Notes

Reactions of the β-Lactone Dimer of Diphenylketene and Derivatives of α,α,γ,γ-Tetraphenylacetoacetic Acid

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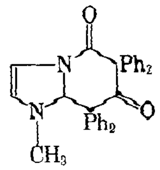
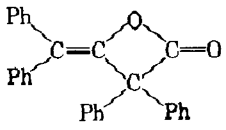
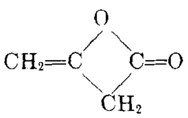
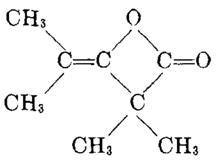
In an investigation of the cycloaddition of diphenylketene to carbon-nitrogen double bonds,[1] the reaction of diphenylketene and *N*-methylimidazole was studied. When 2 moles of diphenylketene was mixed with 1 mole of *N*-methylimidazole, adduct I was formed. In an attempt to obtain cycloaddition at both double bonds of the *N*-methylimidazole, 5 moles of diphenylketene was mixed with 1 mole of *N*-methylimidazole; however, the desired cycloaddition at both double bonds was not obtained. In addition to adduct I, another compound was isolated which was identified as 2,2,4,4-tetraphenyl-3-hydroxy-3-butenoic lactone, the β-lactone dimer of diphenylketene (II) which has been characterized by R. Anet.[2]


I

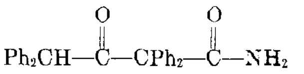

II

Before the identity of II had been established, it was found that ethanol was the solvent of choice for its recrystallization. That II should be stable in boiling ethanol is unexpected, since the β-lactone dimers of ketene[3] (III) and dimethylketene[4] (IV) react with ethanol to give ethyl acetoacetate and ethyl α,α,γ,γ-tetramethylacetoacetate, respectively.

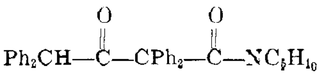

III


IV

Because of this unexpected behavior, the study of II was continued. One of the characteristic reactions of β-lactone dimers of ketenes, such as III or IV, is with ammonia or amines to produce the corresponding acetoacetamides. The reaction of II with an equimolar quantity of ammonia in absolute ethanol at 25° gave the expected amide V, and reaction of II with excess piperidine at 25° gave the expected piperidide VI. That these products were V and VI rather than the

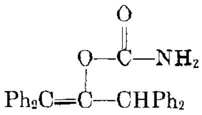

$Ph_2CH-\overset{\overset{O}{\|}}{C}-CPh_2-\overset{\overset{O}{\|}}{C}-NH_2$

V

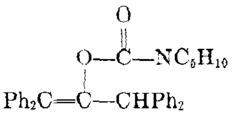

$Ph_2CH-\overset{\overset{O}{\|}}{C}-CPh_2-\overset{\overset{O}{\|}}{C}-NC_5H_{10}$

VI

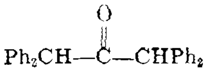
isomeric carbamates, VII and VIII, is evident from the fact that they do not decolor permanganate. The infrared spectra are in agreement with the assigned structures. With excess ethanolic ammonia, both II and V are converted to *sym*-tetraphenylacetone (IX) and urea, but no reaction occurred when VI was treated with ammonia under these conditions.


$Ph_2C=\overset{O-\overset{\overset{O}{\|}}{C}-NH_2}{\overset{|}{C}}-CHPh_2$

VII


$Ph_2C=\overset{O-\overset{\overset{O}{\|}}{C}-NC_5H_{10}}{\overset{|}{C}}-CHPh_2$

VIII

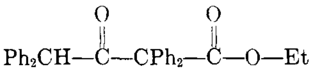

$Ph_2CH-\overset{\overset{O}{\|}}{C}-CHPh_2$

IX

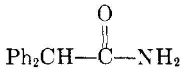
The reaction of an amide with ammonia to give urea under such mild conditions is unusual, although similar reactions under more forcing conditions are known. Acetoacetanilide reacts with aniline at 200° to give acetone and *sym*-diphenylurea,[5] and tetraalkylacetoacetamides react with amines to give the corresponding ketones and ureas at 150–175°.[6]

Several other reactions that are characteristic of the β-lactone dimer of ketene (III) and dimethylketene (IV) were studied with II. Both III[7] and IV[4] react readily with dry hydrogen chloride to give the corresponding acetoacetyl chloride. After II was treated with anhydrous hydrogen chloride in ether at 20°, the starting material was recovered almost quantitatively. Both III[3] and IV[4] react readily with aniline at 100° to give the corresponding acetoacetanilide. After II had been heated with aniline at 100°, no reaction product was obtained and the starting material was recovered (73%).

Ethyl α,α,γ,γ-tetraphenylacetoacetate[8] (X) was found to react with two molecules of ammonia in ethanol at 20° to give diphenylacetamide (XI). The intermediate in this reaction cannot be the amide V, since V with excess ethanolic ammonia yields IX rather than XI. Hence, this reaction must proceed with attack of the ammonia on the keto carbonyl of X giving XI and ethyl diphenylacetate which is converted to XI by the second molecule of ammonia.


