# Epoxidation of Simple Allenes. Role of Cyclopropanones as Reactive Intermediates<sup>1a</sup>

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The peracid oxidation of tetramethylallene, 1,1-dimethylallene, and 1,2-cyclononadiene has been studied. The products of these reactions are rationalized in terms of initial formation of an allene oxide followed by competitive partitioning of this reactive species between valence isomerism to the related cyclopropanone and further oxidation to a dioxaspiropentane derivative. In addition to combining with the carboxylic acid generated during the oxidation to produce  $\alpha$ -acyloxy ketones the cyclopropanones suffer further reaction with peracid to yield  $\beta$ -lactones or undergo "oxidative decarbonylation" to the corresponding olefins which are usually transformed into their epoxides under the reaction conditions. The dioxaspiropentanes also add carboxylic acid yielding  $\alpha$ -acyloxy  $\alpha'$ -hydroxy ketones. Thus, an excess of peracetic acid in buffered methanol gives 1, 8, and 12 as important products from tetramethylallene. A similar reaction under acidic conditions yields only 9. 1,2-Cyclononadiene is transformed to 20, 22, 23, and cyclooctene by peracid in methylene chloride. 1,1-Dimethylallene gives 30, 31, 32, and 33 under these conditions, but only acetone and methyl acetate in methanol solvent.

We have previously reported on the peracetic acid oxidation of tetramethylallene in methylene chloride solution.<sup>2</sup> The formation of products 1-4 in this reaction was rationalized in terms of reactive intermediates 5 and 6 which are derived by straightforward mono- and di-epoxidation of the starting allene. Reasonable transformations of allene oxide 5 and dioxide 6 were postulated to lead to the observed products. This early study provided no information concerning the interesting possibility of valence isomerism of allene oxide 5 to cyclopropanone 7. Subsequent work has resulted in the isolation and characterization of authentic allene oxide derivatives<sup>3-5</sup> and an example of a spiro dioxide.<sup>6</sup> Furthermore, the type of valence isomerism illustrated by the transformation of 5 to 7 has received experimental confirmation.<sup>3,7</sup> The present paper is concerned with further studies on epoxidation of simple allenes.

Merely changing the solvent from methylene chloride to methanol results in a striking modification of the product mixture derived from tetramethylallene. Thus, when 3 equiv of peracetic acid in methylene chloride was added to a methanol solution of the allene containing sodium carbonate, a minimum of nine products could be isolated and identified unambiguously. As in the earlier study the major product was acetoxy ketone 1 (47%). However, an important amount of tetramethylethylene oxide (8) (37%) was found, as were isolable quantities of the following materials: acetone, pinacolone (7%), methoxy ketone 9 (2%), methyl 2,2,3-trimethylbutanoate (10) (1%), methyl  $\alpha$ -hydroxy<br/>isobutyrate (3%), hydroxy methoxy ketone 11 (2%), and 3-hydroxy-2,2,3-trimethylbutanoic acid  $\beta$ -lactone (12) (1%).

In methanol there is a sharp decrease in the products attributed to reactive intermediate 6. For example, ketone 2 is not observed as a product in methanol, whereas it amounts to about 40% in a comparable methylene chloride experiment. Indeed, the only product directly attributable to 6 in the first reaction is ketone 11. (The acetone and methyl  $\alpha$ -hydroxyisobutyrate are probably secondary products of 11 derived by peracid oxidation and methanolysis of intermediate 13.) The reaction is observably slower in methanol, probably a result of hydrogen-bonding interactions between the solvent and peracid.<sup>8</sup> Apparently, the intervention of competing processes prevent substantial conversion of  $\mathbf{5}$  into  $\mathbf{6}$  in methanol. In addition to retarding the epoxidation, the polar hydroxylic solvent may aid the competing reactions for the consumption of the allene oxide by the solvation of polar intermediates involved in these processes. Of course, methanol is also available as a nucleophile for reaction with reactive intermediates. Among the new epoxidation products are four which have suffered skeletal rearrangement, namely pinacolone, epoxide 8, ester 10, and lactone 12 (see Chart I). An attractive rationalization for these products invokes cyclopropanone 7 as an important intermediate.<sup>9</sup> In methanol 7 exists almost exclusively in the form of its hemiketal 14, but reactions involving the small amount of the free ketone presumably present at equilibrium are known.9 The base rearrangement of 7 to give ester 10 is amply documented.<sup>9</sup> Simple Baeyer-Villiger oxidation likewise presents a reasonable pathway to lactone 12. This latter compound is, however, stable to the reaction conditions thereby ruling out a route to epoxide 8 by way of 12 (e.g., decarboxylation<sup>10</sup> followed by epoxidation of the tetramethylethylene thus produced). Nonetheless when an authentic sample of 14 was subjected to the reaction conditions, a product mixture consisting of 8 (55%), methoxy ketone 9 (24%), acetoxy ketone 1 (11%), pinacolone (4%), and rearranged ester 10 (6%) was obtained. A trace of material with the appropriate glpc characteristics for tetramethylethylene was also detected, but this probably arises from decomposition of lactone 12

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<sup>(2)</sup> J. K. Crandall and W. H. Machleder, J. Amer. Chem. Soc., 90, 7292 (1968).

