Barium Dibenzyl Phosphate.—A solution of 212 ml. of benzyl alcohol in 200 ml. of absolute ether was cooled to 0°. With agitation and cooling, there was added 90 g. of phosphorus pentoxide. The resulting solution was refluxed for 24 hours. Differential titration of an aliquot taken at this time indicated that the distribution of phosphorus was 49.5% as dibenzyl phosphate, 41.6% as monobenzyl phosphate and 3.8% as phosphoric acid. In a duplicate experiment the indicated yields were 50.6, 41.6 and 4.5%, respectively. The ether solution was then concentrated to a sirup under reduced pressure and the residue was poured into a slurry of 200 g. of barium carbonate and ice in water. Barium hydroxide solution was added until the pH rose from 4 to 11. The slurry then was heated to 60° with free steam and filtered hot from barium monobenzyl phosphate. The filtrate at this point amounted to about 4 liters. The cake was slurried with one liter of boiling water for 90 minutes and filtered. The combined filtrates were concentrated under reduced pressure. After distillation of about 1200 ml. a small amount of barium monobenzyl phosphate precipitated and was removed by filtration. Concentration was resumed and the barium dibenzyl phosphate began to crystallize. When the residual volume was about 1800

ml., the first crop of barium dibenzyl phosphate was collected and when dry weighed 79.5 g., m.p. 290–295°. Further concentration gave a second crop of 18.55 g., m.p. 293–296°.[19] The total yield (98 g.) corresponds to 45% of that indicated by titration.

Silver Dibenzyl Phosphate.—Barium dibenzyl phosphate (125 g.) was dissolved in 4350 ml. of boiling water. The solution was filtered hot from traces of insoluble material. With agitation and in the dark there was added to the solution a solution of 64.5 g. of silver nitrate in 100 ml. of water. The silver salt began to separate immediately. The suspension was protected from light and chilled. The silver dibenzyl phosphate was collected, washed successively with cold water and cold methanol and dried. The silver salt weighed 114.86 g. (82.5%) and melted upon rapid heating at 229–231°.[20] Titration with standard potassium thiocyanate indicated a purity of 99.7%.

(19) On the same scale Lynen[12] reported a yield of 75 g., m.p. 255–261°.

(20) Lynen[12] reported m.p. 216° dec.

RAHWAY, N. J.

# The Peracetic Acid Oxidation of Dehydronorcamphor

BY JERROLD MEINWALD, MICHAEL C. SEIDEL AND BARRY C. CADOFF

Peracetic acid reacts with dehydronorcamphor (II) to give a mixture of lactones (VI and IX) rather than the epoxide I. The mechanism of this transformation is discussed briefly, and some general conclusions regarding the oxidation of β,γ-unsaturated ketones with peracids are drawn.

In an attempt to prepare dehydronorcamphor epoxide (I), the reaction of dehydronorcamphor[1] (II) with peracetic acid has been investigated. Reaction conditions suitable for the conversion of norbornene to norbornene epoxide[2] were chosen, and a liquid transformation product, b.p. 131–132° (22 mm.), was obtained. Although the elementary analysis of this product corresponded to the expected formula ($C_7H_8O_2$), it soon became evident that the desired ketoepoxide I had not been formed. Thus, although the infrared spectrum of the
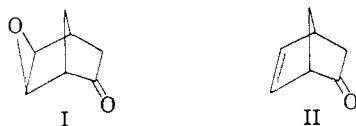
product showed two clearly distinct carbonyl peaks at 5.65 and 5.80 μ, no derivatives could be obtained with either semicarbazide or 2,4-dinitrophenylhydrazine. Since the product appeared to be non-ketonic, it was concluded that the peracetic acid had attacked the carbonyl group of II rather than the olefinic linkage.

The transformation of cyclic ketones into lactones, using persulfuric acid, was described for the first time by Baeyer and Villiger in 1899[3]; closely related reactions involving organic peracids have since been quite extensively studied.[4] Although

