Tetrahedron, 1964, Vol. 20, pp. 1 to 12. Pergamon Press Ltd. Printed in Northern Ireland

A STUDY OF CERTAIN REACTIONS OF TRIHALOGENOACETIC ACIDS

THE REACTION OF TRICHLORO- AND TRIBROMOACETIC ACIDS WITH SCHIFF BASES*

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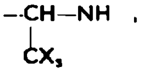
(*Received* 1 *August* 1963; *in revised form* 11 *October* 1963)

Abstract—The reaction of trichloro- and tribromoacetic acids with some imines (the derivatives of aromatic aldehydes and aliphatic as well as some aromatic amines) has been investigated. It has been found that these acids when heated in an organic solvent react with the imines with evolution of carbon dioxide and in the majority of cases the formation of 1,1,1-trihalogeno-2-aminoethane derivatives in good yield. A mechanism has been proposed for this reaction which consists in an intermediate formation and cryptoradical decarboxylation of the esters of α-aminoalcohols.

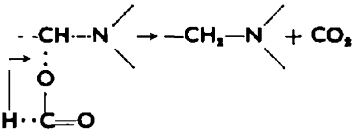
IN A previous communication[1] the reaction between trichloro- and tribromoacetic acids and imines, leading to the formation of the derivatives of trihalogenoaminoethane,



$$-\underset{\displaystyle CX_3}{\underset{|}{CH}}-NH\ ,$$

has been described.

As a result of experimental investigations on the reduction of certain imines and derivatives of methylene-bis-amines with formic acid the following hypothesis[3] has been advanced. In the reaction investigated as well as in Leuckart-Wallach's reaction the esters of α-aminoalcohols and of formic acid are the intermediate products which undergo decarboxylation, in accordance with the following radical or cryptoradical mechanism:



It is probable that besides formic acid, other carboxylic acids could form as intermediate products, the esters of α-aminoalcohols, undergoing analogous decarboxylation. Because of their instability,[4-7] trichloro- and tribromoacetic acids should react

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* For Part 1 see communication[1], for the reaction with methylene-bis-amine derivatives see communication[2].

[1] A. Lukasiewicz, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.* **11**, 15 (1963).

[2] A. Lukasiewicz, *Bull. Acad. Polon., Sér. Sci. Chem.* **11**, 187 (1963).

[3] A. Lukasiewicz, *Tetrahedron* **19**, 1789 (1963).

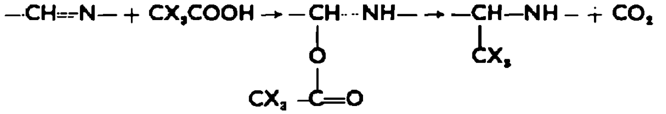
[4] P. Petrenko-Kritschenko and V. Opotzki, *Ber. Dtsch. Chem. Ges.* **59**, 2137 (1926).

[5] R. A. Fairclough, *J. Chem. Soc.* 1188 (1938).

[6] P. Johnson and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* **175**, 122 (1940).

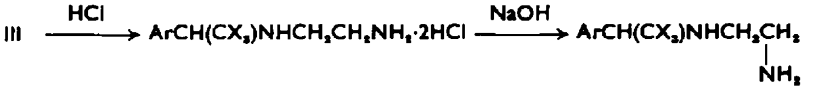
[7] F. H. Verhoek, *J. Amer. Chem. Soc.* **67**, 1062 (1945).

with the imines yielding the corresponding trihalogeno-aminoethane derivatives, according to the following equation:



$$\mathrm{-CH{=}N- + CX_3COOH \rightarrow -\underset{\substack{|\\ O\\ |\\ CX_3-C=O}}{CH}-NH- \rightarrow -\underset{\substack{|\\ CX_3}}{CH}-NH- + CO_2}$$

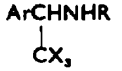
These acids react with Schiff's bases (derived from aromatic aldehydes and aliphatic amines e.g. ethylenediamine, cyclohexylamine, benzylamine, *p*-chlorobenzylamine, n-octylamine, allylamine and some aromatic amines e.g. aniline, *p*-chloroaniline, *p*-phenetidine) evolving carbon dioxide and with formation in the majority of cases of the trihalogenoaminoethane derivatives (Tables 1 and 2) in good yield. In the reaction of Schiff's bases derived from ethylenediamine, $ArCH{=}NCH_2CH_2N{=}CHAr$ (I), a mixture of products, consisting of the derivatives of bis-(trihalogenomethyl)—$ArCH(CX_3)NHCH_2CH_2NH(CX_3)CHAr$ (II) and of the mono-(trihalogenomethyl) derivatives—$ArCH(CX_3)NHCH_2CH_2N{=}CHAr$ (III), is formed. Using two or more moles of the acid for one mole of the base (I), the compounds II are obtained as main products of the reaction. However, in the case of equimolar ratio of the reagents the reaction results predominantly in the compounds III. The latter under the influence of hydrochloric acid undergo hydrolysis to form the hydrochlorides of the amines IV.



