Oxidative Cleavage of 1-Phenyl-dialin with Peracetic Acid

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The present authors, recently, have carried out an extensive study on the oxidative cleavage of various compounds with peracetic acid, and it has been found that the hydroaromatic ring was readily dehydrogenated by peracetic acid. Our previous reports1) indicated that the oxidative cleavage of dialin proceeded in two different reactions in an initial stage; the one was epoxidation and the other, dehydrogenation. On the contrary, the oxidative cleavage of 1-alkyl-dialin (4-alkyl-Δ^1-dialin) was shown to proceed by a predominant epoxidation with no dehydrogenation owing to the influences of alkyl groups.

In order to investigate the substituent-effects of phenyl group, the oxidative cleavage of 1-phenyl-dialin (4-phenyl-Δ^1-dialin) was carried out with peracetic acid. A mixture of 1-phenyl-dialin, ammonium molybdate and glacial acetic acid was heated at 40°C, and then 30% hydrogen peroxide solution was added. After the addition was completed, the reaction mixture was still maintained at the same temperature for further 12 hr.

From the neutral part, melilotine and 1-phenyl-tetralone-2 were isolated, and the presence of monoacetate of 1,2-dihydroxy-1-phenyl-tetralin was confirmed, but unreacted 1-phenyl-dialine was not found. Moreover, the products obtained from the acidic part were benzoic acid, melilotic acid and the benzoate of melilotic acid. The benzoate of melilotic acid was confirmed by elementary analysis, infrared spectrum measurement and hydrolysis. In the ultraviolet spectrum of the compound in 95% ethanol, the maximum absorption is present in 263 mμ (log ε 3.45) and 272 mμ (log ε 3.35). It is very interesting to note that no product formed by dehydrogenation was isolated.

From these results and also by analogy with the case of 1-alkyl-dialin, it was concluded that the reaction of peracetic acid with 1-phenyl-dialin proceeded by a predominant epoxidation with no dehydrogenation, followed by the oxidative cleavage. Although *o*-carboxyethyl-benzophenone could not be isolated, it might be considered to be the precursor of the benzoate of melilotic acid. Thus the essential steps in the reaction were as follows;

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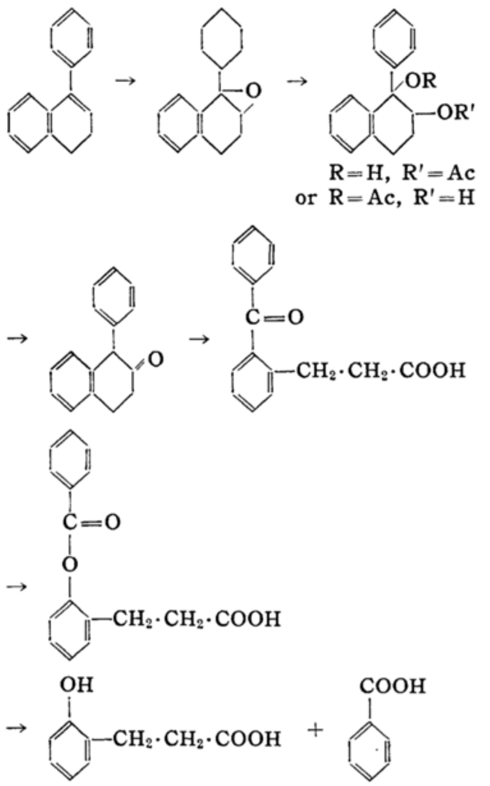
1) Y. Odaira and S. Tsutsumi, *Technol. Repts. Osaka Univ.*, 8, 455 (1958).



In order to obtain further evidence for the above sequence, an authentic 1-phenyl-tetralone-2 was oxidized with peracetic acid and the benzoate of melilotic acid, benzoic acid and melilotic acid were isolated in good yields as the oxidation products.

Compared with the case of 1-alkyl-dialin, it is very interesting that the Baeyer-Villiger reaction occurred because of the effect of phenyl substituent in this case.

It is generally accepted that, in the cleavage of unsymmetrical diaryl ketones[2)] by the Baeyer-Villiger oxidation, the migrating group is normally the more electron-releasing one. For example, treatment of *p*-methyl-benzophenone with peracetic acid gives benzoic acid and *p*-cresol; that is, *p*-tolyl group migrates more readily than phenyl group. On the other hand, the oxidation of *o*-methyl-benzophenone with peracetic acid[3)] leads to the mixture of *o*-tolylbenzoate (12%) and phenyl-*o*-toluate (38%). Therefore, it is obvious that the ortho-effect can even overcome, to some extent, an electronic effect in the opposite direction (*o*-tolyl vs. phenyl).

