Dimerizations of Conjugated γ-Lactones on Reduction with Lithium Aluminum Hydride[1,2]

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The highly conjugated γ-lactone, α-benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (1), and its *o*- and *p*-chloro- and methoxybenzylidene analogs react with a twofold molar excess of lithium aluminum hydride in refluxing ether or tetrahydrofuran to give reduced dilactones, the structures of which were established by molecular weight determination, infrared, ultraviolet, and proton magnetic spectral data, and by chemical degradation. A mechanism for the formation of the dilactones is proposed. When the reaction is conducted at −25°, reduction is followed by oxidative dimerization to form a bislactone.

The reduction of butenolides by lithium aluminum hydride has been studied by several investigators[3,4] and shown to proceed in a manner consistent with the action of this reagent on lactones in general. The reaction involves the hydrogenolysis of the carbonyl–oxygen bond to form aldehyde and alcohol functions. If an enol, rather than an alcohol is formed, tautomerization to the stable keto form may occur. The new carbonyl groups frequently are further reduced to alcohols.

Results and Discussion

As one facet of our studies on highly conjugated γ-lactones,[5] we investigated the reduction of α-benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (1) with lithium aluminum hydride.

When the reaction was carried out by "normal" addition in refluxing ether or tetrahydrofuran using a twofold molar excess of hydride, a white crystalline compound **2** was isolated in 33% yield together with an oil whose infrared spectrum established the presence of a conjugated lactone. The analytical data for **2** indicated the addition of one mole of hydrogen per mole of butenolide. Its infrared spectrum showed that the lactone ring remained intact. The presence of one carbon–carbon double bond was revealed by catalytic hydrogenation, which gave a new lactone **3**. If compound **2** were monomeric, then further hydrogenation should have yielded α-benzyl-γ-phenylbutyrolactone. The latter compound, differing from **3**, was prepared by catalytic hydrogenation of **1**.

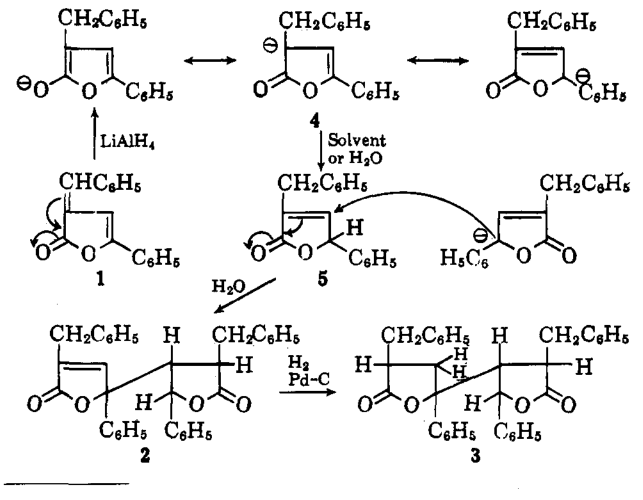
These results strongly suggested that **2** was dimeric and this was confirmed by molecular weight determination. The intense carbonyl absorption at both 1759 and 1787 cm.$^{-1}$ supported a dilactone structure. The band at lower frequency is characteristic of α,β-unsaturated γ-lactones,[4] while the higher frequency mode may be assigned to a butyrolactone ring. The presence of end absorption only in the ultraviolet spectrum was also consistent[6] with the proposed structure (*vide infra*).

The proton magnetic resonance spectrum of **2** is quite complex. However, a partial interpretation may be made by comparing this spectrum with that of the hydrogenated product **3**. Of particular relevance are the bands in **2** which disappear on hydrogenation. These bands, located at 3.28 and 6.28 τ, are attributed to protons astride a center of unsaturation since hydrogenation causes them to disappear with a corresponding increase in the number of hydrogens in the 6.93–7.15-τ region. It is in the latter range that methylene and methinyl hydrogens absorb.[7] The band at 3.28 τ is assigned to an olefinic proton.[8] On the basis of area measurements, only one such proton is present in compound **2** while two protons give rise to the 6.28-τ band. If, as the chemical and spectral evidence indicate, the dimer is composed of an α,β-unsaturated lactone joined to a saturated butyrolactone, then this latter signal may be associated with methylene protons of an α-benzyl group attached to the unsaturated linkage of the lactone ring. This would leave the γ-carbon as the point of junction to the butyrolactone.

