dicyclopentadiene[8] with alkaline permanganate by the method of Bergel and Widman,[16] micro m.p. 181–182° (reported 182–184°).

exo-cis-**Bicyclo[3.3.0]octane-2,4-dicarboxylic Acid Dimethyl Ester (IX).**—A solution of 10.0 g. (0.051 mole) of dicarboxylic acid VIII in 50 ml. of ether was added to a solution of diazomethane in ether cooled in a Dry Ice–acetone-bath. After 30 minutes the excess diazomethane was destroyed with formic acid. Removal of ether and methyl formate yielded a sirupy residue which on distillation gave 9.9 g. (76%) of colorless dimethyl ester, b.p. 135–137° (2 mm.). An additional distillation gave a sample, b.p. 122° (1 mm.), d^{20}_4 1.101, n^{25}_D 1.4711.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.00. Found: C, 63.90; H, 8.27.

trans-**Bicyclo[3.3.0]octane-2,4-dicarboxylic Acid (XI).**—A solution of 10.0 g. (0.044 mole) of the dimethyl ester IX in 200 ml. of ethanol in which 10.0 g. (0.43 g. at.) of sodium had been dissolved was heated under reflux for 4 hours. Methanol was then removed under diminished pressure on a steam-bath and the residue dissolved in water. The aqueous solution was washed twice with ether and the ether discarded. The aqueous solution, acidified with 6 *M* hydrochloric acid, was extracted continuously with ether for 36 hours. Evaporation of the ether gave a brown solid material which was treated in hot water for 4 hours with 1 g. of charcoal. Removal of the charcoal yielded a clear solution from which 4.5 g. (59%) of *trans*-bicyclo[3.3.0]octane-2,4-dicarboxylic acid, m.p. 175–176° (reported[16] 178°), slowly crystallized.

endo-cis-**Bicyclo[3.3.0]octane-2,4-dicarboxylic Acid.**—9-Keto-tetrahydro-*endo*-dicyclopentadine was prepared from the oxime III and oxidized with alkaline permanganate solution to the diacid, m.p. 230° (reported[17] 232°). The methyl ester was prepared as described above, b.p. 111–113° (12 mm.), m.p. 76–77° (reported[16] 77.5–78°), and was, in turn, converted in 47% yield into *trans*-bicyclo [3.3.0] octane-2,4-dicarboxylic acid, m.p. 176–177° (reported[16] 178°); mixed m.p. with the sample from the *exo* isomer, 176–176.5°. The infrared traces of these acids are identical.

For comparison olefin I was oxidized in acetone with potassium permanganate, by the method of Youngblood and Wilder,[17] to the same *endo-cis*-bicyclo [3.3.0] octane-2,4-dicarboxylic acid, m.p. 228–230°; mixed m.p. with the sample from the oxidation of 9-ketotetrahydro-*endo*-dicyclopentadiene, 228–230°.

Acknowledgment.—This work was supported by a grant from the Research Corporation and by a Grant-in-Aid from Allied Chemical and Dye Corporation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Reactions of 1-Substituted Cyclohexenes with Peracids[1-3]

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1-Alkyl- and 1-phenylcyclohexenes react with perbenzoic and monoperphthalic acids to give the 2-substituted cyclohexanones in addition to or instead of the expected epoxide. In some cases, the *trans*-1,2-diol is also isolated. Pure 1-methylcyclohexene oxide does not rearrange to 2-methylcyclohexanone in the presence of perbenzoic acid, but does give the ketone and the hydroxybenzoate with benzoic acid. While some ketone may be formed by thermal rearrangement of epoxide, it is demonstrated that the reaction also occurs in the cold. The mechanism of ketone formation is discussed.

Introduction

The preparation of epoxides is most frequently accomplished by the reaction of olefins with peracids, such as perbenzoic and monoperphthalic acids.[4] There have been a number of cases reported,[5-8] however, in which carbonyl-containing products were formed in addition to or to the exclusion of the expected oxirane, particularly when perbenzoic acid is the reagent.

