Reaction of II with Acetic Acid.—A solution of 3.0 g. of II in 30 ml. of acetic acid was heated at reflux for 16 hr. The product was hydrolyzed and isolated by the method described above for the acetolysis of V. Recrystallization from ligroin yielded 46% of 4,4-dichloro-3-phenyl-3-butenoic acid (VII) as white plates, m.p. 127.8–128.4°.

Anal. Calcd. for $C_{10}H_8O_2Cl_2$: C, 51.97; H, 3.49; neut. equiv., 231.1. Found: C, 52.01; H, 3.46; neut. equiv., 233.6.

The infrared spectrum of VII showed absorptions at 3–4 μ and 5.83 μ characteristic of carboxyl, at 6.18 μ for the carbon–carbon double bond, and 6.88 μ for the phenyl group. From the ultraviolet spectrum (Table II) it is evident that the double bond is not conjugated with the carboxyl group. The nuclear magnetic resonance spectrum had peaks corresponding to carboxyl, phenyl and alkyl hydrogens with areas in the ratio 1:5:2. No absorption due to vinyl hydrogen was observed. The evidence accords with the structure 4,4-dichloro-3-phenyl-3-butenoic acid. An attempt was made to ozonize this acid by the same procedure used for VIII and XVI; however, only starting material could be isolated from the reaction mixture.

Reaction of VI with Aqueous Sodium Hydroxide.—The 4-fluoroketone VI (2.5 g.) was heated with 1.5 M sodium hydroxide solution using the procedure described for V, except that the time of heating was reduced to 5 min. The product was isolated as before, and recrystallization from ligroin gave 4-fluoro-3-phenyl-3-butenoic acid (XVII) as white needles, m.p. 64.2–65.4°, in 33% yield.

Anal. Calcd. for $C_{10}H_9O_2F$: C, 66.66; H, 5.03. Found: 66.72; H, 5.12.

The infrared spectrum of XVII had absorptions at 3–4 and 5.83 μ (carboxyl group) and 6.00 μ (carbon–carbon double bond). The ultraviolet absorption spectrum (Table II) indicates that the double bond is not conjugated with the carboxyl group. The n.m.r. spectrum showed four peaks of areas approximately in the ratio 1:5:1:2 and in the proper positions to be ascribed respectively to carboxyl, phenyl, vinyl and alkyl hydrogens. The structure of XVII was therefore assigned as 4-fluoro-3-phenyl-3-butenoic acid.

Reaction of VI with Acetic Acid.—A solution of 4.4 g. of VI in 50 ml. of acetic acid was heated at reflux for 19 hr., and the product was hydrolyzed and isolated as described above for V. Recrystallization from ligroin yielded 1.4 g. (29%) of α-fluoro-β-methylcinnamic acid (XIII) as white plates, m.p. 129.0–130.2°.

Anal. Calcd. for $C_{10}H_9O_2F$: C, 66.66; H, 5.03. Found: C, 66.69; H, 5.08.

The ultraviolet spectrum of XIII (Table II) is similar to that of β-methylcinnamic acid. The infrared spectrum showed an absorption at 5.88 μ which corresponds to the carbonyl group of an α,β-unsaturated carboxylic acid. The n.m.r. spectrum of XIII possessed three proton absorptions in the weights 5:3:1, identified from their positions as the phenyl, methyl and carboxyl proton resonances, respectively.

A solution of XIII (0.5 g.) in 25 ml. of ethyl acetate was treated with an excess of ozone at 0°. After removal of the solvent, 25 ml. of hot water was added to the residual oil. The mixture was heated on a steam-cone for 1 hr., then cooled and extracted with ether. The ether extracts were washed with sodium bicarbonate solution, dried over magnesium sulfate, and the solvent evaporated. The oily residue was converted to a 2,4-dinitrophenylhydrazone which, after recrystallization from ethyl acetate, gave material of m.p. 248–249°. The m.p. of this material was not depressed on admixture with an authentic sample of acetophenone 2,4-dinitrophenylhydrazone, m.p. 248.4–249.2°.