The position of attachment on the butyrolactone ring is open to question. Position C-2 is ruled out because the hydrogenated product **3** does not correspond to the fully hydrogenated *bislactone* (*vide infra*). Of the other available positions (C-3, C-4, and benzyl), C-3 is most attractive both from mechanistic considerations of formation of **2** and from the behavior of **2** in base.

The reaction may be viewed (Scheme I) as proceeding *via* a reactive resonance-stabilized allylic carbanion **4**, generated by addition of hydride to the cisoid conju-

SCHEME I



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(1) Support of this investigation under Grant NSF G 9985 from the National Science Foundation is gratefully acknowledged.

(2) Submitted by Edmund J. Piasek in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Illinois Institute of Technology, June, 1962.

(3) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 510.

(4) F. Ramirez and M. B. Rubin, *J. Am. Chem. Soc.*, **77**, 3768 (1955).

(5) R. Filler and L. M. Hebron, *ibid.*, **81**, 391 (1959); R. Filler, L. H. Mark, and E. J. Piasek, *J. Org. Chem.*, **24**, 1780 (1959); R. Filler, E. J. Piasek, and L. H. Mark, *ibid.*, **26**, 2659 (1961).

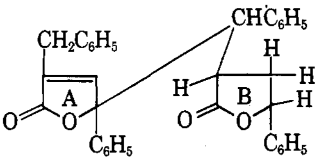
(6) J. F. Grove, and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

(7) H. Conroy, "Advances in Organic Chemistry," Vol II, Interscience Publishers, Inc., New York, N. Y., 1960. p 288.

(8) Ref. 7, p. 290.

gated carbonyl system. Slow protonation from solvent and/or during work-up in weakly alkaline aqueous medium would give a low concentration of conjugated lactone **5**, a substrate susceptible to rapid attack by **4** in a Michael-type addition to form the dilactone **2**. The lactonic material in the reaction mixture which was not characterized may well be compound **5**.

An alternative structure **6**, also consistent with the physical evidence, would have the site of attachment at the benzyl carbon of the butyrolactone ring. This compound could be formed by attack of the anion **4** at the benzylidene carbon of **1** to yield a dilactone allylic anion, which would then add a second mole of hydride to give **6**.

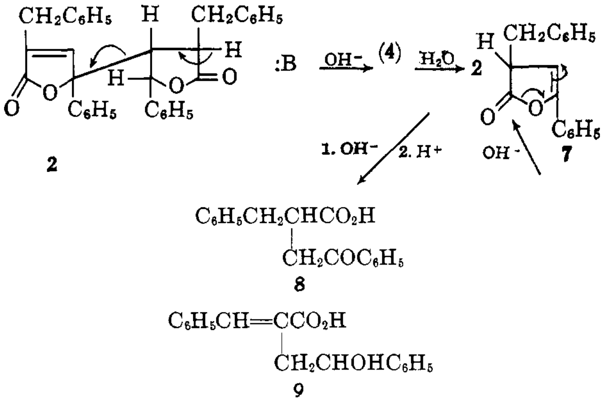


6

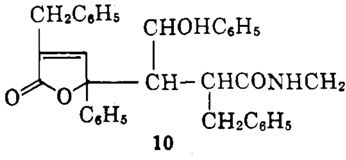
This structure can probably be excluded, since it suffers from several serious disadvantages. (A) In "normal" addition, the hydride ion concentration is overwhelmingly greater than that of the carbanion. Both species are competing for a very low concentration of unchanged butenolide **1**. On these grounds alone, the rate of anion formation probably far exceeds the rate of anion attack. (B) If further reduction of the dilactone anion were to occur, ring A, which does not bear the negative charge, should be preferentially reduced. This would afford an isomer of **6** whose structure with unsaturation in ring B, is inconsistent with the n.m.r. data and would not account for the behavior in alkali. (C) Even if compound **6** were formed, two products would be expected on hydrolysis. In fact, only one of them is actually observed.