In the series $Ph\cdot(CH_2)_n\cdot COOH$ it was found that, whereas the absorption band of benzoic acid is at 268 mμ (ε 1780), the ω-phenyl fatty acids from phenyl-butyric acid upwards have the absorption maximum at 260 mμ with greatly reduced intensity (ε ca. 200), and that this absorption is almost identical in every respect with that of a mixture of ethylbenzene and acetic acid[4)]. Moreover, *o*-toluic acid and *o*-carboxyethyl-benzoic acid have the same maximum band at 278 mμ (log ε 3.15 and 3.08, respectively).

From the above ultraviolet spectra results, it may be assumed that no resonance between carboxyl group and benzoyl group in the molecule of *o*-carboxyethyl-benzophenone exhibits, and the compound will be considered as identical with *o*-methyl-benzophenone from the electronic point of view. If the above concept is true, phenyl group should migrate more easily than *o*-carboxyethyl-phenyl group owing to the ortho-effect, and one would expect the stronger retarding effect of *o*-carboxyethyl group, since this group is bulkier than methyl group. Actually, the reverse result was obtained in our experiments; namely, only the benzoate of melilotic acid was isolated and the migration of *o*-carboxyethyl-phenyl group occurred predominantly.

A more plausible explanation of such an abnormal phenomenon appears to be the steric assistance caused by steric interference of *o*-carboxyethyl group. Further discussion of the problem of the steric assistance in the Baeyer-Villiger reaction now requires more detailed experiments.

Experimental

Reagent.—1-Phenyl dialin, (b. p. 178~180°C/12 mmHg; $n_D^{20.5}$ 1.6323), was prepared from tetralone-1 according to the procedure of Weiss[5)] in 55% yield. Ultraviolet absorption spectrum: λ_{max} 227.5 mμ, log ε 4.26; 265.0 mμ, log ε 3.92; λ_{min} 248.0 mμ, log ε 3.84 (*iso*-octane). Infrared absorption spectrum: ν_{max} 1500, 1600 cm^{-1} (aromatics), 827 cm^{-1} ($CR_1R_2=CHR_3$); no OH band.

Oxidative Cleavage of 1-Phenyl-dialin.—A mixture of 1-phenyl-dialin (15 g.), ammonium molybdate (0.13 g.) and glacial acetic acid (240 cc.) was heated at 40°C, and then 30% hydrogen peroxide solution (30 cc.) was slowly added with stirring in the course of 2 hr. After the addition, the solution was maintained at the same temperature with continued stirring for another 12 hr. To the above solution was added hot water (350 cc.) with stirring to decompose most of unreacted peracetic acid and allowed to stand

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2) C. Hassall, *Org. Reactions*, **9**, 73 (1957).

3) W. Saunders, *J. Am. Chem. Soc.*, **77**, 4679 (1555).

4) P. Ramart-Lucas, *Bull. soc. chim.*, **10**, 13 (1943).

5) R. Weiss, *Org. Syntheses*, **24**, 84 (1944).

for 2 days. The reaction mixture was concentrated as completely as possible on a steam bath under reduced pressure (40°C/20 mmHg).

The orange residue obtained was dissolved in ethyl ether (350 cc.), the ethereal layer was extracted with three 200 cc. portions of 10% aqueous sodium bicarbonate and divided into the ethereal layer (I) and the sodium bicarbonate solution (II). The ethereal layer (I) was washed with water and dried over anhydrous sodium sulfate. After evaporation, 5.5 g. of the yellowish residual oil was distilled under reduced pressure. The product, on fractionation, gave: (i) b. p. 120~140°C/6 mmHg (0.5 g., n_D^{28} 1.5560); (ii) b. p. 180~195°C/6 mmHg (2.7 g., n_D^{28} 1.6080); and (iii) dark orange residue (2.0 g.).

The fraction i, having the perfume like coumarine, showed the presence of lactone group (ν_{max} 1786, 1754 cm^{-1}) and ortho-substitution (ν_{max} 757, 746 cm^{-1}) in the infrared spectrum, and gave 0.32 g. of melilotic acid, m. p. 82~83°C, by hydrolysis with 25% potassium carbonate.

