The results obtained are tenable with those of Barnett and his coworkers.

EXPERIMENTAL

5-Chlorodiphenylmethane-2-carboxylic acid (III). A Grignard reagent was prepared under nitrogen from 8.0 g. (0.028 mole) of 2-bromo-5-chlorodiphenylmethane, 0.68 g. (0.028 mole) of magnesium, *ca.* 100 ml. of anhydrous ether and a crystal of iodine. After all of the magnesium had reacted, the reaction mixture was poured into a slurry of crushed Dry Ice and anhydrous ether. The ethereal solution was treated with dilute sodium hydroxide (trace of charcoal), cooled and filtered. The filtrate was acidified and the white precipitate was filtered. After drying in a desiccator overnight the solid had a melting range of 148–149°, 3.2 g. (46%). Recrystallization from ethanol gave an analytically pure sample, colorless rods, m.p. 149–151°.

Anal. Calcd. for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.50. Neut. Eq. 247. Found: C, 68.00; H, 4.47. Neut. Eq. 250.

3-Chloro-9-anthrone (IV). A mixture of 0.8 g. (0.00032 mole) of 5-chlorodiphenylmethane-2-carboxylic acid and 3 ml. of concentrated sulfuric acid was shaken vigorously and allowed to stand at room temperature for one hour. The mixture was poured into an ice-water mixture and a light yellow precipitate formed. This was filtered, washed with water, and recrystallized from ethanol yielding crystals which melted at 153–154°, 0.62 g. (83%). Further recrystallization from ethanol raised the melting point to 155–156° (Lit.,[2] m.p. 156°).

3-Chloro-9-anthryl acetate. A mixture of 0.4 g. (0.00018 mole) of 3-chloro-9-anthrone, 15 ml. of pyridine and 3 ml. of acetic anhydride was heated on a steam bath for 2 hr. under a nitrogen atmosphere. This was poured into an ice water mixture which gave a yellow powder which was filtered and recrystallized from ethanol. Fine yellow needles, 0.29 g. (42%) were obtained; m.p. 146–146.5° (Lit.,[3] m.p. 146°). The ethanolic solution displayed a strong blue fluorescence.

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An Ozonide of Cholestenone

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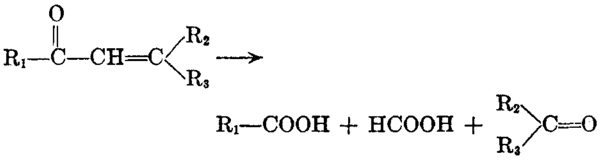
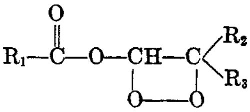
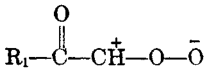
The ozonization of α,β-unsaturated carbonyl compounds occurs with what has been called an "abnormal" course, that is, both the olefinic bond and the adjacent single bond connecting the carbonyl group are cleaved.[1–4] It has been postulated that such a rearrangement occurs (1) through the formation of an abnormal ozonide (I),[1,2] (2) by rearrangement of the intermediate zwitter ion (II),[4] and (3) by abnormal cleavage of a normal ozonide (III) due to the electron release gained by O—H bond heterolysis.[5] In general, in the abnormal reaction, the product of the reaction of the unsaturated carbonyl compound with ozone is not isolated due to its instability.[1]



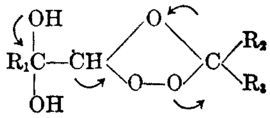
$$R_1-\overset{O}{\overset{\|}{C}}-CH=C\begin{matrix}R_2\\R_3\end{matrix} \longrightarrow R_1-COOH + HCOOH + \begin{matrix}R_2\\R_3\end{matrix}C=O$$



I

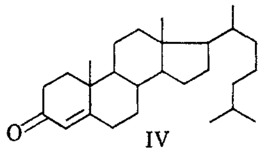


II

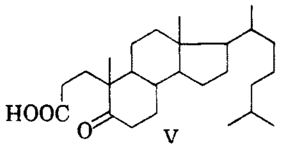


III

In the course of another investigation, the α,β-unsaturated ketone, cholestenone (IV), was ozonized at −15° in a mixture of aqueous acetic acid and ethyl acetate in order to prepare the *seco-nor-keto* acid (V). By concentration of the reaction mixture a 55% yield of crystalline white solid was obtained and this material upon melting decomposed to yield the desired acid V. The composition of the initial product was that expected for the addition of one mole of ozone and one mole of water to the starting enone IV. The compound was peroxidic but not hydroperoxidic as shown by a positive test with potassium iodide and a negative test with lead tetraacetate.[6] The molecular weight was that for a monomer and the infrared spectrum possessed bands for hydroxyl groups but lacked band associated with carbonyl absorption. The material when stored in the dry was stable for many weeks but upon standing in air at room temperature gradually decomposed to give rise to the expected *seco-nor* acid V. Warming the material in benzene transformed it into the acid V and formic acid, demonstrating that it is an intermediate in the "abnormal" ozonization.



IV



V

Based upon the foregoing data, there are at least three structures for a monomeric ozonide derivable from the intermediate hydroxylhydroperoxide VII which would arise by the well-established hydration[4,7] of the zwitterion VI. These structures are

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[1] W. G. Young, A. C. McKinnis, I. D. Webb, and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 293 (1946).

[2] J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949).

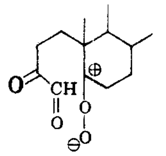
[3] J. Knights and E. S. Waight, *J. Chem. Soc.*, 2830 (1955).