IV

$$\mathrm{III \xrightarrow{HCl} ArCH(CX_3)NHCH_2CH_2NH_2\cdot 2HCl \xrightarrow{NaOH} ArCH(CX_3)NHCH_2\underset{\substack{|\\ NH_2}}{CH_2}} \qquad \mathrm{IV}$$

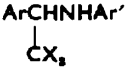
Bis-benzylidenepropylenediamine (Table 1, Nr. 13, 14) reacts in a similar way. During experiments with the imines—the derivatives of aliphatic monoamines—the material used was obtained by heating the components in equimolar ratio and removing the water formed in the reaction as an azeotropic mixture with benzene. The final products of the reaction with the trihalogenoacetic acids were consistent with the formula:



V

$$\mathrm{Ar\underset{\substack{|\\ CX_3}}{CH}NHR} \qquad \mathrm{V}$$

In the reaction of trichloroacetic acid with the aromatic imines, $ArCH{=}NAr'$ (VI, $Ar'{=}C_6H_5^-$ or $Cl{-}C_6H_4^-$) besides evolution of carbon dioxide the formation of the hydrochloride was observed. The product was not as expected but if the group —OR was introduced into Ar′ in the *para* position, the reaction was normal, (Table 2, Nr. 23). Tribromoacetic acid also yields with benzylideneaniline products with the following formula:

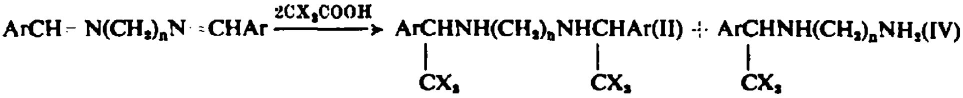


VII

$$\mathrm{Ar\underset{\substack{|\\ CX_3}}{CH}NHAr'} \qquad \mathrm{VII}$$

The structure of the trihalogenoaminoethane derivatives has been determined by analysis and a study of their properties. The compounds II, V and VII form hydrochlorides, undergoing hydrolysis in the presence of water. By shaking the hydrochlorides with benzene and water the corresponding free amines pass quantitatively from the aqueous phase into the benzene. The stability of the amines obtained (even on heating), with regard to mineral acids, and their lower basicity indicate that

TABLE 1. YIELDS AND CONDITIONS (TEMP) OF THE REACTION:

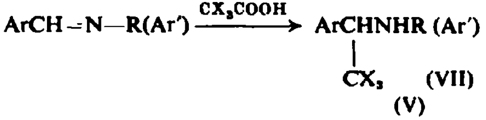


$$\mathrm{ArCH{=}N(CH_2)_nN{=}CHAr} \xrightarrow{2CX_3COOH} \underset{CX_3}{\mathrm{ArCH}}\mathrm{NH(CH_2)_nNH}\underset{CX_3}{\mathrm{CH}}\mathrm{Ar(II)} + \underset{CX_3}{\mathrm{ArCH}}\mathrm{NH(CH_2)_nNH_2(IV)}$$

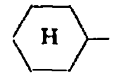
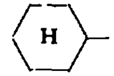
Reaction product					Yield* %	Temp °C
Nr	Ar	n	X	II (IV)		
1	C_6H_5-	2	Cl	II	50 +	70
2	C_6H_5-	2	Cl	IV	27	
3	C_6H_5	2	Br	II	55	50
4	4-CH_3O—C_6H_4-	2	Cl	II	66 +	60
5	4-CH_3O—C_6H_4-	2	Cl	IV	16	
6	4-CH_3O—C_6H_4-	2	Br	II	80	40
7	2-Cl—C_6H_4-	2	Cl	II	18 +	100
8	2-Cl—C_6H_4-	2	Cl	IV	35	
9	3-Cl—C_6H_4-	2	Cl	II	50 –	100
10	3-Cl—C_6H_4-	2	Cl	IV	27	
11	4-Cl—C_6H_4-	2	Cl	II	37 +	100
12	4-Cl—C_6H_4-	2	Cl	IV	37	
13	C_6H_5-	3	Cl	II	†	70
14	C_6H_5-	3	Cl	IV		

* The yields, given in communication (1) concern the rough products, selected in other way.
† The experimental data will be given in a subsequent publication.

TABLE 2. YIELDS AND CONDITIONS (TEMP) OF THE REACTION:



$$\mathrm{ArCH{=}N{-}R(Ar')} \xrightarrow{CX_3COOH} \underset{CX_3}{\mathrm{ArCH}}\mathrm{NHR\,(Ar')}\quad \underset{(V)}{(VII)}$$

Nr	Ar	R(Ar')	X	V (VII)	Yield* %	Temp °C
15	C_6H_5-		Cl	V	62	70
16	C_6H_5-		Br	V	82	50
17	C_6H_5-	$C_6H_5CH_2$-	Cl	V	59	70
18	C_6H_5	4-Cl—$C_6H_4CH_2$-	Cl	V	43,5	70
19	C_6H_5-	4-Cl—$C_6H_4CH_2$-	Br	V	68	50
20	C_6H_5-	n—C_8H_{17}-	Cl	V	46	70
21	4-CH_3O—C_6H_4-	$CH_2{=}CH{-}CH_2$-	Cl	V	56,5	60—70
22	C_6H_5-	C_6H_5-	Br	VII	72	100
23	C_6H_5	4-C_2H_5O—C_6H_4-	Cl	VII	57,5	100

* These yields concern the equimolar ratio of the reagents; the use of the acid in excess increases yields of the reaction.

the imine bond has disappeared and the CX_3 group become attached to the azomethine carbon. The free amines II and V are relatively stable and their hydrochlorides are very stable. The amines VII are less stable and their hydrochlorides very hygroscopic. It has been observed that the derivatives of trichloroethylamines are generally more stable than the analogous derivatives of tribromoethylamines. From the latter, when stored, the evolution of hydrogen bromide has frequently been observed. The instability of N-(1-phenyl-2,2,2,-tribromoethyl)cyclohexylamine should be pointed out (Table 2, Nr. 16). The free amines IV having the consistency of oils, were analysed as dihydrochlorides. These amines when heated with aldehydes yield imines of the type $ArCH(CX_3)NHCH_2CH_2N{=}CHAr'$. Moreover, it is possible to separate the azomethine derivatives (III) from the reaction mixture obtained from an equimolar ratio of the acid and the imines of the type I. In the case of the amines of the type IV, the trichloroethyl derivatives are relatively stable except for a *o*-chlorophenyl derivative (Table 1, Nr. 8); and their hydrochlorides are much more stable; the tribromoethyl derivatives are much less stable and difficult to separate in the form of pure hydrochlorides. However, in the latter form their stability considerably increases.