Only structure **2** adequately accounts for the hydrolysis in sodium hydroxide solution to yield 2-phenacyl-3-phenylpropionic acid (**8**) in 80% yield. This acid also was prepared by hydrolysis of **1** to 2-phenacyl-3-phenylacrylic acid, followed by hydrogenation. The formation of **8** is readily interpreted in terms of a reverse Michael reaction to give, *via* the allylic carbanion **4**, two moles of lactone **7** (isomeric with **5**) per mole of dimer. The facile hydrolysis of **7** leads directly to the keto acid. These transformations are shown in Scheme II. It is to be noted that compound **6**, by the same mechanism, would give theoretically one mole each of **8** and **9**.

SCHEME II



Since strong base induced carbon–carbon bond cleavage, a weaker base benzylamine was used. After 48 hr. under reflux, most of the starting material was recovered, together with a small amount of product, whose infrared spectrum was in accord with the γ-hydroxyamide-$\Delta^{\alpha,\beta}$-lactone (**10**), formed by aminolysis of the butyrolactone ring. When, however, the reaction was allowed to proceed for 5.5 days, both rings were opened to give a low yield of product whose properties suggest structure **11**.



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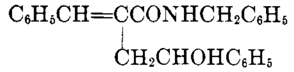


$$\underset{\displaystyle CH_2CHOHC_6H_5}{C_6H_5CH{=}CCONHCH_2C_6H_5}$$

11

The generality of the dimerization of arylidene ring-substituted butenolides to dilactones was demonstrated by the analogous behavior of the *o*- and *p*-chloro and methoxy compounds. The products obtained from the reduction of these lactones at ether reflux temperature had analyses, molecular weights, and infrared spectra in accord with the dilactone structure (see Tables I and II). Except for the *p*-methoxy product, all exhibited the doublet lactone band. The *p*-methoxy compound exhibited a single band at 1765 cm.⁻¹. It may be that the effect of the *p*-methoxy substituent is such as to cause a superposition of the doublet lactone bands of the dimer.

TABLE I

YIELDS AND INFRARED ABSORPTION OF SUBSTITUTED DILACTONES

Arylidene ring substituent	M.p., °C.	Yield, %	Lactone absorption cm.⁻¹
o-Chloro	145	42	1780, 1755
p-Chloro	198	44	1780, 1760
o-Methoxy	136	44	1775, 1760
p-Methoxy	173	37	1765

TABLE II

ANALYSES OF SUBSTITUTED DILACTONES

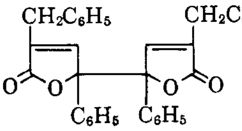
Arylidene ring substituent	Formula	Carbon, %		Hydrogen, %		Mol. wt.	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
o-Chloro	$(C_{17}H_{13}ClO_2)_2$	71.71	71.72	4.60	4.72	579	523
p-Chloro	$(C_{17}H_{13}ClO_2)_2$	71.71	71.74	4.60	4.72	579	512
o-Methoxy	$(C_{18}H_{16}O_3)_2$	77.12	77.03	5.75	5.92	561	500
p-Methoxy	$(C_{18}H_{16}O_3)_2$	77.12	77.02	5.75	6.01	561	528

Preliminary work on the reduction of **1** with sodium borohydride revealed that a high molecular weight lactone is formed. The product melted at 278° and was insoluble in all solvents tried. Elemental analysis indicated the addition of one mole of hydrogen per molecule of **1**.

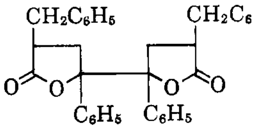
When the reduction of compound **1** was performed at −25°, an amorphous product was obtained which gave a crystalline solid **12** in 20% yield. The elemental analysis was in excellent agreement with a molecular formula in which a dimer of 1 had lost *two* hydrogens. Its infrared spectrum possessed strong carbonyl absorption at 1759 cm.$^{-1}$ only and end absorption in the ultraviolet. A molecular weight determination was inconclusive, possibly because of dissociation of **12**. This low temperature product resisted hydrogenation at ordinary pressures, but, at 2400 p.s.i., gave a solid, **13**, which exhibited a saturated lactone band at 1775 cm.$^{-1}$.

