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1,1-SUBSTITUTED DICHLOROMETHYLENE COMPOUNDS

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Abstract. 1,1-Substituted dichloromethylene compounds are produced in the reaction of carbon tetrachloride or bromotrichloromethane with primary and secondary aliphatic amines containing at least two α-hydrogens on the alkyl group of the amine. The mass spectra of these compounds are reported. A mechanism which depicts the product formation is proposed.

Dichloromethylene compounds are reported to be produced in the reactions of enamines with carbon tetrachloride in diffuse light[1,2] Hydrolysis of these compounds affords α-dichloromethyleneketones. Polyhalogenoalkanes are known to give amine hydrochlorides alongwith several other products[3–8] when reacted with amines. Smith and Malik reported the presence of dichloromethylene compounds in the reaction of butylamine with carbon tetrachloride catalysed by copper salts. In the present investigation the reaction of all the four primary butylamines, diethylamine, di-n-, di-*s*- and di-isobutylamines, morpholine, *N*-methylmorpholine and triethylenediamine with carbon tetrachloride or bromotrichloromethane have been studied to established the presence of 1,1-substituted-dichloromethylene compounds.

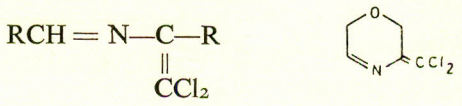
Experimental

All the amines were purified by standard techniques. Carbon tetrachloride or bromotrichloromethane used were spectroscopic grade. Copper acetate used was Analar. Mass spectra were recorded on an AE1 MS 12 mass spectrometer coupled to a Pye-104 gas chromatograph. The glass column used was 2.4 m in length with I.D. 4 mm, packed with 20% Carbowax 20M on alkaline Celite (100–120 mesh).

To 100 ml polyhalogenoalkane (CCl_4 or CCl_3Br) was added 50 ml amine containing 10 mg copper acetate in a flask fitted with a reflux-condenser. The mixture was refluxed for ½ hr and allowed to cool. An aliquote sample of the reaction mixture was taken out from the flask by Hamilton microsyringe and injected on the gas chromatograph fitted with 20% Carbowax 20M celite column. The products of the reaction mixture were resolved on the column under appropriate conditions and analysed by combined GLC–mass spectrometry.

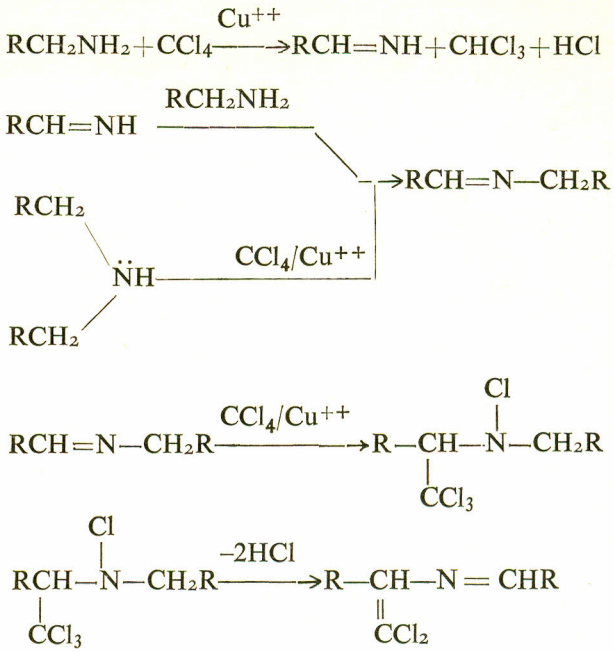
Results and Discussion

The nature of the reaction between amines and polyghalomethanes remains the same at room temperature as at the reflux temperature, except that an extra product is formed in case of amines containing two α-hydrogen on the alkyl group of the amine. (Table 1 and mass plates). The 1,1-substituted-dichloromethylene compound is not formed when the amine has *s*-alkyl groups, *t*-alkyl groups, or is a cyclic *t*-amine with *s*-alkyl groups, *t*-alkyl groups, or is a cyclic has not been characterised fully for various reasons. It is formed in small amounts in the presence or absence of air and is difficult to isolate in pure state either by preparative glc or by solvent extraction method. However, analysis of the peak assigned for this compound by combined GLC–mass spectrometry revealed that the compound contain two chlorine atoms and a possible structure for such compound would be:



where R, ethyl, n-propyl or isopropyl.