In the course of preparing 1-substituted cyclohexene oxides for rearrangement studies,[9] we isolated carbonyl and hydroxyl-containing by-products as well as the epoxide. In most cases, these results differed from those reported in the literature.[4] We therefore examined this reaction in further detail.

Results

The substituted cyclohexenes were generally prepared by dehydration of the tertiary alcohol resulting from reaction of cyclohexanone with the appropriate Grignard reagent. In this way, the 1-methyl, -ethyl, -isopropyl and -phenyl analogs were obtained. 1-*t*-Butylcyclohexene failed to give a hydroxyl-free product by this method[10] and was ultimately prepared in low yield by alkylation of cyclohexene in the presence of bismuth trichloride.[11] Attempts to obtain the isopropyl and *t*-butyl compounds by a Birch-type reduction of the alkylbenzene using lithium–ethylamine,[12] gave inconsistent results with part of the product appearing to be the dihydro product, a conjugated diene (ultraviolet absorption). 1-Acetylcyclohexene was best prepared by acylation of cyclohexene,[13] in preference to the rearrangement of 1-ethynylcyclohexanol.[14] Even after recycling, the ketone obtained by

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[2] Presented before the Division of Organic Chemistry at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[3] This work was supported in part by a grant from the Research Corporation.

[4] D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953.

[5] W. Salzer, *Z. physiol. Chem.*, **274**, 39 (1942).

[6] G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 247 (1945).

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[8] F. L. Weisenborn and D. Taub, THIS JOURNAL, **74**, 1329 (1952).

[9] S. M. Naqvi, J. P. Horwitz and R. Filler, *ibid.*, **79**, 6283 (1957).

[10] H. L. Goering, R. L. Reeves and H. H. Espy, *ibid.*, **78**, 4926 (1956).

[11] L. Schmerling, *ibid.*, **69**, 1121 (1947).

[12] R. A. Benkeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, *ibid.*, **77**, 3230 (1955).

[13] J. English, Jr., and V. Lamberti, *ibid.*, **74**, 1909 (1952).

[14] (a) J. H. Saunders, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 22; (b) J. D. Chanley, THIS JOURNAL, **70**, 246 (1948); (c) M. S. Newman, *ibid.*, **75**, 4740 (1953).

the latter method contained a small amount of starting compound which was detected in its infrared spectrum. The lack of a —C≡C— stretching band could not be taken as evidence that the acetylenic group was absent, for it has been shown that compounds of this type exhibit extremely weak —C≡C— absorption and that the ≡C—H stretching mode is a better criterion for identification.[15]

In Table I are summarized the results of our epoxidation studies using perbenzoic and monoperphthalic acids.

TABLE I

REACTION OF 1-SUBSTITUTED CYCLOHEXENES WITH PERACIDS

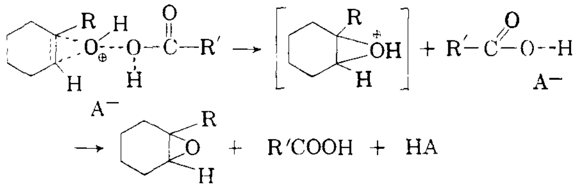
	Yields of products, %					
	Perbenzoic acid			Monoperphthalic acid		
R	Epoxide[a]	Ketone	Diol	Epoxide	Ketone	Diol
CH_3	48	24	2	55	15	2
C_2H_5	60	25		63	28	
i-Pr	44	35		44	21	
t-Bu[b]		30[c]			30[c]	
C_6H_5		53				80

[a] Due to foaming during distillation, product was often contaminated with small amount of ketone. [b] Much starting material recovered unchanged. [c] Pure product not isolated. Both carbonyl and hydroxyl components present (infrared); % is approximate.