In addition to obtaining **12** by the method previously described, this compound also was prepared by cyclization of the keto acid **8** in the presence of acetic anhydride. Pummerer and Buchta[9] and others[10] observed that a similar keto acid, **14**, was converted to a bislactone and an α,β-unsaturated lactone under these conditions. The reaction probably proceeds by initial cyclization of the keto acid to a $\Delta^{\beta,\gamma}$-lactone, followed by isomerization and air oxidation to the bislactone.

That the cyclization of **8** followed an analogous course was demonstrated by conducting the reaction in the absence of oxygen (nitrogen atmosphere); no dimer was formed. Only when the mixture was exposed to air did dimerization occur. These observations lead to the conclusion that compounds **12** and **13** possess bislactone structures with the 2,2′ bridge.



12



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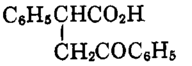

$$\begin{array}{l} C_6H_5CHCO_2H \\ \quad\quad\;\; | \\ \quad\quad\;\; CH_2COC_6H_5 \end{array}$$

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In further support, the n.m.r. spectrum of **12** revealed bands at 6.62, 3.12, and 2.55 τ with relative hydrogen abundances of 2, 1, and 10, respectively. The singlet at 6.62 τ is assigned to the four benzyl hydrogens, the 3.12-τ band to the two olefinic protons, and the band at 2.55 τ to the benzene protons.

The formation of **12** by reduction of compound **1** is therefore a manifestation of the competition between oxidative dimerization of lactone **5** and attack of allylic anion on **5**.

Experimental[11]

Reduction of Butenolide 1 with LiAlH$_4$ at Ether Reflux Temperature.—Lithium aluminum hydride (1.90 g., 0.050 mole) was heated under reflux with anhydrous ether (250 ml.). To the resulting slurry was added with stirring a suspension of 6.2 g. (0.025 mole) of compound 1 in 250 ml. of anhydrous ether during a 15-min. period. After addition was complete the mixture was stirred for 10 min., 30 ml. of moist ether (saturated with water) was slowly added, followed by careful addition of 4 ml. of water. The slurry was stirred for 10 min. and filtered. The inorganic residue was suspended in water and concentrated sulfuric acid was added. Extraction with ether failed to yield any organic product. The ether filtrate, recovered from the reaction, was dried over anhydrous magnesium sulfate, then evaporated on a steam bath until a voluminous white solid had separated and only a small amount of ether remained. Suction filtration of the suspension, followed by an ether wash and air drying, gave 2.06 g. (33%) of the fluffy, white solid **2**, m.p. 158–160°; $\lambda_{\max}^{\mathrm{EtOH}}$ end absorption (below 218 mμ), $\nu_{\max}^{\mathrm{KBr}}$ 1787, 1759, and 1650 cm.$^{-1}$ (lit.[12] m.p. 161–162°, $\lambda_{\max}^{\mathrm{EtOH}}$ end absorption, $\nu_{\max}$ 1757 cm.$^{-1}$). Crystallization from ethanol failed to change the melting point.

Anal. Calcd. for $(C_{17}H_{14}O_2)_2$: C, 81.58; H, 5.64; mol. wt., 500. Found: C, 81.40; H, 5.55; mol. wt. (Rast), 504.

The proton magnetic resonance spectrum of **2** in methylene chloride revealed bands at 6.97, 6.28, 3.28, and 2.65 τ with relative abundances of 4, 2, 1, and 20, respectively. In addition, a doublet at 4.60 τ (relative hydrogen abundance of 1) was observed when chloroform was used as solvent. The apparent absence of this signal in methylene chloride can be attributed to the superimposition of the broad solvent band at 4.60 τ, which obscures the doublet.