The compounds (II) contain two identical asymmetric carbon atoms

$$(Ar\overset{*}{C}H(CX_3)NHCH_2CH_2NH(CX_3)\overset{*}{C}HAr)$$

and form a mixture of DL and meso stereoisomers. Only in some cases could these forms be separated by crystallization owing to a difference in their solubility, but a quantitative separation of all the isomers can easily be achieved owing to a marked difference in their basicity and their ability to form hydrochlorides. Thus, the hydrochloride of the more basic amine (A) can be precipitated by extraction from a benzene or ether solution with a 0·5 N–1 N hydrochloric acid solution, whereas the less basic amine (B) remains in solution. Then by using a more concentrated hydrochloric acid (e.g. 2 N) B can also be transformed into the hydrochloride. Both these forms are more easily extracted from ether than from benzene, when hydrochloric acid is used. Both the hydrochlorides after being shaken with a benzene-water mixture undergo hydrolytic decomposition and the form B decomposes more easily than A. The ability to form hydrochlorides by the amines of the type II also depends on the substituent in the benzene ring (Table 3). Apparently, the basicity of both A and B is diminished by the presence of a chlorine atom in the *ortho*, *meta* or *para* position of the benzene ring.

The presence or lack of hydrogen bonding with a halogen atom could be responsible for the difference in basicity between the amines A and B. Hydrogen bonding of a similar kind has been found in molecules of di- and trichloroethanol.[8] According to stereo-considerations a model containing hydrogen bonding should be proposed for the isomer DL. The possible schematic structure of such a molecule in its most stable state is presented in Fig. 1. A similar model for the meso form shows that steric

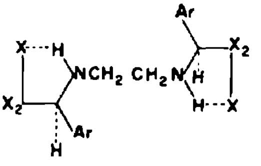


FIG. 1

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[8] J. Cantacuzène, *Bull. Soc. Chim. Fr.* 754 (1962).

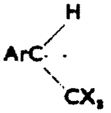
TABLE 3. THE BASICITY (THE ABILITY TO FORM HYDROCHLORIDES) OF SOME AMINES II AND V

Amine		Conc of hydrochloric acid and solvent used						
		0·5 N		1·0 N		2·0 N		
Nr	Form	Benzene	Ether	Benzene	Ether	Benzene	Toluene	Ether
1 II	A	−	+	+				
	B		+		+ (slowly)	−	+ (slowly)	
3 II	A	+	+					
	B		+	−	+	+		
4 II	A	−	−	+				
	B		−		+	−	+ (slowly)	
6 II	A	+ (slowly)	+					
	B		−		+	− (slowly)		
7 II	A				−	−		+
	B					−		−
9 II	A		−	−	+	+		
	B					−	−	−
11 II	A				−	−	+ (slowly)	+
	B				−	−	−	−
13 II	DL + meso		−	−	+	+		
15 V					−			+ (slowly)
17 V					−			+ (slowly)
20 V					+ (slowly)			+ (quickly)

+ The hydrochloride of the amine investigated is precipitated when the solution of the amine is shaken with hydrochloric acid.

− The hydrochloride of the amine is not precipitated.

hindrance caused by the vicinity of two aryl groups precludes a stable configuration (Fig. 2). And, therefore, a structure without hydrogen bonding (or with a weakened tendency towards its formation) and with a limited free rotation of the group



$$\mathrm{ArC}\overset{\mathrm{H}}{\underset{\mathrm{CX_3}}{\cdot}}$$

around the C—N axle should be considered as being more reasonable (Fig. 3). This interpretation is supported by the properties of the derivatives of propylenediamine and benzoic aldehyde. The increase in the length of alkylene bridge by one methylene group diminishes the difference in basicity between the two isomers so that the separation of the forms DL and meso becomes impossible. The more basic form (A) disappears as compared with the analogous derivatives of ethylenediamine (Table 3, comp. nr. 13 with nr. 1).

In view of these facts, the meso form should be considered as being the more basic, although theoretical considerations indicate that the hydrogen bonding with the halogen should tend to increase the electron density at the nitrogen atom and thus enhance the basic character of the dl form. To decide which of the two stereo-configurations should be ascribed to the forms A and B, more detailed investigations are necessary.

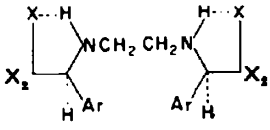


Fig. 2

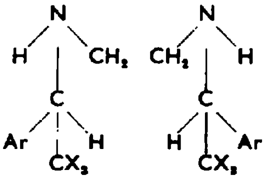
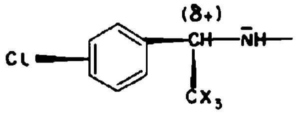


Fig. 3

The decrease in basic character of the trihalogenoaminoethane derivatives is an inductive effect and due to the influence of an electric field around the halogen atoms. A certain role should also be ascribed to the stereo-conditions involved. An additional decrease in the basicity of the amines, containing a chlorine atom in the benzene ring is apparently caused by a rise in the total inductive effect which diminishes the electron density at the α-carbon atom.