Reactions Involving Deuterated Reagents.—The reaction of I with deuterioacetic acid has been described elsewhere.[3] The reactions of I and V with deuterium oxide–sodium deuteroxide were carried out by the methods used in the reactions of I[2] and V with aqueous sodium hydroxide. The acids III and XVI were tested for deuterium exchange by heating them in deuterium oxide–sodium deuteroxide under the conditions of the ring-opening reactions by which they were prepared.

The reaction of 2,4-dichloro-3-phenylcyclobutenone-2-^{2}H[5] with aqueous sodium hydroxide was carried out as described previously for the undeuterated ketone.[2]

The deuterated positions in the resulting carboxylic acids were established with the aid of n.m.r. spectra.

PASADENA, CALIF.

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

A New Method for the Epoxidation of α,β-Unsaturated Ketones

BY N. C. YANG AND R. A. FINNEGAN

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t-Butyl hydroperoxide reacts with α,β-unsaturated ketones in benzene solution in the presence of a few mole per cent. of Triton-B to form the corresponding epoxides. By this method mesityl oxide, methyl vinyl ketone, methyl isopropenyl ketone, cyclohexenone and chalcone were converted to their epoxides. The steric requirements of this epoxidizing agent were indicated by its failure to react with isophorone and 4-cholesten-3-one. This selectivity was demonstrated by the conversion in high yield of 16-dehydroprogesterone to $16\alpha,17\alpha$-epoxy-4-pregnen-3,20-dione. Alternately, the base-catalyzed reaction of *t*-butyl hydroperoxide with acrylonitrile or with methyl acrylate leads to the Michael addition product.

Introduction.—Although the thermal, free radical and acid-catalyzed reactions of hydroperoxides have been studied by several groups,[1] the base-catalyzed reactions have received relatively little attention. Kharasch[2] studied the decomposition of tertiary hydroperoxides in alkaline media and suggested the interaction of a hydroperoxide anion with a neutral hydroperoxide molecule to explain the products. The alkaline decomposition of secondary and primary hydroperoxides has been discussed by Kornblum,[3] who suggested a mechanism in which the removal of a hydrogen atom alpha to the hydroperoxy group occurs as the first step.

The Michael addition of hydroperoxides to olefins bearing a *meta*-directing group attached to one of the doubly-bound carbon atoms has been reported in the patent literature.[4] However, since the products described in this disclosure seemed to be inadequately characterized, and since the Michael reaction appeared to be a promising route to substituted peroxides which might themselves

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(1) For recent discussion and references, see: (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (b) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

(2) M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).

(3) N. Kornblum and H. E. De La Mare, THIS JOURNAL, **73**, 880 (1951).

(4) D. Harman, U. S. Patent 2,508,256.

display interesting chemical properties, the present study of the base-catalyzed reaction of *t*-butyl hydroperoxide with unsaturated compounds was undertaken.

Results.—When mesityl oxide was treated with *t*-butyl hydroperoxide in the presence of a catalytic amount of alkali, there was obtained in fair yield not the anticipated Michael adduct, but the epoxide, 3,4-epoxy-4-methyl-2-pentanone. This epoxidation was best carried out at room temperature in benzene solution using Triton-B as the basic catalyst. Triethylamine and piperidine were found to be ineffective catalysts in benzene or in ethanol solution, even at reflux temperature. When the reaction conditions reported[4] to result in the Michael addition of hydroperoxides to unsaturated ketones were employed, the product again proved to be the epoxide and no Michael adduct was found.

Methyl vinyl ketone was converted to 3,4-epoxy-2-butanone in fair yield on treatment with *t*-butyl hydroperoxide in benzene solution in the presence of a small amount of Triton-B. It was found necessary to use an excess of starting ketone over *t*-butyl hydroperoxide in order to avoid formation of an inseparable mixture of product with unreacted hydroperoxide. When the reaction conditions described by Harman[4] were employed in this instance, the epoxide was again the only product found.