one might at first expect olefin epoxidation to take precedence over the Baeyer–Villiger type reaction, the oxidation of a β,γ-unsaturated ketone to an unsaturated lactone has been observed before. Thus, Mori and Mukawa[5] have shown recently that the so-called "α-epoxide" derived from Δ^5-cholestenone (III), first prepared by Ruzicka and Bosshard,[6] is in reality the lactone IV. In this case,
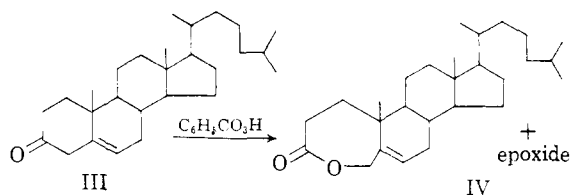
an appreciable amount of the normal epoxide also is formed. However, in the case of dehydronorcamphor it is not hard to understand the reduced reactivity of the olefinic bond, since the carbonyl function is held in a position which is particularly suitable for electron withdrawal (see formula IIa), thus making the double bond unusually resistant to electrophilic attack. A similar phenomenon has been encountered and rationalized in this way by Woodward, et al.,[7] who found that the non-conjugated double bond in the lactone V could not be selectively epoxidized with perbenzoic acid, undoubtedly because of electron release from the double bond to the lactonic carbonyl group.

(1) For a convenient preparation of II, see P. D. Bartlett and B. E. Tate, THIS JOURNAL, 78, 2473 (1956).

(2) H. M. Walborsky and D. F. Loncrini, ibid., 76, 5396 (1954).

(3) A. von Baeyer and V. Villiger, Ber., 32, 3625 (1899).

(4) For a convenient, although not encyclopedic, review of this reaction see C. H. Hassall's article in R. Adams, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York. N. Y., 1957, pp. 73–106.

(5) S. Mori and F. Mukawa, Bull. Chem. Soc. Japan, 27, 479 (1954).

(6) L. Ruzicka and W. Bosshard, Helv. Chim. Acta, 20, 244 (1937).

(7) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey and R. W. Kierstead, Tetrahedron, 2, 1 (1958).

IIa   V
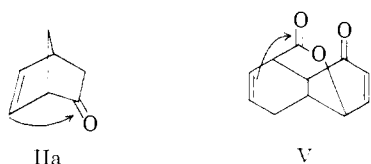
Assuming that the peracid oxidation of ketones to esters proceeds by the addition of the peracid across the carbonyl group, followed by departure of a carboxylate anion (or of a carboxylic acid in the presence of an acid catalyst) accompanied by the migration of a suitable group toward the incipient positive oxygen (equation 1),[4] it is easy to arrive at the lactonic structure VI as one possible product to be derived from II. It is to be noted that VI

$$II \longrightarrow \quad \cdots \quad \xrightarrow{\quad} \quad \xrightarrow{-H^{\oplus}} \quad (1)$$

VI
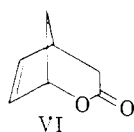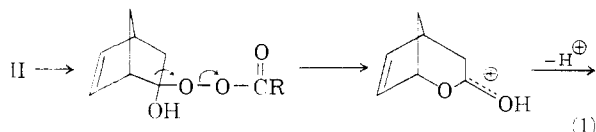
would be formed *via* migration of the bridgehead carbon atom. Purely on the basis of electronic considerations, this would be an excellent migrating group in the case of II. An alternate possibility requiring consideration, however, would involve migration of the methylene group adjacent to the carbonyl, which would give rise to the isomeric product VII.[8]
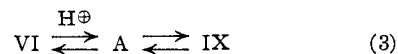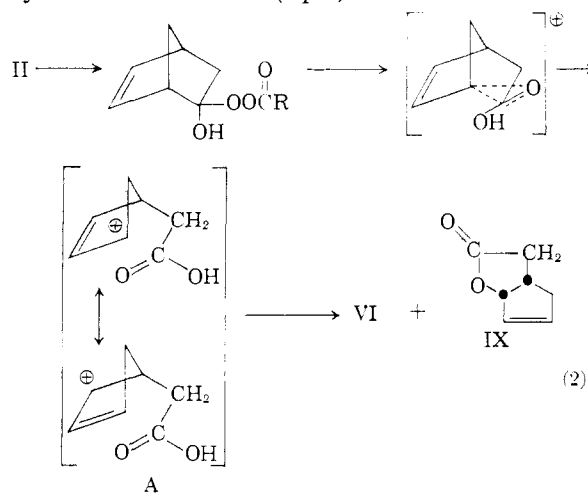
VII   VIII

One striking reaction served to clarify the course of the peracetic acid oxidation. Catalytic hydrogenation of the lactonic product resulted in the rapid uptake of *two* moles of hydrogen, and gave rise to an *acidic* substance in good yield, accompanied by a small amount of neutral material. This acid was identified readily as cyclopentylacetic acid (VIII) by direct comparison of both the free acid and its crystalline amide with authentic, independently prepared specimens of these compounds. The one-step conversion of the Baeyer–Villiger product into VIII is in accord with structure VI, which would be expected to hydrogenolyze and hydrogenate in precisely this fashion; it serves to exclude VII from further consideration.