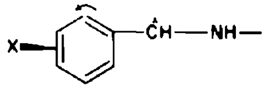
In the group of amines V, a derivative of cyclohexylamine is, for example, less basic than the derivative of n-octylamine (Table 3). This difference may be due to the stereo-conditions and the latter may also be responsible for the lower stability of 1,1,1-tribromo-2-N-cyclohexylaminoethane (Table 2, Nr. 16). The deviation from the normal reaction between the imines VI (derivatives of aniline and chloroaniline) and trichloroacetic acid may be due to the instability (under the reaction conditions) of the product initially formed. Since, for a similar reaction with benzylidene-*p*-phenetidine, the normal course of the reaction may be restored, it may be assumed that a further strong decrease in the basicity of the amines VII (the derivatives of CCl_3) may be the cause of the instability of these products, whereas the Ar′ shows the tendency towards "attraction" of electrons (aniline and chloroaniline).

The amine group of these intermediate products of type VII may be capable of loosing a proton and this fact is very likely responsible for the evolution of hydrogen chloride during the reaction.

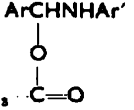
Although the experimental data are still insufficient, the observations made justify the hypothesis of the ester [cryptoradical] mechanism of the reaction between imines and trihalogeno acids.

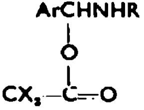
When the reaction of imines with trihalogenoacetic acids is controlled with regard to temperature and the rate of addition of the acids to the imines in a nonpolar medium, the reaction mixture remains homogeneous. But when the temperature of the reaction is too low then a crystalline salt of the reagents may be precipitated. This salt is relatively stable in comparison with the homogeneous reaction mixture. For example, when the trichloroacetic acid is added quickly to the benzene solution of bis-benzylideneethylenediamine at a temperature below 50°, the crystalline salt formed, when dry and stored at a temperature below its melting point, is relatively stable. The salt is insoluble in benzene and on heating to 70° undergoes decarboxylation, the process being however very slow as compared with the high rate of the reaction, occurring in the homogeneous mixture under appropriate conditions (the temperature above 60° and a slow addition of the acid to the base). The salt above its melting point (above 100°) decomposes rapidly with evolution of carbon dioxide and formation of the normal reaction products (a mixture of the mono- and bis-trihalogenmethyl derivatives). Crystalline salts, resulting from the imines and trichloroacetic acid, and with similar properties may be separated in some other cases. The relative stability of these salts may be used as an argument against the ionic mechanism generally accepted for the decarboxylation of trihalogenoacetic acids.[5,9–10]

It may be assumed that in toluene or benzene solutions, the esters decompose at a lower temperature than the crystalline salts. The formation of normal reaction products during decomposition of the salt at its melting point may also be due to the formation of an ester. The generally observed lower reactivity of the imines, containing a chlorine atom in the *ortho*, *meta* or *para* positions in benzene (a higher temperature of the reaction), as compared with the non-substituted imines, or the imines with a *p*-methoxy group, is more easily explained by accepting the crypto-radical (ester) mechanism than the ionic one. This may also explain the higher reactivity of the imines derived from aliphatic amines as compared with those derived from aromatic amines (higher temperatures of the reaction—Table 2). According to these observations, the presence of the chlorine atom in the benzene ring may result in a greater stability of the ester and this effect may be due to a partial positive charge on the α-carbon. The attraction of electrons from the benzene ring to the substituted chlorine may also make a resonant stabilization of an intermediate radical more difficult.



The lower reactivity of the imines (VI) as compared with the imines derived from aliphatic amines can be explained by a higher stability of the ester C than that of the ester D, the effect appearing as a result of a lower mobility of the free electron pair


$$\mathrm{ArCH\bar{N}HAr'}\text{—O—C(=O)—}\mathrm{CX_3}$$
C


$$\mathrm{ArCH\bar{N}HR}\text{—O—C(=O)—}\mathrm{CX_3}$$
D

of the nitrogen in esters C. As a result, the polarizability of the ester bond becomes lower.

Of the acids investigated, the highest reactivity towards imines was shown by the

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[9] F. H. Verhoek, *J. Amer. Chem. Soc.* **56**, 571 (1934).

[10] J. Hine, N. W. Burske, M. Hine and P. B. Langford, *J. Amer. Chem. Soc.* **79**, 1406 (1957).

tribromoacetic acid (lowest temperatures of the reaction), trichloroacetic acid requires higher temperatures, whereas trifluoroacetic acid does not react under the conditions applied. The order of the acids with respect to decarboxylation remains the same as that mentioned above.[5,10–11]

The change in the reactivity of the acids with respect to imines and their tendency to decarboxylate in reverse to the change in inductive effect of the halogen atoms, is not an argument against the cryptoradical mechanism of the reaction, although for the decarboxylation reaction of these acids the ionic mechanism has been accepted.

EXPERIMENTAL

(with the cooperation of Mrs D. Walkowska)

Materials. Anhydrous trichloroacetic acid of chemical grade and tribromoacetic acid of Schuchardt or Fluka were used. *The Schiff bases*—derived from ethylenediamine—were described in an earlier publication.[12] The benzene and toluene were of analytical grade.

The reaction between bis-benzylidene-ethylenediamine and trichloroacetic acid

N,N^1-bis-(1-phenyl-2,2,2-trichloroethyl)ethylenediamine (1 II) and N-mono-(1-phenyl-2,2,2-trichloroethyl)ethylenediamine dihydrochloride (2 IV).

