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THE CONVERSION OF THION ESTERS TO THIOL ESTERS BY $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$(1)

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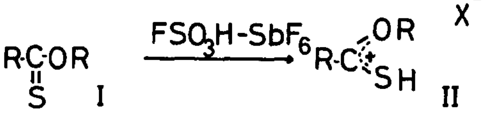
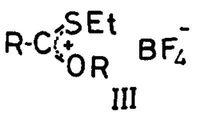
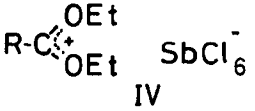
The protonation of the thion ester(1) in the strong acid system(4:1M FSO_3H-SbF_5 solution) was studied by Olah et al.(2) and the site of the protonation was proved to be thiocarbonyl sulfur(cf. II). In continuation of the previous works(3) relating to the activation of weak organic bases through alkylation or acylation, we investigated the alkylation of the thion esters(I) using an effective alkylating reagent, $Et_3\overset{+}{O}$,$\overset{-}{B}F_4$.



I II



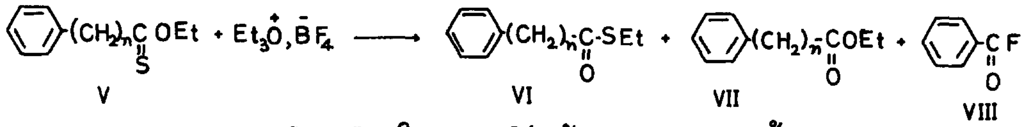
III



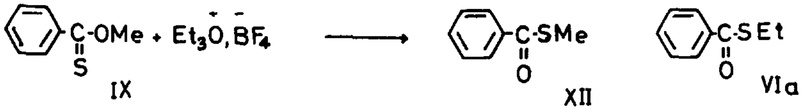
IV

Alkylation is also presumed to occur on the electron rich thiocarbonyl sulfur and the resulting S-alkylated species(III) is anticipated to have a high reactivity toward various nucleophiles because III is structurally related to the diethoxycarbonium ion(IV) which is known to be an effective alkylating reagent(3,4).

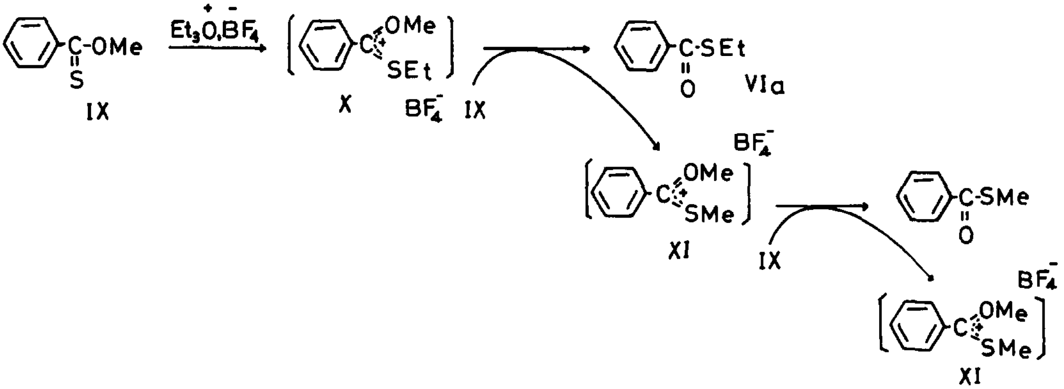
The reaction was very slow when ethyl thionbenzoate(Va)(5) was treated with a molar equivalent of $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$ in dichloroethane at room temperature. However, the starting material was consumed completely within 5 min when the mixture was heated to reflux. After the usual treatment, ethyl thiobenzoate(VIa) was obtained in almost quantitative yield. The i.r. spectrum of the crude reaction product shows a weak absorption band at 1810cm^{-1} which may be ascribed to the acid fluoride(VIII) produced. The reactions of the homologous thion esters(Vb and Vc) with $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$ proceeded smoothly but an appreciable amount of the normal esters(VIIb and VIIc) were obtained along with the expected thiol esters(VIb and VIc). It is of particular interest that both ethyl (VIa) and methyl(XII) thiobenzoate were obtained when methyl thionbenzoate was treated with Et$_3\overset{+}{O}$, $\overset{-}{B}F_4$. These observations suggest that the mechanism of this conversion reaction is by no means simple.



		VI	VII
a	n = 0	94 %	- %
b	1	85.7	14.3
c	2	67	33



The initial step of this conversion would undoubtedly involve the alkylation of thion ester by Et$_3\overset{+}{O}$, $\overset{-}{B}F_4$. Methoxyethylthiocarbonium ion(X) thus formed is considered to be a more effective alkylating agent than Et$_3\overset{+}{O}$, $\overset{-}{B}F_4$ and to attack the remaining methyl thionbenzoate(IX) yielding ethyl thiobenzoate(VIa) and methoxymethylthiocarbonium ion(XI). Here the cleavage of O-Me bond rather than S-Me bond in X is expected to occur predominantly. The resulting salt(XI) would again methylate IX to give XI and methyl thiobenzoate(XII). This process will be repeated until all of the thion ester(IX) is consumed. The relationship may be depicted as follows:



As for alternative pathways, the thermal and/or BF$_3$ catalyzed migration(6) of methyl group from oxygen to sulfur should also be considered. The former was ruled out because the starting thion ester(IX) was recovered unchanged when it was refluxed for two hours in the same solvent.

