

TABLE IV
MELTING POINTS AND EQUIVALENTS OF SUBSTITUTED PHENYL-
ACETIC ACIDS

Substituent	Equiv. wt.		M.p., °C.	
	Calcd.	Found	Lit.	Found
H	136.1	135.1	76.5-77 ^a	77-78
<i>p</i> -I	262.0	259.8	135-136 ^b	139-140
<i>m</i> -I	262.0	256.8	129 ^c	129-130
<i>p</i> -CH ₃ O	166.2	165.6	85-86 ^b	86-87
<i>m</i> -CH ₃ O	166.2	165.1	67 ^d	67-68
<i>p</i> -NO ₂	181.1	180.2	152 ^b	156-157
<i>p</i> -Cl	170.6	167.7	105 ^b	105-106
<i>m</i> -Cl	170.6	169.9	76 ^b	74-75
<i>p</i> -Br	215.1	213.8	114 ^b	113-114
<i>m</i> -Br	215.1	210.8	100 ^e	100-101
<i>p</i> -CH ₃	150.2	147.4	94 ^f	91-92
<i>p</i> -NH ₂	151.2	...	199-200 ^e	200-201
<i>m</i> -NO ₂	181.5	188.6 ^g	120 ^b	117-119

^a A. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 166 (1934).
^b J. F. J. Dippy and F. R. Williams, *ibid.*, 161, 1888 (1934).
^c J. F. J. Dippy, F. R. Williams, and R. H. Lewis, *ibid.*, 644 (1936); 343 (1935). ^d R. Pschorr, *Ann.*, **391**, 44 (1912). ^e H. Berger, *J. prakt. Chem.*, **133**, 331 (1932). ^f Ref. 22. ^g The quantity available was insufficient for further purification.

creased roughly linearly by ca. 50% in the range 0-1 *M* acid.³³ Therefore the present data are reported for solutions initially ca. 0.0025 *M* in DDM and 0.14 to 0.015 *M* in acid where the deviation from the infinite dilution value was within experimental error. Each acid was usually studied at three different concentrations except as indicated (Table II). The slopes of plots of optical density vs. time gave the pseudo-first-order rate constant which was converted to a second-order constant by division by the initial acid concentration. Additional runs were carried out with comparable phenylacetic acid-DDM concentrations of ca.

(33) R. M. O'Ferrall, unpublished results.

0.015 *M*; the second-order rate constants were calculated directly by another method³³ and agreed with those obtained from the pseudo-first-order runs.

The activation parameters listed in Table II were obtained from the expression³⁴

$$k = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

There is some discrepancy in the reported rate constants for DDM-acid reactions in absolute ethanol. For benzoic acid, the second-order rate constant in 1. mole⁻¹ min.⁻¹ at 30° has been found to be 0.99,³¹ 1.08 (1.04),³⁵ 1.00,³² 1.20²⁸; our interpolated value is 0.99; at 25° the rate constant of Taft and Smith appears to be high at 0.96³⁶; our figure is 0.75 at 26.05°. The Taft and Smith rate constants³⁶ for phenylacetic and phenylpropionic acids are also higher than those found in our laboratory, i.e., 1.47 at 25° vs. 0.81 at 26.05° and 1.01 vs. 0.545 at 25°. It is possible that the total change in optical density in their kinetic runs was too low, ca. 0.2 unit or less, and thus susceptible to potential error. Otherwise, our activation parameters indicate that it would require rather improbable errors in the temperature to yield such deviations.

The rate constant for the benzoic acid-DDM reaction increases linearly with the concentration of water (0-8 *M*) added to the ethanol^{18c}; this also appears to hold true for phenylacetic acid.³³ However, the magnitude of this increase is such that the presence of traces of water would not appear to be responsible for these discrepancies in the rate constants. Further, there seems to be no relation between the magnitude of the rate constants and whether the solvent ethanol was redried by the investigators. Until the reasons for these inconsistencies in the DDM-acid reactions are ascertained, some care is needed when the work of different investigators is being compared.

Acknowledgment.—We wish to thank G. R. Ziegler for preparing some of the acids used in this work.

(34) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., Chap. 5.

(35) J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75**, 4102 (1953).