$Ph_2CH-\overset{\overset{O}{\|}}{C}-CPh_2-\overset{\overset{O}{\|}}{C}-O-Et$

X


$Ph_2CH-\overset{\overset{O}{\|}}{C}-NH_2$

XI

The difference in reactivity of the α,α,γ,γ-tetraphenylacetoacetic acid derivatives (V, VI, and X), toward ammonia presents interesting mechanistic possibilities which are to be investigated further.

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(1) R. D. Kimbrough, Jr., *J. Org. Chem.*, **29**, 1242 (1964).

(2) R. Anet, *Chem. Ind.* (London), 1313 (1961).

(3) A. B. Boese, *Ind. Eng. Chem.*, **32**, 16 (1940); C. D. Hurd and C. A. Blanchard, *J. Am. Chem. Soc.*, **72**, 1461 (1950).

(4) R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962); Technical Data Report X-129, Eastman Chemical Products, Inc., Kingsport, Tenn., 1961, p. 14.

(5) L. Knorr, *Ann.*, **236**, 76 (1886).

(6) E. U. Elam and R. H. Hasek, U. S. Patent 3,072,724 (1963).

(7) C. D. Hurd and C. D. Kelso, *J. Am. Chem. Soc.*, **62**, 1548 (1940).

(8) D. C. Dean, W. B. Dickinson, O. R. Quayle, and C. T. Lester, *ibid.*, **72**, 1740 (1950).

Experimental

All analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Infracord.

2,2,4,4-Tetraphenyl-3-hydroxy-3-butenoic Lactone (II).—Freshly distilled diphenylketene[9] (5.0 g.) was added to 0.43 g. of *N*-methylimidazole.[10] The mixture became hot and was stored at room temperature under nitrogen for a day. (The yield of II varied and the details of processing depend on this yield.) Benzene (15 ml.) was added to the reaction mixture and it was heated gently until all the solid dissolved. The solution was cooled and any solid that formed was filtered off. (This solid is the diphenylketene dimer, tetraphenyl-1,3-cyclobutandione.[11]) Petroleum hexane (20 ml.) was added to the benzene solution. (The solid that forms at this point is mostly the adduct I; however, it may contain appreciable amounts of II.) The solid was collected on a filter, and the filtrate was evaporated to dryness. The residue was primarily II. Since I is more soluble in ethanol than II, II was purified readily by recrystallization from ethanol. The yield of II, m.p. 146–148°, lit.[2] m.p. 148°, varied from 0.3 to 1.5 g. (The identity of the dimer can be established by a strong absorption at 5.4 μ in the infrared.) The observed infrared spectrum checks with that in the literature.[2]

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2. Found: C, 86.4; H, 5.1.

Reaction of II with Ammonia.—A mixture of 50 ml. of absolute ethanol containing 2.58 mmoles of ammonia and 1.00 g. (2.58 mmoles) of II was kept stoppered at 25° for a week. The solvent was evaporated and the solid residue was recrystallized from ethanol. The yield of V was 0.79 g. (82%), m.p. 174–175°; infrared spectrum ($CHCl_3$): 2.78, 2.88, 3.23, 5.90, 5.94, 6.68, 6.89, 7.45, 9.27, and 9.98 μ.

Anal. Calcd. for $C_{28}H_{23}NO_2$: C, 82.9; H, 5.7; N, 3.4. Found: C, 82.8; H, 5.5; N, 3.3.

Reaction of II with Excess Ammonia.—A mixture of 50 ml. of absolute ethanol saturated with anhydrous ammonia at 0° and 0.50 g. of II was kept stoppered at 25° for 3 days. The volatile material was evaporated and the residue was boiled with 10 ml. of water. The aqueous solution was decanted and the water was evaporated. The yield of urea was 0.05 g. (67%), m.p. 124–131°, m.m.p. 126–133°. When heated in an oil bath at 150–180°, this substance formed biuret and gave off ammonia, identified by its odor and its effect on moist red litmus. The biuret was identified by the characteristic purple color it gave with a solution of cupric ions which was made basic.[12] The residue from which the water was decanted was recrystallized from ethanol to yield 0.35 g. (75%) of *sym*-tetraphenylacetone, m.p. 133–135°, lit.[8] m.p. 133–134°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.5; H, 6.1. Found: C, 89.6; H, 6.4.

Reaction of V with Excess Ammonia.—The above procedure with 0.50 g. of V gave essentially identical results.

Reaction of II with Piperidine.—A solution of 0.50 g. of II in 5 ml. of piperidine was kept at 25° for 2 days. The white solid precipitate was filtered and washed with 2 ml. of ethanol. This ethanol and 8 ml. more were added to the filtrate and more crystals formed; the total yield of X was 0.45 g. (75%), m.p. 193–195°. After recrystallization from ethanol the melting point was 195–196°; infrared spectrum ($CHCl_3$): 5.79, 6.16, 6.69, 6.93, 8.01, 8.76, 9.41, and 9.78 μ.

