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THE REACTIONS OF SOME 1,1,1-TRIBROMO-ALKYL SYSTEMS WITH THIOLATE ANIONS

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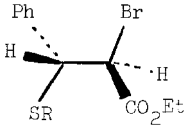
Summary Compounds containing a 1,1,1-tribromoethyl group are normally dehydrobrominated by reaction with sodium thiolates. If a 1,1,1-tribromobut-3-ene fragment is present cyclisation to a 2,2-dibromocyclopropylmethyl thioether or rearrangement are also observed.

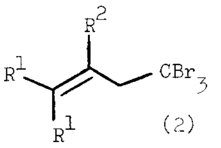
Compounds containing trihalomethyl groups have been reported to undergo a variety of reactions with thiolate anions. 1,1-Diaryl 2,2,2-trichloroethanes undergo 1,2-dehydrohalogenation to 2,2-dichlorostyrenes, apparently by an E_2H mechanism,[1] while compounds XCF_2-CH_2Y (X, Y = halogen) undergo apparent substitution of $X^{\ominus}$ by $RS^{\ominus}$.[2a] In the latter case it is not clear whether a direct nucleophilic substitution at carbon is involved and indeed, when X and Y are both bromine, a debromination is observed; 1,2-dechlorination is also reported in polychloroethane derivatives.[2b] In a related photolytic reaction, the substitution of iodine in CF_3I by certain thiolates, the process appears to be initiated by electron transfer from $RS^{\ominus}$ to the haloform, followed by loss of halide ion.[3] A further alternative is seen in the reaction of $RCCl_3$ with EtSH-Et_3N when reduction to $RCHCl_2$ is observed; this process is however limited to compounds having electron withdrawing R-groups.[4] We now wish to report the reactions of a number of tribromomethyl derivatives with sodium thiolates.

On refluxing for 1 hr with an equivalent of $NaSPr^i$ in MeOH, 2,2,2-tribromoethylbenzene[5] was converted to 2,2-dibromostyrene (47%). Addition of a second equivalent of $NaSPr^i$ led to a 3.6 : 1 mixture of cis- and trans-2-bromostyrenes. A similar reduction has been reported on treatment of PhCH=C(Br).CO_2Et with thiolate anions, when ethyl cinnamate is obtained; in this case an initial addition of RSH across the alkene is thought to lead to (1), which eliminates RSBr on reaction with $RS^{\ominus}$.[6] Such a mechanism may operate in the present case, although a trans-addition followed by a trans-elimination might be expected on conformational grounds to produce largely trans-2-bromostyrene. Direct attack of $RS^{\ominus}$ on the soft halogen to form a vinyl anion or an electron transfer process and loss of halide ion to form a vinyl radical, followed by hydrogen abstraction, seem to be alternatives.[7] Treatment of the mixed 2-bromostyrenes with $NaSPr^{i}$-MeOH at reflux led to conversion of the cis-isomer to cis-2 thioethylstyrene; the trans-isomer was largely unchanged after 4 hr.[8]

Dehydrobromination of a tribromoethyl-fragment was also observed on treatment of $EtS{\cdot}(CH_2)_3{\cdot}CBr_3$ or $EtS{\cdot}CH_2{\cdot}C(Me){=}CH{\cdot}CH_2CBr_3$ with one equivalent of EtSNa-MeOH, when $EtS{\cdot}(CH_2)_2{\cdot}CH{=}CBr_2$ and $EtS{\cdot}CH_2{\cdot}C(Me){=}CH{-}CH{=}CBr_2$ respectively were the only major products. In each case the starting tribromide was obtained from the tetrabromide $Br{\cdot}(CH_2)_3{\cdot}CBr_3$[9] or $BrCH_2{\cdot}C(Me){=}CH{\cdot}CH_2CBr_3$[9] respectively by reaction with EtSNa-MeOH. The former reaction led cleanly to $EtS{\cdot}(CH_2)_3{\cdot}CBr_3$ (69%) with one equivalent of thiolate, indicating that substitution of an alkyl bromine occurs faster than dehydrobromination of a 1,1,1-tribromobutane fragment. In the latter case a mixture of $EtS{\cdot}CH_2{\cdot}C(Me){=}CH{-}CH_2CBr_3$ and $EtS{\cdot}CH_2{\cdot}C(Me){=}CH{-}CH{=}CBr_2$ was obtained, indicating that dehydrobromination of a 1,1,1-tribromobut-3-ene fragment occurs at a comparable rate to the substitution. The related bromotrichloride, $BrCH_2CH{=}CH{-}CH_2CCl_3$ undergoes initial displacement of the allylic bromine.[10]



