in the cold for 3 hr. and then allowed to warm to room temperature over a 3-hr. period. After dilution with 1 l. of water, the solid product was collected by filtration, washed with water, and vacuum dried to a constant weight of 82 g., m.p. 80–85°. Recrystallization from petroleum ether afforded 65 g. (65% yield) of 3,5,5-trimethyl-1,2-cyclohexanedione, m.p. 91–92° (lit.[2a] m.p. 92–93°).

5-Keto-3,3-dimethylhexanoic acid. To a 1-l., 5-neck, round-bottom flask equipped with stirrer, thermometer, *p*H electrodes (connected to a Beckman *p*H meter), and dropping funnel was charged a solution of 38.5 g. (0.25 mole) of 3,5,5-trimethyl-1,2-cyclohexanedione in 300 ml. of methanol. The mixture was stirred at 40° and treated with a solution of 7 g. of potassium hydroxide in 30 ml. of water. One mole of 30% hydrogen peroxide was then added dropwise with cooling over a 15-min. period. During this addition, the meter reading changed from 11 to 8, while indicator paper showed a change from 10 to 7. There was next added dropwise a solution of 21 g. of potassium hydroxide in 90 ml. of water at such a rate as to maintain the meter reading at 9.8–10.0 (true *p*H *ca.* 9). After 1 hr., the alkali addition was complete and another 0.5 mole of hydrogen peroxide was added to compensate for the 0.5 mole loss by decomposition (oxygen evolution followed by means of a wet test meter connected to the system). The mixture was stirred for 1 hr. longer at a steady *p*H of 9.8; no further addition of alkali was necessary

After 12 hr., the mixture was diluted with 200 ml. of water and concentrated under vacuum to a volume of 150 ml. The concentrate was acidified with 30% sulfuric acid and extracted with three 100-ml. portions of chloroform. The combined chloroform extracts were washed with water, dried over magnesium sulfate, and concentrated to low volume on the steam bath. Claisen distillation gave 21.9 g. (55% yield) of 5-keto-3,3-dimethylhexanoic acid, b.p. 73–74° (0.2 mm.), n_D^{20} 1.4469 [lit.[6] values: b.p. 162° (25 mm.), $n_D^{19.5}$ 1.4465] and 11.1 g. of *crude* α,γ,γ-trimethyladipic acid, b.p. 130–135° (0.2 mm.).

Anal. Calcd. for the keto acid, $C_8H_{14}O_3$: C, 60.6; H, 8.9; neut. equiv., 158. Found: C, 60.4; H, 8.9; neut. equiv., 161.

The keto acid gave a positive iodoform test and a crystalline *2,4-dinitrophenylhydrazone* derivative, m.p. 149–150°.

Anal. Calcd. for $C_{14}H_{18}O_6N_4$: N, 16.5. Found: N, 16.4.

The keto acid was cyclized to *dimedone* by the procedure described in the literature[4]: a solution of 5.0 g. of the material in 50 ml. of 72% sulfuric acid was held at 130° for 2 hr. and then poured into 350 ml. of water to precipitate 2.6 g. of dimedone, m.p. and mixed m.p. 145–147°.

α,γ,γ-Trimethyladipic acid. To a stirred solution of 92 g. (0.60 mole) of 3,5,5-trimethyl-1,2-cyclohexanedione, 0.2 g. of magnesium sulfate (stabilizer), and 26 g. (0.65 mole) of sodium hydroxide in 500 ml. of water was added dropwise over 1 hr. 72 g. (0.65 mole) of 30.6% hydrogen peroxide. The temperature was held at 40–45° by means of a cooling bath; the *p*H, as determined by indicator paper, remained about 11 throughout the addition. After completion of the addition, the mixture was allowed to stir for 1 hr. longer before filtration was carried out to allow the recovery of 43 g. (0.28 mole) of starting diketone, m.p. and mixed m.p. 91–92°. Carbon dioxide was bubbled through the filtrate to neutralize excess caustic, and extraction with chloroform gave an additional 2.5 g. of crude starting material. After concentration of the aqueous solution to a volume of 150 ml., it was acidified with 30% sulfuric acid, saturated with solid ammonium sulfate, and extracted with five 200-ml. portions of ether. The combined ether extracts were washed with saturated ammonium sulfate solution, dried over magnesium sulfate, and concentrated to low volume on the steam bath.