1-Acetylcyclohexene failed to react with monoperphthalic acid. It has been shown previously that peroxy acids are not effective for epoxidation of compounds containing the α,β-unsaturated carbonyl moiety.[16] The ketone did give a 50% yield of epoxyketone when treated either with alkaline hydrogen peroxide[17] or peroxytrifluoroacetic acid, CF_3CO_3H.[18] When the peroxy acids were used, there was no evidence of ester formation due to a Baeyer–Villiger reaction.[19]

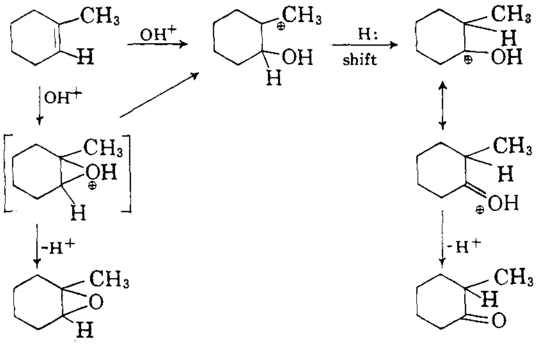
Discussion

It has been suggested by Swern[4] that the epoxide is formed *via* its conjugate acid by the donation of the electrophilic moiety, $[\underset{\cdot\cdot}{\ddot{O}}:H]^+$, to the olefin, by a peracid–general acid complex with subsequent loss of a proton



The mechanism of ketone formation in this reaction has not been clearly determined. In order to establish whether 2-methylcyclohexanone was formed by rearrangment of the free epoxide, 1-methylcyclohexene oxide[20] was treated with perbenzoic acid under epoxidation conditions. Infrared analysis of the reaction mixture showed no carbonyl absorption. It is well known, however, that epoxides rearrange to ketones in the presence of mineral acids and Lewis acids such as magnesium bromide,[9] the postulated intermediate being the conjugate acid of the epoxide. Since benzoic acid is generated during reactions involving perbenzoic acid, we also treated 1-methylcyclohexene oxide with benzoic acid under the same conditions (unfortunately, this reaction was not carried out in the presence of perbenzoic acid as well). Much starting oxide (60%) was recovered, but examination of the residue by infrared revealed appreciable amounts of 2-methylcyclohexanone (identified as its semicarbazone) and a hydroxyester, presumably the hydroxybenzoate, formed by ring opening.[21]

In view of the fact that a hydroxyester has never been detected in any of the epoxidation mixtures we have studied, perhaps a more plausible explanation for ketone formation would be that proposed by Weisenborn and Taub[8] in which reaction proceeds *via* the conjugate acid and carbonium ion intermediate followed by a 1,2-shift to yield the ketone, without the necessity of going through the free epoxide. Alternatively, the conjugate acid may lose a proton to give epoxide



It has been observed in a number of cases that ketones are obtained from epoxides by thermal rearrangement. Thus, ethyl 3,3-diphenylglycidate is converted to ethyl 3,3-diphenyl-2-ketopropionate on distillation.[22]

Similarly, 1-phenylcyclohexene oxide, prepared from the olefin and perbenzoic acid, could only be isolated in crude form, since on distillation, partial rearrangement to carbonyl compound occurred.[21] Even "flash distillation" led to some carbonyl-containing product. It will be noted from Table I that 2-phenylcyclohexanone was the exclusive product when the reaction mixture was dis-

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(16) D. Swern, THIS JOURNAL, **69**, 1692 (1947); H. V. Taylor, *Industrial Chemist*, **29**, 9 (1953).

(17) (a) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921); (b) R. H. Bible, Jr., C. Placek and R. D. Muir, *J. Org. Chem.*, **22**, 607 (1957); (c) H. O. House and D. J. Reif, THIS JOURNAL, **79**, 6491 (1957); (d) H. O. House and R. L. Wasson, *ibid.*, **78**, 4394 (1956).

(18) W. D. Emmons and A. S. Pagano, *ibid.*, **77**, 89 (1955).

