The Peracid Oxidation of Ketones. III. The Reaction of α, β-Unsaturated Ketones with Peroxybenzoic Acid*[1]

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In preceding papers[1] it was reported that the rate sequence of the peracid oxidation of ketones was the reverse to that of their oximation, and that the ketone peroxide was rearranged in the presence of both acid and peracid. It was concluded that the rate-determining step was the rearrangement of the addition intermediate which is formed by the nucleophilic attack of the peracid on the ketone. From the migratory aptitude in cycloalkylphenylketones,[2] it was considered that the most bulky group which is conformationally trans to the leaving carboxyl group migrates preferentially. Recently, Howthorne and his co-workers[3] reported that the rate-determining step was the acid-catalyzed decomposition of the peracid-ketone adduct and suggested that, in migration, although both electronic and steric effects were important, the electronic interpretation appeared to be the most promising.

In the present paper, the peracid oxidation of α, β-unsaturated ketones will be undertaken in an attempt to provide additional information. Böeseken and his co-workers[4] studied the peroxyacetic acid oxidation of 4-phenyl-3-buten-2-one and 3-methyl-4-phenyl-3-buten-2-one; they were found to give mainly the enol acetates of phenylacetaldehyde and of phenylacetone respectively. The authors also carried out the peroxybenzoic acid oxidation of the same ketones and obtained the same products exclusively. These results show that mainly the unsaturated group rearranges. It is interesting to compare the migratory aptitude of the unsaturated group with that of the phenyl group, which has a superior migratory ability. When the peroxybenzoic acid oxidation of 1, 3-diphenyl-2-propen-1-one and 2-methyl-1, 3-diphenyl-2-propen-1-one was carried out, the analysis of the product showed phenyl migrations of 20 and 14% respectively. It is considered that the reaction proceeds through the process described in Scheme 1, that the migratory aptitude of the 1-methyl-2-phenylethenyl group is somewhat larger than that of the 2-phenylethenyl group, and that the migratory ability of the 2-phenylethenyl group is about three times that of the phenyl group.

Meanwhile, it has been reported by Wenkert and Rubin[5] that α-phenyl-α, β-unsaturated

$$RCH=C-COCH \rightarrow$$
$$\overset{|}{C_6H_5}$$

$$RCH=C-COOCH_3 + RCH\overset{O}{\overset{\wedge}{\frown}}C-COCH_3$$
$$\overset{|}{C_6H_5} \qquad\qquad \overset{|}{C_6H_5}$$
$$(I) \qquad\qquad\qquad (II)$$

*[1] Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

1) Y. Yukawa and T. Yokoyama, J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi), 73, 370 (1952); Memoirs of Inst. of Sci. and Ind. Research, IX, 180 (1952); ibid., XII, 159 (1655).
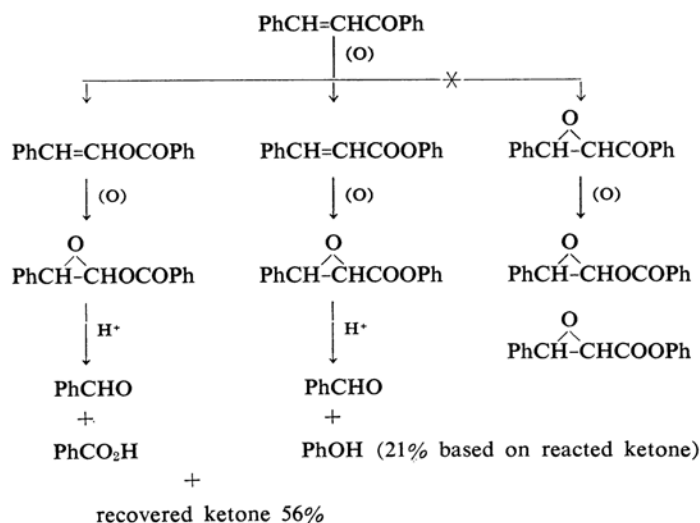
2) Y. Yukawa and T. Yokoyama, J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi), 77, 190 (1956); J. Inst. Polytech., Osaka City Univ., Vol. 5, No. 1., Seri. C., 158 (1956).

3) M. F. Howthorne, W. D. Emmons and K. S. McCallum, J. Am. Chem. Soc., 80, 6393 (1958).

