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Trichloormethaansulfeenchloride met mercaptanen, sulfinaten en olefinen.

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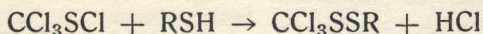
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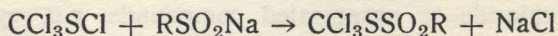
X. SUMMARY.

It is known that asymmetric disulphides can be formed from aromatic sulphenic chlorides and mercaptans. In the work described in this thesis an analogous reaction has been carried out with trichloromethanesulphenic chloride, whereby only the chlorine atom attached to the sulphur atom proved to be reactive. The following reaction has been shown to take place:



In this manner disulphides have been prepared in which R represents an aliphatic, alicyclic or aromatic group. With few exceptions all products are liquids, fuming when exposed to the air.

Trichloromethanesulphenic chloride reacts with aromatic sulphinates, forming trichloromethyl arylthiolsulphonates:

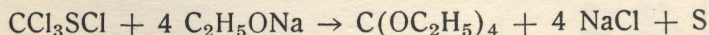


The chlorine analysis of these compounds could be carried out by titration after decomposition by sodium methylate.

The reaction of trichloromethanesulphenic chloride with aliphatic sodium mercaptides yielded chiefly disulphides RSSR and a small quantity of hexa-alkylthio-dimethyldisulphides: $(\text{RS})_3\text{CSSC}(\text{SR})_3$.

Since a sulphenic chloride RSCI and a sodium mercaptide R'SNa always give two symmetric disulphides RSSR and R'SSR', the results reported are not unexpected. These new compounds are, with one exception, liquids, which can be purified by high vacuum distillation. Hexa-tert.butylthio-dimethyldisulphide is a colourless, crystalline compound, volatile with steam.

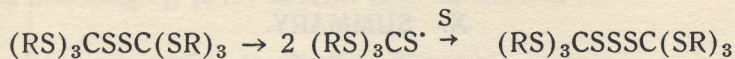
Trichloromethanesulphenic chloride and aromatic mercaptides yield not only disulphides RSSR, but also large quantities of hexa-arylthio-dimethyltrisulphides $(\text{RS})_3\text{CSSSC}(\text{SR})_3$. The latter compounds exhibit a bright yellow colour. To explain the formation of these trisulphides, we can first postulate the intermediate formation of sulphur by the alcoholate present in the alcoholic solution of the mercaptide¹):



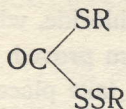
The disulphide originally formed $(\text{RS})_3\text{CSSC}(\text{SR})_3$ can probably

¹) Tieckelmann and Post, J. Org. Chemistry **13**, 265 (1948).

split into free radicals, which may then add to the sulphur atom.



The oxidation of the trisulphides with hydrogen peroxide in acetic acid gave trithiopercarbonic diaryl esters:



Reduction of the m-tolyl ester with lithium aluminium hydride gave methyl alcohol, methyl mercaptan, hydrogen sulphide and m-tolyl mercaptan. Thus it is evident that an oxygen and a sulphur atom (not belonging to a thioaryl group) are attached to the central carbon atom.

In a number of cases it was possible to add trichloromethanesulphenic chloride to unsaturated compounds, e.g. cyclohexene, styrene, phenylacetylene, diallyl, allyl chloride and isobutenyl chloride. In some of the reactions irradiation with U.V. light was required. Several of the addition products formed azeotropic mixtures with trichloromethanesulphenic chloride. In the case of the addition to allyl chloride it was proved that the reaction takes place in the same manner as with aromatic sulphenic chlorides: the chlorine atom adds to the least hydrogenated carbon atom of the double bond, thus:

