(1972); E. J. Corey and C. U. Kim, *J. Am. Chem. Soc.*, **94**, 7586 (1972). Also see E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Vol. II, Chemical Publishing Co., New York, N.Y. 1975.
(22) C. R. Johnson and W. G. Phillips, *J. Am. Chem. Soc.*, **91**, 682 (1969).
(23) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974), and earlier references cited therein.
(24) F. Jung, N. K. Sharma, and T. Durst, *J. Am. Chem. Soc.*, **95**, 3420 (1973).
(25) For a review see J. McMurry, *Org. React.* in press.
(26) G. B. Heisig and F. H. Stodola, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 213.
(27) For alternative cyclobutanone preparations see (a) P. Lipp and R. Köster, *Chem. Ber.*, **64**, 2823 (1931); (b) J. D. Roberts and C. W. Sauer, *J. Am. Chem. Soc.*, 71, 3925 (1949); (c) J. M. Conia, P. Lerivérend, and J. L. Ripoll, *Bull. Soc. Chim. Fr.*, 1803 (1961); (d) D. Seebach and A. K. Beck, *Org. Synth.*, **51**, 76 (1971); (e) J. R. Salaun and J. M. Conia, *Chem. Commun.*, 1579 (1971); (f) M. M. Martin, F. T. Hammer, and E. Zader, *J. Org. Chem.*, **38**, 3422 (1973); (g) K. Ogura, M. Yamashita, M. Suzuki, and G. Tsuchihashi, *Tetrahedron Lett.*, 3653 (1974).
(28) The dianion of phenylthioacetic acid has been reported: K. Iwai, M. Kawai, H. Kosugi, and H. Uda, *Chem. Lett.*, 385 (1974); H. Kosugi, H. Uda, and S. Yamigawa, *J. Chem. Soc., Chem. Commun.*, 192 (1975).
(29) (a) K. Mori and M. Matsui, *Tetrahedron*, **24**, 3127 (1968); (b) K. S. Ayyar and G. S. K. Rao, *Can. J. Chem.*, **46**, 1467 (1968); (c) B. A. Pawson, H. C. Cheung, S. Gurbaxani, and G. Saucy, *J. Am. Chem. Soc.*, **92**, 336 (1970); (d) A. J. Birch, P. L. Macdonald, and V. H. Powell, *J. Chem. Soc. C*, 1469 (1970); (e) A. A. Drabkina and Y. S. Tsizin, *J. Gen. Chem. USSR (Engl. Transl.)*, **43**, 422, 691 (1973); (f) R. J. Crawford, U.S. Patent 3 676 506; *Chem. Abstr.*, 77, 113889e (1972); (g) J. Ficini, J. d'Angelo, and J. Noire, *J. Am. Chem. Soc.*, **96**, 1213 (1974); (h) E. Negishi, M. Sabinski, J. J. Katz, and H. C. Brown, *Tetrahedron*, **32**, 925 (1976). For a recorrection of the stereochemical assignment, see J. F. Manville, *Can. J. Chem.*, **53**, 1579 (1975).
(30) E. J. Corey, N. W. Gilman, and B. Ganem, *J. Am. Chem. Soc.*, **90**, 5616 (1968).
(31) For a recent review see B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides. Emerging Synthetic Intermediates", Academic Press, New York, N.Y., 1975, Chapter 7; A. R. Lepley and A. G. Guimanini, "Mechanisms of Molecular Migrations", Vol. 3, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1971, pp 297–440.
(32) K. Ogura, M. Yamashita, S. Furukawa, M. Suzuki, and G. Tsuchihashi, *Tetrahedron Lett.*, 2767 (1975). S- rather than C-alkylation of a sulfur stabilized vinyl organometallic has also been reported. See H. Westmijze, J. Meijer, and P. Vermeer, *Tetrahedron Lett.*, 2923 (1975).
(33) Obtained by standard ketalization procedures on 4-(4′-carboxycyclohexyl)cyclohexanone or its methyl ester: W. G. Dauben and M. Tanabe, *J. Am. Chem. Soc.*, **75**, 4969 (1953); A. L. Wilds and C. H. Shunk, *ibid.*, **72**, 2388 (1950).
(34) H. Stobbe and A. Lenzner, *Justus Liebigs Ann. Chem.*, **380**, 95 (1911).
(35) A. L. Wilds, C. H. Shunk, and C. H. Hoffman, *J. Am. Chem. Soc.*, 76, 1733 (1954).
(36) P. Wieland and K. Miescher, *Helv. Chim. Acta*, **32**, 1768 (1949).
(37) M. M. Kreevoy, C. R. Morgan, and R. W. Taft, *J. Am. Chem. Soc.*, **82**, 3064 (1960).
(38) We express our thanks to Professor E. J. Corey for making these data available to us.
(39) Prepared from chloroacetic acid, methyl mercaptan, and potassium hydroxide in ethanol: K. S. Bonstarry, *J. Chem. U.A.R.*, **9**, 317 (1966); V. E. Kuvenchik and V. E. Petrun'kin, *Zh. Org. Khim.*, 6, 2227 (1970).
(40) F. Pueschel and C. Kaiser, *Chem. Ber.*, **97**, 2903 (1964).
(41) We wish to thank Dr. V. Van Rheenan of the Upjohn Co. for a very generous gift of this compound.
(42) Freshly prepared solvents and reagents are crucial for a high yield oxidation.

Oxyfunctionalization of Hydrocarbons. 7.[1a] Oxygenation of 2,2-Dimethylpropane and 2,2,3,3-Tetramethylbutane with Ozone or Hydrogen Peroxide in Superacid Media

Norihiko Yoneda[1b] and George A. Olah*

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 8, 1976*

Abstract: The reaction of ozone and hydrogen peroxide with neoalkanes, i.e., 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane, in various superacid solutions has been investigated. Results indicate that the reactions proceed via electrophilic attack by protonated ozone, ^+O_3H, into the involved σ bonds in alkanes through two-electron three-center bonded pentacoordinated carbonium ions. It was also observed that the electrophilic hydroxylation of alkanes with hydrogen peroxide and/or trioxide, which are formed as by-products in the cleavage of the pentacoordinated carbonium ions $[R_3C(H)OOOH]^+$, gives alcohols with no skeletal rearrangement (i.e., neopentyl alcohol from neopentane) again indicative of direct electrophilic hydroxylation with *no* trivalent carbenium ion formation.

