The Peracid Oxidation of Ketones. IV. The Peroxybonzoic Acid Oxidation of Cyclopentenone Derivatives*

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In the preceding paper,[1] the peracid oxidations of 4-phenyl-3-buten-2-one and its 3-substituted derivatives, and of 1, 3-diphenyl-2-propen-1-one and its 2-methyl derivative, were carried out. It was found that the unsaturated group migrated exclusively as compared to the methyl group, that the migratory aptitude of the 2-phenylethenyl group was about three times that of the phenyl group, and that the more bulky group migrated favorably.

In the present paper, the peroxybonzoic acid oxidation of the cyclic α, β-unsaturated ketone was studied. The peracid oxidation of cyclic α, β-unsaturated ketone has not been studied except for one example[2] of the trifluoroperoxyacetic acid oxidation of 2-cyclopentenone, which gave 2-hydroxyadipic acid. In this paper, the peroxybenzoic acid oxidation of 3-phenyl- and 2, 3-diphenyl-2-cyclopentenone was carried out. The acid obtained from the alkaline extract of the oxidation product was polymeric, and its crystalline derivatives could not be obtained. After the oxidation product had been esterified, the ester was hydrolyzed with dilute alkali at room temperature; the crystalline acid could thus be obtained in a 50% yield. This acid showed a m. p. of 115—116°C after recrystallization from petroleum ether and ethyl acetate. This acid and its *S*-benzylisothiouronium salt (m. p. 130—130.5°C) have the compositions of $C_{10}H_{10}O_3$ and $C_{18}H_{20}O_3N_2S$ respectively; the acid was found in a mixed melting point determination to be identical with β-benzoylpropionic acid.

From the alkaline extract of the peracid oxidation product of 2, 3-diphenyl-2-cyclopentenone, the acid A (m. p. 121.5—122°C) was obtained in a nearly quantitative yield, as based on the reacted ketone. The oxidation of A with potassium permanganate gave β-benzoylpropionic acid. The reduction of A with hydroiodic acid gave an acid with a m. p. of 134—135°C. Its methyl ester was identical in melting point and in mixed melting point with methyl γ-benzoyl-γ-phenylbutyrate prepared from desoxybenzoin, methyl acrylate and sodium ethoxide according to the procedure of Bertocchio and Dreux.[5]

It is considered that the peracid oxidation of 3-phenyl- and 2, 3-diphenyl-2-cyclopentenone proceeds through the process described in Fig. 1.

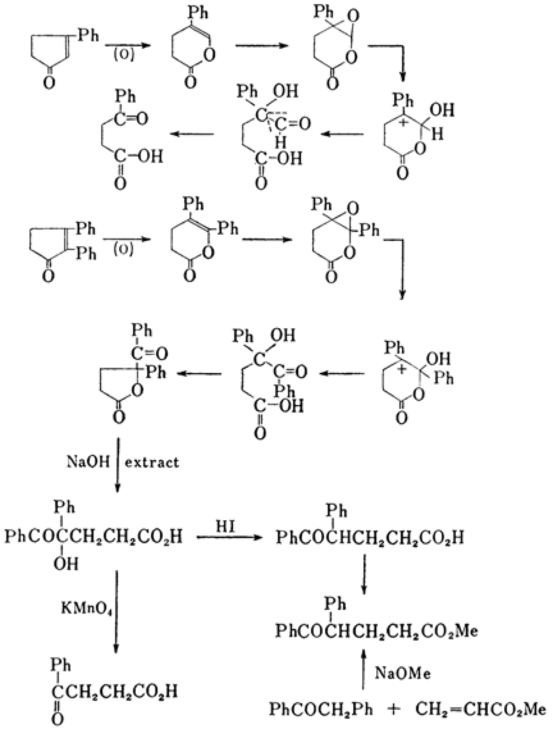

Fig. 1

These results can be explained as follows. In the favored transition state of the peracid rearrangement of cyclic α, β-unsaturated ketone, the ring has a stable half-chair conformation, and the carbon-carbon double bond participate in the oxygen-oxygen fission (Fig. 2).

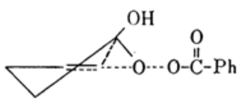

Fig. 2

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[1] T. Yokoyama and F. Nohara, This Bulletin, 38, 1498 (1965).

[2] E. E. Smissman and F. B. Block, *J. Am. Pharm. Assoc. Sci. Ed.*, Vol. XLVIII, No. 9, 526 (1959).

Experimental**

Materials.—*3-Phenyl-2-cyclopentenone* was prepared from 2% sodium hydroxide and ethyl α-phenacyl acetoacetate, which in turn had been prepared from phenacyl bromide and ethyl acetoacetate according to the procedure of Borsche and Fels;[3] m. p. 82.5—83°C (recrystallized from ethyl acetate and petroleum ether).

2,3-Diphenyl-2-cyclopentenone was obtained from 2% sodium hydroxide and ethyl α-phenyl-α-phenacylacetoacetate, which had been prepared from ethyl α-phenacylacetoacetate, phenacyl bromide and sodium in ether according to the procedure of Borsche and Klein.[4] M. p. 94—95°C.