Evaporation of the ether filtrate to dryness gave an oil, which failed to yield any identifiable products. Its infrared spectrum indicated lactone absorption at 1760 and a weak band at 1680 cm.$^{-1}$. The oil failed to form a 2,4-dinitrophenylhydrazone or to undergo hydrolysis. When the reaction was conducted in tetrahydrofuran instead of ether, similar results were obtained. In similar fashion, the chloro and methoxy arylidene analogs of **2** were obtained (Tables I and II).

Alkaline Hydrolysis of the LiAlH$_4$ Product.—2 (1 g., 2 mmoles) was heated on a steam bath with 50 ml. of 3 *N* NaOH. The suspension was swirled for 45 min. to effect solution. The contents were acidified with 18% HCl and the precipitate filtered, washed with water, and dried *in vacuo*. An acid (0.86 g., 80%), m.p. 168–172°, was obtained. Crystallization from ethanol gave a product, m.p. 173–174.5° (cor.), $\nu_{\max}^{\mathrm{KBr}}$ 1710 and 1690 cm.$^{-1}$. This substance showed no depression in melting point when admixed with an authentic sample of 2-phenacyl-3-phenylpropionic acid.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; mol. wt., 268. Found: C, 76.05; H, 5.95; mol. wt. (neut. equiv.), 268.

Concentrated hydrochloric acid failed to hydrolyze **2** even after 12 hr. of reflux.

Preparation of Authentic 2-Phenacyl-3-phenylpropionic Acid (8).—Compound 1 (4.0 g., 0.016 mole) was heated on a steam bath for 1 hr. with 20 ml. of 3 *N* NaOH. After acidification with 18% HCl and work-up of the contents as described previously, 4.0 g. (97%) of 2-phenacyl-3-phenylacrylic acid, m.p. 160–165°, was obtained. Crystallization from 50% ethanol raised the melting point to 170–172° (lit.[12] 171–173°). A mixture melting point with the LiAlH$_4$ hydrolysis product showed a depression.

One gram (3.8 mmoles) of this acid was dissolved in 100 ml. of methanol and hydrogenated over 10% palladium on charcoal at 40 p.s.i. for 2 hr. The catalyst was removed and the methanol evaporated under reduced pressure at room temperature to yield 0.57 g. (57%) of product, m.p. 168–173°, which was crystallized from ethanol to give the keto acid, m.p. 172–173° (cor.). A mixture melting point of this product with the product of dimer hydrolysis showed no depression.

Hydrogenation of 2.—A solution of 430 mg. of **2** in 250 ml. of methanol was hydrogenated over 10% palladium-on-charcoal catalyst for 4.5 hr. at 40 p.s.i. Air evaporation of the solvent yielded 240 mg. (56%) of the white product **3**, m.p. 178–186°, which, after crystallization from methanol, melted at 183–185°, $\nu_{\max}^{\mathrm{KBr}}$ 1777 cm.$^{-1}$, but no band at 1650 cm.$^{-1}$.

Anal. Calcd. for $(C_{17}H_{15}O_2)_2$: C, 81.25; H, 6.02. Found: C, 81.25; H, 6.05.

Compound 2 absorbed 1.01 mole equivalents of hydrogen per mole of dimer in an ethanolic solution containing 10% palladium-on-charcoal catalyst.

A n.m.r. spectrum of **3** in methylene chloride showed bands at 6.93, 4.82, and 2.63 τ, in the ratio, 9:1:20. The absorption at 6.93 consisted of a series of peaks, some of which were unresolved. Generally, the bands were quite similar to those found in 2.

Hydrogenation of 1.—One gram (4 mmoles) of **1** in 250 ml. of glacial acetic acid was hydrogenated over palladium on charcoal

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[9] R. Pummerer and E. Buchta, *Ber.*, **69**, 1005 (1936).

[10] P. Yates and T. J. Clark, *Tetrahedron Letters*, 435 (1961); H. H. Wasserman, R. M. Waters, and J. E. McKeon, *Chem. Ind.* (London), 1795 (1961).

