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NUCLEOPHILIC SUBSTITUTIONS AT OZONIDES

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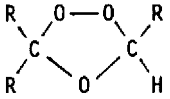
Abstract: Reactions of 3-acetoxy-3,5,5-trimethyl-1,2,4-trioxolane (5a) with methanol, benzyl alcohol or phenol gave the corresponding ether ozonides 5c - e. Reaction of 5b with benzyl alcohol and with acetate ion gave 5d and 5a, respectively.

The known reactions of nucleophiles with ozonides 1 occur either by attack at the peroxide bridge and formation of fragments 2 and 3 or by attack at a CH-bond of the 1,2,4-trioxolane ring and formation of fragments 2 and 4[1]. Nucleophilic substitutions at the C-atoms of the 1,2,4-trioxolane system with retention of the ring are not known.



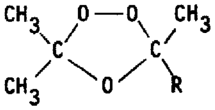
1

$R_2C=O$ RCH=O RCOOH

2 3 4

By ozonolysis of the corresponding unsaturated substrates on polyethylene, we have recently prepared ozonides 5a[2] and 5b[3]. They are slowly decomposed at ca. 40 °C. From the products obtained, we have concluded that the decomposition starts by elimination of R and formation of the ozonide cation 6[2,4]. In the present work, we have tried to trap 6 with nucleophiles with the following results: Reactions of 5a with a 6-fold excess of methanol, benzyl alcohol or phenol at 40 °C in $CDCl_3$ and in the presence of sodium hydrogencarbonate afforded ozonides 5c (62%), 5d (91%) and 5e (46%), respectively. Ozonide 5c was isolated by distillation at room temperature and 10^{-3} torr into a receiver cooled to 0 °C; ozonides 5d and 5e were isolated by chromatographic separation (silica gel; n-pentane/diethyl ether 4:1). The structures of the colorless, liquid ozonides were confirmed by the ^1H- and ^{13}C-NMR data (see Table), by the absence of carbonyl bands in the IR spectra and by reduction to give the acetic esters 7c, 7d and 7e, respectively.

Reaction of 5b with excess benzyl alcohol under similar conditions provided also ozonide 5d (58%). When the decomposition of 5b was carried out in the absence of alcohol yet in the presence of sodium hydrogencarbonate, ozonide 5a (50%) was obtained. This can be rationalized by cleavage of fragment R into acetone and acetate anion. The latter, in turn, traps ozonide cation 6 to give 5a.



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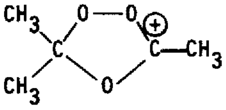

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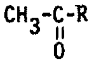
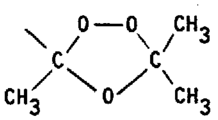


$CH_3\text{-}\overset{}{\underset{\underset{O}{\|}}{C}}\text{-}R$

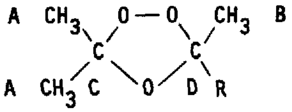
7

a: R = CH_3COO b: R =



c: R = CH_3O d: R = $C_6H_5CH_2O$ e: R = C_6H_5O

^{1}H- and ^{13}C-NMR Data of Ozonides 5a and 5c - 5e



Chemical Shift, δ ppm

^{1}H-NMR Data [a)]				^{13}C-NMR Data [b)]				
	A		B	A		B	C	D
5a	1.50	1.58	1.95	19.56	21.99	22.71	111.58	119.01
5c	1.50	1.59	1.65	21.74	22.64	24.52	109.88	119.98
5d	1.53	1.61	1.72	22.14	22.34	24.56	110.13	119.96
5e	1.34	1.47	1.73	20.80	22.30	24.66	110.67	120.07

a) s-signals b) q-signals for A- and B-atoms; s-signals for C- and D-atoms.

The first successful substitutions at ozonide rings in this work open a new route for the preparation of ozonides. This is particularly suitable in cases where other methods fail. Thus, attempts to prepare 3,5,5-trisubstituted 3-alkoxy- or 3-phenoxy-1,2,4-trioxolanes by ozonolysis of the corresponding enol ethers have been unsuccessful, and ozonides 5c - 5e are the first representatives of permethylated enol ether ozonides.

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