Claisen distillation at 0.5 mm. pressure afforded *A*, b.p. 100–140° (11 g.), *B*, b.p. 140–150° (33 g.), and a residue of 3 g.

Fraction *B* represents a 56% yield of *crude* α,γ,γ-trimethyladipic acid based on unrecovered starting material.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.6; neut. equiv. 94. Found: C, 57.9; H, 8.1; neut. equiv. 120.

Attempts to secure pure acid by recrystallization were unsuccessful, so 24 g. of the crude material was esterified with ethanol using *p*-toluenesulfonic acid catalyst. Distillation of crude ester through a 0.7 × 50 cm. glass spiral-packed column at 5 mm. gave 12.8 g. (23% yield based on unrecovered diketone) of *diethyl α,γ,γ-trimethyladipate*, b.p. 115–117°, n_D^{20} 1.4361 (lit.[7] values: b.p. 124°/9 mm.; n_D^{20} 1.4330).

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.9; H, 9.9; sapon. equiv., 122. Found: C, 63.9; H, 9.7; sapon. equiv., 122.

The *free acid* was obtained by saponification of the ester with alcoholic sodium hydroxide. It was recrystallized from chloroform-isopentane by allowing the solution to stand for several hours at room temperature, then at 0° for several hours, and finally at −20°. From 10 g. of ester there was obtained 4.5 g. (60%) of recrystallized acid, m.p. 67.5–68.5° (lit.[7] m.p. 68.6–69.2°).

Anal. Calcd. for $C_9H_{16}O_4$: Neut. equiv., 94. Found: Neut. equiv., 95.

The *dianilide* was prepared via the acid chloride (not purified) and recrystallized from benzene, m.p. 162.5–163.5° (lit.[7] m.p. 162.8–163.3°).

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[6] M. Qudrat-I-Khuda, *J. Chem. Soc.*, 207 (1929).

[7] S. F. Birch and E. A. Johnson, *J. Chem. Soc.*, 1493 (1951).

Products of the Reaction between γ-Butyrolactone and Phenylmagnesium Bromide

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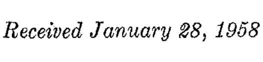
The reaction between phenylmagnesium bromide and γ-butyrolactone has been reported to yield 1,1-diphenylbutane-1,4-diol (I).[1] We have found that an increase in the concentration of acid used to decompose the Grignard adduct results in the formation of two other products, 2,2-diphenyltetrahydrofuran (II) and 1,1-diphenyl-1-butene-4-ol (III). These results are summarized in Table I.

$$(C_6H_5)_2C(OH)CH_2CH_2CH_2OH$$

I



$$(C_6H_5)_2\overline{CCH_2CH_2CH_2O}$$

II

$$(C_6H_5)_2C{=}CH{-}CH_2CH_2OH$$

III

Examples of the formation of cyclic ethers analogous to II seem to be rare in this type of reaction. This structure was assigned on the basis of the infrared spectrum, which shows the characteristic absorption of the tetrahydrofuran ring at about

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[1] C. Weizmann and F. Bergmann, *J. Am. Chem. Soc.*, **60**, 2647 (1938).

TABLE I

Acid Concentration	Product Yield, %		
	I	II	III
2.05M	80–90	—	—
3.50M	56–63	24–27	—
5.00M	35	16	15
6.50M	—	60	15
8.50M	—	—	26

1076 cm.$^{-1}$ and the absence of an olefinic double bond and a hydroxyl group. Also, this compound does not decolorize permanganate or add bromine. Its ultraviolet spectrum with the maximum at 211 mμ is almost identical to that of 2,2-diphenyl-4-*t*-butyltetrahydrofuran.[2]