We have previously reported the electrophilic oxygenation of alkanes with ozone[2] or hydrogen peroxide[3] in superacid media. In both cases the reactions proceed via electrophilic insertion of protonated ozone, i.e., ^+O_3H, and protonated hydrogen peroxide, i.e., $H_3O_2^+ \equiv OH^+(H_2O)$, respectively, into the involved single σ bonds of the alkanes, similarly to such electrophilic reaction as protolysis,[4] chlorolysis,[5] and nitrolysis[6] of alkanes. In continuation of our work on electrophilic oxygenation of alkanes, we considered it to be of interest to extend our investigation to the electrophilic oxygenation of neoalkanes. These systems are expected to provide a fuller understanding of electrophilic oxygenations, particularly their steric requirements, as well as of the question of the involvement of pentacoordinated carbonium ion vs. trivalent carbenium ion intermediates, as the latter would inevitably lead to skeletal rearrangements.

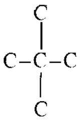
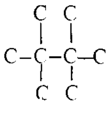
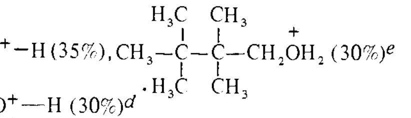
Results and Discussion

2,2-Dimethylpropane (Neopentane). A stream of ~5% ozone containing oxygen was passed through a solution of neopentane (10 mmol) in FSO_3H-SbF_5-SO_2ClF (fourfold excess) held at −78 °C. Because of the limited solubility of neopentane in this acid solution, the reaction is initially carried out in a heterogeneous system. However, upon introduction of ozone, the brownish colored reaction medium becomes homogeneous. ^1H and ^{13}C NMR spectra of the resultant solution (after 40 mmol of ozone was passed through) showed formation of the dimethylethoxy carbenium ion (**1**) as the major product together with dimethylmethoxy carbenium ion (**2**) and protonated neopentyl alcohol (**3**). The conversion of the alkane was found to be almost 100%. The results under varying reaction conditions are summarized in Table I together with those of the reaction of 2,2,3,3-tetramethylbutane.

As discussed previously, the reaction of alkanes with ozone in FSO_3H-SbF_5-SO_2ClF solution can be best described by the electrophilic attack of protonated ozone into the C–C or C–H σ bonds of the alkanes (Scheme I).

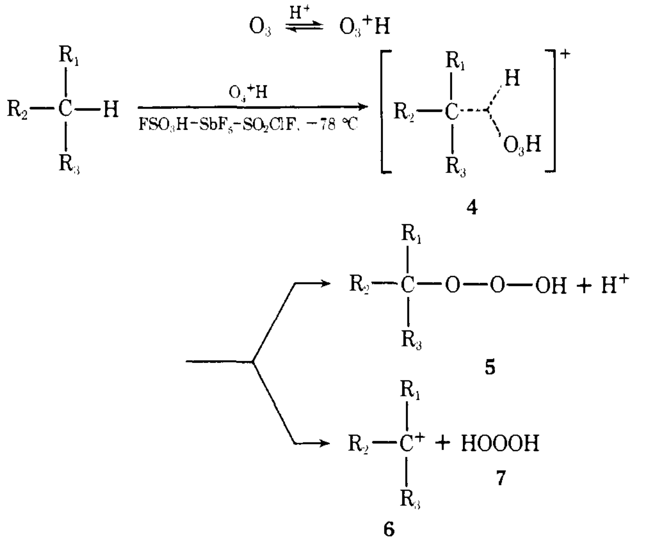
Since ozone has a strong 1,3 dipole, or at least is strongly polarizable, it is not unexpected that it is readily protonated in superacids. Protonated ozone, ^+O_3H, once formed seems

Table I. Products of Reaction of 2,2-Dimethylpropane and 2,2,3,3-Tetramethylbutane with Ozone in Superacids[a]

Alkane	Acid	Rxn temp, °C	Distribution of major products[b]
	$FSO_3H-SbF_5-SO_2ClF$	-78	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (95%), $CH_3C(CH_3)_2CH_2O^+H_2$ (5%)[c]
	$FSO_3H-SbF_5-SO_2ClF$	-20	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (90%), $(CH_3)_2C{=}O^+{-}CH_3$ (10%)[d]
	FSO_3H-SbF_5	0	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (15%) $(CH_3)_2C{=}O^+{-}CH_3$ (85%)[d]
	FSO_3H-SbF_5	+20	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (5%), $(CH_3)_2C{=}O^+{-}CH_3$ (95%)[d]
	$HF-SbF_5-SO_2ClF$	-78	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (25%), $(CH_3)_2C{=}O^+{-}CH_3$ (75%)[d]
	$HF-SbF_5-SO_2ClF$	-20	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (10%), $(CH_3)_2C{=}O^+{-}CH_3$ (90%)[d]
	SbF_5-SO_2ClF	-78	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (70%), $(CH_3)_2C{=}O^+{-}CH_3$ (30%)[d]
	SbF_5-SO_2ClF	-50	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (65%), $(CH_3)_2C{=}O^+{-}CH_3$ (35%)[d]
	SbF_5-SO_2ClF	-20	$(CH_3)_2C{=}O^+{-}CH_2CH_3$ (50%), $(CH_3)_2C{=}O^+{-}CH_3$ (50%)[d]
	$FSO_3H-SbF_5-SO_2ClF$	-78	$(CH_3)_2C{=}O^+{-}CH_3$ (35%), $(CH_3)_2C{=}O^+{-}H$ (35%),  $CH_3-C(CH_3)_2-C(CH_3)_2-CH_2\overset{+}{O}H_2$ (30%)[e]
	$FSO_3H-SbF_5-SO_2ClF$	-50	$(CH_3)_2C{=}O^+{-}CH_3$ (70%), $(CH_3)_2C{=}O^+{-}H$ (30%)[d]
	FSO_3H-SbF_5	0	$(CH_3)_2C{=}O^+{-}CH_3$ (65%), $(CH_3)_2C{=}O^+{-}H$ (35%)[d]
	$HF-SbF_5-SO_2ClF$	-78	$(CH_3)_2C{=}O^+{-}CH_3$ (50%), $(CH_3)_2C{=}O^+{-}H$ (50%)[d]
	$HF-SbF_5-SO_2ClF$	-50	$(CH_3)_2C{=}O^+{-}CH_3$ (60%), $(CH_3)_2C{=}O^+{-}H$ (40%)[d]
	SbF_5-SO_2ClF	-78	$(CH_3)_2C{=}O^+{-}CH_3$ (70%), $(CH_3)_2C{=}O^+{-}H$ (30%)[d]
	SbF_5-SO_2ClF	-20	$(CH_3)_2C{=}O^+{-}CH_3$ (85%), $(CH_3)_2C{=}O^+{-}H$ (15%)[d]