Similarly, methyl isopropenyl ketone, chalcone and cyclohexen-3-one were converted in good to excellent yields to their corresponding epoxides.

From the reaction between isophorone and *t*-butyl hydroperoxide there was isolated a mixture which consisted mainly of starting ketone. The presence of only a small amount of product in the mixture was inferred from its infrared spectrum. Because of the proximity of their boiling points, the components of this mixture could not be separated. Other workers have observed this difficulty.[5] Also from this reaction mixture there was isolated after the appropriate treatment a small yield of an unidentified acid.

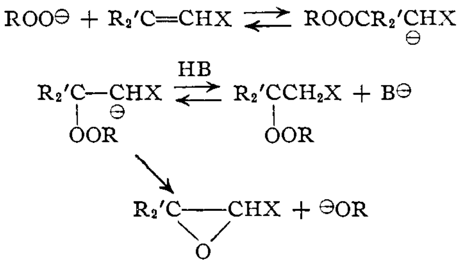
When an attempt was made to epoxidize 4-cholesten-3-one in the manner described above, nearly all of the starting material was recovered along with a minute amount of unidentified acidic material. When excess *t*-butyl hydroperoxide was used as solvent for the reaction, similar results were obtained. Since the 4-dehydro-3-one system in the steroids is apparently inert, the selectivity of this reagent was employed advantageously in the conversion of 16-dehydroprogesterone in good yield to 16α,17α-epoxy-4-pregnen-3,20-dione, an important intermediate in the syntheses of 17α-hydroxy steroids.[6]

β-Nitrostyrene in benzene solution was converted to an insoluble polymer in the presence of *t*-butyl hydroperoxide and a catalytic amount of base. A similar product also was obtained when β-nitrostyrene was treated with catalytic amounts of Triton-B in the absence of *t*-butyl hydroperoxide. The base-catalyzed polymerization of β-nitrostyrene has been observed previously.[7,8]

Acrylonitrile and methyl acrylate were converted to *t*-butyl 2-cyanoethyl peroxide and methyl 3-*t*-butylperoxypropionate, respectively. These Michael adducts have been prepared previously.[4]

Discussion.—The epoxidation of unsaturated ketones is usually carried out using alkaline hydrogen peroxide in aqueous or alcoholic solution. The discovery that *t*-butyl hydroperoxide will cause the epoxidation of unsaturated ketones offers a convenient alternate method by which the epoxidation reaction may be carried out in a completely homogeneous, non-polar medium. The yields of epoxides prepared by this method compare favorably with those obtained by other methods.

The reaction is envisioned as proceeding by the addition of an alkyl-peroxy anion to the β-carbon of the activated double bond. This is followed by the elimination of alkoxide ion with the formation of the epoxide, a mechanism analogous to that suggested by Bunton and Minkoff[9] for the epoxidation of unsaturated ketones with alkaline hydrogen peroxide. If the intermediate anion acquires a proton before cyclization occurs, the Michael adduct is formed. These transformations are illustrated by the reaction scheme



$$\mathrm{ROO^{\ominus} + R_2'C{=}CHX \rightleftarrows ROOCR_2'\underset{\ominus}{C}HX} \tag{1}$$

$$\mathrm{R_2'\underset{OOR}{C}{-}\underset{\ominus}{C}HX \xrightleftharpoons{HB} R_2'\underset{OOR}{C}CH_2X + B^{\ominus}} \tag{2}$$

$$\mathrm{\searrow\ R_2'C{-}CHX\ (\text{-}O\text{-}) + {}^{\ominus}OR} \tag{3}$$

The nature of group X, and consequently the stability of the intermediate anion, apparently determines which pathway is taken. When X is acyl or aroyl, the equilibrium concentration of the anion is sufficiently large to enable the elimination step (3) to compete favorably with the protonation step (2). In fact, since the elimination step is irreversible, the reaction is driven in the direction of epoxide formation. When X is nitrile or carbomethoxy, the concentration of the anions is small and the formation of the Michael adducts is favored. These observations accord with the known relative stabilities of anions alpha to a carbonyl group and to a nitrile or ester group.[10]