<sup>(3)</sup> R. L. Camp and F. D. Greene, *ibid.*, **90**, 7349 (1968).
(4) J. K. Crandall and W. H. Machleder, J. Heterocycl. Chem., **6**, 777

 <sup>(1969).
 (5)</sup> H. M. R. Hoffmann and R. H. Smithers, Angew. Chem., 82, 43

<sup>(1970).
(6)</sup> J. K. Crandall, W. H. Machleder, and M. J. Thomas, J. Amer. Chem.

Soc., 90, 7346 (1968). (7) J. K. Crandall and W. H. Machleder, *ibid.*, 90, 7347 (1968).

<sup>(8)</sup> R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, J. Org. Chem., **35**, 740 (1970).

<sup>(9)</sup> For a review of cyclopropanone chemistry, see N. J. Turro, Accounts Chem. Res., 2, 25 (1969).

<sup>(10)</sup> Y. Etienne and N. Fischer in "Heterocyclic Compounds with Threeand Four-Membered Rings," Part 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 729.





under the glpc conditions. A control experiment demonstrated that this olefin is rapidly transformed to epoxide 8 under the reaction conditions. These results suggest an "oxidative decarbonylation" pathway<sup>11,12</sup> for the conversion of 7 into the olefin precurser of epoxide 8, most likely via fragmentation<sup>13</sup> of the intermediate peracid adduct 15. It is noteworthy that this reaction does not go through the  $\beta$ -lactone 12, a possibility that has not been excluded in other examples of "oxidative decarbonylation."

Accepting this evidence for the involvement of cyclopropanone 7 leads to the suggetion that 7 is formed by isomerization of the initially formed allene oxide. Subsequently performed studies have demonstrated clearly the operation of this type of transformation with other allcnes,<sup>3,7</sup> thereby bolstering substantially this deduction. Evidently an important reaction of allene oxide 5 in methylene chloride is further epoxidation to dioxide 6, whereas this process is not competitive with the isomerism of 5 to 7 in methanol. If this latter transformation involves the intermediacy of zwitterion 16 or some closely related species (e.g.), its protonated form 17), the accelerating effect of a polar hydroxylic solvent can be readily appreciated.

An experiment performed by adding 1 equiv of peracid slowly to a methanol solution of the allene gave a product mixture containing 1 (72%), 9 (9%), 10 (9%), and 11 (9%), but no epoxide 8. In the absence of excess oxidizing agent the cyclopropanone was evidently converted into alternate products in accord with expectations based on the mechanism elaborated above.

A dramatic variation in the reaction was again observed when the sodium carbonate buffer was omitted

(12) J. K. Crandall and W. W. Conover, Tetrahedron Lett., 583 (1971). (13) A free-radical mechanism related to that found for cyclopropyl nitrites may operate here; see C. H. Depuy, H. L. Jones, and D. H. Gibson, J. Amer. Chem. Soc., 94, 3924 (1972).

reaction mixture. These conditions resulted in methoxy ketone 9 as the only oxidation product. Under acidic conditions methanol is the best available nucleophile and its addition occurs cleanly. This addition can conceivably operate on either allene oxide 5 or cyclopropanone 7, although protonation and isomerization to stablized cation 17 probably precedes nucleophilic attack. Hemiketal 14 provides yet a third potential source of 17 in the presence of acid.

In order to better define the chemistry of 7, this intermediate was generated under different conditions by the irradiation of 18.9 Production of the cyclopropanone in the presence of equivalent amounts of methanol and acetic acid in methylene chloride generated only acetoxy ketone 1. A similar experiment to which a trace of strong acid had been added resulted in a 16:84 ratio of 1 to methoxy ketone 9. Performing the photolysis in a methanol solution of sodium acetate yielded 1 (87%) in addition to small amounts of 9 and 10. These results accord well with the proposed role of 7 as the product precursor in the peracid oxidations discussed above. However, the unavailability of allene oxide 5 for independent observation renders it difficult to explore the possibility that this species might be transformed to products without isomerization to 7. Conversely, valence isomerization of 7 to 5 prior to product formation cannot be ruled out.<sup>14</sup>

Rationalization of the variation in products in the photolysis experiments invokes the formation of an ion pair between 17 and acetate as the important step in the addition of acetic acid to 7 in the first experiment. Collapse to covalent product 1 follows logically. In the presence of strong acid, free 17 is generated and combines with the best available nucleophile, methanol. The preponderance of acetate product in methanolic sodium acetate solution is also explicable in terms of nucleophilic competition for the reactive electrophilic species which is probably zwitterion 16.