It has been reported that the reaction between one mole of 2,4-dimethyl-2-hydroxypentanoic acid-4-lactone and three moles of phenylmagnesium bromide yielded 2,2,4-trimethyl-4-hydroxy-5,5-diphenyltetrahydrofuran.[3] In high dilution this reaction gave the trihydroxy open chain compound, 1,1-diphenyl-2,4-dimethylpentane-1,2,4-triol. With methylmagnesium iodide and γ-butyrolactone only 1,1-dimethylbutane-1,4-diol was reported to have been formed.[4] In this investigation it was shown that the course of the reaction is not affected by the molar ratio or the concentration of the reactants. It was also demonstrated that II is formed quantitatively from I by heating the diol above its melting point or by the action of mineral acid at room temperature. It is to be noted that neither of these procedures results in the conversion of I to III.

The unsaturated carbinol (III), which is formed when the Grignard adduct is hydrolyzed with strong hydrochloric acid (above 5.0M) can be obtained as the acetate by refluxing the adduct with acetic anhydride, followed by hydrolysis with hydrochloric acid of any concentration. This ester can be made, also, by refluxing a mixture of I and acetic anhydride in acetic acid.

Structure III was assigned to the unsaturated carbinol on the basis of its dibromo derivative, its oxidation with permanganate and ozone which yielded benzophenone, and its absorption spectra. The infrared spectrum does not show any absorption at 1650 cm.$^{-1}$ (characteristic of 1-butene). This eliminates the tertiary alcohol structure with a terminal double bond. The strong absorption at about 3335, 1600, and 1500 cm.$^{-1}$ indicates the presence of an associated hydroxyl group and a double bond in conjugation with a benzene ring. The ultraviolet spectrum shows the absorption maximum at 250 mμ with an ϵ value of 15,100 (log ϵ = 4.18), confirming the above conclusion regarding the position of the double bond.[5] Compound III was compared, also, to the isomeric tertiary unsaturated carbinol, 1,1-diphenyl-3-butene-1-ol, which was prepared by the method of Kharasch and Weinhouse[6] from allylmagnesium bromide and benzophenone. Permanganate oxidation of this compound yields 3-hydroxy-3,3-diphenylpropanoic acid. Its infrared spectrum shows the terminal methylene group (1650 cm.$^{-1}$) and a weaker absorption of the free hydroxyl group at 3500 cm.$^{-1}$ than the corresponding absorption of compound III at 3335 cm.$^{-1}$

The solid product formed by hydrolyzing the Grignard adduct with hydrochloric acid solutions of 3.5M and 5.0M (Table I) was shown to be a 70:30% mixture of I and II. This composition was assigned to this product on the basis of the similarity of its melting point (88–98°) to that of a synthetic mixture of the same composition. Also, the infrared spectra of these two mixtures are very similar, particularly, since they show approximately the same amount of absorption at 1076, 1447, 1487, 2685, 2950, 3015, 3340, and 3500 cm.$^{-1}$

EXPERIMENTAL

1,1-Diphenylbutane-1,4-diol (I). To the Grignard solution prepared in every case from 31.4 g. (0.2 mole) of bromobenzene and 4.8 g. (0.2 mole) of magnesium in 100 ml. of ether, a solution of 8.6 g. (0.1 mole) of γ-butyrolactone in 100 ml. of ether was added slowly either at 0° or at the reflux temperature of the mixture with vigorous stirring. Stirring was continued for 2 hr. To avoid formation of an agglomerated sticky product, the higher temperature is preferred. The alternate procedure, involving the addition of the ethereal solution of the Grignard reagent to the ethereal solution of the lactone, produced the same result. The cold reaction mixture was treated with 100 ml. of 2.05M hydrochloric acid. An equivalent amount of acetic acid gave the same result. The ethereal layer was separated and treated successively with water, 5.0% sodium hydroxide, and saturated sodium chloride before being dried over anhydrous calcium chloride. After removing the ether, 21.0–23.0 g. of crude material, m.p. 104–107°, was obtained. Recrystallization from light petroleum ether yielded 19.5–22.0 g. (80–90%) of I, m.p. 108–109°. This substance gave a bright red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44. Found: C, 79.56; H, 7.57.

