature gives two main condensation products: a dimer that is 2,2,4,4-tetramethylaldol, and a trimer which has been identified as 2,2,4-trimethyl-3-hydroxypentyl isobutyrate. The structure of the aldol seems to have been fairly well established by means of a number of derivatives and by the ease of decomposition into isobutyraldehyde. The ester, on the other hand,
has been identified by some investigators by the fact that it is converted to the salt of isobutyric acid and to 2,2,4-trimethyl-1,3-pentanediol when refluxed with alcoholic alkali. Such treatment is standard procedure for identifying esters, but it will be shown in the following discussion that in the present case the conclusions drawn from this test were not justified. Actually, this isobutyraldehyde trimer may not have been the ester at all, and failure to recognize this has been the cause of much confusion, not only in the condensation of isobutyraldehyde, but also in the condensation of other aldehydes as well."

Mixture of 2,2,4,4-tetramethylaldol and isobutyraldehyde slowly became viscous and after several days a quantity of isobutyraldehyde trimer was isolated. This transition was followed by Raman spectra, and the lines of the aldol-aldehyde mixture gradually gave way to those characteristic of the trimer.

Distillation of the crude condensation product of isobutyraldehyde in the presence of small amounts of acids or bases yielded approximately equal molar quantities of 2,2,4,4-tetramethylaldol, b.p. 89-90°C (13 mm.), and isobutyraldehyde. Distillation in the absence of catalysts gave the trimer, b.p. 110-111°C (8 mm.), n20 1.4461, d4 0.9670, in yields of 80% and above. The undistilled product, with or without a catalyst, exhibited a spectrum identical with that of the trimer. Thus the crude aldolized product contained no aldol as such, but exhibited only the form of the trimer, 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane.

When the trimer was refluxed with 15% alcoholic potassium hydroxide solution, both isobutyric acid and 2,2,4-trimethyl-1,3-pentanediol were isolated. The course of this reaction possibly involved the dissociation of the trimer into isobutyraldehyde and isobutyraldol, followed by a crossed Cannizzaro reaction.


The crude aldolized reaction products from acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde were each treated with equal volumes of acetic anhydride and pyridine, and the acetates of the corresponding 6-hydroxy-1,3-dioxanes were obtained in about 70% yields. The acetates had the following properties: 2,4-dimethyl-6-acetoxo-1,3-dioxane, b.p. 85.5°C (10 mm.), n20 1.4278, d20 1.068; 2,4-diethyl-5-methyl-6-acetoxo-1,3-dioxane, b.p. 100°C (7 mm.), n20 1.4328, d20 1.009; 2,4-diisopropyl-5-ethyl-6-acetoxo-1,3-dioxane, b.p. 114°C (3 mm.), n20 1.4378, d20 0.9758; and 2,4-diisopropyl-5,5-dimethyl-6-acetoxo-1,3-dioxane, b.p. 93.5°C (2 mm.), n20 1.4355, d20 0.9726.
A mixture of 300 g. of 1% methyl alcoholic hydrogen chloride and 60 g. of 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane yielded, after 18 days, 19 g. of the corresponding methyl ether, b.p. 110° (20 mm.), n\textsuperscript{25}D 1.4310, d\textsuperscript{25} 0.9220, MRD 64.70 (calcd. 64.98).

An aldol condensation was conducted with 14.4 g. of isobutyraldol. There was obtained 8.7 g. of 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane and 3.5 g. of a white solid which, after recrystallization from petroleum ether, melted at 105-107°. This was the same melting point found for the paraldol of isobutyraldol when the same solvent was used. When different solvents were employed, the melting point varied as much as 15°. This variation was attributed to the presence of isomeric forms of the product.

Shilov, E. A.
The Limit of the Aldol Condensation of Acetaldehyde.

The aldol condensation of acetaldehyde was carried out by using 2.5% sodium hydroxide solution as the catalyst. It was concluded that the condensation of acetaldehyde to acetaldol is not caused by conditions of an equilibrium, but by the formation of a compound resulting from the reaction between acetaldehyde and acetaldol. The addition compound was assigned the structure of a cyclic hemiacetal, 2,4-dimethyl-6-hydroxy-1,3-dioxane, although no evidence for such a structure was presented.