(19) C. H. Hassall, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957.

(20) We also prepared this compound in 50% yield, free of by-products, by dehydrobromination of *trans*-2-bromo-1-methylcyclohexanol, obtained by treating the olefin with N-bromosuccinimide and water (C. O. Guss and R. Rosenthal, THIS JOURNAL, **77**, 2549 (1955)). This is the method of choice for this bromohydrin and epoxide. However, no epoxide was isolated when this method was applied to 1-phenylcyclohexene (C. O. Guss, private communication).

(21) In this connection, it is of interest to note that 1-phenylcyclohexene oxide on treatment with nitrous acid in glacial acetic acid gave a small amount of 2-phenylcyclohexanone in addition to phenylcyclohexane diols and the hydroxyacetate; D. Y. Curtin and S. Schmukler, *ibid.*, **77**, 1105 (1955).

(22) E. P. Kohler, N. K. Richtmyer and W. F. Hester, *ibid.*, **53**, 205 (1931).

tilled. Monoperphthalic acid, on the other hand, gave a high yield of diol.

In order to test the possibility that 2-alkylcyclohexanones might arise as a result of thermal rearrangement, 1-methylcyclohexene was treated with perbenzoic acid at 0°. After working up the mixture, solvent was removed under reduced pressure and the crude product kept at room temperature. The presence of some 2-methylcyclohexanone in this material was suggested by a medium intensity band in the ketone carbonyl region. This was confirmed by preparation of its semicarbazone.[23]

It should also be mentioned that there is no rearrangement when ketone-free 1-methylcyclohexene oxide is distilled at about 40° (under reduced pressure).

These observations demonstrate that at least some ketone is formed at room temperature and below, though further conversion of epoxide to ketone may occur at elevated temperatures. Certainly, high distilling temperatures should be avoided, where possible, when purifying epoxides.

It may be seen from Table I that the total yield of products using either peroxy acid may be arranged in the decreasing order with reference to the 1-alkyl group: $-C_2H_5 > -CH_3 \cong -CH(CH_3)_2 > -C(CH_3)_3$.

The nucleophilicity (toward attack by $[OH]^+$) of the olefins increases as the electron-donating power of the alkyl group increases, *i.e.*, from methyl to *t*-butyl. However, the **steric factor**, operating in the opposite direction, becomes increasingly significant as the R group becomes more bulky and appears to predominate with the *t*-butyl compound. In this extreme case, the *t*-butyl group is equatorial,[24] thereby requiring that either the 6-membered ring be a deformed chair with the two C–O bonds, which compose the epoxide structure, having an equatorial–axial conformation or the cyclohexane ring be in one of two possible boat structures which are interconvertible without bond rupture.[25]

The reason for the exclusive formation of 1-phenylcyclohexane-*trans*-1,2-diol when monoperphthalic acid was used is not readily apparent. It presumably could arise during work-up of the reaction mixture with base.

Discrepancies between our results and those of earlier workers may be accounted for in part when it is recognized that the physical properties of epoxides and their isomeric ketones are often very similar and percentage composition would not be affected if a mixture were present. Infrared analysis, which was not available in earlier work, was invaluable in detecting the ketones and diols.

Experimental

1-Alkylcyclohexenes.—1-Methylcyclohexene was prepared by the method described by Bartlett and Rosenwald.[26] The main fraction was collected at 109–111°, n^{22}D 1.4489, yield 60–64% (lit.[27] b.p. 111–112°, n^{20}D 1.4496).

1-Ethylcyclohexene was prepared by the same method in 65–67% yield, b.p. 40–42° (20 mm.), n^{20}D 1.4560 (lit.[28] b.p. 134–135° (751.5 mm.), $n^{22.3}$D 1.4547).

