391. *The Reaction of Carbon Tetrachloride with Sulphide Ions.*

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A vigorous exothermic reaction was noticed when the sulphides or hydrosulphides of aliphatic primary or secondary amines were brought into contact with carbon tetrachloride. Examination of the ultraviolet spectra of the products indicated the presence of dithiocarbamates and thioureas. Further work showed that reasonable yields of dialkylthioureas could be obtained from primary amines.

Experimental.—The following are examples of the type of reaction effected.

(i) A solution of n-octylamine (13·5 g., 0·105 mole) in 2,2,4-trimethylpentane (200 ml.) was saturated with hydrogen sulphide, and carbon tetrachloride (8 g., 0·052 mole) was added. The mixture was boiled under reflux for 2 hr., and the product washed with water to remove amine hydrochloride. The solvent was evaporated, leaving a crystalline product (Found: C, 67·7; H, 12·0; N, 9·3; S, 10·1. Calc. for $C_{17}H_{36}N_2S$: C, 67·8; H, 12·1; N, 9·3; S, 10·7%). The yield of crude material was 4·8 g. and purity, estimated from the ultraviolet spectrum, was 95%. After recrystallisation from alcohol–water, the product had m. p. 53° and $\lambda_{max.}$ (in $Pr^{\beta}OH$) 241 mμ (ε 13,000; in agreement with an authentic sample); a sample of *NN'*-di-n-octylthiourea prepared by established methods had m. p. 56°. Octyl dithiocarbamate ions were present in the aqueous extract of the reaction mixture, as shown by $\lambda_{max.}$ (in $Pr^{\beta}OH$) 286 and 256 mμ.

(ii) Carbon tetrachloride (0·05 mole), n-hexylamine (0·1 mole) and sodium sulphide nonahydrate (0·05 mole) did not react when shaken together for 18 hr. After addition of water (5 ml.), the solution rapidly darkened and the temperature rose to the b. p. of carbon tetrachloride in about 30 min. After 1 hr., more water (200 ml.) was added and the oil which separated was washed with dilute hydrochloric acid and water; the residue solidified overnight (yield 6·0 g.). It was found by ultraviolet spectroscopy to be ~90% pure *NN'*-di-n-hexylthiourea. The yield was 90% of that required for the reaction, $CCl_4 + 4R{\cdot}NH_2 + Na_2S \longrightarrow R{\cdot}NH{\cdot}CS{\cdot}NHR + 2R{\cdot}NH_3^+Cl^- + 2NaCl$. Several other primary amines also yielded the corresponding dialkylthioureas. Dithiocarbamate was also detected in many of the solutions. Secondary aliphatic amines also react, but do not readily give the tetra-alkylthioureas; the products will be described elsewhere.

(iii) To a 9% w/v solution (30 ml.) of sodium sulphide nonahydrate in methanol was added carbon tetrachloride (1 ml.) (~$3Na_2S : CCl_4$). Next morning the precipitated sodium chloride was removed; the solution contained xanthate ions ($\lambda_{max.}$ 303 and 225 mμ [2]). On the basis of an extinction coefficient of 15,000 for xanthate ions, the yield was 50% for the reaction: $ROH + 2S^{2-} + CCl_4 \longrightarrow RO{\cdot}CS{\cdot}S^- + 3Cl^- + HCl$. Impure sodium methyl xanthate was obtained by evaporation of the excess of methanol.

(iv) When alcoholic solutions of primary amines were treated with carbon tetrachloride and sodium sulphide, both xanthate and dithiocarbamate ions were formed, as shown by the ultraviolet spectra of the solutions. Overnight, a new absorption band, at 252 mμ, appeared, partly masking the short-wave dithiocarbamate maximum; this was possibly due to the thioncarbamate, RO·CS·NHR.[2] There was evidence of trithiocarbonate formation when an aqueous solution of sodium sulphide was shaken for several days with carbon tetrachloride (red solution with an ultraviolet spectrum resembling that of sodium trithiocarbonate).

Discussion.—The mechanism of the reaction has not been established in detail, but the common factor appears to be a reaction between carbon tetrachloride and sulphide ions, involving (*a*) replacement of one chloride by S^{2-}, to give an anion or (*b*) replacement of two chlorine atoms by one S^{2-}, to give a thione group. If the latter were the initial reaction, the key intermediate would be thiocarbonyl chloride; the known reactions of this compound would account for the observed products. It is unlikely that attack by amine on the carbon tetrachloride initiates the reaction, because (i) the reaction between carbon tetrachloride and amine in the absence of sulphide is relatively slow unless

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[1] Treiber, *Monatsh.*, 1951, **82**, 53.

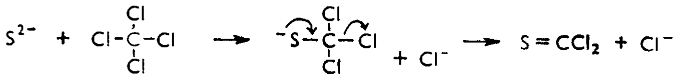
[2] Janssen, *Rec. Trav. chim.*, 1960, **79**, 454.

catalysed,[3] and (ii) the reaction between alcohols, carbon tetrachloride, and sulphide is comparable in rate with that between an amine, carbon tetrachloride, and sulphide, *i.e.*, the rate is determined mainly by the sulphide. There is an interesting parallel between this work and that of Milligan and Swan,[4] who showed that dialkylthioureas could be prepared from a primary amine, sulphur, and methylene chloride or chloroform, but not carbon tetrachloride. We, on the other hand, obtained dialkylthioureas from amine, sulphide ions, and carbon tetrachloride, but found no thiourea when chloroform replaced carbon tetrachloride. Writing the carbon tetrachloride as involving hydrogen sulphide, enables the oxidation levels to be compared:

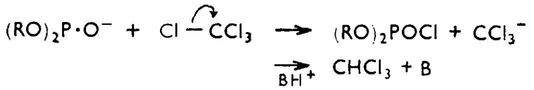
$$2R{\cdot}NH_2 + H_2S + CCl_4 \longrightarrow CS(NHR)_2 + 4HCl$$
$$2R{\cdot}NH_2 + S + CHCl_3 \longrightarrow CS(NHR)_2 + 3HCl$$
$$2R{\cdot}NH_2 + 2S + CH_2Cl_2 \longrightarrow CS(NHR)_2 + 2HCl + H_2S$$
$$\text{[cf. also} \quad 2R{\cdot}NH_2 + 3S + CH_3Cl \longrightarrow CS(NHR)_2 + HCl + 2H_2S\text{]}$$

The reaction between carbon tetrachloride and sulphide ions may provide a useful alternative to established methods for preparing sulphur derivatives of carbonic acid. There are indications that the experimental conditions can be altered to yield dithiocarbamates as major products of the reaction in the presence of amines. Spectroscopic evidence has been obtained for the formation of other products, some not yet identified.

[Addendum]. A Referee has drawn the authors' attention to Steinberg's work [5] on the reaction between dialkyl phosphites and carbon tetrachloride. Our reaction can be considered as involving nucleophilic displacement on carbon:



Steinberg's reaction involves nucleophilic displacement on chlorine:



where B = base (tertiary amine).

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[3] Cromwell, Foster, and Wheeler, *Chem. and Ind.*, 1959, 228.
[4] Milligan and Swan, *J.*, 1960, 1194.
[5] Steinberg, *J. Org. Chem.*, 1950, **15**, 637.