Spath, E., Lorenz, R. and Freund, E.
Derivatives of Aldol and of Crotonaldehyde. V. An Addition Product of Acetaldehyde with Aldol.

The formation of paraldol from monomeric acetaldol was described as proceeding through an acetaldol hydroxy group and the carbonyl group of another acetaldol molecule to form a hemiacetal type of structure upon ring closure. Other simple aldehydes should react with acetaldol to form compounds having a similar cyclic structure.

To 20 g. of paraldol was added 25 ml. of acetaldehyde, and the mixture was placed in a sealed tube and heated for 4 hours at 100°, then was allowed to remain at 18° for 24 hours. There was obtained 20.5 of a product, b.p. 68-72° (2 mm.), which corresponded to a trimer of acetaldehyde. Two aldehyde determinations, in which acetaldehyde was determined quantitatively as its p-nitrophenylhydrazone, gave values of 32% and 31.6%, as compared with the theoretical acetaldehyde value of 33.3%.

By repeated distillations of the dioxane, or upon long standing in dry air, this compound was partially converted into acetaldol, as
evidenced by the lowering of the boiling point of the product in successive distillations.

The dioxane formed an acetate, b.p. 86° (10 mm.), and a crystalline benzoate, m.p. 92-93°.

Spath, E., Lorenz, R. and Altmann, E.
Derivatives of Aldol and of Crotonaldehyde. VII. The Stritar Condensation Product from Isobutyraldehyde and Benzaldehyde.

A mixture composed of 72 g. of isobutyraldehyde, 53 g. of benzaldehyde, and 135 ml. of saturated potassium carbonate solution was shaken for 30 hours at 17°. The crystalline mass which formed was taken up in ether, the solution was filtered, and the ether was removed under reduced pressure. There was obtained 116.5 g. of a white, crystalline product which, after two recrystallizations from petroleum ether, melted at 97-98.5°. The properties of this substance corresponded to 2-isopropyl-4-phenyl-5,5-dimethyl-6-hydroxy-1,3-dioxane. Calcd. for C₁₅H₂₂O₃: C, 71.97; H, 8.86. Found: C, 72.07; H, 8.50.

This compound formed an acetate, b.p. 145-150° (1 mm.), and a benzoate, m.p. 130°. Upon oxidation with potassium permanganate in pyridine, it yielded a small amount of α,α-dimethyl-β-hydroxy-β-phenylpropionic acid, m.p. 136.5°.

Distillation of the dioxane at 12 mm. gave α,α-dimethyl-β-hydroxy-β-phenylpropionaldehyde, m.p. 55-55.5°, and a quantity of benzaldehyde. The aldol thus formed yielded a dimer, m.p. 143-144°, whose melting point was found to vary in different preparations. This dimer again yielded the aldol upon distillation at 1 mm., and yielded a diacetate, b.p. 180-190° (0.01 mm.), when treated with acetic anhydride in dry pyridine.

Spath, E. and Szilagyi, I.
Derivatives of Aldol and of Crotonaldehyde. X. Formisobutyraldol.

When 5 g. of dimeric formisobutyraldol was heated for 2 hours at 70° with 10 ml. of freshly distilled acetaldehyde, there was obtained 3 g. of product, b.p. 50° (1 mm.), consisting of 2,5,5-trimethyl-6-hydroxy-1,3-dioxane, which partially decomposed upon distillation. It was found advantageous to treat the crude reaction product with acetic anhydride in order to obtain the more stable acetate, b.p. 40-42° (1 mm.).

Similarly, when the product resulting from the reaction between 5 g. of dimeric formisobutyraldol and 17.6 ml. of propionaldehyde was

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acetylated, there was obtained 6 g. of 2-ethyl-5,5-dimethyl-6-acetoxyl-
1,3-dioxane, b.p. 50-52° (1 mm.).