(a) To a benzene solution (10 ml), containing 2·4 g (0·01 mole) imine, 3·4 g (0·02 mole) trichloroacetic acid in 10 ml benzene was added dropwise at 70°. During this addition vigorous evolution of gas from the homogeneous reaction mixture was observed. After 1·5 hr at 70° (evolution of gas nearly ceased) the mixture was cooled, washed with NaOH aq. and water and dried. After the benzene had been distilled off (red. press.) 10 ml ethanol was added. The precipitate (1B) formed was filtered off, yield 1·52 g, m.p. 126–129°, after crystallization from ethanol m.p. 131–132°*. (Found: C, 45·55; H, 3·6; N, 6·45. $C_{18}H_{16}N_2Cl_6$ requires: C, 45·55; H, 3·8; N, 5·9%). To the filtrate 3 ml conc. HCl was added, the precipitate (I) filtered off (yield 1·1 g) and shaken with a benzene–water mixture. After the benzene had been distilled off a small amount of ethanol was added to the oily residue, yielding after a few days a precipitate (1A), 0·85 g, m.p. 47–49°. (Found: C, 45·6; H, 3·8; N, 5·85; $C_{18}H_{16}N_2Cl_6$ requires: C, 45·55; H, 3·8; N, 5·9%).

The residue obtained after the hydrochloride (I) was evaporated to dryness under red. press. was treated with acetone, the precipitate formed filtered off, dissolved in water and made alkaline. The oil, brought down, was extracted with ether, the ether was distilled off, 1 ml conc. acid and ethanol added and the mixture evaporated under red. press. The residue was treated with dry acetone, which precipitated 0·75 g (2 IV). The product was purified by crystallization from dry ethanol (with a small addition of dry HCl), m.p. 177–178°. (Found: C, 35·3; H, 4·8; N, 8·25; $C_{10}H_{15}N_2Cl_5$ requires: C, 35·3; H, 4·4; N, 8·25%).

(b) The imine (4·8 g) was heated as described with 6·8 g trichloroacetic acid in benzene. After the reaction was complete, the mixture was shaken with 50 ml 1N HCl, yielding 2·63 g (1A).

The benzene layer was again shaken with HCl (1 : 3)† and the hydrochloride filtered off (3·89 g, 1B). The acidic layer from 1A was made alkaline, the oil was extracted with ether, the ether distilled off. The oil was dissolved in dry benzene and hydrogen chloride passed through, yielding the hydrochloride 2 IV (1·6 g), m.p. 177–178° after purification. The hydrochloride 1A was decomposed by shaking with a benzene-water mixture yield 1·95 g amine (1A), m.p. 47–49°.

From the hydrochloride (1B) in an analogous way (rapid decomposition, ethanol 2 : 1‡ added) the amine 1B (2·83 g) was obtained, after crystallization m.p. 131–132°.

(c) *The separation of the salt of bis-benzylideneethylenediamine with trichloroacetic acid.* To an imine solution in benzene (2·4 g in 10 ml) trichloroacetic acid (3·4 g) in benzene (10 ml) was added at 40°. A crystalline precipitate formed was filtered off, washed with benzene and dried in a vacuum

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* All m.p. are uncorrected.

† 1 part conc. HCl : 3 parts water.

‡ 2 parts ethanol : 1 part water.

[11] I. Auerbach, F. H. Verhoek and A. L. Henne, *J. Amer. Chem. Soc.* **72**, 299 (1950).

[12] Z. Eckstein and A. Lukasiewicz, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.* **7**, 789 (1959).

desiccator (4·8 g). (Found: N, 5·65%; $C_{20}H_{18}O_4N_2Cl_6$ requires: N, 5·0%). The precipitate (1·5 g) was heated in benzene for 2 hr at 70°. Insignificant evolution of gas was observed, while the precipitate remained insoluble. The salt recovered amounted to 1·38 g. The precipitate (1·5 g) was heated for several min at above 100° and decomposed with rapid evolution of gas. A liquid formed which had the odour of chloroform. After cooling the mixture was dissolved in ether and shaken with 2N HCl, yielding 1 II (0·32 g) and 2 IV (0·18 g).

N-(1-*phenyl-2,2,2-trichloroethyl)benzylideneethylenediamine*. Bis-benzylideneethylenediamine (4·8 g, 0·02 mole) was heated as in (a) and (b) with 3·4 g (0·02 mole) trichloroacetic acid. After cooling the mixture was washed with NaOH aq. and water and dried. The benzene was distilled off under red. press., ethanol 3:1 added, yielding 3·75 g (I), m.p. 69–78°. To the filtrate from I, 3 ml conc. HCl was added and evaporated to dryness, acetone added and the precipitate (II) filtered off. The precipitate (I) was dissolved in hot ethanol and crystallized in part on cooling, m.p. 126–130°. The ethanol was distilled off and the residue (III) repeatedly crystallized from hexane, m.p. 74–75·5°. (Found: N, 8·1%; $C_{17}H_{17}N_2Cl_3$ requires: N, 7·9%).

The precipitate (II) was treated with a benzene–water mixture and the benzene layer shaken with HCl, yielding the hydrochlorides (1A + 1B; 0·18 g). From the aqueous phase the hydrochloride (2 IV, 0·12 g) was obtained. The product (III), when treated with HCl yielded 2 IV and benzaldehyde (odour). By heating the free amine (2 IV) with benzaldehyde in ethanol and precipitation with water the compound III was obtained, m.p. 75·5–76·5 (from hexane).

The reaction of dibenzalethylenediamine with tribromoacetic acid

N,N¹-Bis(1-phenyl-2,2,2-tribromoethyl)ethylenediamine (3 II). Tribromoacetic acid (3·0 g) in benzene (10 ml) was added to 1·2 g amine in benzene (5 ml) at 50°. After 1 hr the reaction mixture was shaken, first with 1N HCl and then 1:3 HCl, yielding 0·98 g (3 A) and 1·25 g (3 B). The aqueous phase from I A was made alkaline, the oil extracted with ether, conc. HCl and ethanol added and the mixture evaporated to dryness, yielding 0·35 g of the hydrochloride difficult to purify on account of its instability.