Anal. Calcd. for $C_{33}H_{31}NO_2$: C, 83.7; H, 6.6; N, 3.0. Found: C, 83.5; H, 6.6; N, 2.9.

Reaction of X with Excess Ammonia.—A mixture of 20 ml. of absolute ethanol, saturated with anhydrous ammonia at 0°, and 50 mg. of X[8] was kept stoppered at 25° for 3 days. The volatile material was evaporated and the solid residue was triturated with 2 ml. of ethanol to yield 40 mg. (77%) of diphenylacetamide, m.p. 164–167°, lit.[13] m.p. 168°, m.m.p. 165–167°.

For comparison purposes, *N*-**(diphenylacetyl)piperidine** was made from diphenylacetyl chloride[14] and excess piperidine; the yield, recrystallized from aqueous ethanol, was 1.0 g. (83%), m.p. 117–118°; infrared spectrum ($CHCl_3$): 6.12, 6.71, 6.95, 7.89, 8.83, 9.30, 9.88, 10.51, and 11.73 μ.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.7; H, 7.5; N, 5.0. Found: C, 81.3; H, 7.4; N, 5.0.

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[9] L. I. Smith and H. H. Hoehn, *Org. Syn.*, **20**, 47 (1940).

[10] M. Hoering, *Helv. Chim. Acta*, **42**, 1845 (1959).

[11] H. Staudinger, *Ber.*, **44**, 530 (1911).

[12] L. Gattermann, H. Wieland, and T. Wieland, "Die Praxis des organischen Chemikers," Walter DeGruyter and Co., Berlin, 1959, p. 122.

[13] F. Klingemann, *Ann.*, **275**, 85 (1893).

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Lactone Formation in the Free-Radical Addition of Iodoperfluoroalkanes to Alkenoic Acids and Esters

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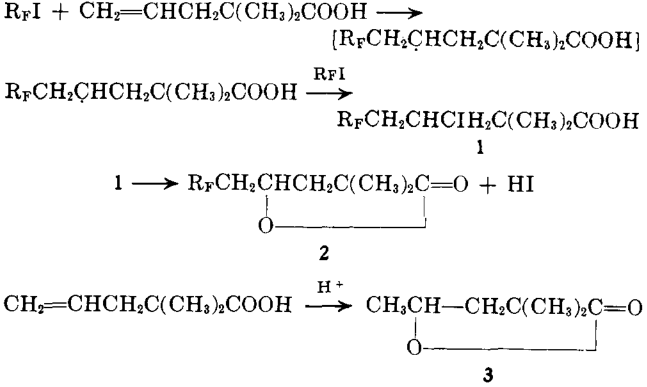
The tendency for acids with unsaturation in the γ- or δ-position to cyclize to lactones is well-known.[1,2] The primary adduct, $R_FCH_2CHI(CH_2)_3COOH$, was obtained[3] by free-radical-induced reaction of iodoperfluoroalkanes (R_FI) with 5-hexenoic acid or esters, using azonitrile initiator at 75°. By contrast, the products from thermally induced reaction of 5-hexenoic acid and R_FI at 175 or 200° included both the primary adduct and the derived δ-lactone. This has precedent in the thermal conversion at 150 to 180° of $CH_3CHBr(CH_2)_2COOC_2H_5$ to ethyl bromide and 4-hydroxypentanoic acid γ-lactone.[4] The formation of *γ-lactone* from $R_FCH{=}CH(CH_2)_3COOH$ (the expected dehydrohalogenation product)[3] or from the primary adduct would have required shifting of the double bond in our case.

In reaction of R_FI with 2,2-dimethyl-4-pentenoic acid, lactone formation was unusually facile, occurring even at 75° with the cleavage of hydrogen iodide. Soon after initiator was added to the 2,2-dimethyl-4-pentenoic acid–R_FI mixture, a reddish color of hydrogen iodide–iodine appeared; samples analyzed by gas–liquid chromatography (g.l.c.) showed both γ-lactones **3** and **2** were present. That γ-lactone rather than δ-



$$R_FI + CH_2{=}CHCH_2C(CH_3)_2COOH \xrightarrow{R\cdot} [R_FCH_2\dot{C}HCH_2C(CH_3)_2COOH]$$

$$R_FCH_2\dot{C}HCH_2C(CH_3)_2COOH \xrightarrow{R_FI} R_FCH_2CHCIH_2C(CH_3)_2COOH \quad \mathbf{1}$$

$$\mathbf{1} \longrightarrow R_FCH_2\underset{|\_\_O\_\_|}{CHCH_2C(CH_3)_2C}{=}O + HI \quad \mathbf{2}$$

$$CH_2{=}CHCH_2C(CH_3)_2COOH \xrightarrow{H^+} CH_3\underset{|\_\_O\_\_|}{CH{-}CH_2C(CH_3)_2C}{=}O \quad \mathbf{3}$$

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[1] See, for example, L. F. Fieser and Mary Fieser, "Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1956, p. 324.

[2] M. F. Ansell and M. H. Palmer, *J. Chem. Soc.*, 2640 (1963).

[3] N. O. Brace, *J. Org. Chem.*, **27**, 4491 (1962).

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