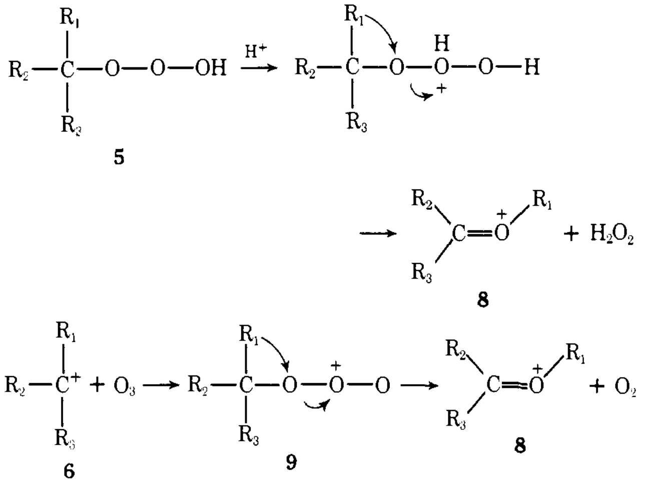
[a] In all experiments, a 3-mol excess of acids and a 3–4-mol excess of ozone to alkanes were used. Conversion of alkanes was almost 100% in all cases. [b] Major products as shown in the table represent up to 90–95% of all products. Assignments of carboxonium ion products were made by comparison of their NMR spectra with previously reported data. See G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89**, 3582, 3586 (1967); G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *ibid.*, **96**, 884 (1974); G. A. Olah, D. G. Parker, N. Yoneda, and A. Pellizar, *ibid.*, **98**, 2245 (1976). [c] $(CH_3)_2C{=}O^+CH_3$, $H_2C{=}O^+H$, $CH_3C^+{\equiv}O$, CO_2 were found as minor products. [d] CO_2, $CH_3{}^+C{\equiv}O$, $H_2C{=}O^+H$, and minor unidentified products were also found. [e] $CH_3CH_2(CH_3)C{=}O^+H$, $H_2C{=}O^+H$, $CH_3{}^+C{\equiv}O$, CO_2, and minor unidentified products were also found.

Scheme I



(R_1, R_2, R_3 = alkyl or hydrogen)

Scheme II



to have a significant affinity (i.e., is a powerful electrophile) for the σ-donor single bonds of alkanes through pentacoordinated carbonium ion transition state **4**. The pentacoordinated carbonium ion subsequently cleaves to neutral trioxide **5** or trivalent carbenium ion **6** and hydrogen trioxide (**7**), satisfactorily explaining all the results of the reactions of alkanes with ozone in strong acid media, as shown in Scheme II.

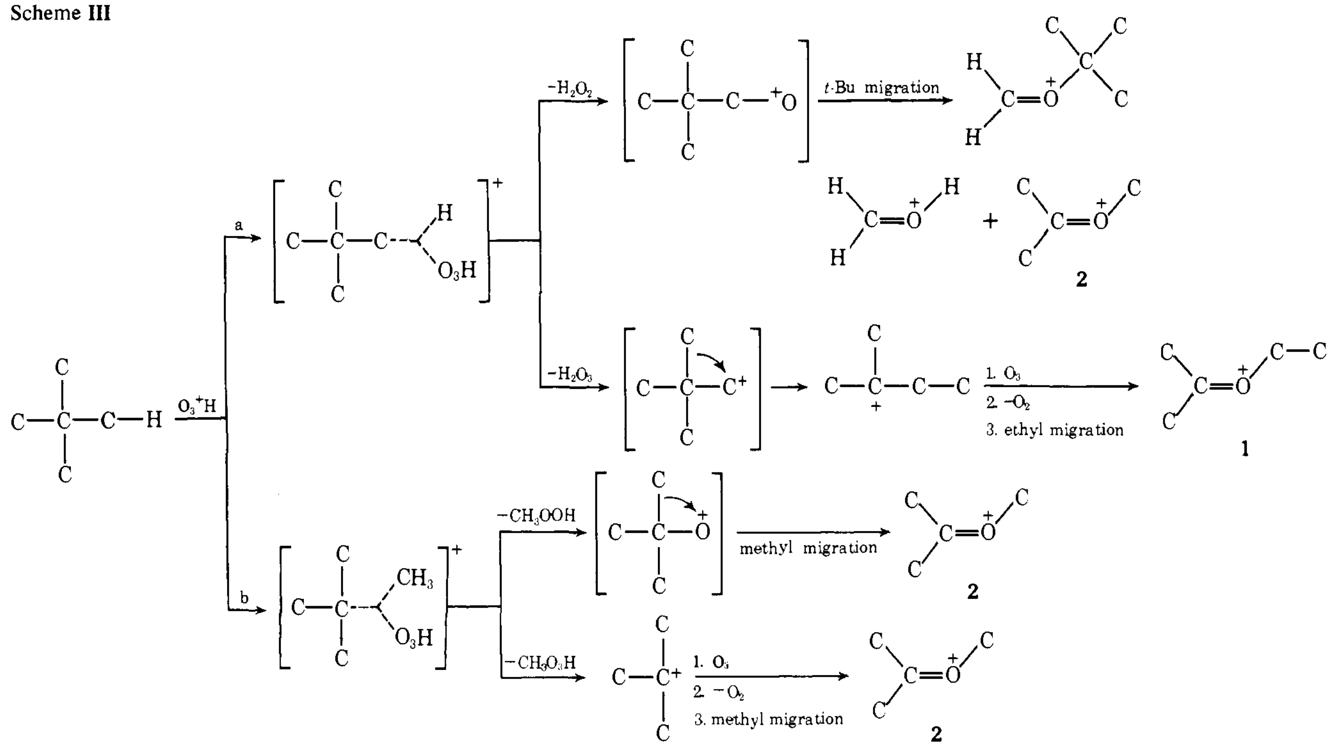
Neutral trioxides (**5**), which have been proposed as intermediates in the decomposition of tertiary alkyl hydroperoxides with lead tetraacetate[7] and in the ozonation of ethers,[8] aldehydes,[9] and alcohols[10] or have been isolated more recently as the crystalline trioxide by ozonolysis of *tert*-butyl hydroperoxide, the sodium salt of *tert*-butyl hydroperoxide, or the sodium salt of cumyl hydroperoxide,[11] may be easily decomposed in acid media yielding carboxonium ion **8** and hydrogen peroxide. On the other hand, alkylcarbenium ion **6**, derived from the alternate cleavage path of carbonium ion **4**, can be attacked by ozone as a nucleophilic agent giving intermediate trioxide **9**, which then cleaves to carboxonium ion **8** and oxygen.[12]

When considering Schemes I and II, the possible reaction pathways of the reaction of neopentane with ozone in $FSO_3H-SbF_5-SO_2ClF$ at −78 °C can be described as shown in Scheme III.