(36) R. W. Taft, Jr., and D. J. Smith, *ibid.*, **76**, 305 (1954); D. J. Smith, B.S. Thesis, Pennsylvania State College, June, 1953.

[CONTRIBUTION NO. 2945 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF., AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Structure and Rearrangement of Neutral Phenylketene Dimer¹

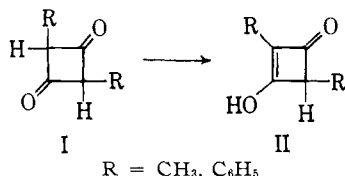
BY JOHN E. BALDWIN² AND JOHN D. ROBERTS

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Neutral phenylketene dimer has been identified as 3-hydroxy-2,4-diphenyl-3-butenolactone. It was converted in the presence of base to an acidic isomer, 2,4-diphenylcyclobutenol-3-one.

Introduction

Base-catalyzed rearrangements of neutral phenylketene dimer to an acidic isomer³ and of neutral methylketene dimer to an acidic form⁴ have been reported. These rearrangements were interpreted in terms of conversion of I to II by simple tautomerizations.^{3,4}



Since this early work, investigations of various ketene dimers have led to fairly secure structural assignments for diketene⁵ (IIIa), neutral methylketene and other alkylketene dimers (IIIb),⁶ acidic methyl- and ethylketene dimers (IVb or Vb)⁷, and ketoketene dimers (IVd, IVe).⁸

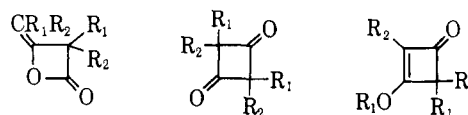
(1) Supported in part by the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1960-1962; Department of Chemistry, University of Illinois, Urbana, Ill.

(3) H. Staudinger, *Ber.*, **44**, 533 (1911).

(4) H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 42. H. Staudinger, *Ber.*, **53**, 1085 (1920).

(5) See V. V. Perekalin and T. A. Sokolva, *Uspekhi Khim.*, **25**, 1351 (1956), and R. N. Lacey in "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 240-241, for references to the original structural studies.



IIIa, R₁ = R₂ = H
 b, R₁ = H, R₂ = alkyl
 c, R₁ = H, R₂ = aryl

IV
 Vd, R₁ = R₂ = alkyl
 e, R₁ = R₂ = aryl

Two new representatives of this series of compounds have been reported recently: cyclobutane-1,3-dione (which exists as the enol Va)⁹ and 3-hydroxy-2,4-trimethyl-3-pentanoic lactone (IIIId, R = CH₃).¹⁰

From the evidence now available it seems clear that the neutral dimers reported by Staudinger^{3,4} are likely to be lactonic-type dimers and, if so, then the reported

(6) J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, *J. Am. Chem. Soc.*, **71**, 843 (1949); C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950); R. L. Wear, *ibid.*, **73**, 2390 (1951); A. S. Spriggs, C. M. Hill, and G. W. Senter, *ibid.*, **74**, 1555 (1952); J. R. Johnson and V. J. Shiner, *ibid.*, **75**, 1350 (1953); J. Bregman and S. W. Bauer, *ibid.*, **77**, 1955 (1955).

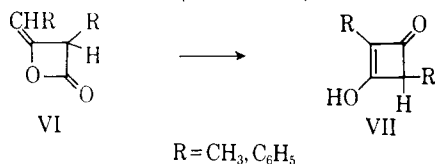
(7) (a) R. B. Woodward and G. Small, Jr., *ibid.*, **72**, 1297 (1950); (b) E. B. Reid and S. J. Grosz, *ibid.*, **75**, 1655 (1953).

(8) W. E. Hanford and J. C. Sauer in "Organic Reactions," Vol. III, edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 127 ff.

(9) H. H. Wasserman and E. V. Dehmow, *J. Am. Chem. Soc.*, **84**, 3786 (1962).

(10) R. H. Hasek, R. D. Clark, E. V. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).

rearrangements must involve rather extensive alteration in molecular structures (VI \rightarrow VII).



Earlier attempts to confirm the occurrence of this type of molecular rearrangement were unsuccessful.^{7a}

The present paper reports evidence indicative of the structures of both the neutral and acidic phenylketene dimers and confirms the reported base-catalyzed rearrangement of the neutral phenylketene dimer to the acidic isomer.