In the same way, from 5 g. of dimeric formisobutyraldol and 22 ml.
of isobutyraldehyde there was obtained, after acetylation, 4.7 g. of
2-isopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane, b.p. 65-66° (1 mm.).

Structures were assigned to the various products on the basis of
elemental analyses.

Spath, E., Lorenz, R. and Freund, E.
Derivatives of Aldol and of Crotonaldehyde. XI. Aliphatic Aldols.

The base-catalyzed condensations of propionaldehyde, butyral-
dehyde, and isobutyraldehyde were effected by stirring the aldehyde
with saturated potassium carbonate solution. The dioxanes thus
prepared gave the phenylhydrazones of the corresponding aldehyde and
aldol when treated with phenylhydrazine; formed stable acetates upon
treatment with acetic anhydride; and yielded the corresponding aldehyde
and aldol when distilled repeatedly in the presence of adipic acid.
The p-nitrophenylhydrazones of the liberated aldols were prepared. The
physical properties of the dioxanes, their acetates, and the aldols
obtained from the above aldehydes and from acetaldehyde are shown below.

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<th>Aldehyde Used</th>
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<td>68-70° (2)</td>
<td>1.4407</td>
<td>86° (10)</td>
<td>1.4301</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>89-90° (1.2)</td>
<td>1.4463</td>
<td>85-5.5° (1.4)</td>
<td>1.4355</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>decomp.</td>
<td>1.4495</td>
<td>105-6° (1)</td>
<td>1.4405</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>95° (0.8)</td>
<td>1.4487</td>
<td>93-3.5° (0.9)</td>
<td>1.4381</td>
</tr>
</tbody>
</table>

Spath, E., Lorenz, R. and Freund, E.
Derivatives of Aldol and of Crotonaldehyde. XII. Aldoxanes.

Monomeric aldehydes and aldols, on standing for several hours to
days, yield 4-methyl-6-hydroxy-1,3-dioxane and its homologs. Because
of the difficulty of purification, these compounds have been studied in the form of their acetates.

Acetaldol (5.06 g.) and 200 ml. of 3.8% ethereal formaldehyde solution were mixed and allowed to stand at 18° for 24 hours, after which the lower boiling components were removed and the crude reaction product was acetylated with a mixture of 6 ml. of acetic anhydride and 6 ml. of pyridine. Rectification yielded 4-methyl-6-acetoxyl-1,3-dioxane, b.p. 59-60° (0.8 mm.), nD20 1.4306. This compound (2.6 g.) was prepared also by acetyllating the product which formed by heating 20 g. of paraldol and 15 g. of trioxane on a water bath for 20 hours. When the acetate was heated at 50° with 2% hydrochloric acid, acetaldelyde and crotonaldehyde were formed.

A mixture of 10 g. of acetaldol and 11 ml. of propionaldehyde was treated with acetic anhydride after 24 hours. There was obtained 11.98 g. of 2-ethyl-4-methyl-6-acetoxyl-1,3-dioxane, b.p. 67.8° (1.3 mm.), nD20 1.4330. The benzoate melted at 46.5-47.5°.

By the method described above, 9.47 g. of acetaldol and 11.5 g. of butyraldehyde gave 2-propyl-4-methyl-6-acetoxyl-1,3-dioxane, b.p. 81.5-82.5° (1.2 mm.), nD20 1.4330. Similarly, from 10.12 g. of acetaldol and 12 ml. of isobutyaldehyde there was obtained 11.1 g. of 2-isopropyl-4-methyl-6-acetoxyl-1,3-dioxane, b.p. 64.5-65.5° (0.9 mm.), nD20 1.4305. The benzoate melted at 67.5-68.5°. Acetaldol and isovaleraldehyde yielded 2-isobutyl-4-methyl-6-acetoxyl-1,3-dioxane, b.p. 85-95° (1 mm.). From acetaldol and heptanal was obtained 2-hexyl-4-methyl-6-acetoxyl-1,3-dioxane, b.p. 114-115° (1.2 mm.), nD20 1.4400.