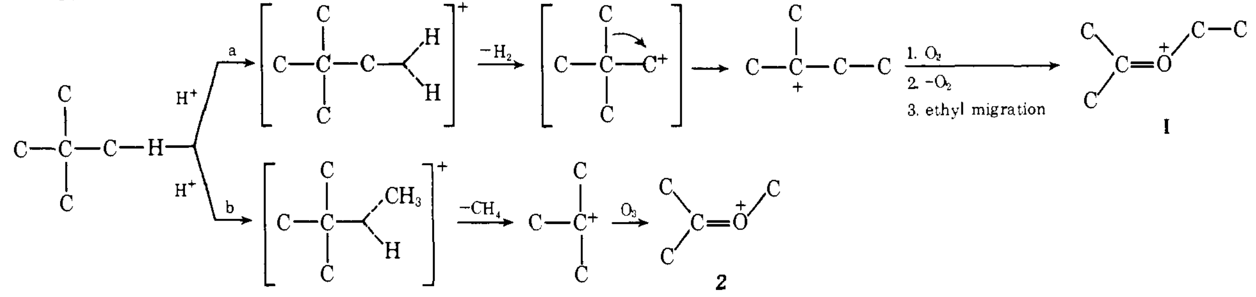
The results, as obtained under the reaction conditions where the dimethylethoxy carbenium ion (**1**) is formed almost exclusively, can be best accounted for by alternate reaction path (a) involving C-H bond ozonolysis, H_2O_3 elimination from transition state **10**, *tert*-amyl cation formation by immediate rearrangement of the neopentyl cation, and its quenching by ozone as nucleophilic agent.

It should be emphasized that the protolysis of σ bonds in neopentane in $FSO_3H-SbF_5-SO_2ClF$ solution at −78 °C is very slow and thus can be neglected. In fact, below −40 °C during 5 h, no formation of any alkylcarbenium ion can be detected by NMR spectroscopy. It was only when ozone was introduced into the system that rapid reaction took place under the reaction condition. However, when the reaction was carried

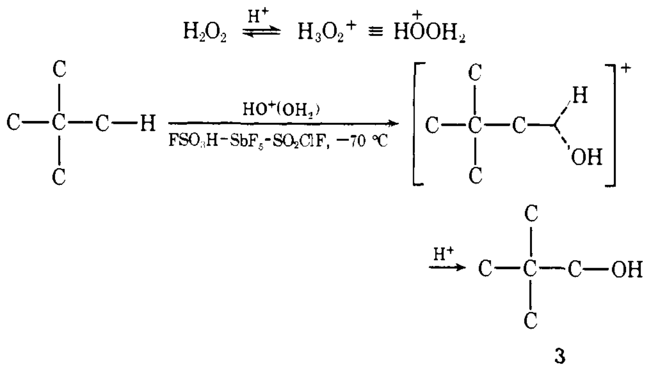
Scheme III



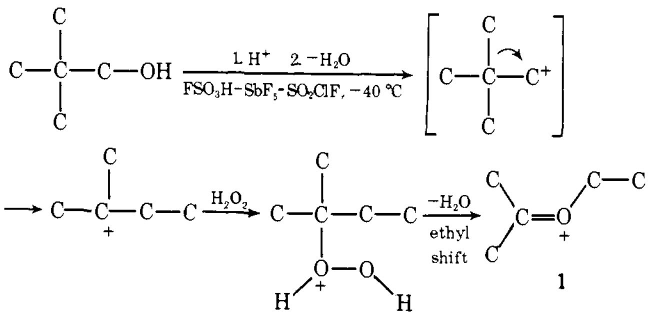
Scheme IV



Scheme V



Scheme VI



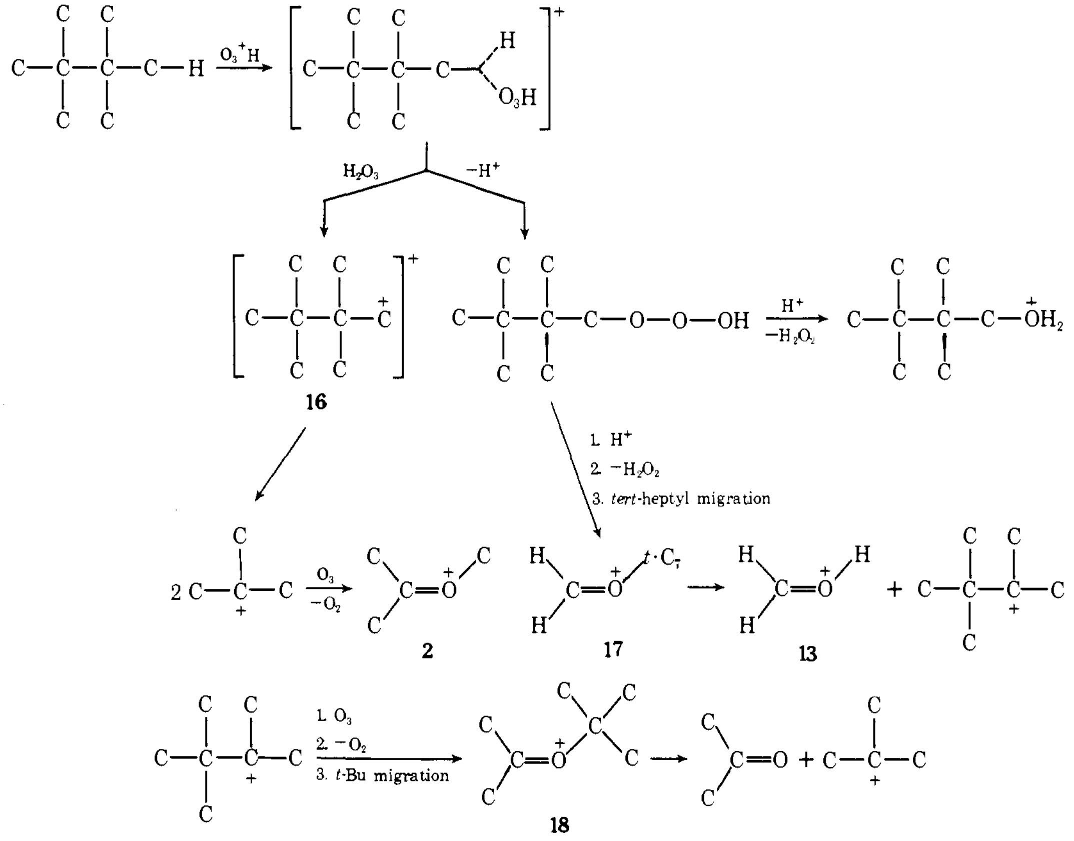
out at temperatures higher than −20 °C, the formation of dimethylmethoxy carbenium ion (**2**) became predominant indicating that under these conditions C-C bond protolysis of neopentane is preferential, with formation of the *tert*-butyl cation which then reacts with ozone to give the carboxonium ion. Indeed, when the reaction was carried out with less than stoichiometric amount of ozone corresponding to that of neopentane, the resultant solution showed the presence of the *tert*-butyl cation.