Results and Discussion

Neutral phenylketene dimer was synthesized by the dechlorination of chlorophenylacetyl chloride.³ The elemental analysis, spectral properties, and conversion of this dimer to α, γ -diphenylbutyric acid upon consumption of two moles of hydrogen are consistent with structure VI ($R = \text{C}_6\text{H}_5$). The infrared spectrum of the dimer was particularly informative, there being strong absorptions at 1910, 1875, and 1710 cm^{-1} indicative of a β, γ -unsaturated β -lactone.¹¹

The geometry about the *exo*-cyclic double bond in neutral phenylketene dimer (3-hydroxy-2,4-diphenyl-3-butenolide), as in neutral alkylketene dimers, was not established. The n.m.r. spin-spin coupling constants between the olefinic and methine hydrogens in neutral methylketene dimer, 1.41 c.p.s., the same pair of hydrogens in neutral phenylketene dimer, 1.4 c.p.s., and the olefinic and methylene protons in diketene, 1.48 and 1.89 c.p.s.,¹² suggest that neutral methylketene dimer and neutral phenylketene dimer have the same geometry. While lacking a rigorous assignment for the two 1,4-coupling constants in diketene,¹³ no decision as to the geometry of neutral aldoketene dimers based on n.m.r. evidence alone can be made.

When neutral phenylketene dimer was treated with aqueous sodium hydroxide,³ an exothermic reaction occurred and acidification provided a colorless crystalline solid. The elemental analysis, molecular weight, neutralization equivalent, pK_a , and spectral properties support structure VII ($R = \text{C}_6\text{H}_5$) for this acidic phenylketene dimer.

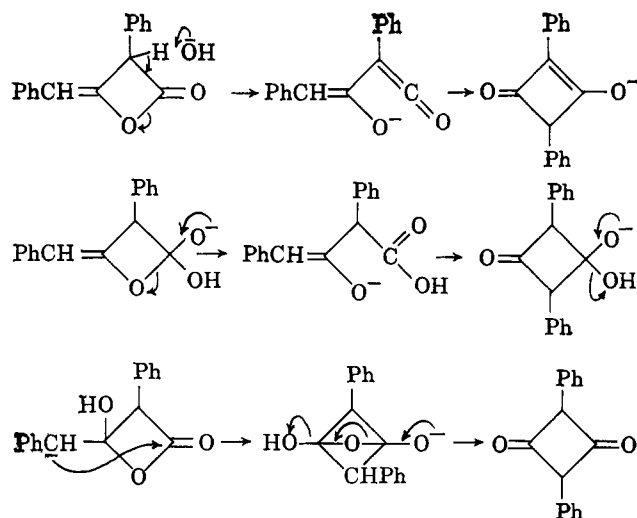
The pK_a of 3.0 determined for acidic phenylketene dimer is quite similar to $\text{pK}_a = 2.8$ reported for acidic methylketene dimer^{7a} and $\text{pK}_a \sim 3$ for cyclobutane-1,3-dione.⁹

A plausible mechanistic route has been suggested for the rearrangement IVd \rightarrow IIIId ($R_1 = R_2 = \text{CH}_3$).¹⁰ Several mechanisms for the base-catalyzed conversion of neutral phenylketene dimer to acidic phenylketene dimer may be considered. Hydroxide ion may abstract the α -hydrogen to produce a ketene intermediate, or attack the carbonyl carbon, or add to the *exo*-cyclic double bond.

No more detailed mechanistic description for this rearrangement is now possible.

Experimental¹⁴

Neutral Phenylketene Dimer.³—To a dry 1-l. three-necked flask containing 40 g. (0.61 mole) of zinc dust and 500 ml. of absolute ether was added under a nitrogen atmosphere with efficient mechanical stirring a solution of 84 g. (0.44 mole) of



phenylchloroacetyl chloride, (prepared from mandelic acid and phosphorus pentachloride), b.p. 68–69° (1 mm.), in 100 ml. of absolute ether. The reaction started several minutes after the beginning of the addition and the ether refluxed throughout the 25-min. addition. The reaction mixture was stirred another hour and filtered. The filtrate was washed repeatedly with water, 5% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, dried over magnesium sulfate, filtered, and, when concentrated under reduced pressure, gave 44 g. of oily dark-red residue.