One remaining difficulty is that VI should show 5.80 μ absorption (δ-lactone) but not 5.65 μ absorption. It therefore seemed that the Baeyer–

(8) The problem of predicting the product of the Baeyer–Villiger oxidation of bicyclic ketones is an interesting one, and is receiving attention in this Laboratory. Camphor itself has been shown to undergo methylene rather than bridgehead migration.[3] Apocamphor behaves similarly (see O. Komppa, *Ber.*, **47**, 933 (1914)). In contrast, recent work of E. X. Frauenglass has shown that norcamphor suffers bridgehead migration when treated with peracetic acid. It is hoped to present the results of these experiments in THIS JOURNAL in the near future.

Villiger product was a mixture of compounds, the second component being a γ-lactone which would also hydrogenolyze and hydrogenate to give VIII. Attempts to separate this mixture into individual components were unsuccessful, but gave some additional information. Thus, attempted fractional distillation gave rise to fractions where the ratio of the two carbonyl intensities varied, but in which the 5.80 μ band was always of lesser intensity than in the original mixture. In fact, different runs of the peracetic acid reaction gave products with varying relative carbonyl intensities. Finally, chromatography of the product on Magnesol–Celite or treatment with sulfuric acid resulted in the obtention of a material showing only the 5.65 μ band in the carbonyl region.

The most likely structure for this 5.65 μ component is that shown below as IX. This would have the proper infrared absorption, would behave exactly as VI on hydrogenation, and could arise either directly in the peracid oxidation (eq. 2) or by isomerization of VI (eq. 3).

$$II \longrightarrow \cdots \longrightarrow \cdots \longrightarrow$$

A

$$\longrightarrow VI \; + \quad IX$$

$$(2)$$

$$VI \underset{\xleftarrow{\quad}}{\overset{H^{\oplus}}{\rightleftharpoons}} A \rightleftharpoons IX \qquad (3)$$

As a confirmatory measure, the neutral portion of the product obtained by catalytic reduction of a sample of the Baeyer–Villiger product showing only the 5.65 μ carbonyl band was examined, and found to be identical with an authentic sample of the lactone X, prepared by acid cyclization of Δ²-cyclopentenylacetic acid. Finally, the neutral

X   XI

product obtained by hydrogenation of the original Baeyer–Villiger lactone mixture (VI + IX) was identified as a mixture of the two saturated lactones X and XI on the basis of an infrared spectral comparison.[9]

Generalizing from these results, it may be concluded that the peracid oxidation of β,γ-unsaturated ketones is likely to give rise to unsaturated esters

(9) An authentic sample of lactone XI was synthesized in this Laboratory by E. X. Frauenglass. This is the same lactone formed in the Baeyer–Villiger oxidation of norcamphor (*cf.* footnote 8).

(lactones) rather than epoxides when there is an opportunity for appreciable interaction between the two functional groups. The formation of allylically isomeric esters (lactones) is also to be anticipated.

Acknowledgment.—This work was supported in part by a research grant from the National Science Foundation. This support is acknowledged with pleasure.

Experimental

Reaction of Dehydronorcamphor (II) with Peracetic Acid. —A solution of 5.4 g. of sodium acetate in 27 ml. of 40% peracetic acid was added slowly to a stirred solution of 10 g. of dehydronorcamphor in 15 ml. of chloroform. During the addition the temperature of the reaction mixture was not allowed to rise above 0°, and this temperature was maintained for one hour after the addition had been completed. The reaction mixture was neutralized with 40% sodium hydroxide solution, again maintaining a 0° temperature. The organic product was extracted into ether, the ether dried over anhydrous magnesium sulfate, and the product was distilled under reduced pressure after removal of the solvents. A single product, b.p. 131–132° (22 mm.), n^{25}D 1.4908, d^{25} 1.1642, was obtained in 56% yield (6.4 g.). This product showed infrared maxima in the carbonyl region at 5.65 and 5.80 μ.

Anal. Calcd. for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.77.

In some subsequent experiments, a similar product missing the 5.80 μ band was obtained. Furthermore, slow distillation of the original material showing both carbonyl peaks gave rise to fractions all of which showed diminished intensities at 5.80 μ. Finally, treatment of the mixture with sulfuric acid, or even chromatography on Magnesol–Celite, caused complete conversion to the 5.65 μ form.

