

**Potentiometric Titration.**—Polyacrylic anhydride (B) (0.1838 g.) was allowed to dissolve in carbonate-free sodium hydroxide solution (0.338 *N*, 100 ml.) over a period of two days, carbon dioxide-free nitrogen being bubbled slowly through the solution during this time. The excess sodium hydroxide was then estimated by potentiometric titration (glass and calomel electrodes) with hydrochloric acid solution (0.05 *N*). The sodium hydroxide solution consumed in the reaction (77.0 ml.) represents reaction with 90% of the anhydride units. Direct potentiometric titration of a solution of polyacrylic anhydride with sodium hydroxide solution was less efficient, reaction occurring with only 80% of the anhydride units in this case.

**Determination of X-Ray Diffraction Patterns.**—For this work polyacrylic anhydride (B) was hydrolyzed to polyacrylic acid by allowing it to dissolve in water at 5° and removing the excess water by freeze-drying. The polyacid was ground to <200 mesh particle size and redried. Normal

polyacrylic acid was prepared by a potassium persulfate-initiated polymerization of acrylic acid in aqueous solution, and ground and dried as above. The two polyacrylic acid samples had identical infrared spectra. The X-ray diffraction patterns were run on a General Electric XRD-5 diffractometer, using copper  $K\alpha$  radiation at 50 KVP and 16 MA. A 1° beam slit and a 0.2° detector slit were used, with a 3° beam slit positioned in the Soller slit position preceding the detector slit. Figure 1 shows the diffraction patterns obtained.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

## The Spontaneous Polymerization of Phenylacetaldehyde<sup>1</sup>

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Phenylacetaldehyde polymerizes slowly to yield a crystalline trimer, which has been identified as a sesquiacetal, 2,4-dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane (I).

When phenylacetaldehyde is allowed to stand for several weeks it undergoes a gradual but noticeable change as evidenced by increased viscosity and other changes in physical properties. Over a longer period of time, apparently as the result of a spontaneous polymerization process, phenylacetaldehyde yields a very viscous oil from which a crystalline substance is continuously separating. Measurements<sup>2,3</sup> involving rates of change in physical properties appear to have been of little value in determining the nature of this process. Stobbe and Lippold<sup>2</sup> and later Treibs and Krumbholz<sup>4</sup> treated phenylacetaldehyde with alkali and obtained a number of viscous oils and resins, but efforts to identify them failed, and suggestions as to the structure of these substances are not convincing. Pound<sup>3</sup> 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.

The stabilization of phenylacetaldehyde against polymerization has been a problem of much concern to manufacturers and users of this substance, and our investigation has been directed toward the identification of the crystalline substance and the nature of the process by which it is formed. We have found that phenylacetaldehyde upon storage for a period of 8 to 10 months becomes very viscous, and there is deposited a solid which may be collected by filtration and purified to yield 20 to 30% of a well-defined crystalline substance melting at 114.5–115°. The filtrate continues 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. It was found that the rate of formation of this substance may be catalyzed by bases, and that potassium hydroxide at the rather critical concentration of 0.03% in phenylacetaldehyde increases the rate about fifty-fold, so that uniform yields of 25 to 30% may be obtained within 5 to 7 days, and much larger yields result over a longer period of time. Manifestly, this polymer is not identical with the paraldehyde-type trimer, 2,4,6-tribenzyl-*s*-trioxane (Ia), m.p. 155–156°, obtained by Stobbe and Lippold<sup>2</sup> 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 its structure correspond to that of a trimer of phenylacetaldehyde. It yields a monoacetate and a monobenzoate, and its infrared spectrum shows strong absorption bands at 2.98 and 8.74  $\mu$ , 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 phenylacetal-dol (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 phenylacetal-dol. Sesquiacetals of this type have been obtained as liquids by a number of workers<sup>5,6</sup> from acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde.

The proposed structure (I) for the trimer of phenylacetaldehyde was confirmed by reducing the

(1) Taken from a part of the dissertation submitted by G. N. Grammer in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Louisiana State University, June, 1958.