1-Isopropylcyclohexene. A. Grignard Method.—A 2:1 molar ratio of isopropylmagnesium iodide to cyclohexanone gave a product which after dehydration exhibited an infrared band (strong) at[29] 1170 cm.$^{-1}$ and yielded the 2,4-dinitrophenylhydrazone of cyclohexanone. A threefold excess of Grignard was therefore employed and the pure olefin was obtained in 20% yield, b.p. 43–45° (15 mm.), n^{20}D 1.4574 (lit.[30] b.p. 45° (15 mm.), n^{20}D 1.4578), with no absorption at 1705 cm.$^{-1}$.

B. **Lithium Reduction.**[12]—1-Isopropylcyclohexene was prepared by the method described by Benkeser and his co-workers. The main fraction was collected at 46–49° (15 mm.), n^{17}D 1.4683, $\lambda_{\max}^{\mathrm{EtOH}}$ 262 mμ.[31] *Anal.* Calcd. for C_9H_{16} (olefin): C, 87.02; H, 12.98. Calcd. for C_9H_{14} (diene): C, 88.37; H, 11.55. Found: C, 87.67; H, 11.94. An attempt to form a maleic anhydride adduct failed.

1-*t*-Butylcyclohexene. A. Grignard Method.—A 2:1 and even a 3:1 excess of *t*-butylmagnesium bromide to cyclohexanone, followed by dehydration, gave a product which exhibited an infrared band at 1705 cm.$^{-1}$, and 2,4-dinitrophenylhydrazone of cyclohexanone was obtained in both cases.

B. **Lithium Reduction.**—The same method as used for 1-isopropylcyclohexene was employed. A liquid, b.p. 55–56° (12.5 mm.), n^{20}D 1.4672, was obtained with ultraviolet and infrared spectra different from that of *t*-butylbenzene. A maximum was observed at 261 mμ (EtOH). *Anal.* Calcd. for $C_{10}H_{18}$ (Olefin): C, 86.88; H, 13.13. Calcd. for $C_{10}H_{16}$ (diene): C, 88.16; H, 11.84. Found: C, 87.54; H, 12.54. No maleic anhydride adduct could be isolated.

C. **Alkylation.**—*t*-Butylcyclohexene was obtained by the Schmerling procedure[11] in 3 to 5% yield, b.p. 53–58° (14 mm.), n^{20}D 1.4600. (lit.[11] b.p. 62–65° (14 mm.), n^{20}D 1.4590).

1-Phenylcyclohexene was obtained in 42–44% yield, b.p. 135–138° (25 mm.), n^{20}D 1.5668 (lit.[32] b.p. 136° (25 mm.), n^{20}D 1.5670) by the Grignard dehydration procedure.[26]

1-Acetylcyclohexene. A. Rearrangement of 1-Ethynylcyclohexanol.[33]—1- Acetylcyclohexene[14] was prepared by the previously known procedure in 56–70% yield, b.p. 87–90° (22 mm.), n^{26}D 1.4872 (lit.[14] b.p. 85–88° (22 mm.), n^{20}D 1.4892). The infrared spectrum of this material showed the presence of bands at 3325 (-OH) and 3200 cm.$^{-1}$ (≡C—H) due to unreacted 1-ethynylcyclohexanol. The product obtained was therefore heated under reflux in 250 ml. of dry benzene with 10 g. of P_2O_5 for 2.5 hours. The infrared spectrum of the 1-acetylcyclohexene thus obtained, b.p. 88–92° (22 mm.), n^{25}D 1.4882, still exhibited the presence of small amounts of starting material.

B. **Acylation.**—When the procedure described by English and his co-workers[13] was used, 1-acetylcyclohexene was obtained in 75% yield, b.p. 89–90° (20 mm.), n^{20}D 1.4917 (lit.[13] b.p. 88–90° (19.5 mm.), n^{20}D 1.4914); semicarbazone, m.p. 220° (lit.[34] m.p. 218–220°).

Preparation of Peracids.—Perbenzoic acid[35] was prepared by the procedure of Kolthoff in 75–80% yield.