The Schotten-Baumann reaction in dioxane-water solution yielded the monobenzoate, m.p. 123–124°. This product also gave a bright red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.77; H, 6.36. Found: C, 79.81; H, 6.55.

1,1-Diphenyl-1-butene-4-ol (III). Decomposition of the Grignard adduct with 25.0 ml. of 8.5M hydrochloric acid yielded 5.8 g. (26.0%) of III, b.p. 135–137° (0.6 mm.), n_D^{25} 1.5948, D_{25}^{25} 1.1024; infrared spectrum of liquid film on salt plate: 3335, 1600, and 1500 cm.$^{-1}$; ultraviolet spectrum in 95% ethyl alcohol: 250 mμ, ϵ = 15,100 (log ϵ = 4.18).

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(2) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951, Plate 118.

(3) M. Kohn, *Monatsh.*, **34**, 1729 (1913).

(4) A. Losanitsch, *Compt. rend.*, **153**, 390 (1911).

(5) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951, Plates 117 and 119.

(6) M. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.62; H, 7.26.

Treatment of a carbon tetrachloride solution of III with bromine yielded the dibromo derivative, m.p. 96–97°.

Anal. Calcd. for $C_{16}H_{16}OBr_2$: C, 50.00; H, 4.17. Found: C, 50.28; H, 4.24.

Permanganate oxidation and ozonolysis of III yielded benzophenone, identified by its 2,4-dinitrophenylhydrazone and phenylhydrazone.

Distillation of III resulted in the formation of an appreciable amount of a viscous, nonvolatile residue, which was readily soluble in ether and gave a bright red color with concentrated sulfuric acid.

The reaction between allylmagnesium bromide and benzophenone yielded 1,1-diphenyl-3-butene-1-ol, b.p. 135–138° (0.5 mm.), n_D^{25} 1.5875, d_{25}^{25} 1.0756; infrared spectrum of liquid film on salt plate: 3500 and 1645 cm.$^{-1}$ Kharasch and Weinhouse reported the boiling point, 150–155° (3.0 mm.) and no other constants.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.58; H, 7.35. This product yielded a dibromo derivative, m.p. 186–188°.

Anal. Calcd. for $C_{16}H_{16}OBr_2$: C, 50.00; H, 4.17. Found: C, 50.22; H, 4.32.

4,4-Diphenyl-3-butenyl acetate. The Grignard adduct was treated with 20.4 g. (0.2 mole) of acetic anhydride, and the mixture was allowed to stir for 2 hr. at the reflux temperature of the ethereal mixture. The cold mixture was then treated with 120.0 ml. of 1.7*M* hydrochloric acid. The ether layer, after being treated in the usual manner, yielded 14.5 g. (54.5%) of the unsaturated ester, b.p. 144–146° (0.8 mm.), n_D^{25} 1.5740, d_{25}^{25} 1.0960; infrared spectrum of liquid film on salt plate: 1735, 1600, and 1245 cm.$^{-1}$

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.20; H, 6.76. Found: C, 81.27; H, 6.82.

Saponification of this ester in ethanolic potassium hydroxide yielded the unsaturated carbinol (III), which was identified by its physical constants and its dibromo derivative, m.p. 96–97°. The odor of ethyl acetate was also very prevalent in the saponification mixture.

Method 2. A mixture of 10.0 g. (0.041 mole) of I and 4.2 g. (0.041 mole) of acetic anhydride in 15 ml. of glacial acetic acid was refluxed for 1 hr. The cold mixture was diluted with 100 ml. of water and extracted with 150 ml. of ether in two portions. The ether solution of the ester was treated with water, sodium bicarbonate, and saturated sodium chloride before drying it over anhydrous sodium sulfate. After removing the ether and a small amount of forerun, 1.5 g. of viscous liquid, b.p. 110–122° (0.6 mm.) was distilled. This substance solidified on standing, m.p. 64–68°. It did not depress the melting point of a pure sample of II (68–69°). Further distillation produced 6.3 g. (66.0%) of the unsaturated acetate, b.p. 140–143° (0.6 mm.), n_D^{25} 1.5738.

