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SUPERACID CATALYZED OXYGENATION OF ALIPHATIC ETHERS WITH OZONE

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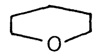
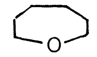
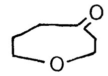
Electrophilic insertion of protonated ozone into tertiary or secondary C-H bonds located at γ or farther away positions from the oxygen atom in aliphatic ethers was observed to produce oxoalkyl ethers in $HF-SbF_5$ superacid media at -40 °C.

The chemistry of the reactions of single σ-bonds with electrophiles generated in superacid media is an interesting and developing field.[1)] In this connection, electrophilic oxygenation of alkanes with protonated ozone (O_3H^+) generated in superacid media such as $HF-SbF_5$ and the like are particularly noteworthy, in that they produce carboxonium ions[2)] ($R_2C=O^+R$) which can subsequently be hydrolyzed to ketones and alcohols. We extended our investigations of this novel reaction toward the functionalized organic compounds and wish to report here the reaction of aliphatic ethers to synthesize oxoalkyl ethers.

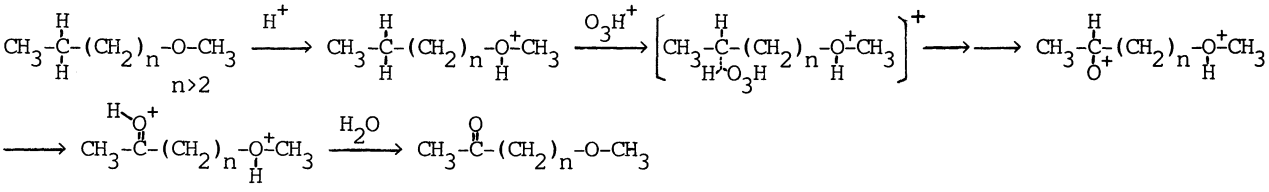
The solution of substrate (2-25 mmol) in $HF-SbF_5$ (SbF_5 10-125 mmol; HF/SbF_5 molar ratio 10) was placed in the reaction vessel made of Kel-F (150 cm^3) at -20 — -40 °C. Then, a stream of oxygen gas containing 2.5% ozone (0.29 mmol/min) was passed through the solution until it acquired a blue color (usually 15-90 min). The products were obtained by working up in the usual manner and were identified by IR and NMR spectroscopy. Typical experimental results are summarized in the Table.

Ethers having alkyl groups of three or less carbon atoms did not react. As ethers are completly protonated to dialkyloxonium ions (R_2OH^+) in superacid media, O_3H^+ can not readily react with σ-bonds located near the protonated oxygen atom in the substrates. Rather complex mixtures of products, on the other hand, were observed in the reaction of substrates having tertiary C-H bond, such as that of 3-methyl butyl, located at γ or farther away positions from the charged center which proceed almost completely. These reactions involve cleavage of C-C bonds in intermediate oxenium ions (R_3O^+) derived from the initial insertion of O_3H^+ at the tertiary C-H bond in the substrate. In contrast, the reaction of O_3H^+ toward ethers having n-butyl or longer straight chain alkyl takes place cleanly to give rise to the oxoalkyl ethers. An important feature of the reaction is that O_3H^+ undergoes insertion almost exclusively into the farthest located secondary C-H bonds from the oxygen atom in ethers having straight chain alkyl groups with more than four carbon atoms[3)] as shown in Scheme.