From the hydrochloride (3 A) by shaking with a benzene–water mixture (slow decomposition) the amine (3 A) was obtained, m.p. 89·5–90·5° (from ethanol 95%). (Found: C, 29·3; H, 2·4; N, 4·4; $C_{18}H_{18}N_2Br_6$ requires: C, 29·1; H, 2·4; N, 3·8%).

From the hydrochloride (3 B; quick decomposition) the amine (3 B, 0·93 g) was obtained, m.p. about 160° decomp. (from a benzene–ethanol mixture), partial decomp. occurs at above 140° (Found: C, 29·1; H, 2·85; N, 3·85%).

The reaction of bis-(p*-methoxybenzylidene)ethylenediamine with trichloroacetic acid*

N,N¹-Bis-(1-(*p*-methoxyphenyl)-2,2,2-trichloroethyl)ethylenediamine (4 II) and N-mono-1-(*p*-methoxyphenyl)-2,2,2-trichloroethyl)-ethylenediamine dihydrochloride (5 IV).

(a) To a benzene solution (5 ml), containing 1·5 g of the imine, 1·7 g trichloroacetic acid in benzene (5 ml) was added at 60°. The temp was gradually raised to 70° and the mixture heated for 1 hr. By extraction with 1N HCl and then with 1:3 HCl, 1·07 g (4 A) and 0·93 g (4 B) was obtained. From the aqueous phase of (4 A), using the usual procedure, the hydrochloride (5 IV) was obtained, yield 0·28 g, m.p. 157° dec. (from a benzene–ethanol mixture with dry HCl). (Found: C, 35·85; H, 4·8; N, 7·65. $C_{11}H_{17}ON_2Cl_5$ requires: C, 35·65; H, 4·85; N, 7·55%). The hydrochlorides were decomposed by shaking with a benzene–water mixture yielding 0·87 g (4 A), m.p. 102·5–104°, after crystallization from ethanol m.p. 103–104°, and 0·72 g (4 B), m.p. 120·5–121·5° (from ethanol).

(b) After the reaction was complete, by distilling off the benzene and adding ethanol to the residue, a mixture of the amines (4 A + 4 B) was obtained, m.p. 99–103°. Separation of the amines could not be achieved by crystallization from ethanol. (Found: C, 44·9; H, 4·0; N, 5·5; $C_{20}H_{22}O_2N_2Cl_6$ requires: C, 44·45; H, 4·05; N, 5·2%).

By extraction from a benzene solution with 1N HCl, the mixture was separated, yielding the hydrochloride (4 A) and the amine (4 B) m.p. 120–121·5°. The amine (4 A) obtained from its hydrochloride melted at 103–104°.

The reaction of bis-(p*-methoxybenzylidene)ethylenediamine with tribromoacetic acid*

N,N¹-bis-(1-(*p*-methoxyphenyl)-2,2,2-tribromoethyl)-ethylenediamine (6 II).

Tribromoacetic acid (3·0 g) in benzene (10 ml) was slowly added to the imine (1·5 g) in benzene

(5 ml) at 40°. After 1 hr 15 ml ether was added and the mixture shaken with 0·5N HCl for 1 hr, yield 2·5 g (I), and then with 1:3 HCl, yielding 1·0 g (6 B_1). The precipitate (I) was shaken for a few min with a benzene–water mixture, the hydrochloride (6 A) filtered off, the solvent from the organic phase removed and ethanol added, yielding 0·43 g (6 B_2), m.p. about 130°dec. From the hydrochloride (6 B_1) the amine (6 B_1, 0·77 g) was obtained, m.p. 132° dec. Both amines (6 B_1 and 6 B_2) were combined and recrystallized from a benzene–ethanol mixture, m.p. 133° dec. (Found: C, 30·15; H, 2·7; N, 3·75; $C_{20}H_{22}O_2N_2Br_6$ requires: C, 29·9; H, 2·75; N, 3·5%).

From the hydrochloride (6 A), after prolonged shaking with a benzene–water mixture, the amine (6 A, 1·5 g) was obtained, m.p. 100–102° (from ethanol). (Found: C, 29·85; H, 2·8; N, 3·95%). When stored, the amine (6 A) evolves hydrogen bromide, the process occurring more easily on heating (e.g. during crystallization).

*The reaction between bis-(*o*-chlorobenzylidene)ethylenediamine and trichloroacetic acid*

N,N^1-bis-(1-*o*-chlorophenyl-2,2,2-trichloroethyl)ethylenediamine (7 II) and N-mono-(1-*o*-chlorophenyl)-2,2,2-trichloroethyl)ethylenediamine dihydrochloride (di $_x$)hydrate)(8 IV).

The imine (3·0 g) and trichloroacetic acid (3·4 g) in toluene (20 ml) were heated for 2 hr at 100°. The mixture was washed with water, the excess toluene distilled off (red. press.), the residue dissolved in ether (solution I) and shaken with 1N HCl. The aqueous phase was basified and the precipitated oil extracted with ether. The etheral layer was shaken with 7 ml HCl (2:1) and left for one day. The precipitate (8 IV) was filtered off (1·32 g) and recrystallized from HCl (2:1), m.p. 81° dec. (Found: C, 29·6; H, 4·45; N, 7·15; $C_{10}H_{18}O_2N_2Cl_6$ requires: C, 29·15; H, 4·4; N, 6·8%). On heating with benzene the product evolved water of crystallization and hydrogen chloride.