[11] All melting points are uncorrected unless specified (corrected). The elemental analyses were run by Micro-Tech Laboratories, Skokie, Illinois. The infrared absorption spectra were determined on a Perkin-Elmer Model 21 double beam infrared recording spectrophotometer with a sodium chloride prism. The ultraviolet spectra were measured on a Beckman DK-2 spectrophotometer. N.m.r. spectra were measured with a Varian Associates Model A-60 analytical n.m.r. spectrophotometer. The chemical shifts are reported in values of τ, where tetramethylsilane is arbitrarily assigned a value of 10.00 p.p.m.

[12] L. H. Mark, M.S. thesis, Illinois Institute of Technology, 1959.

for 2.5 hr. at 40 p.s.i. Evaporation of the filtrate gave an oil, which was dissolved in petroleum ether (b.p. 60–80°) and chloroform (1:1) and refrigerated for several weeks. A solid separated and was crystallized from ethanol to yield 0.47 g. (47%) of α-benzyl-γ-phenylbutyrolactone, m.p. 78–80°, $\nu_{\max}^{\mathrm{KBr}}$ 1775 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.07; H, 6.51.

Reaction of 2 with Benzylamine.—A solution of 5 ml. of benzylamine in 25 ml. of dry benzene was refluxed with 500 mg. of **2** for 48 hr. The contents were taken up in 50 ml. of ether and extracted several times with 18% hydrochloric acid, followed by water. Evaporation of the solution gave an oil, which was treated with a large volume of petroleum ether and heated on a steam bath until all of the oil had been converted to a white solid. Filtration of the mixture under suction gave 300 mg. of material, m.p. 125–130°. Crystallization from ethyl acetate gave several mg. of solid **9**, m.p. 135–139°, $\nu_{\max}^{\mathrm{KBr}}$ 1760 (α,β-unsaturated lactone), 1660 cm.$^{-1}$ (amide), and 3300–3400 cm.$^{-1}$ (-OH and -NH). The filtrate yielded **2**, m.p. 155–160°, upon evaporation.

When 200 mg. of **2** was heated under reflux with a solution of 2 ml. of benzylamine in 10 ml. of dry benzene for 5.5 days, and the reaction worked up as described previously, 40 mg. of a substance, m.p. 120–125°, was obtained. After crystallization from ethyl acetate–petroleum ether the melting point was 120–121°, $\nu_{\max}^{\mathrm{KBr}}$ 1660, 3490, and 3350 cm.$^{-1}$. This compound gave a positive test when treated with bromine in carbon tetrachloride.

Anal. Calcd. for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.48; mol. wt., 357. Found: C, 80.46; H, 6.31; mol. wt. (Rast), 337.

Reduction of 1 with LiAlH$_4$ at Low Temperature.—One gram (0.026 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether was stirred vigorously and heated under reflux for 0.5 hr. A suspension of 3.1 g. (0.012 mole) of **1** in 125 ml. of ether was added to the slurry, which was maintained at $-25 \pm 5°$, in a carbon tetrachloride–Dry Ice bath. After 40 min., addition was complete and the mixture was stirred for 5.5 hr. The contents were hydrolyzed with 20 ml. of wet ether followed by 4 ml. of water. The filtrate was dried over anhydrous magnesium sulfate and evaporated to an oil. A solution of the oil in acetone was stored in a refrigerator for several days to yield 0.62 g. (20%) of a compound, m.p. 224–226° (red decomposition), $\lambda_{\max}^{\mathrm{EtOH}}$ end absorption, $\nu_{\max}^{\mathrm{KBr}}$ 1759 and 1550 cm.$^{-1}$. Crystallization from ethyl acetate narrowed the melting point to 225–226°.

Anal. Calcd. for $(C_{17}H_{13}O_2)_2$: C, 81.91; H, 5.25; mol. wt., 498. Found: C, 81.84; H, 5.17; mol. wt. (Signer–Barbier), 340.

The molecular weight was obtained only after many months of equilibration. We suspect that decomposition may have occurred during this time giving rise to the low value. Similar results were obtained using tetrahydrofuran in place of ether.