The behavior of 1,2-cyclononadiene (19), a 1,3disubstituted allene, towards peracid oxidation was also studied.<sup>15</sup> Reaction of 19 with 1 equiv of peracetic acid in methylene chloride solution, followed by glpc isolation yielded cyclooctene, unreacted 19, cyclooctene oxide (20), and 1,2-cyclononadione (21) in an 11:16:29:44 ratio. Column chromatography of the crude product produced a small amount of an additional material which is tentatively identified as  $\beta$ -lactone 22 on the basis of its spectral characteristics, most notably a carbonyl band at 5.47  $\mu$  in the ir and loss of CO<sub>2</sub> as an important mass spectral fragmentation. Utilizing 3 equiv of peracid resulted in a 31:69 mixture of 20/21 as the only important products observed by glpc. However, examination of the crude reaction mixtures demonstrated that dione 21 was not present, but rather the data were consistent with the presence of an acetate ester, most probably 23a (vide infra).

One equivalent of *m*-chloroperbenzoic acid (MCPBA) transformed 19 into a 12:4:84 mixture of 19/20/21 as viewed by glpc analysis. In this instance crystalline 23b was isolated from the reaction mixture and

<sup>(11)</sup> J. E. Baldwin and J. H. I. Cardellia, Chem. Commun., 558 (1968).

<sup>(14)</sup> There is no concrete evidence for the presence of detectable amounts of the allene oxide isomer in equilibrium with 7.8

<sup>(15)</sup> Subsequent to initiation of this work, a publication on the same subject appeared: W. P. Reeves and G. G. Stroebel, Tetrahedron Lett., 2945 (1971).



**a**,  $\mathbf{R} = \mathbf{CH}_3$ ; **b**,  $\mathbf{R} = m \cdot \mathbf{ClC}_6\mathbf{H}_4$ ; **c**,  $\mathbf{R} = p \cdot \mathbf{NO}_2\mathbf{C}_6\mathbf{H}_4$ 

shown to decompose cleanly to dione 21 upon injection onto the glpc column. An experiment performed with 3 equiv of *p*-nitroperbenzoic acid (PNPBA) gave a product mixture indicating an 18:72 ratio of 20/21by glpc, but from which crystalline 23c was isolated. This ester also yielded 21 cleanly by glpc decomposition.

These results can be accommodated within the general framework of allene epoxidation mechanisms as depicted in Chart II. Epoxidation of 19 leads to the reactive allene oxide intermediate 24, which serves as a branching point for further reaction. On one hand, 24 is further epoxidized to a second reactive species, spiro dioxide 25, which is the precursor of the major product 23 by addition of the appropriate acid. This pathway to 23 is supported by the isolation and characterization of an analogous compound in a different allene epoxidation.<sup>6</sup> Of course, dione 21 is a secondary decomposition product of 23 formed only upon injection into the gas chromatograph. It is noteworthy that 23 (analyzed as 21 by glpc) increases in relative quantity as the amount of peracid increases. The other mode of reaction for 24 involves valence isomerization to cyclopropanone 26. This hypothesis is supported most strongly by the presence of lactone 22, its further peracid oxidation product, in the crude product mixture. However, the major pathway for utilization of this reactive species is "oxidative decarbonylation" yielding cyclooctene and its epoxide 20 by yet another peracid oxidation. The isolation of cyclooctene itself in the reaction utilizing 1 equiv of peracetic acid is particularly significant since, in the reactions of tetramethylallene, the corresponding olefin was only postulated as an intermediate on the way to epoxide 8. The relative efficiencies of the two productforming routes from 24 as a function of available peracid is consistent with a balanced competition between valence isomerization and further epoxidation of 24.

It was somewhat surprising to note that 24 does not give appreciable quantities of the simple carboxylic acid adduct 27, normally the major product from allene epoxidations. An understanding of this observation is complicated by the ambiguity of the mechanistic pathway leading to this type product, which can conceivably be generated by addition of acid to either an allene oxide or cyclopropanone intermediate. The methylene chain of 24 is situated such as to retard SN2-type attack at the saturated epoxide center, a feature which could account for the predominance of other processes. Alternatively, reaction of cyclopropanone 26 with acid via a cationic intermediate analogous to 17 may be impeded by the paucity of stabilizing alkyl groups. It is not presently known what role is played by the strain inherent in these medium-ring derivatives.

Finally, it is now clear that dione 21 is not a primary product of the peracid oxidation as had been suggested earlier by Reeves and Stroebel.<sup>15</sup> The nature of this unanticipated transformation of 23 merits brief consideration. A most intriguing possibility involves pyrolytic 1,3 elimination of carboxylic acid to give hydroxycyclopropanone 28, the anticipated tautomerism of which produces the dione. A related 1,3 elimination has been suggested to account for the pyrolytic conversion of 2-acetoxycycloalkanones into ring-contracted olefins, carbon monoxide, and acetic acid.<sup>16</sup> An alternate mechanism calls for tautomerization of 23 to isomeric ketol 29 prior to 1,2 elimination of acid and subsequent tautomerization to 21. Experimental differentiation between these possibilities is not obvious.