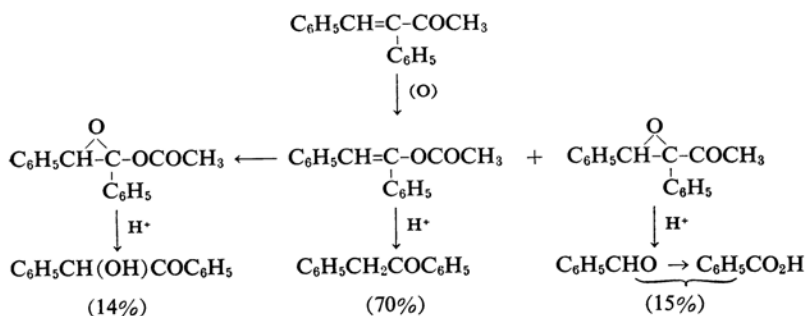4) L. Böeseken and A. L. Soeman, Rec. trav. chim., 52, 874 (1933); J. Böeseken and J. Jacobs, ibid., 55, 786 (1936).
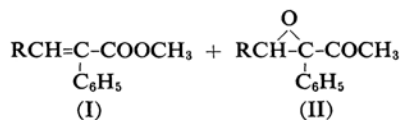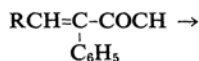
5) E. Wenkert and M. Rubin, Nature, 170, 708 (1952); C. H. Hassall, "Organic Reaction," Vol. 9, 81 (1957).

PhCH=CHCOPh
|(O)

PhCH=CHOCOPh　　　　PhCH=CHCOOPh　　　　$\overset{O}{\overset{\triangle}{PhCH-CHCOPh}}$
|(O)　　　　　　　　　　|(O)　　　　　　　　　　　|(O)

$\overset{O}{\overset{\triangle}{PhCH-CHOCOPh}}$　　　$\overset{O}{\overset{\triangle}{PhCH-CHCOOPh}}$　　$\overset{O}{\overset{\triangle}{PhCH-CHOCOPh}}$
|H+　　　　　　　　　　|H+

PhCHO　　　　　　　　　PhCHO　　　　　　　$\overset{O}{\overset{\triangle}{PhCH-CHCOOPh}}$
+　　　　　　　　　　　+

PhCO₂H　　　　　　　　PhOH (21% based on reacted ketone)

+

recovered ketone 56%

Scheme 1

C₆H₅CH=C-COCH₃
|
C₆H₅
|(O)

$\overset{O}{\overset{\triangle}{C_6H_5CH-C-OCOCH_3}}$ ⟵ C₆H₅CH=C-OCOCH₃ + $\overset{O}{\overset{\triangle}{C_6H_5CH-C-COCH_3}}$
|　　　　　　　　　　　|　　　　　　　　　　　　　　|
C₆H₅　　　　　　　　　C₆H₅　　　　　　　　　　　　C₆H₅
|H+　　　　　　　　　　|H+　　　　　　　　　　　　　|H+

C₆H₅CH(OH)COC₆H₅　　C₆H₅CH₂COC₆H₅　　　C₆H₅CHO → C₆H₅CO₂H
(14%)　　　　　　　　　(70%)　　　　　　　　　(15%)

Scheme 2

ketone reacted with peroxyacetic acid to give a mixture consisting mainly of compounds I and II.

This indicates that the methyl group migrates exclusively. To confirm this point, the proxybenzoic acid oxidation of 3, 4-diphenyl-3-buten-2-one was carried out. The hydrolysis of the peracid oxidation products gave desoxybenzoin as a main product, plus small amounts of bezoin, benzaldehyde and benzoic acid. On the other hand, the peroxybenzoic acid oxidation of methyl α-phenyl cinnamate gave neither benzoin nor desoxybenzoin. These results show that the reaction proceeds through the process described in Scheme 2 and that the unsaturated group migrates exclusively.

These results indicate that the unsaturated group migrates exclusively as compared to the methyl group, that the migratory aptitude of the 2-phenylethenyl group is about three times that of the phenyl group, and that the more bulky groups migrate favorably. These results and the kinetic results[*2] (the rate of the peroxybenzoic acid oxidation of 4-phenyl-

3-buten-2-one was 2×10^2 faster than that of acetophenone) suggest that the favored transition state involves the participation of the carbon-carbon double bond.

Experimental[*3]

Materials.—*1, 3-Diphenyl-2-propen-1-one* was prepared from benzaldehyde and acetophenone according to the procedure of Kohler and Chadwell[6]; m. p. 56—57°C.

2-Methyl-1, 3-diphenyl-2-propen-1-one was prepared from benzaldehyde and propiophenone according to a procedure similar to the above one. B. p. 173—174°C/3 mmHg.

3, 4-Diphenyl-3-buten-2-one was prepared from benzaldehyde, phenylacetone, benzene and piperidine with a Dean and Stark distillation apparatus according to the procedure of Zimmerman, Singer and Thyagarajan.[7] B. p. 162—163°C/3 mmHg, m. p. 55—56°C.

The Peroxybenzoic Acid Oxidation of 1, 3-Diphenyl-2-propen-1-one.—10.69 g. (0.0514 mol.) of the ketone was added to a chloroform solution

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*2 The kinetic studies are now in progress.