The failure of the reaction with isophorone and 4-cholesten-3-one can reasonably be ascribed to steric inhibition. The addition of the bulky *t*-butylperoxy anion to isophorone would result in a cyclohexane derivative with two axial substituents in the 1,3-positions, a conformationally unfavorable structure. Steric hindrance to the reaction of *t*-butyl hydroperoxide with 4-cholesten-3-one is ap-

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[5] H. O. House and R. L. Wasson, THIS JOURNAL, **79**, 1488 (1957).

[6] P. L. Julian, E. W. Meyer and I. Ryden, *ibid.*, **72**, 367 (1950).

[7] D. E. Worrall, *ibid.*, **49**, 1598 (1927).

[8] P. Vorlander and D. Herrmann, *Abhandlungen der Naturforschenden Gesellschaft zu Halle*, **21**, 251 (1899); *Chem. Zentr.*, **70**, 730 (1899).

[9] C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

[10] A. C. Cope, H. L. Holmes and H. O. House, in R. Adams, "Organic Reactions," Vol. IX, Chapter 4, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 110.

parently offered by the axial hydrogen atoms in the 1-, 7- and 9-positions.

Acknowledgments.—The authors are grateful to Mr. William Saschek for microanalyses and to Mr. Ihor Masnyk for molecular weight determinations. They are also indebted to the G. D. Searle Co. for a sample of 16-dehydroprogesterone and to the Celanese Corporation of America for a sample of methyl isopropenyl ketone. They wish also to express their gratitude to Dr. Stephen H. Levin for many valuable discussions. A fellowship to R. A. F. from the Shell Development Co. is gratefully acknowledged.

Experimental[11]

Starting Materials.—*t*-Butyl hydroperoxide (Lucidol Division, Wallace and Tiernan, Inc.) was distilled through a 10″ Vigreux column. The fraction used had b.p. 48° (35 mm.) and $n^{20}\mathrm{D}$ 1.4000. The purity of this material was estimated by titration to be 90%. Mesityl oxide (Eastman Kodak Co.) was distilled before use, b.p. 50° (43 mm.), $n^{20}\mathrm{D}$ 1.4413. Methyl vinyl ketone (Aldrich Chemical Co.) was distilled before use, b.p. 80–82°. Methyl isopropenyl ketone (Celanese Corporation) was fractionated before use, b.p. 52° (53 mm.), $n^{20}\mathrm{D}$ 1.4222. Cyclohexen-3-one was prepared by the method of Whitmore and Pedlow,[12] b.p. 67° (25 mm.), $n^{20}\mathrm{D}$ 1.4880. Chalcone (Eastman Kodak Co.) was recrystallized from benzene–petroleum ether, m.p. 56–58°. 16-Dehydroprogesterone was obtained from the G. D. Searle Co., m.p. 184–186°. 4-Cholesten-3-one was prepared by a recorded procedure,[13] m.p. 79–80°. Isophorone (Eastman Kodak Co.) was distilled before use, b.p. 94° (18 mm.), $n^{20}\mathrm{D}$ 1.4774. Acrylonitrile (Eastman Kodak Co.) was distilled before use, b.p. 75–76°, $n^{20}\mathrm{D}$ 1.3913. Methyl acrylate (Rohm and Haas) was distilled before use, b.p. 77–78°, $n^{25}\mathrm{D}$ 1.3997. β-Nitrostyrene (Aldrich Chemical Co.) was recrystallized from absolute ethanol, m.p. 56–58°. Triton-B (benzyltrimethylammonium hydroxide) was obtained as a 35% solution in methanol from Mid-West Laboratories, Inc.