The geminally disubstituted compound, 1,1-dimethylallene, was also briefly examined. The addition of this allene to 3 equiv of peracetic acid in methylene chloride solution proceeded with the evolution of  $CO_2$  and the formation of 3-acetoxy-3-methyl-2-butanone<sup>17</sup> (**30**) and isobutylene oxide (**31**) as major products. Appreciable quantities of acetone and 3-hydroxy-2,2-dimethylpropanoic acid  $\beta$ -lactone (**32**) were also isolated. The relative proportions of the latter four products were 50:25:17:8. In addition the presence of the isomeric  $\beta$ -lactone **33** was indicated by nmr examination of the crude product which displayed signals at the same chemical shifts as an authentic sample. Furthermore, **33** was shown to lose  $CO_2$  under

 <sup>(16)</sup> R. G. Carlson and J. H. Bateman, J. Org. Chem., 32, 1608 (1967).
 (17) J. Boeseken, Recl. Trav. Chim. Pays-Bas, 54, 657 (1935).

the reaction conditions. Lactone **32** was stable to similar treatment. Interestingly the use of methanol as solvent with an excess of peracetic acid gave only acetone and methyl acetate as products.

Chart III provides the familiar rationale for the observed results. As usual, epoxidation of the allene



is the presumed initial step. In the case of this unsymmetrical allene, it is assumed that the normal accelerating effect of alkyl substituents will direct peracid attack to the more substituted double bond yielding 34. It is possible that valence isomerism interconverts 34 and its isomer 35, but transformation to cyclopropanone **36** is probably the prevailing process. Acetoxy ketone **30** arises by addition of acetic acid to the cyclopropanone and/or the allene oxide as discussed above. The lactones are Baeyer-Villiger products of the former and epoxide 31 is presumably derived from isobutylene also formed by peracid oxidation of 36. The availability of a sample of 36 allowed confirmation of the  $36 \rightarrow 30$  reaction with acetic acid.<sup>18</sup> Reaction of 36 with 40% peracetic acid in acetic acid at  $-78^{\circ}$  resulted in rapid gas evolution (presumably  $CO_2$ ) and the production of **30**.

The oxidation in methanol is puzzling. A conceivable route to the observed products involves nucleophilic addition of peracid to one of the intermediates leading to 37, which could serve as a source of acetone and methyl acctate by the indicated fragmentation. The role of the solvent in directing reaction along this new pathway is not altogether clear, although several reasonable hypotheses can be put forth.

In conclusion, strong circumstantial evidence has been accrued for the involvement of cyclopropanones in the epoxidation reactions of representative allenes.

#### **Experimental Section**

**General.**—All nmr spectra were recorded on a Varian A-60 spectrometer using CCl<sub>4</sub> as solvent. Infrared spectra were obtained as liquid films with a Perkin-Elmer Infracord Model 137 spectrophotometer. Gas chromatography (glpc) was performed on Aerograph A600 (flame ionization detector) and A700 (preparative) instruments. The analytical columns were 5 ft  $\times$  1/s in. 15% Carbowax 20M on 60/80 Chromosorb W and 5 ft  $\times$  1/s in. 10% SE-30 on 80/100 Chromosorb W; preparative columns

were 10 or 20 ft  $\times$   $^{3}/_{8}$  in 15% Carbowax on 60/80 Chromosorb W. Percentage composition data on product mixtures were estimated by peak areas and are uncorrected for compound response except where noted. Anhydrous magnesium sulfate was used as a drying agent.

**Peracetic Acid Solutions.**—Acetic acid was removed from commercially available 40% peracetic acid by adding the peracid dropwise to a cold mixture of excess anhydrous sodium carbonate suspended in methylene chloride. After the mixture was stirred for 45 min, the inorganic salts were removed by suction filtration through a layer of glass wool and anhydrous magnesium sulfate. The peracid solution was used immediately in the oxidation reaction. Nmr analysis indicated a 95:5 mixture of peracetic and acetic acids. When peracid is mentioned below, this implies that the given amount of 40% peracetic acid was treated according to the above procedure and used as the resulting acetic acid-free methylene chloride solution. Titration indicated that the total oxidizing activity of the peracid was undiminished.<sup>19</sup>

Epoxidation of Tetramethylallene with 3 Equiv of Peracetic Acid in Methanol.—To an ice-cold mixture of tetramethylallene (2.0 g) and sodium carbonate (20 g) in 80 ml of methanol was added 12 g of peracetic acid. After stirring for 3 hr, the excess peracetic acid was destroyed by the addition of 2-methyl-2butene. The reaction mixture was then filtered and the solvent removed on the flash evaporator to give 2.4 g of crude material. Glpc analysis indicated nine reaction products in addition to a small amount of unreacted allene. All the components were isolated by preparative glpc. These were acetone, tetramethylethylene oxide, pinacolone, methyl 2,2,3-trimethylbutanoate, methoxy ketone 9, methyl  $\alpha$ -hydroxyisobutyrate, methoxy hydroxy ketone 11, acetoxy ketone 1, and 3-hydroxy-2,2,3-trimethylbutanoic acid  $\beta$ -lactone (12).