In FSO_3H-SbF_5(-SO_2ClF) solution, above −20 °C, 2,2-dimethylpropane is known to undergo protolytic C-C bond cleavage (path b in Scheme IV) giving *tert*-butyl cation.[14] The *tert*-butyl cation subsequently, upon reaction with ozone, can give the carboxonium ion **2**.[13]

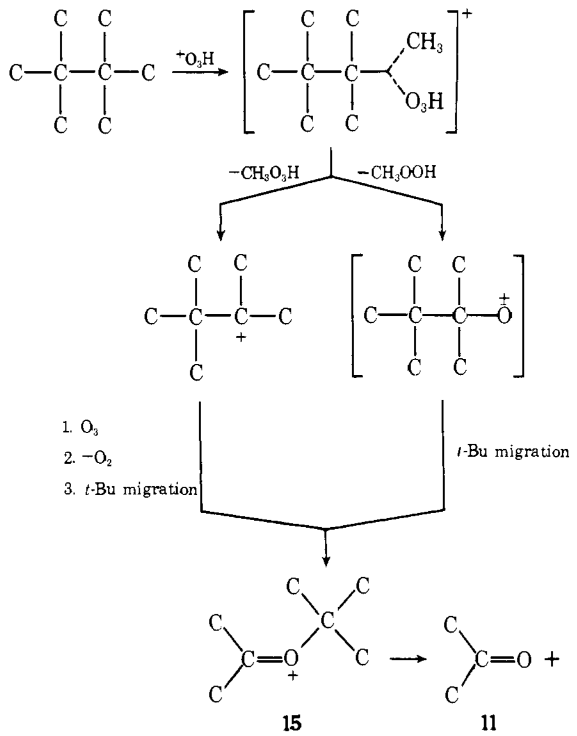
Similar results were also obtained when the reactions were carried out in HF-SbF_5-SO_2ClF or SbF_5-SO_2ClF solution, even at temperatures as low as −78 °C. In these systems, neopentane was shown to have a different protolytic behavior, i.e., path a or b in Scheme IV. In the HF-SbF_5-SO_2ClF solution at −78 °C neopentane undergoes protolytic C-C bond cleavage to give the *tert*-butyl cation (and methane) (path b in Scheme IV) and in the presence of ozone under the same condition thus can give the dimethylmethoxy carbenium ion (**2**) as the major product. On the other hand, in SbF_5-SO_2ClF solution (which always can be considered to contain sufficient protic acid impurity to act as superacid), protolytic C-H bond cleavage (path a in Scheme IV) takes place preferentially giving at −78 °C the *tert*-amyl cation and consequently, in the

Scheme VII

A. C-H Bond Ozonolysis



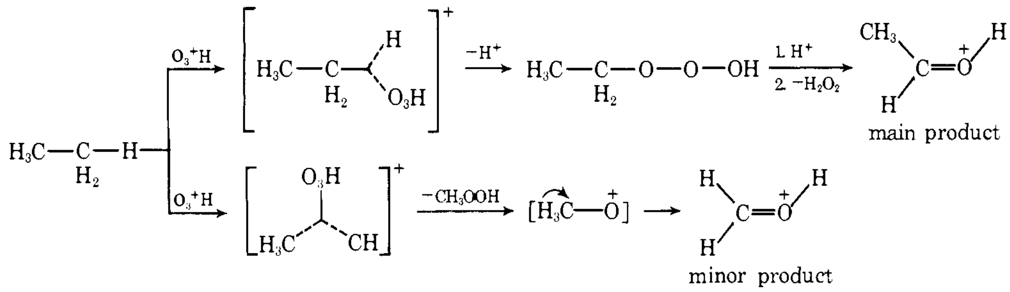
B. C_1-C_2 Bond Ozonolysis



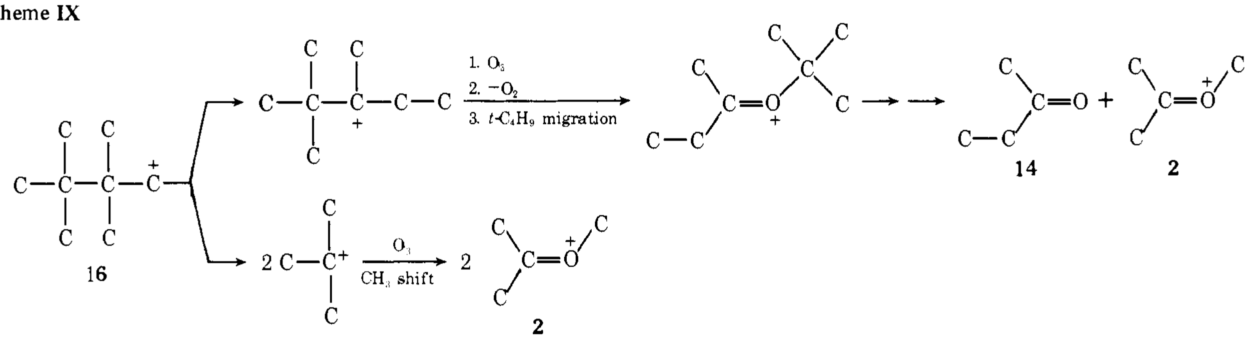
presence of ozone, the dimethylethoxy carbenium ion (**1**) is observed as the major product. The differing reactivity of neopentane depending on the kind of superacid media seems to reflect the differing nature of the electrophilic agent, i.e., solvated proton, toward the σ bonds of the alkane. The nature of each system, particularly steric requirements, may affect the relative reactivity of C–C or C–H bonds.[13]

The major difference between the reaction of neopentane with ozone in FSO_3H-SbF_5-SO_2ClF at −78 °C and reactions at more elevated temperatures in HF-SbF_5-SO_2ClF or SbF_5-SO_2ClF solutions is the formation of neopentyl alcohol (**3**) in the latter cases. In the reaction of alkylcarbenium ions with ozone there is not observed formation of any alcohol. On the other hand, in reactions involving the electrophilic attack