3,4-Epoxy-4-methyl-2-pentanone.—To a stirred solution of *t*-butyl hydroperoxide (15 ml., 0.135 mole) and mesityl oxide (22.6 ml., 0.20 mole) in 100 ml. benzene at 15° was added 2.88 g. of a 35% methanolic solution of Triton-B (0.006 mole). After 5 hours stirring at room temperature, the mixture was washed with water. The aqueous washings were saturated with salt and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and carefully fractionated through a 60 × 0.7 cm. tantalum wire column. After removal of solvents and starting materials there was obtained 10.05 g. (65%) of the product, b.p. 67–68° (30 mm.), $n^{20}\mathrm{D}$ 1.4229. A sample was redistilled for analysis, b.p. 55° (17 mm.), $n^{20}\mathrm{D}$ 1.4232 (lit.[14] b.p. 61–62° at 20 mm., $n^{20}\mathrm{D}$ 1.4235); $\nu_{\max}$ (pure liquid) 1718 (saturated carbonyl), 920, 877 and 835 cm.$^{-1}$ (epoxide).[15]

The boiling point, refractive index and infrared spectrum of this product were identical with those of an authentic sample prepared by the method of Bunton and Minkoff.[9]

When *t*-butyl hydroperoxide (0.10 mole) was caused to react for 24 hours at 0° with mesityl oxide (0.10 mole) in 325 ml. of an aqueous solution containing sodium hydroxide (0.02 mole), there was obtained a 53% yield of 3,4-epoxy-4-methyl-2-pentanone. The infrared spectrum of this product indicated the presence of a small amount of hydroxyl-containing impurity.

In an attempt to effect the Michael addition of *t*-butyl hydroperoxide to mesityl oxide, a procedure outlined by Harman[4] for the analogous preparation of *t*-butyl 2-cyanoethyl peroxide was followed. Thus, from 22 ml. (0.20 mole) *t*-butyl hydroperoxide, 5.8 ml. of water, 6.85 ml. (0.06 mole) of mesityl oxide and 1.8 ml. of a 40% aqueous solution of potassium hydroxide, there was obtained a 21% yield of pure 3,4-epoxy-4-methyl-2-pentanone. No product corresponding to the Michael adduct was found.

t-Butyl hydroperoxide and mesityl oxide, when caused to react in anhydrous *t*-butyl alcohol in the presence of 10 mole % sodium *t*-butoxide, produced a tarry mixture, and isolation of products was not attempted.

Even after prolonged refluxing, no product was observed when *t*-butyl hydroperoxide and mesityl oxide were mixed in either benzene or ethanol solution, in the presence of either triethylamine or piperidine, or in piperidine alone as solvent.

3,4-Epoxy-2-butanone.—To a stirred solution of *t*-butyl hydroperoxide (10 ml., 0.09 mole) and methyl vinyl ketone (16.7 ml., 0.20 mole) in 200 ml. benzene maintained at ice-bath temperature was added 0.48 g. of a 35% methanolic solution of Triton-B (0.001 mole) in 3 portions over a period of 2 hours. The temperature then was allowed to rise to 15° and, after a total reaction time of 4.5 hours, the benzene solution was washed with water. The aqueous washings were saturated with salt and extracted several times with ether. The combined organic layers were dried over anhydrous magnesium sulfate. After removal of the solvents through a 10″ Vigreux column at 180 mm. pressure, the residue was fractionated through a 60 × 0.7 cm. tantalum wire column. A 49% yield of product was obtained, b.p. 71.5° (77 mm.), (46° at 30 mm.), $n^{19}\mathrm{D}$ 1.4228, $\nu_{\max}$ (pure liquid) 1718 (saturated carbonyl) 925 and 870 cm.$^{-1}$ (epoxide).

Anal. Calcd. for $C_4H_6O_2$: C, 55.80; H, 7.03; mol. wt., 86.09. Found: C, 56.02; H, 7.18; mol. wt., 85.