*3 All melting points are uncorrected.
6) E. P. Kohler and H. W. Chadwell, "Organic Syntheses," Coll. Vol. I, 78 (1948).
7) H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

containing 0.0624 mol. of peroxybenzoic acid. The reaction mixture was swirled at intervals and then kept for 45 hr. in a thermostat maintained at 25°C. The reaction mixture was then extracted with an aqueous sodium bicarbonate solution in order to remove acids; then it was extracted 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 under reduced pressure, the residue was hydrolyzed by refluxing it for 10 hr. with 15% sulfuric acid and the hydrolysate was extracted with ether in a continuous extraction apparatus for 10 hr. The ethereal solution was shaken with a 15% sodium hydroxide solution and distilled under reduced pressure. The following fractions were obtained:

Fraction I: 1.64 g., b. p. 41—48°C/3 mmHg
Fraction II: 5.99 g., b. p. 159—187°C/3 mmHg
Residue: 1.62 g.

Fraction I was benzaldehyde (0.0155 mol.), identified as its 2,4-dinitrophenylhydrazone, m. p. 236 237°C; when it was mixed with an authentic sample, its melting point was not depressed.

Fraction II was the recovered ketone (0.0288 mol.); melting point and mixed melting point with an authentic sample, 54—55°C after recrystallization from ethyl acetate and petroleum ether.

To the alkaline solution dilute hydrochloric acid was added until a small amount of precipitate appeared, and then sodium bicarbonate was added. The mixture was then shaken violently and extracted with ether 10 hr. in a continuous extraction apparatus. The removal of the solvent gave 0.43 g. (0.0047 mol.) of phenol, which was then converted to tribromophenol (m. p. 87—89°C, melting point and mixed melting point with an authentic sample, 94—95°C after recrystallization from ethanol). To the aqueous solution, concentrated hydrochloric acid was added and then extracted with ether. The ethereal extracts were dried over anhydrous sodium sulfate. After the removal of the solvent, 1.89 g. (0.0155 mol.) of benzoic acid was obtained. The ratio of phenol to the reacted ketone, which corresponds to the extent of phenyl migration, was 20.8%. The repetition of the experiment showed a 21.3% phenyl migration.

The ester content in the products was analyzed by a saponification test. Thus, 0.576 g. of the peracid oxidation product mixture was stirred with 50 ml. of a 0.096 N sodium hydroxide solution for 20 hr. at room temperature, and then the excess alkali was back-titrated with 0.102 N hydrochloric acid. 11.9 ml. of the alkaline solution was consumed. It was ascertained that the starting ketone and 2,3-epoxy-1,3-diphenyl-2-propen-1-one consumed only 0.3 ml. and 0.5 ml. of the alkaline solution, respectively, under the same conditions. These results indicate that the product mixture was exclusively made up of the epoxy ester (0.0012 mol.) and the starting ketone (0.0013 mol.).

The Peroxybenzoic Acid Oxidation of 1,3-Diphenyl-2-methyl-2-propen-1-one.—15.81 g. (0.071 mol.) of the ketone was treated with peroxybenzoic acid (0.0763 mol.) at 25°C for 118 hr. When the reaction product was then treated as above, 1.98 g. (0.0187 mol.) of benzaldehyde and 8.66 g. (0.0389 mol.) of the recovered ketone were obtained from the neutral fraction. From the acidic fraction, 3.08 g. (0.0253 mol.) of benzoic acid and 0.49 g. (0.00477 mol.) of phenol were obtained. The yield of phenol based on the reacted ketone was 14.3%; the extent of phenyl migration was estimated to be 14.3%. The repetition of the experiment showed 13.6%.

The Peroxybenzoic Acid Oxidation of 3,4-Diphenyl-3-buten-2-one. — 13.380 g. (0.060 mol.) of the ketone was treated with peroxybenzoic acid (0.0712 mol.) at 27°C. From the acidic fraction of the hydrolysate, 0.854 g. (0.007 mol.) of benzoic acid was obtained. From the neutral fraction, the following fractions were obtained.

Fraction I: 1.353 g., b. p. ~110°C
Fraction II: 0.216 g., b. p. 52—57°C/6 mmHg
Fraction III: 10.110 g., b.p. 162—182°C/6 mmHg
Residue: 0.844 g.

Fraction II was benzaldehyde (0.002 mol.) identified as its 2,4-dinitrophenylhydrazone; a mixed melting point determination with an authentic sample showed no depression. From fraction III, crystals of benzoin (1.74 g.) were separated; melting point and mixed melting point with an authentic sample, 131—132°C after recrystallization from ethanol. The 2,4-Dinitrophenylhydrazone of the liquid part was fractionally crystallized from ethyl acetate and an orange yellow crystal (m. p. 198—199°C) was obtained. This was identified with the 2,4-dinitrophenylhydrazone of desoxybenzoin on the basis of a mixed melting point determination. From the mother liquor, small amounts of red crystals (m. p. 200—201°C) were obtained. A mixed melting point determination with the 2,4-dinitrophenylhydrazone of the starting ketone gave no depression. It was shown that the neutral fraction was made up of 1.74 g. (0.0082 mol.) of benzoin, 8.37 g. (0.043 mol.) of desoxybenzoin, 0.22 g. (0.002 mol.) of benzaldehyde, 0.85 g. (0.007 mol.) of benzoic acid, and a small amount of the recovered ketone.

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