A 36.8-g. portion of this residue was diluted with 25 ml. of nitromethane and extracted with twelve 50-ml. portions of cyclohexane. Concentration of the cyclohexane extracts gave 18.6 g. of clear yellow residue. When treated with cyclohexane, petroleum ether, b.p. 30–60°, and methylene chloride, this residue deposited crystals amounting to 4.7 g. (14%), m.p. 53–57°. Recrystallization from pentane-cyclohexane gave the neutral dimer of phenylketene, m.p. 69–70° (lit.³ m.p. 73°); $\lambda_{\text{max}}^{\text{cyclohexane}}$ 289 μ (ϵ 784), 253 μ (ϵ 32,200); $\nu_{\text{max}}^{\text{C}_{16}\text{H}_{12}\text{O}_2}$ 1910, 1875, 1850 (wk), and 1710 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_2$: C, 81.34; H, 5.12. Found: C, 80.98; H, 5.17.

The neutral dimer gave no color with methanolic ferric chloride.

Hydrogenation of Neutral Phenylketene Dimer.—Hydrogenation of 2.91 mg. of neutral phenylketene dimer with 5% palladium-on-carbon in ethanol resulted in absorption of 2.19 equivalents of hydrogen.¹⁵

A solution of 0.2 g. of crude neutral phenylketene dimer, m.p. 55–59°, in 20 ml. of ethyl acetate was reduced with hydrogen over 10 mg. of 5% palladium-on-carbon. The product was isolated and recrystallized twice from hexane to give material of m.p. 69–73°. The infrared spectrum of this solid was identical with that of an authentic sample of α, γ -diphenylbutyric acid¹⁶ of m.p. 73–74.5°. A mixture of a α, γ -diphenylbutyric acid and the hydrogenation product from neutral phenylketene dimer melted at 68–73°.

Rearrangement of Neutral Phenylketene Dimer to an Acidic Isomer.—Neutral phenylketene dimer (160 mg.) was treated with 0.5 ml. of dioxane and 2.5 ml. of 8% aqueous sodium hydroxide. The reaction mixture was heated briefly, cooled to room temperature, and filtered. When the filtrate was acidified with acetic acid-sulfuric acid, a colorless precipitate was obtained; 157 mg. (98%), m.p. 143–145°. Recrystallization from acetonitrile gave crystals, m.p. 149–150.5° (lit.³ m.p. 150°); $\lambda_{\text{max}}^{\text{EtOH}}$ 204 (log ϵ 6.56), 218 (log ϵ 6.38), 274 (log ϵ 6.49); $\nu_{\text{max}}^{\text{KBr}}$ 1708, 1540, 1455, 1360, 1325, 765, 708, and 695 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_2$: C, 81.34; H, 5.12; mol. wt., 236. Found: C, 81.13; H, 5.00; mol. wt., 222 (determined by isothermal distillation in acetone according to Barger.¹⁷)

Treatment of 10.0 mg. of dimer with excess standard sodium hydroxide and back-titration with standard hydrochloric acid gave 246 for the neutralization equivalent (calcd. 236, lit.³ 237.7) and pK_a 3.0.¹⁸

(15) The equipment used was that described by N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **1**, 884 (1947).

(16) α, γ -Diphenylbutyric acid was synthesized by the procedure of H. M. Crawford, *J. Am. Chem. Soc.*, **61**, 608 (1939).

(17) Cf. R. P. Linstead, J. A. Elvidge, and M. Whalley, "A Course in Modern Techniques of Organic Chemistry," Butterworths, London, 1955, p. 150.

(18) The potentiometric titrations were done with an automatic recording titrator, model AT-2A, Polarad Electronics Corporation, L. I. City, New York. This instrument was made available through the courtesy of Dr. S. G. Smith.

(11) The corresponding bands for diketene are at 1900, 1867, and 1708 cm^{-1} : F. A. Miller and G. L. Carlson, *J. Am. Chem. Soc.*, **79**, 3995 (1957).

(12) J. E. Baldwin and J. D. Roberts, unpublished data.

(13) Cf. D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2252 (1962); R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961).

(14) Melting points are corrected. Analyses are by A. Elek, Los Angeles, Calif., and J. Nemeth and associates, Urbana, Ill.