To the etheral solution (I) HCl (2:1) was added, the precipitate (1·0 g) filtered off and shaken with an ether–water mixture. The etheral layer was shaken with 2N HCl (1 hr), the hydrochloride (7 A) filtered off, the layer washed with water, the ether removed and ethanol (2:1) added, yield 0·35 g (7 B), m.p. 89–91°, after crystallization from ethanol m.p. 91–92°. (Found: C, 40·0; H, 3·0; N, 5·3; $C_{18}H_{16}N_2Cl_8$ requires: C, 39·7; H, 2·95; N, 5·15%).

The amine (7 A) was obtained from its hydrochloride by shaking with a benzene–water mixture, yield 0·32 g, m.p. 104·5–119° (from ethanol). The amine was retransformed into its hydrochloride by treating with conc. HCl in ethanol; the hydrochloride was decomposed with a water–benzene mixture. The amine thus obtained had m.p. 127–129° (from ethanol). (Found: C, 39·8; H, 2·75; N, 5·55%).

*The reaction of bis-(*m*-chlorobenzylidene)ethylenediamine with trichloroacetic acid*

N,N^1-bis-(1-(*m*-chlorophenyl)-2,2,2-trichloroethyl)ethylenediamine (9 II) and N-mono-(1-(*m*-chlorophenyl)-2,2,2-trichloroethyl)ethylenediamine dihydrochloride (10 IV).

The imine (1·5 g) and trichloroacetic acid (2·6 g) in toluene (15 ml) were heated at 100° for 1·5 hr. After the toluene had been distilled off some ether was added, the mixture shaken with 1N HCl and HCl (1:3) yielding 0·7 g (9 A) and 0·8 g (9 B). The aqueous phase from 9 A was made alkaline, the oily amine dissolved in ethanol, conc. HCl added and the mixture evaporated to dryness, yielding 0·45 g (10 IV). After crystallization from HCl (1:2) m.p. 178° dec. (Found: C, 31·6; H, 3·75; N, 7·5; $C_{10}H_{14}N_2Cl_6$ requires: C, 32·0; H, 3·75; N, 7·45%).

The amine (9 A) 0·45 g (m.p. 114–115·5°*. Found: C, 39·3; H, 2·9; N, 5·75; $C_{18}H_{16}N_2Cl_8$ requires: C, 39·7; H, 2·95; N, 5·15%), and (9 B) (0·54 g m.p. 82·5–83·5°* from ethanol. Found: C, 39·9; H, 3·0; N, 5·5%), were obtained from their hydrochlorides by decomposition with a benzene–water mixture.

*The reaction between bis-(*p*-chlorobenzylidene)ethylenediamine and trichloroacetic acid*

N,N^1-bis-(1-*p*-chlorophenyl)-2,2,2-trichloroethyl)ethylenediamine (11 II) and N-mono-(1-(*p*-chlorophenyl)-2,2,2-trichloroethyl)ethylenediamine dihydrochloride (12 IV).

The imine (1·5 g) and trichloroacetic acid (1·7 g) in toluene (10 ml) were heated at 100° for about 2 hr. By shaking the mixture (~1 hr) with 2N HCl the hydrochloride (11 A), (0·54 g) was obtained, and with 1:3 HCl (a few ml of ether added) the hydrochloride (11 B), (0·60 g) was obtained. The hydrochloride (12 IV) was obtained from the aqueous phase as decribed above, yield 0·62 g, m.p.

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* In the communication[1] m.p. have been reported for the forms separated by crystallization from ethanol.

166° dec. (from ethanol with dry HCl). (Found: C, 32·45; H, 3·85; N, 7·55; $C_{10}H_{14}N_2Cl_6$ requires: C, 32·0; H, 3·75; N, 7·45%).

The amines (11 A, 0·40 g, m.p. 105·5–107°) and (11 B, 0·40 g, m.p. 111–112·5°) were obtained from their hydrochlorides. A mixture of both amines was obtained by distilling off the toluene from the reaction mixture. After three crystallizations from ethanol m.p. 94–96°. (Found: C, 39·6; H, 2·9; N, 5·6; $C_{18}H_{16}N_2Cl_8$ requires: C, 39·7; H, 2·95; N, 5·15%). Both the amines were separated by extraction with 2N HCl from the toluene solution and by decomposition the precipitated hydrochloride (11 A); m.p. 106–107·5° for (11 A) and 112–113° for (11 B) (from ethanol).

N-(1-*phenyl*-2,2,2-*trichloroethyl*)*cyclohexylamine hydrochloride* (15 V). Benzaldehyde (5·3 g) and cyclohexylamine (5·0 g) in benzene were heated and the water formed removed. Part of the benzene was distilled off and 9·0 g trichloroacetic acid dissolved in benzene added at 60–70°. When the reaction was complete the benzene was distilled off, the residue dissolved in dry ethyl acetate and geseous HCl passed through (heating). The precipitate was shaken with a benzene–water mixture, the benzene distilled off, the oily amine retransformed into its hydrochloride (15 V), yielding 10·5 g. The latter is also formed when the ether solution of the amine is shaken with HCl (1:3). (Found: C, 49·0; H, 5·5; N, 4·25; $C_{14}H_{19}NCl_4$ requires: C, 49·0; H, 5·55; N, 4·1%).