A mixture of 5.15 g. of propionaldol and 5 ml. of acetaldehyde was allowed to stand for 39 hours and was acetylated to yield 7.19 g. of 2,5-dimethyl-4-ethyl-6-acetoxyl-1,3-dioxane, b.p. 69-70° (1 mm.), nD20 1.4350.

Similarly, 4.7 g. of butyraldol and 6 ml. of acetaldehyde gave 6.85 g. of 2-methyl-5-ethyl-4-propyl-6-acetoxyl-1,3-dioxane, b.p. 77-78° (0.4 mm.), nD20 1.4388.

Isobutyaldehyde (4.34 g.) and 5.1 ml. of acetaldehyde gave, after acetylation, 5.07 g. of 2,5,5-trimethyl-4-isopropyl-6-acetoxyl-1,3-dioxane, b.p. 62-63° (0.3 mm.), nD20 1.4389.

Stephán, H.
A New Synthesis of Aldehydes.

It is stated that myristaldehyde, m.p. 23°, palmitaldehyde, m.p. 34°, and stearaldehyde, m.p. 38°, all polymerize readily to yield white solids melting at 65°, 73-74°, and 80°, respectively.
A mixture of equal molecular proportions of isobutyraldehyde and benzaldehyde was shaken with an equal volume of saturated potassium carbonate solution for about 36 hours and yielded a solid condensation product. The compound was dissolved in benzene, washed with water, dried over calcium chloride, and concentrated under reduced pressure over paraffin. The yield was about 75%. By careful recrystallization from aqueous acetic acid, the product was obtained as fine needles, m.p. 94°. It analyzed for $C_{15}H_{22}O_3$ and had a molecular weight corresponding to a product formed from two moles of isobutyraldehyde and one mole of benzaldehyde.

The condensation product was partially converted into benzaldehyde and isobutyraldehyde by distillation at reduced pressure in the presence of 10% sulfuric acid. When it was heated with dilute potassium hydroxide solution, the odor of benzaldehyde was apparent.

Attempts to establish the presence of a free aldehyde group by the preparation of an oxime were unsuccessful, for there was obtained only a quantity of isobutyraldehyde and a mixture of the oximes of benzaldehyde and isobutyraldehyde. The condensation product yielded a phenylhydrazone, m.p. 117°, which corresponded in analysis to the phenylhydrazones of an aldol, formed from one mole of isobutyraldehyde and one mole of benzaldehyde.

Permanganate oxidation of the unknown condensation product gave a mixture of benzoic acid, isobutyric acid, and a small amount of $\omega,\omega$-dimethyl-$\beta$-hydroxy-$\beta$-phenylpropionic acid, m.p. 133°, which was identified by conversion to the silver and barium salts.

The unidentified condensation product was believed to be one in which a second molecule of isobutyraldehyde was bound loosely in some way to the aldol formed from benzaldehyde and isobutyraldehyde.

Uelzmann, H.
The Structure of the Hydrolysis Product, $C_9H_{14}O_4$, from Vinyl Acetate.

Vinyl propionate (1000 g.) was stirred vigorously for 100 minutes in 400 ml. of water at 5-10° while 266 g. of potassium hydroxide, dissolved in 800 ml. of water, was added. An additional 100 g. of vinyl propionate was added after 1 hour. The mixture was made weakly acidic with acetic acid and the upper layer was dried over sodium sulfate. Distillation yielded 400 g. (64%) of $2,4$-dimethyl-$6$-propionoxy-1,3-dioxane, b.p. 108-114° (20 mm.). The pure product boiled at 110° (17 mm.). The structural assignment was based on the elemental analysis. Calcd. for $C_9H_{16}O_4$: C, 57.38; H, 8.57. Found: C, 57.57; H, 8.57.
It was suggested that the product, C₇H₁₄O₄, isolated after the saponification of vinyl acetate (Herrmann and Haehnel, German Patent 844,441), was the known 2,4-dimethyl-6-acetoxyl-1,3-dioxane.

Villani, F. J. and Nord, F. F.
Glycol Esters from Aldehydes.

Simple esters, polymers, aldols, glycol monoesters, and 6-hydroxy-1,3-dioxanes have reportedly been isolated from the condensation of aldehydes, the product depending on the nature of the condensing agent. This work describes the preparation of both the dioxanes and glycol esters from acetaldehyde and isobutyraldehyde.

