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FACILE ISOMERIZATION AND OXIDATION BY $^{3}O_{2}$ OF 1,2-DIALKOXY-1-HALOGENOETHENES

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In connection with our studies on acetylene diethers[1], we have been concerned with the preparation and manipulation of 1,2-dialkoxy-1-halogenoethenes (**2**). Although some of these compounds had been previously described[2], almost nothing is known about their stereochemistry and chemical reactivity.

The general procedure for the preparation of the title compounds involve the low temperature elimination of hydrogen halide, from the corresponding 1,2-dialkoxy-1,2-dihalogenoethanes (**1**), by potassium *tert*-butoxide in pentane solution. The yields of the dehydrohalogenation and the *Z*/*E* ratios are given in Table I

Whereas no significant variation is observed in the isomeric composition of the chloro derivatives (**2b**), either upon distillation or after remaining at room temperature for long periods of time, the corresponding bromoalkenes (**2a**) exhibit a facile *E* → *Z* isomerization, even at room temperature. On the other hand, both halogenoalkenes are isomerized, in an atmosphere of pure nitrogen, under non sensitized photochemical conditions (254 nm).

$$(RO)(X)CH{-}CH(X)(OR) \longrightarrow (RO)(X)C{=}CH(OR)$$

1 **2**

a, X = Br
b, X = Cl

TABLE I

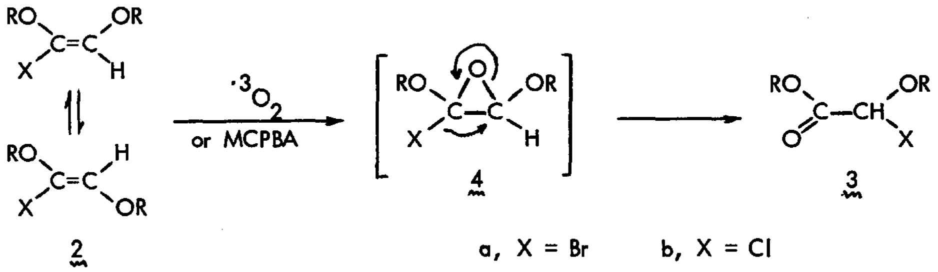
R	X	**1** (rac/meso)	**2**, Z/E			yield (%)
			crude	distilled	photochem.	
Me	Cl	85/15	78/22	78/22	-	57
Et	Cl	35/65	58/42	58/42	-	63
i-Pr	Cl	56/44	33/67	33/67	20/80	82
tert-But	Cl	0/100	0/100	0/100	-	90
Me	Br	40/60	40/60	50/50	-	38
Et	Br	33/67	8/92	22/78	-	73
i-Pr	Br	45/55	0/100	12/88	54/46	87
tert-But	Br	44/56	0/100	0/100	-	83

Moreover, both halogenoalkenes (**2a** and **2b**) are sensitive to atmospheric oxygen to afford carbonylic compounds, which have been identified as the corresponding alkyl alkoxyhalogenoacetates (**3**) by independent synthesis[3]. In fact, when pure oxygen was bubbled into a dilute pentane solution of 1-bromo-1,2-diisopropoxyethene (**2a**, R = i-Pr), in the dark, an exothermic reaction ensued and the oxidation was complete in a 90 min period. After elimination of the solvent and distillation, isopropyl bromoisopropoxyacetate (**3a**, R = i-Pr) was isolated in 87% yield. By contrast, the oxidation of 1-chloro-1,2-diisopropoxyethene (**2b**, R = i-Pr) occurred at slower rate, the conversion being only 65% after 16 h.

The oxidation of halogenoalkenes **2** probably occurs *via* the epoxides **4**, as Griesbaum and his associates have shown in the case of dichlorinated ethylenes[4]. In this context, it is worth noting that the low temperature epoxidation of 1-chloro-1,2-diisopropoxyethene (**2b**, R = i-Pr) with *meta*-chloroperbenzoic acid (MCPBA) in methylene chloride affords exclusively the rearranged isopropyl chloroisopropoxyacetate (**3b**, R = i-Pr) (Scheme 1).

As an exception, both (*E*)-1-bromo- and (*E*)-1-chloro-1,2-di-*tert*-butoxyethene (**2a** and **2b**, R = *tert*-But) neither isomerize nor oxidize in the presence of pure oxygen.

All the reported facts are consistent with a low lying perpendicular triplet state, as supported by MNDO calculations[5] ($E_T - E_{S_0} \sim 18.7$ kcal/mol, for **2b**, R = Me)[6], the singlet → triplet transition being favored by heavy atoms effects.



Scheme 1

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