Reaction of Keto Acid 8 with Acetic Anhydride.—A mixture of 500 mg. (1.9 mmoles) of **8** and 5 ml. of acetic anhydride in an Erlenmeyer flask was heated on a hot plate, maintained at 70–80°, for 3 hr. After partial evaporation of the solvent by air, the heavy white precipitate was filtered by suction, washed with ethyl acetate, and dried *in vacuo*. A product, 133 mg., 28%, m.p. 226°, was obtained. Admixture of a sample with that obtained from the low temperature reduction of **1** failed to depress the melting point.

The aforementioned procedure was repeated, except that the reaction was conducted in a 50-ml. three-necked flask, equipped with a reflux condenser and gas inlet tube through which nitrogen was passed. After 3 hr., the acetic anhydride was removed under reduced pressure in a rotating evaporator. Only an oil was obtained, from which the product described previously could not be obtained. The oil was redissolved in 5 ml. of acetic anhydride and heated for 2 hr. while air was bubbled through the solution. Evaporation in air caused 40 mg. of product **12** to precipitate from solution.

Hydrogenation of 12.—The bislactone (30 mg.) was suspended in 60 ml. of methanol and hydrogenated for 3 hr. over palladium on charcoal at 2400 p.s.i. and 60°. A large volume of acetone was added to dissolve the suspended white solid. Evaporation of solvent yielded 10 mg. of a fine, white solid, m.p. 250–254°. Crystallization from benzene gave several milligrams of product, m.p. 256–257°, $\nu_{\max}^{\mathrm{KBr}}$ 1775 (saturated butyrolactone), no band at 1650 cm.$^{-1}$.

Anal. Calcd. for $(C_{17}H_{15}O_2)_2$: C, 81.25; H, 6.02. Found: C, 80.11; H, 6.23.

Attempted hydrogenation of **12** at 40 p.s.i. with palladium on charcoal or platinum oxide failed.

Reduction of 1 with Sodium Borohydride.—Sodium borohydride (0.85 g., 0.022 mole) was dissolved in 50 ml. of 95% ethanol and cooled in an ice–water bath. The solution was stirred magnetically and a suspension of 2.78 g. (0.011 mole) of **1** in 125 ml. of ethanol was added over a period of 30 min. After addition was complete, the contents were stirred for 4 hr. while the temperature was maintained at 0°. The reaction mixture was carefully poured into cold 18% HCl, and a white solid separated. Suction filtration gave 1.82 g. (66%) of product, m.p. 260–270°. This material was insoluble in all solvents tried and could only be purified in the following manner: The compound was refluxed in a large volume of chloroform for 12 hr. Undissolved solid was removed and the filtrate evaporated to an oily residue. Methanol was added to precipitate a white solid, m.p. 278–280° (red decomposition), $\nu_{\max}^{\mathrm{KBr}}$ 1760 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.21; H, 5.21.

Acknowledgment.—The authors thank Professor Scott Searles for helpful discussions.

3,3-Diphenylglutaric Acid. A Novel Carbanion Condensation Reaction

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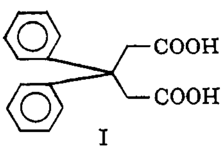
A compound previously assigned the structure of 3,3-diphenylglutaric acid has been established to be β-(4-carboxymethylphenyl)hydrocinnamic acid (II). The preparation of II *via* condensation of dichlorodiphenylmethane with sodium diethyl malonate represents a novel carbanion condensation reaction on an aromatic ring. Details are provided for the synthesis of 3,3-diphenylglutaric acid (I).



I

In extending the studies of the Thorpe–Ingold effect[2] on the rates of anhydride formation from the monoesters of 3,3-disubstituted glutaric acids and the rates of hydrolysis of the intermediate anhydrides[3] we desired to obtain 3,3-diphenylglutaric acid (I). The present paper describes the synthesis of 3,3-diphenylglutaric acid and the correct assignment of structure to a structural isomer of I that had previously been assumed to be I. In the course of this study a novel carbanion condensation reaction was encountered.

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[1] The experimental data contained herein will form a portion of the Ph.D. dissertation of W. C. B.

[2] R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915).

[3] T. C. Bruice and U. K. Pandit, *J. Am. Chem. Soc.*, **82**, 5858 (1960).