In one experiment the relative product percentages (excluding acetone) were determined by calibrated glpc analysis: **8** (37%), pinacolone (7%), **10** (1%), **9** (2%), methyl  $\alpha$ -hydroxyisobutyrate (3%), **11** (2%), **1** (47%), and **12** (1%).

Epoxidation of Tetramethylallene with 1 Equiv of Peracetic Acid in Methanol.—Peracetic acid (2.0 g) was added very slowly to an ice-cold solution of allene (1.0 g) in 30 ml of methanol. After 4 hr a negative peracid test was obtained, and the reaction solution was poured into saturated sodium bicarbonate. The aqueous layer was extracted with methylene chloride and dried. A crude product of 1.4 g was obtained after solvent removal on the flash evaporator. Four products were isolated by preparative glpc and identified as acetone, 1, 11, and 10. A fifth component was identified as 9 by glpc retention time. The ratio of 1/11/10/9was 72:9:9:9.

3-Hydroxy-2,2,3-trimethylbutanoic Acid  $\beta$ -Lactone (12).— Tetramethylcyclobutane-1,3-dione (10 g) was pyrolyzed by passing through a vacuum flow system at 700° and 0.2 mm. The dimethyl ketene was trapped in a solution of 150 ml of acetone and 1.3 g of freshly distilled boron trifluoride etherate maintained at  $-75^{\circ}$ . After 1 hr the reaction mixture was allowed to come to room temperature, and 2 g of dicyclohexylamine was added to destroy the boron trifluoride etherate. The solvent was removed on the flash evaporator to give crystalline material. Washing with cold hexane gave 4.3 g of a white crystalline material which was recrystallized from carbon tetrachloride to give pure 12:<sup>20</sup> mp 127-128°; ir 5.49  $\mu$ ; nmr  $\delta$  1.50 (s, 6) and 1.29 (s, 6).

**Reaction of 12 with Peracetic Acid.**—To an ice-cold mixture of 0.5 g of 12, 2 g of sodium carbonate, and 0.1 g of benzene (internal standard) in 10 ml of methanol was added 0.8 g of peracetic acid. After 2.5 hr the reaction mixture was washed with saturated sodium bicarbonate and dried. The solvent was removed by distillation. Nmr and glpc analysis indicated that 12 had not been destroyed.

Epoxidation of Tetramethylallene in the Presence of Sulfuric Acid and Methanol.—A solution of 2.0 g of peracetic acid containing 10 drops of concentrated sulfuric acid was added at a moderate rate to an ice-cold solution of 1.0 g of allene in 30 ml of methanol. After 2.5 hr the reaction solution gave a negative peracid test. The solution was poured into saturated sodium carbonate, the aqueous layer was extracted with methylene chloride, and the extract was dried. A crude yield of 0.7 g was

<sup>(18)</sup> We thank Professor Turro for kindly providing us with this sample.

 <sup>(19)</sup> F. P. Greenspan and D. G. Mackellar, Anal. Chem., 20, 1061 (1948).
 (20) G. Natta, G. Mazzanti, G. Pregaglia, and M. Binaghi, J. Amer. Chem. Soc., 82, 5511 (1960).

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obtained upon removal of the solvent. Glpc analysis indicated the presence of two components which were identified as 9 (43%)and 4-methoxy-2,4-dimethyl-2-pentene (57%). There was less than 1% of 1.

Photolysis of 18 in the Presence of Acetic Acid and Methanol.—A methylene chloride solution (400 ml) containing 10.0 g of 18, 4.3 g of acetic acid, and 2.3 g of methanol was irradiated for 1.25 hr using a 450-W Hanovia Type L medium-pressure quartz mercury vapor lamp fitted with a Pyrex filter. The resulting clear solution contained a single product identified as 1. There was less than 1% of 9.

Photolysis of 18 in the Presence of Methanol, Acetic Acid, and Sulfuric Acid .- A methylene chloride solution (400 ml) containing 10.0 g of 18, 4.3 g of acetic acid, 2.3 g of methanol, and 12 drops of concentrated sulfuric acid was irradiated as described above for 1.25 hr at which point the reaction solution darkened. The solvent volume was reduced by flash evaporation, and the solution was washed with saturated sodium bicarbonate and dried. Glpc analysis indicated two reaction products which were identified as 1 and 9 in the ratio of 16:84.