Monoperphthalic acid was prepared in 75–80% yield by the previously described procedure.[36]

Peroxytrifluoroacetic Acid.—The procedure of Emmons and Pagano[18] was used.

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[23] The use of 2,4-dinitrophenylhydrazine in testing for possible ketone in such mixtures must be avoided since the acid medium of the reagent readily converts epoxide to ketone.

[24] S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

[25] H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954).

[26] P. D. Bartlett and R. H. Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[27] O. Wallach, *Ann.*, **359**, 297 (1908).

[28] B. A. Kazanskii and H. F. Glushnev, *J. Gen. Chem., U.S.S.R.*, **8**, 642 (1938).

[29] Infrared spectra were determined on a double beam Perkin-Elmer model 21 recording infrared spectrophotometer with sodium chloride cells of 2.0 mm. thickness or on the Perkin-Elmer model 137 Infracord spectrophotometer with sodium chloride cells of either 0.2 mm. or 0.1 mm. thickness. The solvent was carbon tetrachloride.

[30] S. S. Nametkin and M. A. Volodine, *J. Gen. Chem., U.S.S.R.*, **17**, 325 (1947).

[31] The ultraviolet spectra were determined on a Beckman recording spectrophotometer model DK-2; ethanol was used as solvent.

[32] C. R. Noller and G. K. Kaneko, THIS JOURNAL, **69**, 1121 (1947).

[33] We wish to thank the Air Reduction Products Co. for a sample of this compound.

[34] G. A. Kon, *J. Chem. Soc.*, 1801 (1926).

[35] I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

[36] M. A. Stahmann and M. Bergmann, *J. Org. Chem.*, **11**, 589 (1946).

1-Methylcyclohexene with Monoperphthalic Acid.[37]—1-Methylcyclohexene oxide was obtained in 55% yield, b.p. 40–42° (12 mm.), $n^{20}\mathrm{D}$ 1.4434, (lit.[38] b.p. 138°, $n^{20}\mathrm{D}$ 1.4430). A 15% yield of 2-methylcyclohexanone was also isolated, b.p. 63–68° (20 mm.), $n^{18}\mathrm{D}$ 1.4492 (lit.[39] b.p. 166°, $n^{20}\mathrm{D}$ 1.4483); m.p. of semicarbazone, 189° (lit.[40] m.p. 189°); mixed melting point with semicarbazone of authentic 2-methylcyclohexanone, 189°. The residue solidified on standing, and recrystallization with ether gave 1–2% *trans*-1-methylcyclohexane-1,2-diol, m.p. 84–85° (lit.[26] m.p. 85°).

1-Methylcyclohexene with Perbenzoic Acid.[41]—An impure 1-methylcyclohexene oxide[42] boiling at 40–42° (12 mm.), $n^{20}\mathrm{D}$ 1.4455, was obtained in 48% yield, showing infrared band at 1705 cm.$^{-1}$. A 24% yield of the ketone was isolated, b.p. 58–62° (14 mm.), $n^{24}\mathrm{D}$ 1.4472. The *trans*-glycol was also isolated in 1–2% yield, m.p. 85°.

1-Methylcyclohexene with Perbenzoic Acid without Distillation.—The reaction was carried out in the same manner as above. However, no heat was applied in removing the solvent. The infrared spectrum of the crude material exhibited a band of medium intensity at 1705 cm.$^{-1}$, indicating that the ketone was present.

1-Methylcyclohexene with N-Bromosuccinimide and Water.[20]—The bromohydrin was isolated, distilling at 96–98° (8.5 mm.), $n^{25}\mathrm{D}$ 1.5150, yield 71.5% (lit.[43] b.p. 100–101° (16 mm.)). By stirring the bromohydrin with sodium hydroxide, the epoxide was obtained in 29% yield, b.p. 36–37° (12 mm.), $n^{25}\mathrm{D}$ 1.4415. The infrared spectrum showed no carbonyl peak. *Anal.* Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.68; H, 10.82.