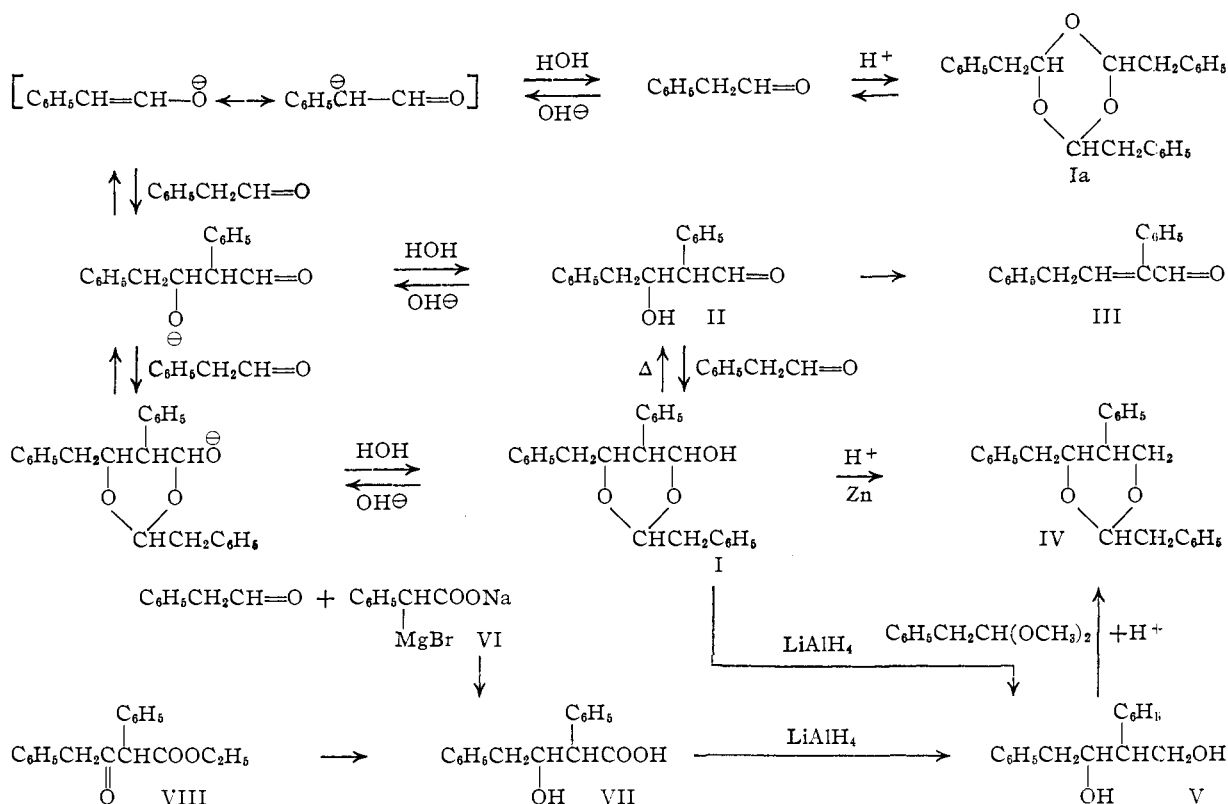
(2) H. Stobbe and A. Lippold, *J. prakt. Chem.*, **90**, 277 (1914).

(3) J. R. Pound, *J. Phys. Chem.*, **35**, 1174 (1931).

(4) W. Treibs and K. Krumbholz, *Chem. Ber.*, **85**, 1116 (1952).

(5) E. Spath, R. Lonrenz and E. Freund, *Ber.*, **76**, 57, 1196 (1943); E. Hanschke, *ibid.*, **76**, 180 (1943).

(6) R. H. Saunders, M. J. Murray, *et al.*, *THIS JOURNAL*, **65**, 1309, 1714 (1943); **66**, 206 (1944).



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.

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  $\beta$ -phenylethyl alcohol and also a crystalline substance, which was identified as 2,4-diphenyl-1,3-butanediol (V), the reduction product of phenylacetaldehyde, by comparing it with an authentic sample of V obtained by an independent method.  $\beta$ -Hydroxy- $\alpha,\gamma$ -diphenylbutyric acid (VII) was synthesized by treating phenylacetaldehyde with the Ivanoff reagent (VI),<sup>7</sup> 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.<sup>8</sup> 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 phenylacetaldehyde (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.

(7) D. Ivanoff and A. Spasoff, *Bull. soc. chim. France*, [4] **49**, 377 (1931); D. Ivanoff and N. I. Nicoloff, *ibid.*, [4] **51**, 1325 (1932).

(8) J. S. H. Davies and D. S. Morris, *J. Chem. Soc.*, 1697 (1947).

Thermal decomposition of the sesquiacetal I in a closed system at pressures ranging from 5 to 20  $\mu$ , 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 phenylacetaldehyde. The residue, a viscous, sticky liquid, presumably consisted of almost pure phenylacetaldehyde, 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  $\alpha,\gamma$ -diphenylcrotonaldehyde (III), which is the dehydration product of phenylacetaldehyde (II).

While the isolation and identification of these decomposition products seem to furnish ample evidence for the existence of phenylacetaldehyde, 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 phenylacetaldehyde (II), since it yields, when mixed with an equivalent quantity of phenylacetaldehyde, the sesquiacetal I.