Scheme VIII



Scheme IX



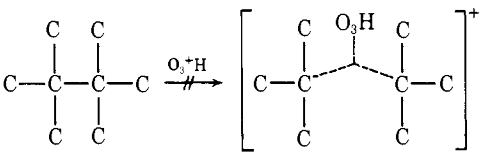
of protonated ozone on σ bonds of alkanes, as shown in Schemes I and II, these reactions form hydrogen peroxide (or trioxide) which itself can then further react to give alcohols. Hydrogen peroxide (or trioxide) is an effective hydroxylating agent in superacid media. Indeed, when neopentane was treated with hydrogen peroxide in FSO_3H-SbF_5-SO_2ClF solution at −70 °C, the formation of neopentyl alcohol was observed. Hydrogen peroxide is protonated and undergoes rapid exchange with the superacid system, but under the reaction conditions there is no indication of formation of persulfuric acid (Caro's acid). The reaction thus can be described as electrophilic hydroxylation (Scheme V). Since no other products than neopentyl alcohol were observed under the reaction condition, the attack of protonated hydrogen peroxide (i.e., the incipient hydroxyl cation, OH^+ for convenience) must be exclusively in the C–H bonds and involves a five-coordinated carbonium ion. Ionization leading to trivalent neopentyl cation would lead to immediate rearrangement to the *tert*-amyl cation and products derived from it, which are not observed. By raising the temperature to −60 °C, the amount of neopentyl alcohol markedly increased. At −40 °C *tert*-amyl cation formation is observed, because when excess hydrogen peroxide was used in the reaction dimethylethoxy carbenium ion (**1**) was obtained, formation of which can be described in Scheme VI.

Hydrogen trioxide is reported to be an extremely unstable species, decomposing into water and oxygen.[14] In superacids, however, it can be considered to have the ability to act as a hydroxylating agent. Alkyl trioxides[15] (**5**) may also be considered as hydroxylating agents in an analogous way.

$$\mathrm{HOOOH} \xrightarrow{\mathrm{H^+}} \mathrm{HO\overset{H}{\underset{+}{O}}OH} \equiv \mathrm{H\overset{+}{O}(O_2H_2)}$$

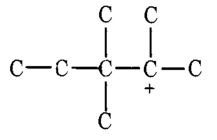
Consequently, when the reaction proceeds by electrophilic attack of protonated ozone on the σ bonds of alkanes via transition states of pentacoordinated carbonium ion nature (**10**), there is expected formation of alcohols with hydrogen peroxide (trioxide) liberated as by-product of the reaction.

2,2,3,3-Tetramethylbutane, when reacted with ozone in FSO_3H-SbF_5-SO_2ClF solution at −78 °C, gave (as analyzed by ^1H NMR spectroscopy) the dimethylmethoxy carbenium ion (**2**) and acetone (**11**) (protonated) together with 2,2,3,3-tetramethylbutyl alcohol (**12**) as the major products. The molar ratio of ion **2** and **11** was found to be 1:1. Product analysis by ^{13}C NMR showed also the formation of formaldehyde (**13**), methyl ethyl ketone (**14**), acetylium ion $CH_3C{\equiv}^+O$, and carbon dioxide in small amounts. We feel that these data again show that the reaction takes place initially by electrophilic insertion of protonated ozone into the single σ bond of the alkane as shown in Scheme VII. The third possible route, i.e., direct C_2–C_3 bond ozonolysis, is improbable for steric reasons. Instead formation of the *tert*-butyl cation can take place through initial attack on the C–H bond with the neooctyl cation undergoing β-cleavage, with subsequent reaction with ozone to yield **2**.

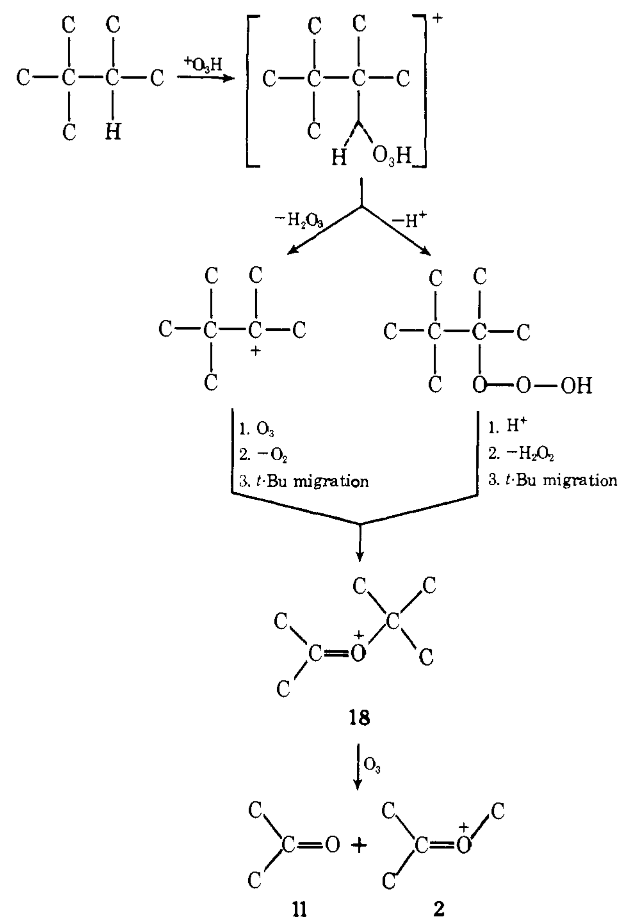


Although it can be considered, in principle, that reaction takes place by attack of protonated ozone into the C–H or C_1–C_2 σ bonds, respectively, as shown in Scheme VII, the reactivity of the C–H bonds is much higher than that of the C–C bonds. Further, the product distribution obtained shows that there is no direct C_2–C_3 bond reaction (owing to steric reasons). Although C_1–C_2 or C–H bond cleavage can both be in good accordance with the experimental results (product ratio of **2** and **11** is about equal), previous results showed that ethane gave acetaldehyde almost exclusively under the same conditions, suggesting again that attack of protonated ozone preferentially took place with the C–H bonds (being more accessible). As pointed out previously, the nature of each system (particularly steric hindrance) can influence the reactivity of δ bonds. The bulkiness of protonated ozone may cause the higher reactivity of C–H over C–C bonds.