When the crude bromohydrin was converted directly to the epoxide by the method and conditions described above, the yield of pure 1-methylcyclohexene oxide was 50%, b.p. 35–39° (12 mm.), $n^{24}\mathrm{D}$ 1.4420.

1-Ethylcylohexene with Monoperphthalic Acid.—Pure epoxide was obtained in 53% yield, b.p. 56–58° (20 mm.), $n^{20}\mathrm{D}$ 1.4490 (lit.[44] b.p. 165°, $n^{25}\mathrm{D}$ 1.4520, $n^{25}\mathrm{D}$ 1.4473[11]). A 28% yield of 2-ethylcyclohexanone, b.p. 62–63° (20 mm.), $n^{20}\mathrm{D}$ 1.4629, was also obtained; m.p. of semicarbazone, 165° (lit.[38] m.p. 165°); 2,4-dinitrophenylhydrazone, m.p. 158–159° (lit.[9] m.p. 159°).

1-Ethylcyclohexene with Perbenzoic Acid.—Impure epoxide was obtained, 60% yield, b.p. 56–59° (20 mm.), $n^{20}\mathrm{D}$ 1.4508, infrared absorption at 1705 cm.$^{-1}$. The ketone was isolated in 25% yield, b.p. 64–66° (20 mm.), $n^{20}\mathrm{D}$ 1.4630; 2,4-dinitrophenylhydrazone, m.p. 158°.

1-Isopropylcyclohexene with Monoperphthalic Acid.—Pure epoxide was isolated, yield 44%, b.p. 67° (15 mm.), $n^{20}\mathrm{D}$ 1.4496 (lit.[12] b.p. 67° (15 mm.), $n^{25}\mathrm{D}$ 1.4575). *Anal.* Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.55; H, 11.28. 2-Isopropylcyclohexanone was also isolated in 21% yield, b.p. 72° (15 mm.), $n^{24}\mathrm{D}$ 1.4526 (lit.[45] b.p. 83° (17 mm.), $n^{15}\mathrm{D}$ 1.4564; m.p. of semicarbazone, 180° (lit.[46] m.p. 180°); 2,4-dinitrophenylhydrazone, m.p. 138°. *Anal.* Calcd. for $C_{15}H_{20}O_4N_4$: N, 17.49. Found: N, 17.55.

1-Isopropylcyclohexene with Perbenzoic Acid.—A 44% yield of impure epoxide was obtained, b.p. 62–65° (15 mm.), $n^{25}\mathrm{D}$ 1.4475, infrared absorption at 1705 cm.$^{-1}$. In addition, 35% of the ketone was also isolated, b.p. 72–74° (15 mm.), $n^{25}\mathrm{D}$ 1.4525; m.p. of semicarbazone, 180°; 2,4-dinitrophenylhydrazone, m.p. 138°.

1-*t*-Butylcyclohexene with Monoperphthalic Acid.—Some starting material (50%) was recovered. Only one product was obtained, b.p. 76–80° (14 mm.), $n^{20}\mathrm{D}$ 1.4518; infrared bands at 1705 (>C=O) and 3400 cm.$^{-1}$ (-OH).

1-*t*-Butylcyclohexene with Perbenzoic Acid.—Again, some starting material (26%) was recovered. A liquid, b.p. 73–75° (14 mm.), $n^{24}\mathrm{D}$ 1.4492, with infrared bands at 1705 and 3400 cm.$^{-1}$, was the only product isolated. A 2,4-dinitrophenylhydrazone derivative was obtained, m.p. 126°.

Anal. Calcd. for $C_{16}H_{22}O_4N_4$: N, 16.76. Found: N, 15.70.