Photolysis of 18 in the Presence of Sodium Acetate.--A solution of 18 (2 g) and sodium acetate (13 g) in 26 ml of methanol was photolyzed with 3000-Å light in a Rayonet photochemical reactor for 24 hr. The reaction solution was then poured into water, extracted with methylene chloride, and dried. After removing the solvent by flash evaporation, 2 g of crude product was obtained which glpc analysis indicated to be 87% of 1. There was less than 5% of 9 or 10. 1-Methoxy-1-hydroxy-2,2,3,3-tetramethylcyclopropane (14).<sup>21</sup>-

A solution of 10 g of 18 in 400 ml of dry methanol was irradiated at 0° for 3.5 hr as described above. After the disappearance of starting material was indicated by glpc, the solvent was removed cautiously on the flash evaporator to give a clear, colorless liquid which was shown by nmr to contain 85% of 14: ir 5.79, 8.21, 8.80, 9.03, and 9.11  $\mu$ ; nmr  $\delta$  3.34 (s) and 1.05 (s). (Contaminants were 10 and methyl isobutyrate.) This material was stored at  $-20^{\circ}$  and subsequent reactions were performed without further purification.

Reaction of 14 with Sodium Carbonate.—Approximately 1 g of 14 was added to a slurry of 4 g of sodium carbonate in 25 ml of methanol and 25 ml of methylene chloride at 0°. After stirring for 5 hr, the reaction mixture was filtered and washed with saturated sodium bicarbonate solution; the organic layer was dried. The solvent was removed cautiously to give unchanged starting material.

Reaction of 14 with Peracetic Acid.-To approximately 1 g of 14 and 4 g of sodium carbonate in 25 ml of methanol at 0° was added approximately 1.4 g of peracetic acid in 25 ml of methylene chloride. After 4 hr at  $0^\circ$  the reaction mixture was diluted with methylene chloride and filtered. The organic layer was washed with saturated sodium bicarbonate and dried. Analysis indicated 55% of 8, 24% of 9, 11% of 1, 4% of pinacolone, and 6% of 10.

Reaction of 14 with Peracetic Acid in the Presence of Tetramethylethylene.-To approximately 1 g of 14 and 5 g of sodium carbonate at 0° was added 1.4 g of peracetic acid in 25 ml of methylene chloride. Immediately after the peracetic acid solution was added, 60 mg of tetramethylethylene was introduced into the reaction flask. After stirring at 0° for 4 hr, the reaction mixture was processed as in the preceding experiment. Glpc analysis indicated that 60% of the product was 8 and no tetramethylethylene remained.

Reaction of 19 with Peracetic Acid .-- To a slurry of 1 g of anhydrous Na<sub>2</sub>CO<sub>3</sub> and 500 mg of 19 in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> at 0° was added 1 equiv of peracetic acid in 20 ml of cold CH<sub>2</sub>Cl<sub>2</sub>. The mixture was allowed to warm to room temperature and stirred for 8 hr at which time a negative starch-iodide test was obtained. The mixture was filtered and the solvent was removed from the filtrate to give 543 mg of a colorless oil: ir 2.8, 5.47, 5.60, 5.73, 5.80, and 8.0  $\mu;~\mathrm{nmr}~\delta$  2.04 (s) and 3.6 (m). Analytical glpc showed four major peaks in a ratio of 11:16:29:44. The first two materials were identified as cyclooctene and unreacted starting material by glpc and mass spectral comparisons with authentic samples. The remaining peaks were isolated and identified as 20 and 21: ir 5.87  $\mu$ ; nmr  $\delta$  2.64 (t, 4, J = 6 Hz), 1.83 (m, 4), and 1.47 (m, 6).  $^{\boldsymbol{22}}$ 

Column chromatography of the crude reaction mixture on silica gel gave a small quantity of a further product tentatively identified as 22: ir (CCl<sub>4</sub>) 5.47  $\mu$ ; nmr  $\delta$  4.42 (m, 1), 3.36 (m, 1), and 2.2 (m, 12); mass spectrum m/e (rel intensity) 154 (6), 110 (15), 96 (121), 80 (18), 63 (42), 50 (64), and 46 (100)

A similar reaction using 3 equiv of peracid for 2 days gave a 20/21 ratio of 31:69.

**Reaction of 19 with MCPBA**.—To 1.8 g of 19 in 10 ml of  $CH_2Cl_2$  at 0° was added 2.4 g (1 equiv) of MCPBA in 30 ml of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 40 min a copious white precipitate had formed and a negative starch-iodide test was obtained. The reaction mixture was filtered and the filtrate washed with NaHCO<sub>3</sub> solution after diluting with ether. The solution was dried and the solvent was removed to give 2.4 g of a light vellow oil which showed three peaks corresponding to 19, 20, and 21 in a 12:4:84 ratio by glpc. The addition of a small amount of ether resulted in the formation of crystalline 23b: mp 96-97.55 (dec); ir (CCl<sub>4</sub>) 2.85, 5.82, and 8.0  $\mu$ ; nmr (220 MHz)  $\delta$  7.96 (s, 1), 7.89 (d, 1, J = 6 Hz), 7.52 (d, 1, J = 8 Hz), 7.36 (t, 1, = 10 Hz), 5.22 (d of d, 1, J = 10, 3 Hz), 4.65 (d of d, 1, J =6, 3 Hz), 3.34 (s, 1), and 2.4-1.8 (m, 12); mass spectrum m/e

(rel intensity) 310 (11), 154 (54), 139 (57), 126 (64), and 98 (100). *Anal.* Calcd for  $C_{16}H_{19}O_4Cl$ : C, 61.84; H, 6.16; Cl, 20.59. Found: C, 61.8; H, 6.4; Cl, 20.7.