It seems that substituted-dichloromethylene compound in the reaction of amines investigated arises somehow by the addition of CCl_4 or CCl_3 Br to the Schiff's base produced in the reaction followed by dehydrochlorination. A possible mechanism is proposed below:



From the results it is concluded that at least two α-hydrogens are necessary on the alkyl group of the amine to form the substituted-dichloromethylene compound, otherwise a similar compound would have

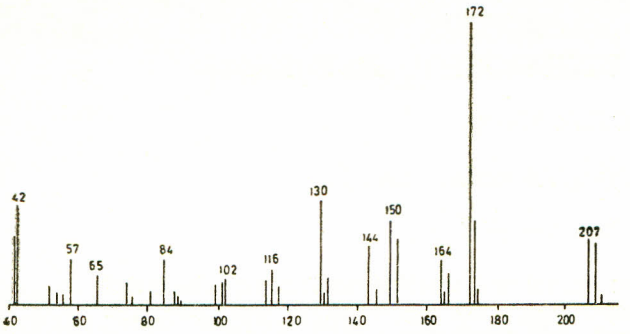


Fig. 1. Dichloromethylene compound from n-ButNH$_2$ or (n-But)$_2$ NH and CCl_4 reaction.

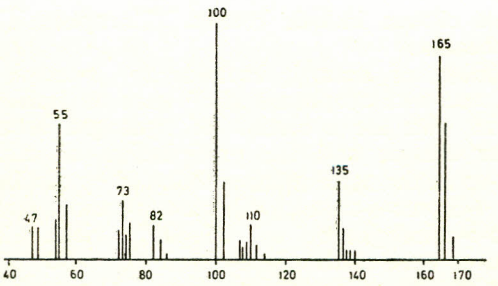
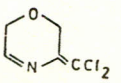


Fig. 3. Dichloromethylene compound from morpholine and CCl_4 reaction.

TABLE 1.

Substrate	Possible structure	Mass	Product formed in CCl_4 CCl_3 Br
n-Butylamine	C_3H_7—C(=CCl_2)—N=CH—C_3H_7	207	+
Di-n-butylamine		207	+
Isobutylamine	C_3H_7—C(=CCl_2)—N=CH—CH(CH_3)(CH_3)	207	+
Diisobutylamine		207	+
s-Butylamine	—	—	
Di-s-butylamine	—	—	
t-Butylamine	—	—	—
Diethylamine	CH_3—C(=CCl_2)—N=CH—CH_3	151	+
Morpholine		165	
N-Methylmorpholine		—	—
Triethylendiamine		—	—

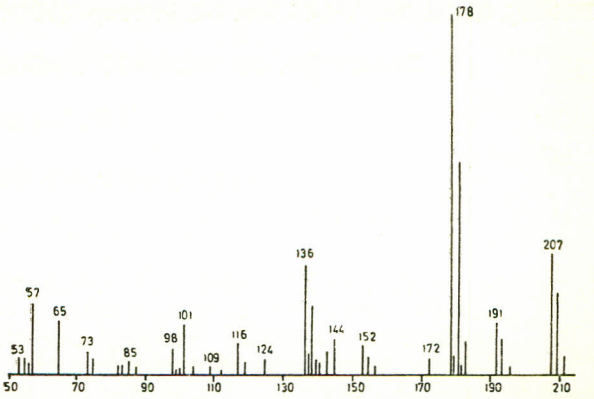


Fig. 2. Dichloromethylene compound from iso-ButNH$_2$ or (iso-But)$_2$ NH and CCl_4 reaction.

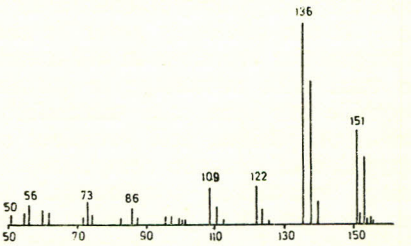


Fig. 4. Dichloromethylene compound from (C_2H_5)$_2$ NH and CCl_4 reaction.

been produced with s- or t-mono and dibutylamines The structure proposed for the compound fits well with the present findings.

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