[4] R. Criegee, *Record. Chem. Progr.*, **18**, 111 (1957).

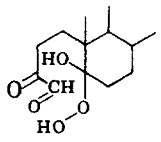
[5] D. H. R. Barton and E. Seone, *J. Chem. Soc.*, 4150 (1956).

[6] R. Criegee, *Fortschr. Chem. Forsch.* **1**, 536 (1950).

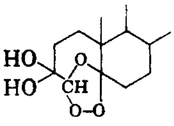
[7] H. Lettre and A. Jahn, *Ann.*, **608**, 43 (1957).



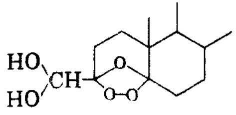
VI



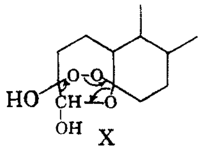
VII



VIII



IX



X

VIII, IX, and X, the first two representing hydrates of normal ozonides and the last a hemiketal-acetal. On the basis of the work of Criegee,[8] IX would seem to be the preferred structure since in the presence of a protic solvent cyclic monomeric ozonides appear to form only when a bicyclo-3:2:1-system results. The formation of a stable hydrate of a carbonyl group, however, should only occur if the ozonide linkage is strongly electronegative and from the acid strength of hydrogen peroxide such seems unlikely.

At the present time, structure X would appear to represent the most probable formulation for the product.[9] The decomposition of X to products most likely follows the intramolecular pathway indicated.

EXPERIMENTAL[10]

Ozonization of cholestenone. A solution of 7.78 g. (20.2 mmoles) of cholestenone, 135 ml. of C.P. ethyl acetate, 135 ml. of glacial acetic acid, and 8 ml. of water was cooled in an ice salt bath and then 2.5 mole-equivalents (at 0.5 mmole/min.) of ozone was passed through the solution. After standing at room temperature for 1 hr., the solution began to deposit white crystals and by removal of three fourths of the solvent under reduced pressure (20-mm. pressure at room temperature), a total of 5.0 g. (55%), m.p. 112–115° (dec.), of white crystalline solid was obtained. The crude material was dried for 24 hr. at room temperature under 20-mm. pressure. The dried material first melts at 117° with evolution of gas and then solidifies and remelts at 152–153°, the melting point of authentic seco-keto-acid V.[11] The infrared spectrum possessed bands at 2.94 μ (OH) and at 9.2, 9.5, 9.6 μ (ether—O).

Anal. Calcd. for $C_{27}H_{46}O_5$: C, 71.96; H, 10.29; peroxide, 7.10; mol. wt. 450.6. Found: C, 71.26; H, 10.50; peroxide, 6.86; mol. wt.[12] 439–481.

When the ozonide was heated with benzene and the solvent distilled and collected in an ice-cooled receiver, the residue after recrystallization from hexane amounted to 86% of the expected *seco-nor*-acid, m.p. 150–152°. To the benzene distillate (200 ml.) were added 2 ml. of glacial acetic acid and 4.8 g. of mercuric acetate and the mixture was refluxed for 3 hr. The evolved CO_2 was swept with nitrogen into a gas collection flask containing sodium hydroxide (CO_2-free). Precipitation of CO_2 as $BaCO_3$ with $BaCl_2$ yielded 70% of theory, based upon the oxidation of one mole of formic acid.

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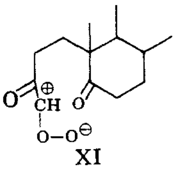
[8] R. Criegee, A. Kerchow, and H. Zinke, *Ber.*, **88**, 1878 (1955).

[9] The alternate zwitterion XI, which would appear to be a less favored intermediate, upon hydration and cyclization would give rise to a similar series of structures. Such structures cannot be differentiated from the above on the basis of the present work.



XI

[10] All melting points corrected. Analyses by the Microanalytical Laboratory, University of California.

[11] R. Tschesche, *Ann.*, **498**, 185 (1932); R. B. Turner, *J. Am. Chem. Soc.*, **72**, 579 (1950).

[12] The mol. wt. determination was kindly performed for us by Professor P. S. Bailey, University of Texas, by the cryoscopic method using dioxane as solvent.

Preparation of Trialkylboranes or Primary Alcohols from Pyridine-Borane and Terminal Olefins

M. Frederick Hawthorne

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Two new synthetic methods for the preparation of trialkylboranes from olefins have recently been described. The first of these consists of treating the olefin with the sodium borohydride–aluminum chloride reagent of Brown and Rao.[1] The second new method is based on the direct addition of diborane to the olefin in diglyme solution at room temperature.[2] The diborane may be introduced as a gas or produced *in situ* by the reaction of sodium borohydride with boron trifluoride. The present paper describes a third method which is probably chemically similar to, but experimentally quite different from the second method above[3] and probably involves the electrophilic attack of thermally produced diborane upon the terminal olefin.

During the course of an examination of the chemistry of amine boranes it was observed that pyridine-borane would react with olefins in diglyme solvent and at temperatures near 100° to produce trialkylboranes. The reaction was conveniently carried out overnight in pressure bottles on the steam bath and with stoichiometric quantities of reactants.

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[1] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

[2] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[3] It was pointed out by a referee that Dr. R. Koster reported to the Inorganic Division of the XVIth International Congress of Pure and Applied Chemistry, Paris, France, that he had successfully added triethylamine borane to terminal olefins. This is not apparent in the abstracts (page 161) of the meeting.