Anal. Calcd. for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.60; H, 6.61.

Quantitative Hydrogenation of Lactone Mixture (VI + IX).—A methanol solution of 0.151 g. of the lactone mixture obtained above was hydrogenated over prereduced Adams catalyst. After 10 minutes, 97% of the total hydrogen had been taken up. The reaction was stopped after 40 minutes. A total of 60.5 ml. of hydrogen (29° and

738 mm.), corresponding to 1.94 moles per mole of lactone, was absorbed.

Hydrogenation of Lactone IX.—A solution of 5 g. of lactone IX in methanol was hydrogenated over prereduced Adams catalyst in a Parr apparatus for 2 hours. After removal of solvent, 4.4 g. of product was collected, b.p. 101–106° (5 mm.). This material was dissolved in ether and extracted with 10% sodium hydroxide solution.

The ether solution was dried over anhydrous magnesium sulfate. Upon removal of the ether a liquid residue remained which showed a single carbonyl peak at 5.65 μ, yield 0.30 g. (6%). This was shown to be lactone X by comparison with an authentic sample prepared as described by Linstead and Meade[10] using cyclopentadiene as starting material. The infrared spectra and gas chromatograms of the two products were identical; synthesized material, b.p. 121–123° (12 mm.), n^{25}D 1.4727, infrared maxima 2.85, 5.65 μ (lit.[11] b.p. 69° (0.5 mm.), n^{25}D 1.4727, infrared maxima 2.84, 5.69 μ).

The basic aqueous layer was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and the product was distilled under reduced pressure after removal of the solvent. A single fraction b.p. 123–125° (20 mm.), was obtained in 71% yield (3.6 g.). This material was shown to be identical with an authentic sample of cyclopentylacetic acid, prepared according to the method of Verwey,[12] by comparison of infrared spectra. The amides of both acids melted at 150–151°, and no depression of melting point was noted upon admixture of the amides.[13]

Comparison of Infrared Spectra.—When a mixture of unsaturated lactones VI and IX was hydrogenated, the neutral fraction of the hydrogenation product had maxima in the carbonyl region at 5.65 and 5.80 μ. By comparing the spectrum of this mixture (containing X and XI) with that of the pure lactone X it was necessary to attribute several peaks to lactone XI. These peaks occurred at 5.80, 7.27, 8.85, 9.37, 9.83, 11.85 and 12.02 μ. Finally it was shown that an authentic sample of lactone XI showed characteristic absorption bands at these wave lengths.[9]

(10) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

(11) W. E. Noland, J. H. Cooley and P. A. McVeigh, THIS JOURNAL, **79**, 2976 (1957).

(12) A. Verwey, *Ber.*, **29**, 1996 (1896).

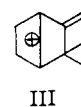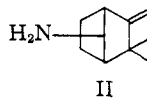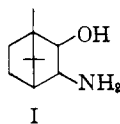(13) C. D. Nenitzescu, D. A. Isăcescu and T. A. Volrap, *ibid.*, **71**, 2056 (1938).

ITHACA, N. Y.

Reactivity of 7-Substituted Camphenes.   Structure of β-Isocamphor

BY EUGENE E. VAN TAMELEN AND CLAUDE I. JUDD[1]

β-Isocamphor, the nitrous acid deamination product of camphenamine, has been shown to be *anti*-7-camphenol(Va). The solvolytic behavior of tosylates obtained from *anti*-7-camphenol, *syn*-7-camphenol and *syn*-7-camphanol, has been studied. 2,2,3-Trimethyl-3-cyclohexene-1-carboxaldehyde has been identified as the product resulting from the action of sulfuric acid on β-isocamphor.

More than fifty years ago Duden[2] described the conversion, by successive treatment with phosphorus pentachloride and aqueous alkali, of 3-aminoborenol (I) to the unsaturated base camphenamine, which was shown more recently[3] to be *anti*-7-aminocamphene (II). This finding thus brought the opportunity of studying the 7-camphenyl carbonium ion III, and the present contribution is concerned with several aspects of this reaction system.

I   II   III

(2) (a) P. Duden and A. E. Macintyre, *Ann.*, **313**, 59 (1900); (b) *Ber.*, **33**, 477 (1900).

(3) E. E. van Tamelen, W. F. Tousignant and P. E. Peckham, THIS JOURNAL, **75**, 1297 (1953).