Melilotic acid obtained showed no melting point depression by mixing with the authentic melilotic acid prepared from coumarine. From these facts, the above fraction i was determined as melilotine.

The fraction ii gave a positive Brady's test and showed the presence of carbonyl group in the infrared spectrum. Oxime of the fraction ii was obtained as colorless needles, m. p. 184~185°C.

Anal. Found: N, 5.97. Calcd. for $C_{16}H_{15}ON$: N, 5.90%.

Lit. b. p. 156~158°C/1 mmHg (n_D^{24} 1.6089) for 1-phenyltetralone-2; m. p. 184~185°C for oxime of 1-phenyltetralone-2.

From these facts, the carbonyl compound obtained in the fraction ii was confirmed to be 1-phenyl-tetralone-2. A mixture of the fraction iii and 30% sulfuric acid (15 cc.) was heated under reflux for 3.5 hr. After cooling, the reaction mixture was treated in the usual ways and gave 0.8 g. of brown oil. The oxime obtained from the above oil melted at 184~185°C and weighed 0.34 g. Since the oxime was identified as the oxime of 1-phenyl-tetralone-2, it might be considered that monoacetate of 1,2-dihydroxy-1-phenyl-tetralin was contained in the fraction iii, the yield calculated from the oxime obtained was 0.402 g.

The above sodium bicarbonate solution II was acidified with dilute hydrochloric acid and saturated with sodium chloride and extracted with ethyl ether. The ethereal extract was washed with water and dried over anhydrous sodium sulfate. After the solvent was evaporated, 10.7 g. of crude acid was isolated. The crude acid was distilled under reduced pressure. The product, on fractionation, gave: i b. p. 125~200°C/7 mmHg (3.2 g.); and ii brown viscous residue.

The fraction i was recrystallized from water to 1.1 g. of colorless needles, m. p. 121°C. *p*-Bromo-phenacyl-ester of this crystal was obtained as colorless needles, m.p. 119°C. Since this crystal showed no melting point depression by mixing with pure benzoic acid, and the infrared spectrum of this crystal was in good agreement with that of pure benzoic acid, the above crystal was confirmed to be benzoic acid.

The above recrystallization mother liquor was extracted with ethyl ether and dried over anhydrous sodium sulfate. After the solvent was evaporated, the yellowish residual oil was distilled, giving a colorless oil, b. p. 265~275°C. Hydrolysis of this oil with 25% potassium carbonate gave 0.45 g. of colorless needles, m. p. 82~83°C, identified as melilotic acid by mixed fusion.

The fraction ii, a brown viscous residue, was dissolved in benzene-light petroleum ether (1 : 1) and chromatographed by passing the solution through a silica-gel column. The column was then eluted with benzene and evaporation of benzene from the effluent left 3.3 g. of colorless crystals, m. p. 144~145°C. Recrystallization from benzene afforded colorless needles, m. p. 145.5°C.

Anal. Found: C, 70.96; H, 5.47. Calcd. for $C_{16}H_{14}O_3$: C, 71.10; H, 5.22%.

Infrared analysis showed the absence of diaryl-ketone group and hydroxyl group, whereas the presence of the hydroxyl stretching vibration of carboxyl group (ν_{max} 2700 cm^{-1}) and carbonyl group (ν_{max} 1730, 1706 cm^{-1}). *p*-Bromo-phenacyl-ester of the above crystals was obtained as colorless needles, m. p. 166~167°C.

In the ultraviolet spectrum of the above crystals, m. p. 145.5°C, the maximum absorption lies at 263 mμ (log ε 3.447) and 272 mμ (log ε 3.555) in 95% ethanol.

Moreover, hydrolysis of 2 g. of the above substance by sodium-alcoholat gave 0.78 g. of benzoic acid and 0.86 g. of melilotic acid. From these facts, the above substance was identified to be the benzoate of melilotic acid.

Oxidative Cleavage of 1-Phenyl-tetralone-2.—A mixture of 1-phenyl-tetralone-2 (2.5 g.), ammonium molybdate (0.02 g.) and glacial acetic acid (40 cc.) was heated at 40°C, and then 30% hydrogen peroxide solution (50 cc.) was slowly added with stirring. After the addition, the reaction mixture was kept at the same temperature with continued stirring for 14 hr. The reaction mixture was treated in the usual ways. Remaining 1-phenyl-tetralone-2, the benzoate of melilotic acid, benzoic acid and melilotic acid were obtained, and the yields were 1.6 g., 12 mg., 0.25 g. and 0.22 g., respectively.

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