(1)



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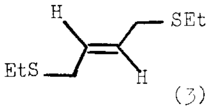

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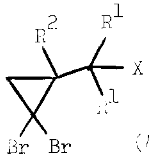

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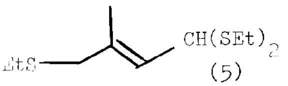

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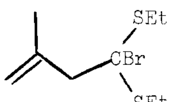

(6)

Treatment of 4,4,4-tribromobut-1-ene (2, $R^1 = R^2 = H$)[11] with one equivalent of EtSNa or $Pr^{i}SNa$ in MeOH for 17 hrs at 20° led to complete reaction and the formation of 1,1-dibromobuta-1,3-diene (27%) and dialkyldisulphide as the only isolable products. However, if the tribromid was treated with one equivalent of EtSNa in DMF, only partial reaction occurred and trans-1,4-di(thioethyl)but-2-ene (3) was produced. With two equivalents of the reagent the starting material was completely consumed and (3) was isolated in 38% yield. The product was identical to a sample obtained by treatment of trans-1,4-dibromobut-2-ene with NaSEt-MeOH (85%). The formation of (3) from (2, $R^1 = R^2 = H$) apparently involves an overall reduction together with either a rearrangement of the carbon skeleton or removal of a proton from C-3 and addition of two protons at C-4. 1,1-Dibromobuta-1,3-diene can be ruled out as an intermediate in this process as treatment with NaSEt-DMF under the reaction conditions led to complex products which did not include (3). The thioether (4, X = SEt, $R^1 = R^2 = H$)[9] can also be excluded as it was stable to the reaction conditions. A third possible intermediate, 1-thioethylbuta-1,3-diene, also seems unlikely as it too appears to be stable to thiolate anions.[12]

The methylated derivative (2, R^1 = Me, R^2 = H) was also dehydrobrominated, to produce 1,1-dibromo-4-methylpenta-1,3-diene, (50%) on reaction with one equivalent of Pr^iSNa-MeOH. In DMF or HMPT, however, the cyclopropane (4, R^1 = Me, R^2 = H, X = SPr^i) (5%) was obtained in addition to the diene (53%). In the case of (2, R^1 = H, R^2 = Me) the corresponding cyclopropane (4, X = SPr^i, R^1 = H, R^2 = Me) was obtained even with $NaSPr^i$-MeOH (47%), while with $NaSPr^i$-DMF the thioacetal (5) (28%) was also produced, together with a very minor component whose spectroscopic properties were consistent with structure (6). The formation of compounds (4) from (2) appears to result from homoallyl-cyclopropylmethyl rearrangement during nucleophilic displacement of $Br^\ominus$ by $RS^\ominus$, analogous to the cyclisation observed in solvolytic reactions of 4-bromobut-1-enes.[13] A cationic rearrangement seems less likely, however, in the present case and rearrangement of an anion[14] or radical[15] derived respectively by attack of $RS^\ominus$ on the soft halogen or by electron transfer and loss of halide ion, must be considered - although in both cases the open chain form is generally favoured. It is interesting to note that the reaction of bromoform with $EtS^\ominus$-DMF leads to both $CH(SEt)_3$ and $CH_2(SEt)_2$, and that no build up of CH_2Br_2 occurs during the reaction. Iodoform reacts with $EtS^\ominus$-DMF to give $CH_2(SEt)_2$ together with CH_2I_2 - which is converted to the disulphide by excess $EtS^\ominus$-DMF. It seems likely again that these reductions also involve initial attack on halogen. The reactions of chloroform and bromoform with $ArS^\ominus$ have previously been extensively analysed and found to occur through an α-elimination of HBr to form a carbene, followed by trapping.[16,17]

The great variety of processes involved in reactions of thiolates with halides mean that detailed studies are needed to identify the mechanisms of the above reactions.

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