In Scheme VIIA, the elimination of hydrogen trioxide from pentacoordinated carbonium ion **5** can give the neooctyl cation (**16**) which immediately rearranges to the more stable tertiary ion



Scheme X



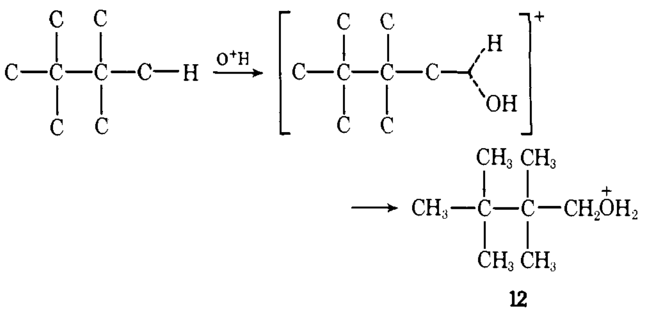
or cleaves to the *tert*-butyl cation as shown in Scheme IX. However, the low yield of methyl ethyl ketone (**14**) and the product distribution in Table I suggest that the rearrangement or cleavage of neooctyl cation is only a minor reaction path.

The formyl-*tert*-heptoxy carbenium ion (**17**) has never been observed as a long-lived species in solution. It readily cleaves giving formaldehyde (**13**) and the dimethyl-*tert*-butyl carbenium ion which then readily reacts with ozone giving dimethyl-*tert*-butoxy carbenium ion (**18**) subsequently. Ion **18** also has never been observed. The observed products were acetone (protonated) (**11**) and dimethylmethoxy carbenium ion (**2**). Indeed, the reaction of triptane (2,2,3-trimethylbutane) under the same condition showed the formation of ions **2** and **11** exclusively in the ratio of 1:1 which can be explained according to Scheme X.

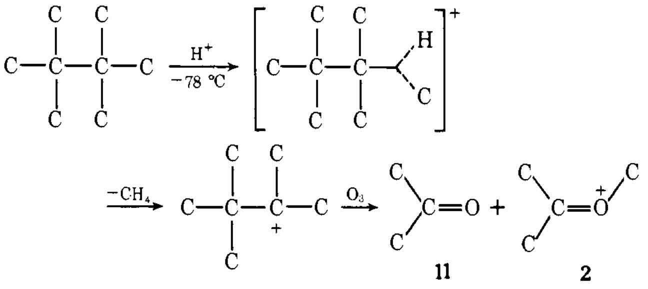
2,2,3,3-Tetramethylbutane under the same condition gave the corresponding neo alcohol (2,2,3,3-tetramethylbutyl alcohol (**12**)) in higher yield (30%) than in the case of neopentane (5%). The formation of **12** can be explained as in Scheme XI.

The differing yield of corresponding alcohol **12** from neooctane seems to reflect the reactivity of hydroxylating agent toward the methyl C-H bonds without isomerization. A similar observation of the reactivity for C-H bond was made in the reaction of hydrogen peroxide in the presence of FSO_3H-SbF_5-SO_2ClF. The lowest temperature at which the reaction takes place giving significant quantity of the corresponding alcohols is for methane, ethane, neopentane, and 2,2,3,3-tetramethylbutane around −20, −40, −70, and −78 °C, respectively. The difference in reactivity of C-H bonds in these alkanes is significant and reflects inter alia steric effects, as well as neighboring group substituent effects on the reactivity of the involved C-H bonds.

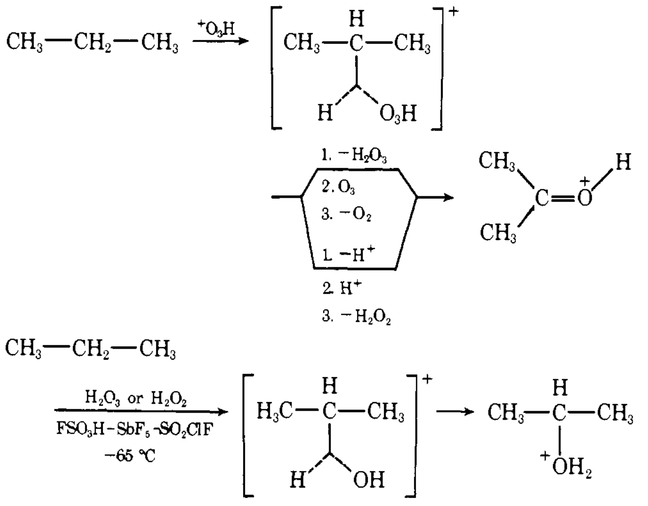
Scheme XI



Scheme XII



Scheme XIII



In HF-SbF_5-SO_2ClF solution, the reaction of 2,2,3,3-tetramethylbutane with ozone gave as the main products dimethylmethoxy carbenium ion (**2**) and protonated acetone (**11**) in a molar ratio of about 1:1, with no alcoholic product formed. This clearly demonstrates the protolysis of alkane prior to ozonolysis as shown in Scheme XII.

Similar results were also obtained when the reactions were carried out at somewhat higher temperature or in the presence of SbF_5-SO_2ClF at −78 °C. Under these conditions protolysis (or oxygenative cleavage) would take place more easily than in the FSO_3H-SbF_5-SO_2ClF system at −78 °C.

Previously[2] we have described the reaction of straight chain alkanes with ozone in FSO_3H-SbF_5-SO_2ClF solution at −78 °C. Further more detailed studies of the reactions by changing the temperature with an equimolar amount of ozone led to the observation of the formation of alcohols, further suggesting the initial attack of protonated ozone on the involved δ bonds of alkanes. For example, when propane was reacted with an equimolar amount of ozone in FSO_3H-SbF_5-SO_2ClF at −78 °C the NMR of the resultant solution shows almost exclusive formation of acetone (protonated) with an about 30% conversion of propane. By raising the temperature of the solution to −65 °C with no further introduction of ozone and keeping

Table II. Secondary Hydroxylation of Straight Chain Alkanes by H_2O_2 (or H_2O_3) Formed in Their Ozonolysis in Superacids[a]

Alkane	Temp, °C	Rxn time, min	Product distribution, %[b]
CH_3CH_3	−78	<1	$CH_3(H)C{=}O^+H$ (∼95%)[c]
CH_3CH_3	−78	120	$CH_3(H)C{=}O^+H$ (∼95%)
CH_3CH_3	−40	60	$CH_3(H)C{=}O^+H$ (90%), $CH_3CH_2{}^+OH_2$ (10%)
$CH_3CH_2CH_3$	−78	<1	$(CH_3)_2C{=}O^+H$ (∼95%)[c]
$CH_3CH_2CH_3$	−78	120	$(CH_3)_2C{=}O^+H$ (∼95%)
$CH_3CH_2CH_3$	−65	60	$(CH_3)_2C{=}O^+H$ (85%), $CH_3CH(O^+H_2)CH_3$(15%)
$CH_3CH_2CH_2CH_3$	−78	<1	$CH_3CH_2(CH_3)C{=}O^+H$ (40%), $CH_3(H)C{=}O^+$-CH_2CH_3 (60%)[c]
$CH_3CH_2CH_2CH_3$	−78	120	$CH_3CH_2(CH_3)C{=}O^+H$ (40%), $CH_3(H)C{=}O^+$-CH_2CH_3 (60%)
$CH_3CH_2CH_2CH_3$	−65	60	$CH_3CH_2(CH_3)C{=}O^+H$ (30%),$CH_3(H)C{=}O^+$-CH_2CH_3 (50%), CH_2CH_2-$CH(O^+H_2)CH_3$ (20%)[d]