Table 1. Products in the Reaction of Aliphatic Ethers with Ozone in HF-SbF_5[a]

Substrate	SbF_5/Subst.[b]	Product Yield/%[c]	NMR (CCl_4, δ/ppm, Ho=90 MHz); IR(Neat, ν/cm^{-1})
$CH_3(CH_2)_2OCH_3$	50	NR[d]	
$CH_3(CH_2)_3OCH_3$	10	$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_2OCH_3$ (80.3)[e]	NMR [2.09(3H,s), 2.52(2H,t), 3.23(3H,s), 3.53(2H,t)] IR [1720(C=O), 1120(C-O-C)]
$CH_3(CH_2)_4OCH_3$	5	$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_3OCH_3$ (89.0)[e]	NMR [1.75(2H,p), 2.09(3H,s), 2.44(2H,t), 3.25(3H,s), 3.32(2H,t)]; IR [1720(C=O), 1120(C-O-C)]
$CH_3(CH_2)_5OCH_3$	5	$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_4OCH_3$ (87.7)[f]	NMR [1.53(4H,m), 2.09(3H,s), 2.36(2H,t), 3.22(3H,s), 3.30(2H,t)]; IR [1720(C=O), 1120(C-O-C)]
$(CH_3)_2CH(CH_2)_2OCH_3$	10	$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_2OCH_3$ (19.8)[g]	
$[CH_3(CH_2)_3]_2O$	10	$[CH_3\overset{O}{\overset{\|}{C}}(CH_2)_2]_2O$ (75.6)[h]	NMR [2.10(6H,s), 2.55(4H,t), 3.65(4H,t) IR [1720(C=O), 1120(C-O-C)]
$[CH_3(CH_2)_4]_2O$	10	$[CH_3\overset{O}{\overset{\|}{C}}(CH_2)_3]_2O$ (65.5)[i]	NMR [1.75(4H,p), 2.09(6H,s), 2.41(4H,t), 3.33(4H,t)] IR [1712(C=O), 1115(C-O-C)]
	50	NR[d]	
	20	 (85.7)[e]	NMR [1.76(2H,p), 2.53(4H,m), 3.73(4H,t)] IR [1710(C=O), 1125(C-O-C), 1258,1080]

a) Reaction conditions: HF/SbF_5 molar ratio 10; substrate 2-25 mmol; reaction temperature -40 °C. b) Molar ratio. c) Based on substrate. d) Reaction temperature -20 °C, no reaction. e) Another is the substrate. f) Methyl 4-oxohexyl ether and methyl 3-oxobutyl ether were detected by GLC less than 1% in total. g) Other products are complicated. h) Pentyl 4-oxopentyl ether(10.5%) is also found. IR [2960,2865,1720,1360,1120]; NMR [0.90(3H,t),1.35(6H,m),1.76(2H,m),2.09(3H,s) 2.42(t.3H),3.35(m,4H)]. i) Hexyl 5-oxohexyl ether(18%) is also found. IR [1720,1115]; NMR [0.97(3H, t),1.2-1.7(6H,m),2.09(3H,s), 2.38(2H,t),3.35(4H,m)].



Scheme 1.

Such an almost exclusive attack of O_3H^+ on the methylene C-H bonds at the ω-1 position of the alkyl groups can not be fully accounted for only by the electron withdrawing effect of the protonated oxygen atom since such an effect is known not to serve two or three carbon atoms.[4] Hence, high reactivity of such C-H bonds may be partly also due to the inductive effect of the adjacent terminal methyl group. Also interestingly, oxepane gave exclusively 3-oxepanone in good yield, although oxolane, having the same positional methylene group as oxepane, showed no significant reaction. This may be explained by the fact that the secondary C-H bonds in the former are of rather higher energetic configuration (eclipsed position) than those in the latter.

References

1) G.A.Olah, Science, 206, 13(1979); N.Yoneda and Y.Takahashi, J.Jpn.Petroleum Inst., 20, 468(1977).
2) G.A.Olah, D.G.Parker, and N.Yoneda, Angew.Chem.,Int.Ed.Engl., 17, 909(1978).
3) For the ethers having straight chain alkyl group with more than seven carbon atoms, electrophilic insertion of O_3H^+ tended to take place at the secondary C-H bonds located at δ or farther away from oxygen atom in the substrate. Even in such cases, ω-1 oxoalkyl ethers are major products.
4) E.S.Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt & Co., New York(1960),p.39.

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