For acetaldehyde, potassium hydroxide and diethylamine were used in preparing the 1,3-dioxane, and magnesium aluminum ethoxide was used for preparing the glycol monooester. For isobutyraldehyde, potassium hydroxide and diethylamine were used in preparing the 1,3-dioxane, and magnesium aluminum isobutoxide was used for the glycol ester. The products were shown not to be identical.

In preparing the glycol esters, a quantity of the coordination catalyst equal to 5% of the weight of aldehyde was added to the aldehyde in a flask, which was quickly stoppered and cooled under the tap. The mixture was allowed to stand for 24 hours at room temperature, and then was fractionated without further treatment.

The dioxanes were prepared by adding 10% potassium hydroxide solution to a mixture of aldehyde, ether, and a few drops of diethylamine at 5-10°. The ether layer was then separated, washed with water, dried over sodium sulfate, and the product was distilled.

Wakayama, S.
Higher Aliphatic Aldehydes. I. Octanal.

The trimer, m.p. 33.5-34°, is prepared from octanal by the use of such catalysts as ferric chloride, sulfuric acid, hydrochloric acid, aluminum chloride, or stannous chloride dihydrate. The product does not give the typical aldehyde reactions, but regenerates the monomeric aldehyde when distilled with traces of sulfuric or hydrochloric acid.

Weidenbusch, H.
Products from the Action of Alkali and Acids on Acetaldehyde.

Paraldehyde was synthesized by treating acetaldehyde with a trace of sulfuric acid. When the reaction flask was cooled to 0°,
a quantity of needle-like crystals, presumably metaldehyde, was observed. The liquid portion was separated, washed with water, dried, and distilled to yield paradehyde, b.p. 125°. Upon warming this trimer with a trace of sulfuric acid, acetaldehyde was regenerated. Calcd. for \((\text{C}_2\text{H}_4\text{O})_3\): C, 54.53; H, 9.15. Found: C, 54.15, 54.35; H, 9.13, 9.11.
VITA
George Neal Grammar is the son of Mr. and Mrs. George Cornelius Grammar of Benton, Louisiana. He was born in Dallas, Texas on February 2, 1931. His primary education was obtained in the public schools of Dallas, Texas, Rocky Mount, Louisiana, Edgewood, Texas, and Benton, Louisiana. He was graduated from the grade school of Benton, Louisiana in May, 1944.

In high school, he was a member of the varsity basketball, softball and track teams, and represented Benton High School in English, Spanish and chemistry in scholastic competition rallies held at Ruston, Louisiana. Upon graduation from Benton High School in May, 1948, he received the American Legion Award and a scholarship to Northwestern State College of Natchitoches, Louisiana, where he entered in September, 1948. He was a member of Phi Kappa Nu, social fraternity, and served as president of this organization during the year, 1950-1951. Before graduating, he was named to the Senior Hall of Fame. He received the degree of Bachelor of Science in Chemistry in May, 1952.

In September, 1952, he entered the Graduate School of Louisiana State University and worked under the direction of Professor J. J. E. Erickson until he received the degree of Master of Science in Chemistry in August, 1954.

He was married to Martha Jane Ivey, a graduate of Louisiana State University, on August 14, 1954. In the following September, he again entered the Graduate School of Louisiana State University, where he served as a teaching assistant and was given a University Graduate Assistantship in Chemistry and an Esso Standard Oil Company Research Fellowship during the terms of 1954-1955 and 1956-1957, respectively. He has been employed since May 1, 1958, as a Research Chemist in the Department of Research and Development of the Ethyl Corporation. He is now a candidate for the degree of Doctor of Philosophy in Chemistry.
EXAMINATION AND THESIS REPORT

Candidate: George Neal Grammer

Major Field: Organic Chemistry

Title of Thesis: The Trimerization of Aldehydes

Approved:

[Signatures]

J. L. E. Erickson
Major Professor and Chairman

Richard Russell
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

May 9, 1958