Phenylacetaldehyde polymerizes spontaneously to yield a crystalline trimer I and also 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°, and gave an infrared spectrum identical, except for very small differences in the region of 10 to 12  $\mu$ , 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. Our experiments suggest that the 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<sup>9</sup>

**Spontaneous Polymerization of Phenylacetaldehyde.**—A sample of phenylacetaldehyde (Givaudan-Delawanna, Inc.) b.p. 81–83° (12 mm.),  $n_D^{20}$  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 then were 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  $\mu$  and for ether at 8.74  $\mu$ , but no carbonyl band.

*Anal.* Calcd. for  $(C_8H_8O)_3$ : 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  $\mu$ .

*Anal.* Calcd. for  $C_{26}H_{26}O_4$ : C, 77.59; H, 6.51. Found: C, 77.28; H, 6.60.

The benzoate melted at 158.5–159° after recrystallization from a benzene-petroleum ether mixture.

*Anal.* Calcd. for  $C_{31}H_{30}O_4$ : 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.),  $n_D^{20}$  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 the Trimer.**—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  $\mu$ , but no hydroxyl band near 3.0  $\mu$ .

*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 seems 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 mixture 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°,  $n_D^{20}$  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°. Recrystallization from ligroin and then from methyl alcohol raised the melting point to 100–101°. 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°, and a filtrate which was distilled to give 2.01 g. (60%) of  $\beta$ -phenylethyl alcohol, b.p. 219–221°;  $\alpha$ -naphthylurethane, m.p. 117.5°, mixed m.p. 117.5°. 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°. 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 and 9.33  $\mu$ , but no absorption in the 8.0–9.0  $\mu$  region.

*Anal.* Calcd. for  $C_{16}H_{18}O_2$ : 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  $C_{30}H_{28}O_4$ : C, 79.98; H, 5.82. Found: C, 79.84; H, 5.87.

(9) Melting points are corrected and boiling points are uncorrected. Microanalyses were determined by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer model 21, infrared spectrophotometer.

**B. By Catalytic Hydrogenation of the Trimer.**—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  $\beta$ -Hydroxy- $\alpha,\gamma$ -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.

**$\beta$ -Hydroxy- $\alpha,\gamma$ -diphenylbutyric Acid (VII). A. By the Reaction between Phenylacetaldehyde and the Ivanoff Reagent (VI).**—Isopropyl bromide (1.0 g.) was added to 4.8 g. (0.20 g. 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 140 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  $C_{16}H_{16}O_2$ : neut. equiv., 256.3. Found: neut. equiv., 256.

**B. By the Reduction and Subsequent Hydrolysis of Ethyl  $\alpha,\gamma$ -Diphenylacetoacetate (VIII).**—Two molecules of ethyl phenylacetate were condensed according to the method of Conant and Blatt<sup>10</sup> to yield VIII (71%), melting at 78–78.5° (lit.<sup>10</sup> m.p. 78°). This ester was converted into  $\beta$ -hydroxy- $\alpha,\gamma$ -diphenylbutyric acid (VII) according to the procedure of Davies and Morris<sup>8</sup> by the catalytic hydrogenation of VIII to yield, as an intermediate, ethyl  $\beta$ -hydroxy- $\alpha,\gamma$ -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.<sup>8</sup> 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°. This compound was not identified, but its analysis corresponds closely to that of an isomer of V. The infrared spectrum showed a hydroxyl band at 2.93  $\mu$ .

*Anal.* Calcd. for  $C_{16}H_{16}O_2$ : 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  $\mu$ , 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 phenylacetaldehyde) and 3.10 g. (93%) of distillate, which was identified as phenylacetaldehyde, b.p. 82.5–83.5° (13 mm.),  $n_D^{20}$  1.5227. When the distillation was conducted as above and continued for 24 hours, it was found that compound I almost completely dimerized 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, these several 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, 1.8 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  $\alpha,\gamma$ -diphenylcrotonaldehyde (III), m.p. 39.5–40° (lit.<sup>4</sup> m.p. 39°),  $n_D^{20}$  1.5938. The infrared spectrum showed strong absorption bands at 5.91, 6.11 and 6.24  $\mu$ .

*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)  $\mu$ .

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  $\mu$ ; 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)  $\mu$ .

**Distillation of the Polymeric Oil.**—The viscous oil (130 g.), obtained from the polymerization of phenylacetaldehyde, was distilled to yield the 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.

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(10) J. B. Conant and A. H. Blatt, *THIS JOURNAL*, **51**, 1227 (1929).