The Novel Transesterification of Quaternary Ammonium Dithiocarbonates and Thiolesters

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It is well known that transesterification occurs when an ester is heated with an alcohol in the presence of acid or a base.

In the previous papers[1] the present authors have reported that methylxanthates reacted with trimethylamine at room temperature to form quaternary ammonium dithiocarbonates, as in Eq. 1.

$$\mathrm{MeOCS_2R + Me_3N \rightarrow \underset{(I)}{Me_4\overset{+}{N}\overset{-}{S}COSR}} \qquad (1)$$

When the ammonium salts were mixed with esters in acetonitrile, transesterification was observed; this reaction will be described in this communication.

Reactions were carried out in acetonitrile homogeneously for about 20 min. at room temperature. After the solvent had been evaporated in vacuo, the residue was separated into an ether-soluble part (A) and an insoluble part (B). A was a mixture of esters, and B was a mixture of quaternary ammonium dithiocarbonates. B was then treated with methyl iodides, as has previously been reported.[1] The products were identified through comparison with authentic samples via their gas chromatographic retention times (silicone grease column, 130—180°C). The results are shown below.

$$\left.\begin{array}{l} \mathrm{I(R=Me) + MeSCOSEt^{1a)}} \\ \mathrm{I(R=Et) + MeSCOSMe^{1a)}} \\ \mathrm{I(R=Et) + MeSCOSEt} \end{array}\right\} \rightarrow$$

$$\mathrm{MeSCOSMe + MeSCOSEt + EtSCOSEt + I(R=Me) + I(R=Et)} \qquad (2)$$

$$\mathrm{I(R=Et) + MeSCSSMe^{2)} \rightarrow MeSCSSMe + MeSCSSEt^{3)} + I(R=Me) + I(R=Et)} \qquad (3)$$

$$\mathrm{I(R=Et) + C_6H_5COSMe^{4)} \rightarrow C_6H_5COSMe + C_6H_5COSEt^{4)} + I(R=Me) + I(R=Et)} \qquad (4)$$

Reactions 2—4 showed that almost all of the ethyl radicals of I(R=Et) were transferred to the esters and that a large amount of I(R=Me) was found in the residual ammonium salts. Although thiolesters reacted easily with I(R=Et), esters such as methyl benzoate, dimethyl carbonate[5] did not react under similar reaction conditions.

These experimental results show that I(R=Me) is more stable than I(R=Et), that carbonyl-SR bond fisson may occur, and that then mercapto groups may exchange with each other.

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