When the conditions reported to cause the Michael addition of a hydroperoxide to methyl vinyl ketone[4] were followed to effect the reaction between *t*-butyl hydroperoxide and methyl vinyl ketone, 3,4-epoxy-2-butanone was identified as the only product by means of its infrared spectrum; however, it was contaminated by *t*-butyl hydroperoxide, which could not be removed even by repeated fractionation through a 60 × 0.7 cm. tantalum wire column.

3,4-Epoxy-3-methyl-2-butanone.—To a stirred solution of *t*-butyl hydroperoxide (10 ml., 0.09 mole) and methyl isopropenyl ketone (19.7 ml., 0.20 mole) in 175 ml. of benzene maintained at ice-bath temperature was added 0.72 g. of a 35% methanolic solution of Triton-B (0.005 mole) in 3 portions over a period of 0.5 hour. The reaction mixture was then allowed to warm to room temperature. After approximately 10 hours, the reaction mixture was worked up in the manner described above. The product weighed 6.25 g. (69%), b.p. 54° (44 mm.), $n^{19}\mathrm{D}$ 1.4193 (lit.[16] b.p. 130–138°, $n^{20}\mathrm{D}$ 1.4192); $\nu_{\max}$ (pure liquid) 1721 (saturated carbonyl), 922 and 842 cm.$^{-1}$ (epoxide).

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05; mol. wt., 100.11. Found: C, 60.16; H, 8.00; mol. wt., 99.

2,3-Epoxycyclohexanone.—To a stirred solution of cyclohexen-3-one (9.6 g., 0.10 mole) and *t*-butyl hydroperoxide (15 ml., 0.135 mole) in 80 ml. of benzene was added at 10° 0.96 g. of a 35% methanolic solution of Triton-B (0.002 mole). The reaction was allowed to proceed for 12 hours at room temperature before it was worked up in the usual manner. The product weighed 7.42 g. (66%), b.p. 74° (11 mm.), 76–78° (15 mm.), $n^{22}\mathrm{D}$ 1.4736 (lit.[5] b.p. 75–78° (10 mm.), $n^{25}\mathrm{D}$ 1.4725), $\nu_{\max}$ (pure liquid) 1718 (saturated carbonyl) and 822 cm.$^{-1}$ (epoxide).

***trans*-Chalcone Epoxide.**—Chalcone (10.41 g., 0.05 mole), *t*-butyl hydroperoxide (7.5 ml., 0.068 mole) and a 35% methanolic solution of Triton-B (0.72 g., 0.0015 mole) were dissolved in 80 ml. of benzene at 10°. After being stirred for 5 hours at room temperature, the benzene solution was washed with water. The aqueous washings were saturated with salt and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and the solution was evaporated to dryness. A 95% yield of a white solid, m.p. 83–85°, was obtained. Crystallization from a benzene–petroleum ether (b.p. 60–68°) solution gave crystals which melted at 88.5–89.5° (lit.[17] m.p. 89–90°),

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[11] Boiling points and melting points are uncorrected. Molecular weights were determined by the cryoscopic method in benzene. Infrared spectra were determined on a Perkin Elmer Infracord.

[12] F. C. Whitmore and G. W. Pedlow, Jr., THIS JOURNAL, **63**, 758 (1941).

[13] J. F. Eastham and R. Teranishi, *Org. Syntheses*, **35**, 39 (1955).

[14] G. B. Payne, *J. Org. Chem.*, **23**, 310 (1958).

[15] R. N. Jones and C. Sandorfy, in A. Weissberger, "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 436.

[16] R. S. Wilder and A. A. Dolnick, U. S. Patent 2,431,718.

[17] E. P. Kohler, N. K. Richtmyer and W. F. Hester, THIS JOURNAL, **53**, 205 (1931).

$\nu_{\max}$ (potassium bromide pellet) 1686 (conjugated carbonyl) and 893 cm.$^{-1}$ (epoxide).

