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THE SULFHYDROLYSIS OF DIALKOXYCARBONIUM IONS. A NOVEL ROUTE TO THIONESTERS

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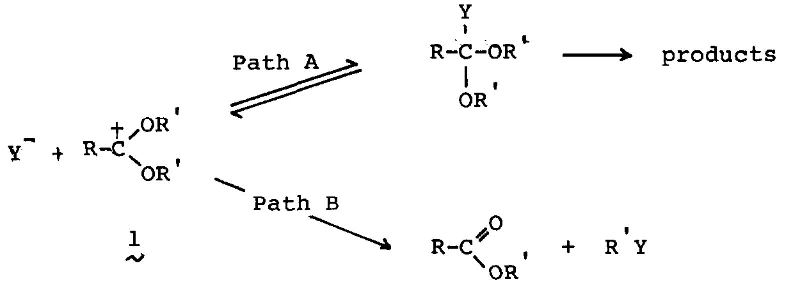
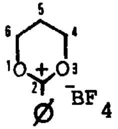
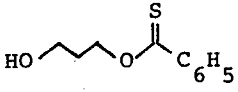
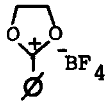
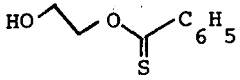
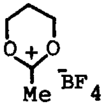
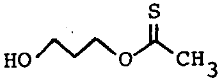
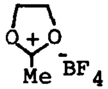
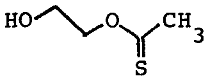
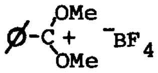
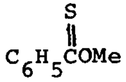
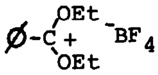
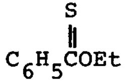
Acyclic and cyclic dialkoxycarbonium salts[1] have been subjected to various structural[2] and chemical studies.[3] Under kinetic control, a nucleophile is expected to add to 1 at the atom of greatest electron deficiency viz. the proacyl carbon (Path A); the resulting adduct may be isolable or trappable if it is kinetically stable, or else it may either revert to starting materials or convert to other products. The electrophile is also subject to attack at an alkyl position in R' (Path B) to give $RCOOR'$ and $R'Y$.



The relative importance of these two pathways depends on the nucleophile, the ambident cation, the temperature and duration of the reaction, and the solvent; for a negatively charged nucleophile, Path A is favored since the ion combination generally has the lower activation energy.[4] A judicious choice of these experimental variables sets the course for chemospecific and/or regiospecific synthetic transformations.

We have found that the reaction of dialkoxycarbonium ions 2-7 with sodium sulfide (or anhydrous sodium hydrosulfide) in solvent acetonitrile (followed by hydrolytic work-up) provides a novel and convenient way for the synthesis of thionbenzoates and monothionesters of 1,2- and 1,3-diols.[5] The following Table summarizes our results:

Compound		T (^{o}C)	Reagent	Work-up	Reaction Time (hr)	Isolated Product[d]	% Yield
	**2**[b]	-23	Na_2S[a]	H_2O	3		85
	**3**	-23	Na_2S	satd. aq. Na_2S	2		77
	**4**	0	NaSH[c]	--	$8\frac{1}{2}$		78
	**5**	0	NaSH[c]	--	$5\frac{1}{2}$		60
 $C_6H_5C^{+}(OMe)_2\ ^{-}BF_4$	**6**	-23	Na_2S	H_2O	$1\frac{1}{2}$	 $C_6H_5C(=S)OMe$	46
 $C_6H_5C^{+}(OEt)_2\ ^{-}BF_4$	**7**	-23	Na_2S	ethereal HBF_4	2	 $C_6H_5C(=S)OEt$	40

[a] 96% Na_2S is conveniently prepared from $Na_2S.9H_2O$ as described in ref. 6.

[b] The hexachloroantimonate salt led to the formation of an orange precipitate, presumably Sb_2S_3.

[c] Two-fold excess; prepared as described in ref. 7.

[d] All new compounds gave satisfactory elemental and spectral (pmr, ir, uv) analyses; the thionbenzoates were isolated as bright yellow oils, the thionacetates as pale yellow oils.

In a typical procedure, to a mixture of 2-phenyl-1,3-dioxan-2-ylium fluoroborate (0.44 mmol) and sodium sulfide[6] (0.44 mmol) cooled, under nitrogen, in a Dry Ice-CCl_4 bath was added pre-cooled dry acetonitrile (1.8 ml). The mixture was stirred at -23° for 3 hr and then quenched with water (0.5 ml) with vigorous stirring. The resulting mixture was quickly poured over $CHCl_3$ (10 ml) and the product was extracted with additional $CHCl_3$ (3x5 ml); the combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was then chromatographed on a dry Silica Gel (100-200 mesh) column eluting with $CHCl_3$-CH_3CN (9:1 v/v) to give 73.0 mg (85%) of the yellow oily thionester.

The sulfhydrolytic reactions of **2**-**5** by the above procedure do not lead (as revealed by TLC) to the formation of any mercaptoesters resulting from Path B; that is, the nucleophilic attack is virtually exclusively at C-2 (Path A). Compounds **6** and **7**, on the other hand, undergo partial dealkylation (Path B) to give lesser yields of the thionbenzoate esters. This is not surprising since aryl-substituted dialkoxycarbonium ions are known to be powerful alkylating agents.[8] While the cleavages of 1,3-dioxan-2-ylium and 1,3-dioxolan-2-ylium fluoroborate with Na_2S by the procedure above were successful (TLC evidence), several attempts at isolating the ω-hydroxythionformates were thwarted by the apparent high reactivity of the thionesters. Attempts at extending the above procedure to other acyclic salts $R\overset{+}{C}(OEt)_2\,\overset{-}{B}F_4$ (R = H, Me, Et) were unsuccessful.

It is interesting to note that cleavage of **3** with H_2S in acetonitrile (0°, 38 hr) gave mercaptoester $HSCH_2CH_2OC(=O)C_6H_5$ (13.5% isolated yield) but no thionester. Reaction of **3** with anhydrous NaSH in acetonitrile (27°, 21.5 hr) yielded, after aqueous work-up, a mixture of mercaptoester (8%), hydroxythionester (19%) and hydroxyester (27%). However, reaction of **3** with Na_2S (see Table) gave mostly hydroxythionester (77%), negligible amounts of hydroxyester ($<$3%) and no mercaptoester.

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