Injection of pure 23b unto a glpc column gave only 21. Reaction of 19 with PNPBA.—To 111 mg of 19 in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> at 0° was added 594 mg (3.5 equiv) of PNPBA in 5 ml of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 24 hr, ir indicated the absence of 19. Excess peracid was destroyed by the addition of trimethylethylene, the mixture was filtered, and the filtrate was washed with  $NaHCO_3$  solution and dried. Removal of the solvent gave 207 mg of a yellow oil. Glpc showed a 20/21 ratio of 18:72: The addition of CCl, resulted in the formation of a yellow solid which was recrystallized from ether-pentane to give light yellow 23c: mp 92.5-93°; ir (CCl<sub>4</sub>) 2.83, 5.79, and 7.85 μ; nmr δ 8.20 (s, 4), 5.38 (d of d, 1, J = 10, 4 Hz), 4.69 (d of d, 1, J =7, 2 Hz), 4.6 (s, 1), and 2.6-1.1 (m, 12).

Anal. Calcd for C16H19O6N: C, 59.81; H, 5.96. Found: C, 59.8; H, 5.8.

Injection of 23c onto the glpc column gave a single peak with the retention time of 21.

Epoxidation of 1,1-Dimethylallene.-To an ice-cold slurry of 16.7 g of acetic acid-free peracetic acid and 27 g of sodium carbonate was added slowly a methylene chloride solution of 2.0 g of the allene. After several hr the reaction mixture warmed to room temperature and stirring was continued for a total of 70 hr. The crude product was filtered, most of the solvent was removed by spinning band distillation, and the products were isolated by preparative glpc. The first component was 31; the second, acetone. The third component was 30 [ir 5.75, 5.80, and 8.0  $\mu$ ; nmr  $\delta$  2.03 (s, 6) and 1.41 (s, 6) (the 2.03 absorption split into two equivalent singlets upon the addition of benzene to the nmr sample)] and the fourth was 3-hydroxy-2,2dimethylpropanoic acid  $\beta$ -lactone (32). In one experiment the ratio of acetone/30/31/32 of 17:25:50:8 was determined by nmr. The appearance of absorption at  $\delta$  3.18 and 1.53 in a 1:3 ratio in the nmr of the crude product indicates the presence of 33.

In a similar epoxidation the allene was treated with 40%peracetic acid, and the evolving gases were passed through a solution of barium chloride. Rapid evolution of carbon dioxide was noted.

Epoxidation of 1,1-Dimethylallene in Methanol.-To an icecold slurry of 1.0 g of allene and 15 g of sodium carbonate in 25 ml of methanol was added 3 equiv of acetic acid-free peracetic acid. After 3 hr the reaction mixture was filtered and washed with saturated sodium bicarbonate solution. The aqueous phase was extracted with methylene chloride, and the combined organic layers were dried. Nmr and glpc analysis indicated that the only significant products were acetone and methyl acetate in 1:1 ratio. These compounds were identified by isolation.

3-Hydroxy-2,2-dimethylpropanoic Acid  $\beta$ -Lactone.<sup>23</sup>—Dimethylketene was generated by the  $700^{\circ}$  pyrolysis of 10 g of 18 in a flow system and collected in a Dry Ice trap containing 50 mg of zinc chloride. Gaseous formaldehyde generated by heating 3.0 g of paraformaldehyde with a microburner was bubbled into the ketene-zinc chloride solution. The crude product was diluted with 20 ml of methylene chloride, stirred

<sup>(21)</sup> P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, J. Amer. Chem. Soc., 86, 4213 (1964).

<sup>(22)</sup> A. J. Blomquist, L. H. Liu, and J. C. Bohrer, ibid., 74, 3643 (1952).

<sup>(23)</sup> H. E. Zaugg, Org. React., 7, 305 (1954).

over sodium carbonate for 1 hr, and filtered. The filtrate was distilled to give 2 g of material, bp 56-61° (19 mm), containing starting dione. A pure sample of **32** was obtained by preparative glpc: ir 5.47, 9.1, and  $10.9 \mu$ ; nmr  $\delta 4.08$  (s, 2) and 1.43 (s, 6).

Reaction of 32 with Acetic Acid.—To an nmr sample of 32 containing methylene chloride as an internal standard, was added 1 equiv of acetic acid. After 63 hr at room temperature, no reaction had occurred. In a similar experiment 32 was treated with excess 40% peracetic acid with the same result.