Base-catalyzed Reactions of *t*-Butyl Hydroperoxide with Isophorone.—Isophorone (0.10 mole) and *t*-butyl hydroperoxide (0.25 mole) were allowed to react in benzene solution in the presence of Triton-B (0.005 mole). After 18 hours at room temperature, the reaction mixture was washed with water. The aqueous washings were saturated with salt and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and evaporated. The residue consisted primarily of starting ketone, along with a small amount of product. This mixture could not be separated on a spinning band column.[5]

From the aqueous washings, after acidification and extraction with ether, there was isolated 0.43 g. of an acid. This acid was distilled in a Kragen tube at 0.03 mm. (bath temperature approximately 95°), $n^{21}D$ 1.4492. It was not further characterized.

This acid also was isolated from the reaction of isophorone in aqueous medium with alkaline hydrogen peroxide.[18]

Base-catalyzed Reaction of *t*-Butyl Hydroperoxide with 4-Cholesten-3-one.—When 4-cholesten-3-one (3.85 g., 0.01 mole) was treated with *t*-butyl hydroperoxide (2 ml., 0.018 mole) in benzene solution in the presence of Triton-B (0.0002 mole) for 4 hours at room temperature and 19 hours at 50°, the starting ketone was recovered.

When 4-cholesten-3-one (1.93 g., 0.005 mole) was treated with Triton-B (0.0005 mole) in 15 ml. of *t*-butyl hydroperoxide as solvent for 19 hours at room temperature, the starting ketone was again recovered.

16α,17α-Epoxy-4-pregnen-3,20-dione.—16-Dehydroprogesterone (1.0 g., 0.0032 mole), *t*-butyl hydroperoxide (0.6 ml., 0.0054 mole) and Triton-B (0.05 g. of a 35% methanolic solution, 0.0001 mole) were dissolved in 6 ml. of benzene and allowed to stand for 12 hours at room temperature. The reaction mixture was then washed 3 times with water. The aqueous washings were saturated with salt and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and, after evaporation of the solvents at reduced pressure, there was obtained 0.98 g. (93%) of a white crystalline solid, m.p. 165–183°. The infrared spectrum of the analytical sample was indistinguishable from that of the crude product. After recrystallization from methanol there was obtained 0.59 g. of crystals, m.p. 205–207°, $[\alpha]^{27}D$ +156.6° (34.0 mg. in 5 ml. chloroform), αD +2.13° (*l* 2 dm.) (lit.[6] m.p. 205–207°), $[\alpha]^{27}D$ +160.8° (34.5 mg. in 5 ml. chloroform), αD +1.11° (*l* 1 dm.); $\nu_{\max}$ (potassium bromide pellet) 1700 (saturated carbonyl), 1665 (unsaturated carbonyl), 1613 (conjugated double bond, and 885 cm.$^{-1}$ (epoxide)).

From the mother liquor was obtained an additional 0.09 g. of pure product, m.p. 204–206° (total yield 65%). From the aqueous washings was isolated, after appropriate treatment, 0.04 g. of an unidentified acidic material.

The Base-catalyzed Reaction of *t*-Butyl Hydroperoxide with β-Nitrostyrene.—β-Nitrostyrene (7.45 g., 0.05 mole) and *t*-butyl hydroperoxide (7.5 ml., 0.068 mole) were dissolved in 75 ml. of benzene at ice-bath temperature. Triton-B (0.48 g. of a 35% methanolic solution, 0.001 mole) was added and after a few minutes a precipitate was observed. The mixture was warmed to room temperature and stirred an additional 90 minutes before the precipitate was collected on a filter. There was obtained 6.56 g. of a powdery white solid which melted at 200–210° with some charring. This material was insoluble in the usual solvents. A similar polymeric material precipitated almost immediately when Triton-B (2 mole %) was added to a benzene solution of β-nitrostyrene.[7,8] When β-nitrostyrene and *t*-butyl hydroperoxide were mixed in ether solution in the presence of 4 mole % of triethylamine, no reaction was observed after 20 hours at room temperature. However, when the reaction mixture was warmed during evaporation of the solvent, the formation of polymeric material was observed.