2,2-Diphenyltetrahydrofuran (II). Decomposition of the Grignard adduct with 32.0 ml. of 6.5*M* hydrochloric acid yielded a viscous liquid, which on cooling in an ice bath for 4 hr. deposited 10.7 g. of crystals, m.p. 64–68°. Recrystallization from light petroleum ether gave 9.8 g. of II, m.p. 68–69°. Distillation of the liquid which was filtered from the crude solid yielded 3.5 g. of product, b.p. 100–120° (0.5 mm.) which solidified, m.p. 66–68°, bringing the total yield to 13.3 g. (59.5%). Compound II gave a bright red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.45; H, 7.19; infrared spectrum in CCl_4: 1076 cm.$^{-1}$; ultraviolet spectrum in 95% ethyl alcohol: 211, 227, 252, 258, and 264 mμ.

Compound II did not decolorize permanganate or add bromine.

Distillation of the residue remaining after removing product II yielded 3.4 g. (15.0%) of III.

Method 2. Compound I (5.0 g.) was heated in an oil bath at 130° for 2 hr. On cooling, 4.5 g. (97%) of crystals, m.p. 66–68° was obtained. This product did not depress the melting point of II.

Method 3. A mixture consisting of 1.0 g. of I, 15.0 ml. of dioxane, 30.0 ml. of water, and 10.0 ml. of sulfuric acid was allowed to stand at room temperature for 6 hr. and then was poured into 200 ml. of water. This yielded 0.84 g. (92%) of product, m.p. 67–69°. This product did not depress the melting point of compound II.

Mixture of 1,1-diphenylbutane-1,4-diol (I) *and 2,2-diphenyltetrahydrofuran* (II). Decomposition of the Grignard adduct with 60.0 ml. of 3.5*M* hydrochloric acid yielded 20.0–22.0 g. (80–90%) of crude material, m.p. 88–98 . This product has the same melting point as a synthetic mixture of I and II in a 70:30 weight ratio. The infrared absorption curves of the two mixtures are very similar, showing approximately the same amount of absorption at 1076, 3340, and 3500 cm.$^{-1}$ in particular.

Attempts to separate the two components of the mixture by four crystallizations from cyclohexane yielded a fraction, m.p. 61–75° (pure II, m.p. 68–69°) and another product, m.p. 99–106° (pure I, m.p. 108–109°).

Mixture of 1,1-diphenylbutane-1,4-diol (I), *2,2-diphenyltetrahydrofuran* (II), *and 1,1-diphenyl-1-butene-4-ol* (III). Decomposition of the Grignard adduct with 43.0 ml. of 5.0*M* hydrochloric acid gave a product, which on cooling for 4 hr. in an ice bath deposited 12.3 g. (51.0%) of crystals, m.p. 86–96°, which is the 70:30% mixture of I and II. The liquid which was obtained by filtration was distllled, yielding 3.5 g. (15.0%) of compound III.

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Polarographic Reduction of Some Aliphatic Ketones

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Aliphatic ketones are reduced at a dropping mercury electrode only at fairly negative potentials. Neiman and Markina[1] reported the half-wave potentials of acetone and methyl ethyl ketone as −2.20 and −2.25 v., respectively, in 0.025 *M* tetramethylammonium iodide solution. Von Stackelberg and Stracke[2] reported the reduction of acetone and cyclohexanone in 0.05*M* tetraethylammonium iodide–75% dioxane, with half-wave potentials of −2.45 v. and −2.46 v., respectively. The number of electrons involved in the electrode process has not been measured for such ketones. However, diffusion current values reported in the literature[2] suggest a one-electron electrode process. On the other hand, it is known that it is difficult to obtain bimolecular reduction products from aliphatic ketones other than acetone when the reduction is carried out either chemically or electrolytically.[3,4] Swann[4] has reported that electrolytic

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(1) M. B. Neiman and Z. V. Markina, *Zavodskaya Lab.*, **13**, 1177 (1947).

(2) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

(3) E. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Inc., New York, 1954, p. 711.