The Peroxybenzoic Acid Oxidation of 3-Phenyl-2-cyclopentenone.—a) Ten grams of the ketone was added to a chloroform solution of peroxybenzoic acid and kept for 45 hr. at 25°C. The reaction mixture was then extracted with sodium bicarbonate solution in order to remove acids, and then it was extracted with water. The aqueous layer was combined and extracted with ether. The ethereal layer was combined with the chloroform solution and extracted with a 5% sodium hydroxide solution. When the neutral solution remaining after the sodium hydroxide extraction was evaporated, 4.8 g. of a crystalline solid was obtained. This was recovered ketone (0.03 mol.); melting point and mixed melting point with an authentic sample, 82—83°C after recrystallization from ethyl acetate and petroleum ether. The basic extracts were acidified with concentrated hydrochloric acid and extracted with ether. After the removal of the ether, 3.8 g. of an acid was obtained. This was again dissolved in ether and extracted with a sodium bicarbonate solution. From the basic extracts, 2.1 g. of an acid was obtained. This acid was a brown, viscous oil; no crystalline derivatives could be obtained.

b) 25.01 g. (0.158 mol.) of the ketone was treated with peroxybenzoic acid (0.233 mol.) at 28°C. The reaction mixture was extracted with a sodium bicarbonate solution, and then with water. The aqueous phase was combined and extracted with ether. The ethereal layer was combined with the chloroform solution and dried over anhydrous sodium sulfate. After the solvent had been removed the residual oil was refluxed 8 hr. with 240 ml. of ethanol and 12 ml. of concentrated sulfuric acid. The reaction mixture was then extracted with ether. The ethereal solution was extracted with a sodium bicarbonate solution, and the ethereal layer was dried over anhydrous sodium sulfate. The solvent was then removed, and the residue was distilled under reduced pressure. The following fractions were obtained:

Fraction I: 36.689 g., b. p. 90—100°C/20 mmHg
Fraction II: 17.411 g., b. p. 132—197°C/4 mmHg
Residue: 6.90 g.

Fraction I was ethyl benzoate. Fraction II was stirred for 2.5 hr. with 100 ml. of a 10% sodium hydroxide solution at room temperature and then the hydrolysate was extracted with ether. From the ethereal layer, the recovered ketone was obtained, (2.592 g. 0.0164 mol.). The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. After the removal of the ether, 11.003 g. of an acid was obtained, m. p. 115—116°C. The infrared spectrum of this acid showed no band in the 3000—4000 cm^{-1} region originating in the hydroxyl group.

Found for this acid: C, 66.88; H, 5.53. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%.

S-Benzylisothiouronium salt of this acid, m. p. 130—130.5°C.

Found: C, 63.28; H, 5.64. Calcd. for $C_{18}H_{20}O_3N_2S$: C, 62.80; H, 5.81%.

From these results, this acid was confirmed to be β-benzoylpropionic acid; identification was established by a mixed melting point determination with an authentic sample. The yield of β-benzoylpropionic acid was 50% on the basis of the reacted ketone.

The Peroxybenzoic Acid Oxidation of 2,3-Diphenyl-2-cyclopentenone.—24.59 g. (0.105 mol.) of the ketone was added to 0.14 mol. of peroxybenzoic acid at 28°C for 24 hr. After the acids had been removed with sodium bicarbonate, 30.76 g. of a crude reaction product was obtained. This was dissolved in ether and extracted with a 10% sodium hydroxide solution. From the ethereal solution after the sodium hydroxide extraction, 13.016 g. (0.0556 mol.) of the recovered ketone was obtained. To the basic extracts, concentrated hydrochloric acid was added and then extracted with ether. The ethereal solution was extracted with the sodium bicarbonate solution. From the ethereal solution after the sodium bicarbonate extraction, 1.73 g. of an oil was obtained. The morpholide of this oil showed a m. p. of 188—188.5°C and showed no depression on a mixed melting point determination with the morpholide of the crude oxidation product. It was confirmed that this oil was the lactone of the acid A and that the peracid oxidation product contained this lactone.

To the sodium bicarbonate extracts, concentrated hydrochloric acid was added and then extracted with ether. After the removal of the ether, 12.088 g. of an acid A was obtained (m. p. 121.5—122°C, recrystallized from ethyl acetate and petroleum ether). This acid showed an infrared absorption band at 3450 cm^{-1} (OH) and gave a benzoyl derivative, m. p. 40—41.5°C. The oxidation of A with potassium permanganate in an acidic media gave an acid, m. p. 115—116°C, a mixed melting point determination with β-benzoylpropionic acid showed no depression. To the acid A, was added an excess of 57% hydroiodic acid; this mixture was then refluxed for one hour under a constant stream of dry nitrogen. The mixture was then dissolved in ether and dried. The removal of the solvent gave an acid, m. p. 134—134.5°C; its methyl ester had a m. p. of 60—61.5°C. This methyl ester was methyl γ-benzoyl-γ-phenylbutyrate; identification was made by means of a mixed melting point determination with an authentic sample which had been prepared from methyl acrylate, desoxybenzoin and sodium ethoxide according to the procedure of

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** All melting points are uncorrected.

[3] W. Borsche and A. Fels, *Ber.*, 39, 1809, 1922 (1906).

[4] W. Borsche and A. Klein, ibid., 72B, 2082 (1939).

Bertocchio and Dreux.⁵⁾ The acid A also showed no depression on admixture with an authentic specimen. The yield of A was 86% and that of the lactone of A was 12% on the basis of the reacted ketone.

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5) R. Bertocchio and J. Dreux, *Bull. soc. chim. France*, **1962**, 823.