3-Hydroxy-3-Methylbutanoic Acid  $\beta$ -Lactone (33).—Lactone 33 was prepared as described:<sup>24</sup> ir 5.49, 9.3, and 12.6  $\mu$  (doublet); nmr  $\delta$  3.18 (s, 2) and 1.53 (s, 6).

Reaction of 33 with Peracetic Acid.—To an nmr sample of 33 in  $\rm CH_2Cl_2$  (containing benzene as an internal standard) was

(24) T. L. Gresham, J. E. Jansen, F. W. Shaver, and W. L. Beears, J. Amer. Chem. Soc., 76, 486 (1954).

added 4 equiv of 40% peracetic acid. Gas evolution was immediate and in 45 min **33** was completely gone. No new peaks appeared in the spectrum.

**Reaction of 36 with Acetic Acid.**—A  $CH_2Cl_2$  solution of **36** was treated with 1 equiv of glacial acetic acid at  $-70^\circ$ . Glpc analysis showed a single component identified as **30**.

**Reaction of 36 with Peracetic Acid.**—A  $CH_2Cl_2$  solution of 36 was treated with 2 equiv of 40% peracetic acid at  $-70^{\circ}$ . As the reaction warmed to room temperature, vigorous  $CO_2$  evolution was observed. Ir analysis of the crude product indicated that acetoxy ketone 30 was the predominant product.

Registry No.--12, 10008-69-2; 18, 933-52-8; 19, 1123-11-1; 23b, 38202-51-6; 23c, 38202-52-7; 32, 1955-45-9; MCPBA, 937-14-4; PNPBA, 943-39-5; tetramethylallene, 1000-87-9; 1,2-dimethylallene, 598-25-4.

# Photochemical Oxidations. VII. Photooxidation of Cyclohexylamine with Oxygen

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The presence of a charge-transfer ultraviolet absorption band for an oxygen-saturated cyclohexylamine solution has been reconfirmed. The absorption of light by this band causes cyclohexanone oxime and N-cyclohexyldinecyclohexylamine to be formed in the initial stages of the reaction, *i.e.*, to 0.6% conversion. The oxime is not the precursor of the imine. N-Cyclohexyl-1-hydroperoxycyclohexylamine, 1-hydroperoxycyclohexylamine, and the cyclohexylamine-hydrogen peroxide adduct give only the imine under the conditions of the reaction.

The destructive ability of a combination of oxygen and sunlight on organic substances is great and costly. We have been studying the consequences of light on charge-transfer (CT) complexes between various organic materials<sup>1</sup> and oxygen because these are instrumental in a number of degradations. The most dramatic demonstration to date is the fact that saturated hydrocarbons exhibit CT interactions<sup>2a,b,c</sup> with molecular oxygen and the excitation of this uv absorption band causes product formation.<sup>1e-g</sup>

A distinction must be made between those oxidation reactions initiated by sensitization and those by excitation of the CT band though similarities in products and product composition may occur. Among the reports of dye-sensitized oxygenation of amines, Gaffron<sup>3</sup> found that erythrosin photosensitized the oxygenation of *n*-propylamine and chlorophyll photosensitized the oxygenation of *n*-isoamylamine. More recently Schenck<sup>4</sup> reported that the dye-sensitized photooxygenation of primary, secondary, and tertiary amines resulted in the uptake of one, two, or three molecules of oxygen, respectively, indicating that the number of CH groups  $\alpha$  to the nitrogen determines the stoichiometry. The products of these reactions were amine

(3) H. Gaffron, Chem. Ber., 60, 2229 (1927).

(4) G. O. Schenck, Angew. Chem., 69, 579 (1957).

hydroperoxides. Others have reported that a variety of reactions occur when amines are irradiated in the presence of dyes and oxygen:  $\alpha$  oxidation,<sup>5-9</sup> dehydrogenation,<sup>10,11</sup> and dealkylation.<sup>10</sup> Kinetic studies on the oxygen uptake in the photosensitized oxidation of triethylamine have also been done.<sup>12</sup>

In contrast, no work has been reported concerning the direct photooxidation of amines without sensitizers being present. Evans<sup>2a</sup> has suggested that oxygen charge-transfer complexes could provide a plausible initial stage in these photooxidations. Since it is known that amines also exhibit CT bands with oxygen, we wished to determine the chemical consequences of direct absorption of light by the oxygen-amine chargetransfer band. A number of aliphatic amines, *i.e.*, primary, secondary, and tertiary, were photochemically oxidized with oxygen in the initial studies. All of the aliphatic amines tested reacted; however, since the primary aliphatic amines gave more simple product mixtures than secondary and tertiary amines, these were selected for the initial study. For primary aliphatic amines, our attention was focused on the photooxidation of cyclohexylamine because a procedure for the synthesis of the  $\alpha$  hydroperoxide of cyclohexylamine was available.

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