1-Phenylcyclohexene with Monoperphthalic Acid.—No epoxide was formed. Phenylcyclohexane-*trans*-1,2 diol was obtained in 80% yield, m.p. 96° (lit.[47] m.p. 96°). *Anal.* Calcd. for $C_{12}H_{12}O$: C, 75.00; H, 8.39. Found: C, 75.25; H, 8.37. Monobenzoate derivative of the glycol, m.p. 159°. *Anal.* Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: *C*, 76.92; H, 6.86.

1-Phenylcyclohexene with Perbenzoic Acid.—The only product isolated was 2-phenylcyclohexanone (53% yield), b.p. 146–153° (12 mm.), infrared band at 1705 cm.$^{-1}$; *anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.72; H, 7.87; semicarbazone, m.p. 190° (lit.[46] m.p. 190°).

1-Acetylcyclohexene with Monoperphthalic Acid.—No reaction occurred. The starting material was recovered unchanged.

1-Acetylcyclohexene with Alkaline Hydrogen Peroxide.[17a]—1-Acetylcyclohexene (14.88 g., 0.12 mole) was dissolved in 240 ml. of absolute methanol. About 0.24 mole (30 ml.) of 30% hydrogen peroxide and then 30 ml. of 4 *N* sodium hydroxide were added. The mixture became warm and external cooling was necessary to keep the temperature below 40°. When the mixture had cooled, water was added. No turbidity was shown even after the addition of about 500 ml. of water. The solution was extracted with ether, the ether extract dried over anhydrous sodium sulfate and distilled. The product was obtained in 50% yield, b.p. 88–92° (22 mm.), $n^{25}\mathrm{D}$ 1.4650, infrared band at 1675 cm.$^{-1}$ (>C=O). *Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.63; H, 8.63. Found: C, 69.76; H, 8.92.

1-Acetylcyclohexene with Peroxytrifluoroacetic Acid.[18]—To a well-stirred boiling mixture of 18.8 g. (0.15 mole) of 1-acetylcyclohexene, 150 ml. of methylene chloride and 84.7 g. (0.6 mole) of Na_2HPO_4 (which had been ground to a fine powder and dried in a vacuum oven at 50° for 20 hours before use), was added through a dropping funnel 19.5 g. (0.15 mole) of peroxytrifluoroacetic acid (in methylene chloride). After the exothermic reaction had subsided, the solution was heated under reflux for 30 minutes. The resulting mixture was stirred with 500 ml. of water until all the inorganic salt had dissolved. The organic layer was separated and the aqueous layer extracted with 50 ml. of methylene chloride. The combined methylene chloride extracts were washed with water, then with 100 ml. of 10% sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was removed by distillation, and the product obtained by distillation under reduced pressure was the epoxide in 50% yield, b.p. 89–92° (22 mm.), $n^{20}\mathrm{D}$ 1.4673.

1-Methylcyclohexene Oxide with Perbenzoic Acid.—Pure 1-methylcyclohexene oxide (11.2 g., 0.1 mole) was allowed to react with 13.8 g. (0.1 mole) of perbenzoic acid in benzene for 24 hours under epoxidation conditions. No reaction occurred and 1-methylcyclohexene oxide was recovered unchanged, as evidenced by the physical constants and the infrared spectrum which showed the absence of the carbonyl group.

1-Methylcyclohexene Oxide with Benzoic Acid.—Pure 1-methylcyclohexene oxide (11.2 g., 0.1 mole) was added dropwise to a solution of 12.2 g. (0.1 mole) of benzoic acid in anhydrous benzene. The reaction was carried out for 24 hours under epoxidation conditions. Distillation under reduced pressure (after removal of benzene at atmospheric pressure) gave 6.72 g. (60%) of 1-methylcyclohexene oxide and the residue (3.85 g.) had an infrared spectrum which indicated the presence of 2-methylcyclohexanone (1695s, cm.$^{-1}$), and presumably a hydroxyester (3380m, 1725s, cm.$^{-1}$). The semicarbazone of 2-methylcyclohexanone was obtained which gave no depression when admixed with the authentic semicarbazone.

Microanalysis.—The microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

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