[a] Equimolar amount of ozone and alkane was used in the presence of threefold excess of FSO_3H–SbF_5 in SO_2ClF at −78 °C. Conversion of propane and *n*-butane was around 30–40%. The reaction mixture was then kept at given times and specified temperature. In the case of ethane, the mixture of alkane and ozone (1:1 molar ratio) was passed through the acid solution at −78 °C. [b] Product assignments were made as described in Table I. Neopentyl and neooctyl alcohols were assigned by their NMR spectra (in the protonated forms present in superacids): $C^1C^2(CC)C^3OH^4{}_2{}^+$ ^1H NMR 1, 1.51 (s); 3, 4.85 (t); 4, 9.28 ppm (t). ^{13}C NMR 1, 23.84; 2, 37.14; 3, 87.71 ppm (FSO_3H-SbF_5–SO_2ClF, −78 °C, external Me_4Si). $C^1H_3C^2(CH_3)_2C^3(C^4H_3CH_3)C^5H_2{}^+OH_2$ ^1H NMR 1, 1.03 (s); 4, 1.06 (s); 5, 4.80 (t); $^+OH_2$, 9.21 ppm (t). ^{13}C NMR 1, 25.03; 2, 34.4; 3, 39.06; 4, 24.36; 5, 85.38 ppm. [c] $CH_3C{=}O^+$ was found as minor product, together with other unidentified products. [d] $(CH_3)_2$-$C{=}O^+CH_3$ was found as minor product.

it for about 2 h, the formation of isopropyl alcohol was observed. A similar observation was made for ethane at −40 °C and butane at −65 °C (results are summarized in Table II).

The results can be best explained, as shown in Scheme XIII, as proceeding in two steps: primary ozonolysis followed by hydroxylation with H_2O_2 (H_2O_3) formed in the former reaction. Indeed the reaction of propane with H_2O_2 in FSO_3H-SbF_5-SO_2ClF at −65 °C confirmed the suggested path, giving isopropyl alcohol (protonated).

On the other hand, tertiary isoalkanes did not give any observable alcohol under the reaction conditions. It is considered that tertiary alcohols, once formed, easily ionize giving *tert*-alkyl carbenium ions and undergo further reaction with ozone or hydrogen peroxide. Indeed, for example, *tert*-butyl alcohol in FSO_3H-SbF_5-SO_2ClF gives readily and quantitatively the trimethyl carbenium ion even at −78 °C. In the presence of ozone or hydrogen peroxide the dimethylmethoxy carbenium ion (**2**) is formed.

From the results obtained we conclude that the reaction of studied neoalkanes with ozone in the presence of FSO_3H–SbF_5-SO_2ClF at low temperature proceeds by electrophilic insertion of protonated ozone ^+O_3H into the affected σ bonds of the alkanes. The initially formed hydrocarbon-^+O_3H complex is of pentacoordinated carbonium ion nature and cleaves to a trivalent carbenium ion or neutral trioxide. Hydrogen or alkyl trioxide or hydrogen peroxide formed in the course of the reactions subsequently can hydroxylate excess alkane giving alcohols.

Experimental Section

Materials. All alkanes were commercially available, of high purity (>99.5%), and used without further purification. SbF_5 and FSO_3H were doubly distilled. The ozone generator (Welsbach Model T-816) gave about 8% ozone at a rate of 0.2–0.5 L/min oxygen gas flow.

Reaction Apparatus. The reaction apparatus (15 mL volume) was constructed of glass, except when using HF, and was provided with suitable gas inlet and outlet for sampling and introduction of reagents. When using HF the reaction vessel was made out of Teflon.

Ozonolysis. The solution of alkanes (5–10 mmol) and acid (20–40 mmol) in SO_2ClF (to give a 5–10% solution) was placed into the reaction vessel at given reaction temperatures. Ozone (5–50 mmol) was then passed through the solution. After completion of the reaction the solutions were directly subjected to analysis by ^1H and ^{13}C NMR, without isolation of products. The experimental conditions and analytical procedures used were similar to those used and described in our preceding work.[2-4]

References and Notes

(1) (a) Part 6: G. A. Olah, N. Yoneda, and R. Ohnishi, *J. Am. Chem. Soc.*, **98**, 7341 (1976). (b) Hokkaido University, Sapporo 060, Japan.
(2) G. A. Olah, N. Yoneda, and D. G. Parker, *J. Am. Chem. Soc.*, **98**, 5261 (1976).
(3) G. A. Olah and N. Yoneda, *J. Am. Chem. Soc.*, in press.
(4) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 4960 (1973).
(5) G. A. Olah, R. Renner, P. Schilling, and Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 7686 (1973).
(6) G. A. Olah, A. Germain, H. C. Lin, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 2928 (1975).
(7) (a) P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, **88**, 3288 (1966); (b) P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).
(8) R. E. Erickson, R. T. Hansen, and J. Harkins, *J. Am. Chem. Soc.*, **90**, 6777 (1968).
(9) H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).
(10) (a) R. W. Murray, W. C. Cumma, Jr., and J. W. P. Lin, *J. Am. Chem. Soc.*, **92**, 3205 (1970); (b) F. E. Stary, D. E. Emge, and R. W. Murray, *ibid.*, **97**, 5761 (1975).
(11) P. D. Bartlett and M. Laha, *Isr. J. Chem.*, **10**, 101 (1972).
(12) G. A. Olah, N. Yoneda, and D. S. Parker, *J. Am. Chem. Soc.*, **98**, 2251 (1976).
(13) G. A. Olah, D. G. Parker, N. Yoneda, and F. Pelizza, *J. Am. Chem. Soc.*, **98**, 2245 (1976).
(14) G. Czapski and B. H. J. Belsi, *J. Phys. Chem.*, 67, 2180 (1963); **72**, 3836 (1968).
(15) P. D. Bartlett and M. Laha, *Isr. J. Chem.*, **10**, 101 (1972).