On the other hand, the migration was found to occur with BF_3-etherate as a catalyst but was slow and incomplete when a molar equivalent of the reagent was used. Only 16% of the converted thiol ester(VIa) was detected when an equimolar mixture of Va and BF_3-etherate was kept for 6 hr at 51°(Fig. 1), whereas almost half of the thion ester was consumed within 16 min when $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$ was used(Fig. 2) at the same temperature. These data clearly exclude the importance of the BF_3-etherate catalyzed reaction in the above conversion reaction.

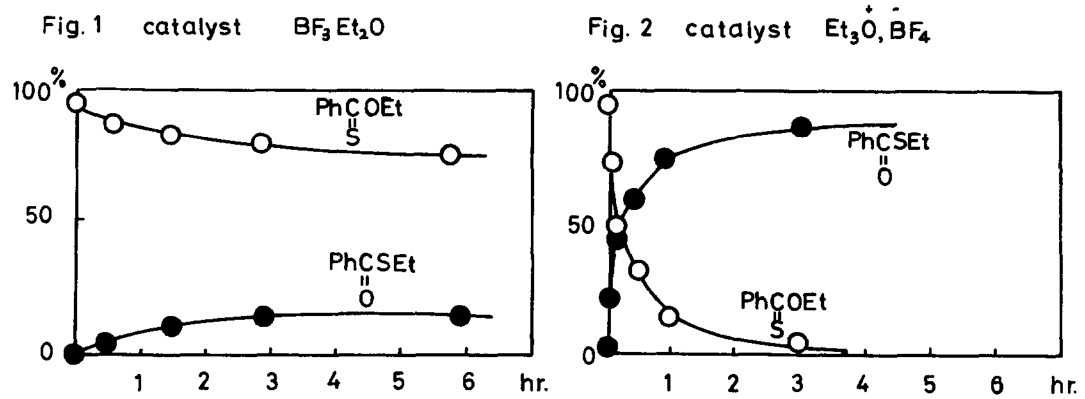


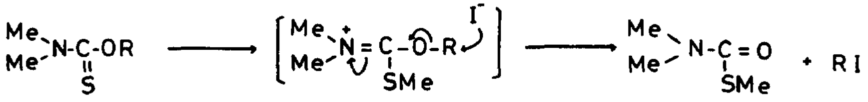
Fig. 1 catalyst BF_3Et_2O

Fig. 2 catalyst $Et_3\overset{+}{O}, \overset{-}{B}F_4$

Plots of the concentrations of reactant and product against time, for the conversion of ethyl thionbenzoate into ethyl thiolbenzoate.
$[Ph\underset{S}{\overset{\|}{C}}\text{-}OEt] = 3.01 \times 10^{-1}M$

If the afore mentioned mechanism is actually in operation, then only a small amount of $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$ would be necessary to initiate the reaction. In fact, when the reaction was carried out using only one tenth molar equivalent of $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$, the conversion was found to proceed expectedly yielding 51% of methyl thiobenzoate(XII) and 8.3% of ethyl thiobenzoate (VIa).

Wheeler and Barnes(7) reported that alkyl thioncarbamates(XIII) were converted to methyl thiocarbamate(XIV) via S-methylated species(XV) by treating them with CH_3I. The mechanism is formally similar to that of the present reaction but in their case the liberated iodide ion(I^-) is nucleophilic enough to attack the alkyl group adjacent to oxygen affording XIV directly.


XIII XV XIV

It should be emphasized here the simple alkyl thion esters are unaffected by alkyl halides. They are also stable under the conditions for the usual Schönberg rearrangement (8) which involves the intramolecular thermal migration of aryl groups from oxygen to sulfur. In this work, we have demonstrated the first example of the conversion of the simple alkyl thion ester(V) to the alkyl thiol esters(VI) by $Et_3\overset{+}{O}$, $\overset{-}{B}F_4$ catalysis.

REFERENCES

1. Part IV in the series "Activation of Weak Organic Bases".
2. G. A. Plah and A. T. Ku, J. Org. Chem., 35, 331 (1970).
3. T. Oishi, K. Kamata and Y. Ban, Chemical Communications, 777 (1970).
4. S. Kabuss, Angew. Chem., Inter., Ed. Engl., 5, 675 (1966).
5. A variety of thion esters were prepared from the corresponding N-methylanilides by the modified Eilingsfeld's method[H. Eilingsfeld, M. Seefelder and H. Weidinger, Chem. Ber., 96, 2671 (1963)] in good yield. The details will be published in the forthcoming paper.
6. In the above experiment, benzoyl fluoride was detected from the reaction product, which means that BF_3 was liberated during the reaction. BF_3-catalized conversion of alkyl thion carbamate to alkyl thiocarbamate has been reported by Kinoshita et al. [Y. Kinoshita, S. Uchiumi, S. Chokai and Y. Oshima, Agr. Biol. Chem., 30, 710 (1966)].
7. H. L. Wheeler and B. Barnes, Am. Chem. J., 22, 141 (1899); ibid., 24, 60, 424 (1900).
8. H. R. Al-Kazimi, D. S. Tarbell and D. H. Plant, J. Am. Chem. Soc., 77, 2479 (1955); D. H. Powers and D. S. Tarbell, ibid., 78, 5363 (1956).