***t*-Butyl 2-Cyanoethyl Peroxide.**—Following the method of Harman,[4] acrylonitrile (2.0 ml., 0.03 mole) slowly was added with stirring to a solution containing 11 ml. (0.10 mole) of *t*-butyl hydroperoxide, 2.9 ml. of water and 0.9 ml. of 40% aqueous potassium hydroxide. After stirring 0.5 hour at room temperature, the two phases were separated and the upper (organic) layer washed several times with distilled water. The organic layer was then dried and distilled at reduced pressure. After removal of the forerun, which was identified as *t*-butyl hydroperoxide, there was obtained 0.93 g. (22%) of product, b.p. 57–59° (1.4 mm.), $n^{20}D$ 1.4189 (lit.[4] $n^{20}D$ 1.4142); $\nu_{\max}$ (pure liquid) 2268 (saturated nitrile), 1383, 1366 and 1244 cm.$^{-1}$ (*t*-butyl group).

Anal. Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; mol. wt., 143.18. Found: C, 58.81; H, 9.39; mol. wt., 140.

The same product was obtained in 18% yield when the reaction was carried out in dilute aqueous solution.

Methyl 3-*t*-Butylperoxypropionate.—To a stirred solution of methyl acrylate (9.1 ml., 0.10 mole) and *t*-butyl hydroperoxide (15 ml., 0.135 mole) in 175 ml. of benzene was added 1.44 g. of a 35% methanolic solution of Triton-B (0.003 mole) in small portions over a period of one hour at ice-bath temperature. The reaction mixture was then allowed to warm to room temperature. After 8 hours, an additional 1.44 g. of 35% methanolic Triton-B solution was added. After being allowed to remain an additional 12 hours at room temperature, the reaction mixture was worked up in the usual manner. The product, after fractionation through a 60 × 0.7 cm. tantalum wire column, weighed 3.91 g. (22%), b.p. 75° (13 mm.), $n^{25}D$ 1.4140 (lit.[4] $n^{20}D$ 1.4142); $\nu_{\max}$ (pure liquid) 1748 (saturated carbonyl), 1383, 1366 and 1244 cm.$^{-1}$ (*t*-butyl group).

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15; mol. wt., 176.21. Found: C, 54.55; H, 9.11; mol. wt., 175.

When the reaction was carried out at room temperature for 12 hours in dilute aqueous solution there was obtained a 2.2% yield of product, which was identified by its infrared spectrum.

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[18] Ketone cleavage presumably occurred; see H. O. House and R. L. Wasson, *J. Org. Chem.*, **22**, 1157 (1957).

[CONTRIBUTION FROM THE TEXACO RESEARCH CENTER]

Mechanism of the Dehydrocyclization of *n*-Heptane

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The mechanisms already in the literature for the dehydrocyclization of *n*-heptane to toluene all predict that the dehydrocyclization of *n*-heptane-1-C^{14} would produce toluene with 50% of the C^{14} in the methyl group. One run, at conditions which gave a product containing 56 mole per cent. toluene, gave 27 ± 1% of the C^{14} in the toluene methyl group; another, at conditions yielding a product containing 74 mole per cent. toluene, gave 29 ± 1% of the C^{14} in the methyl group. Two possible mechanisms leading to this lower value of methyl C^{14} content and a test to distinguish between them are proposed.

Introduction

The mechanism of catalytic dehydrocyclization has been the subject[1] of considerable study because the process is one of obvious commercial, as well as scientific, importance. It was shown quite early after the discovery of dehydrocyclization that, in the conversion of *n*-heptane to toluene, *n*-

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[1] See the review of C. Hansch, *Chem. Revs.*, **53**, 353 (1953).