N-(1-*phenyl*-2,2,2-*tribromoethyl*)*cyclohexylamine hydrochloride* (16 V). Benzaldehyde (1·06 g) and cyclohexylamine (1·0 g) were heated as described. After removal of the water tribromoacetic acid (3·0 g) in benzene was added dropwise at 50°. After 0·5 hr the mixture was shaken with 1N HCl, washed with water and the benzene distilled off under red. press. The residue was treated with 3 ml conc. HCl in ethanol, evaporated to dryness and dry acetone added, yielding 3·94 g (16 V). The hydrochloride was purified by decomposition with a benzene–water mixture and precipitated as hydrochloride, m.p. 166·5° dec. (Found: C, 35·8; H, 4·3; N, 3·15; $C_{14}H_{19}NClBr_3$ requires: C, 35·3; H, 4·0; N, 2·95%).

N-(1-*phenyl*-2,2,2-*trichloroethyl*)*benzylamine hydrochloride* (17 V). Bezaldehyde (2·15 g) and benzylamine (2·15 g) were treated as described. After the water had been removed, trichloroacetic acid (3·4 g) in benzene was added dropwise at 70°. After the reaction was complete the mixture was shaken with 2N HCl and the benzene distilled off. Following the procedure described, 4·14 g (17 V) was obtained, m.p. 182°. (Found: C, 51·4; H, 4·85; N, 4·2; $C_{15}H_{15}NCl_4$ requires: C, 51·3; H, 4·25; N, 4·0%). The hydrochloride (17 V) can be also obtained by extraction from ether with 1:3 HCl.

N-(1-*phenyl*-2,2,2-*trichloroethyl*)-p-*chlorobenzylamine* (18 V). Benzaldehyde (2·1 g) and *p*-chlorobenzylamine (2·8 g, Light) in benzene were heated. The water formed was removed, trichloroacetic acid (3·4 g) in benzene added at 70° and the mixture after heating 1·5 hr, was treated as above, yielding 3·35 g hydrochloride (18 V). The amine (18 V) was obtained by decomp. of hydrochloride, m.p. 41–42·5°. (Found: C, 51·4; H, 3·95; N, 4·25; $C_{15}H_{13}NCl_4$ requires: C, 51·3; H, 3·75; N, 4·0%).

N-(1-*phenyl*-2,2,2-*tribromoethyl*)-p-*chlorobenzylamine* (19 V). Benzaldehyde (2·1 g) and *p*-chlorobenzylamine (2·8 g) in benzene were heated and treated as above with 6·0 g tribromoacetic acid at 50°. After 1 hr the mixture was shaken with 2N HCl, washed with water, the benzene removed and ethanol added, yielding 6·54 g (19 V), m.p. 120–123°, after recrystallization from ethanol 124–125°. (Found: C, 37·4; H, 2·8; N, 3·35; $C_{15}H_{13}NClBr_3$ requires: C, 37·35; H, 2·7; N, 2·9%).

N-(1-*phenyl*-2,2,2-*trichloroethyl*)-n-*octylamine hydrochloride* (20 V). Benzaldehyde (2·1 g and n-octylamine (2·6 g, Fluka) in benzene were heated and treated as above with 3·4 g trichloroacetic acid at 70°. After 1·5 hr the mixture was washed with water, the benzene removed, conc. HCl in ethanol added and evaporated to dryness. To the residue dry acetone was added, the hydrochloride filtered off and decomposed by treating with a benzene–water mixture. The oily amine was retransformed into the hydrochloride (20 V), yielding 4·35 g, m.p. 180–181° dec. (Found: C, 51·55; H, 6·7; N, 3·55; $C_{16}H_{25}NCl_4$ requires: C, 51·45; H, 6·7; N, 3·75%). The hydrochloride (20 V) can be also obtained by extraction from ether with 2N HCl.

N-(1-(p-*methoxyphenyl*)-2,2,2-*trichloroethyl*)-*allylamine hydrochloride* (21 V). *p*-Methoxybenzaldehyde (4·0 g) and allylamine (1·7 g, Schuchardt) in ethanol were heated for 1 hr. The ethanol was distilled off (red. press.) and to the residue, dissolved in benzene (15 ml) trichloroacetic acid (5·0 g) in benzene was added dropwise at 70°. After 1·5 hr the mixture was washed with water, the benzene removed, the residue dissolved in ethyl acetate and dry hydrogen chloride passed through the solution.

The precipitate was filtered off, decomposed with a benzene–water mixture and the oily amine re-transformed into the hydrochloride (21 V), yielding 5·3 g, m.p. above 175° dec. (Found: C, 43·6; H, 4·35; N, 4·65; $C_{12}H_{15}NCl_4$ requires: C, 43·5; H, 4·55; N, 4·25%).

The reaction between benzylideneaniline and trichloroacetic acid

The benzylideneaniline was obtained by heating aniline and benzaldehyde in ethanol, m.p. 51–52·5°. Trichloroacetic acid (2·5 g) in toluene (5 ml) was added to benzylideneaniline (2·0 g) in toluene (5 ml) at 100°. During heating (2 hr) evolution of highly acidic gases were observed. The mixture was washed with water and the toluene distilled off under red. press. The syrupy residue was treated with 7 ml ethanol and 4 ml conc. HCl. The resin-like precipitate was dissolved in hot ethanol, cooled, some water added and the precipitate filtered off (1·83 g). This operation was repeated several times and resulted in a white precipitate of small irregular crystals (microscopic), m.p. 79–81°, becoming soft at 75°. (Found; C, 61·70; H, 4·5; N, 4·9%). After additional purification the product melted at 80–81° and softened at 75°. (Found: C, 61·65; H, 4·2; N, 4·5%).

The reaction of benzylideneaniline with tribromoacetic acid

N-(1-phenyl-2,2,2-tribromoethyl)aniline (22 VII).

Benzylideneaniline (1·8 g) and tribromoacetic acid (4·0 g) in toluene (20 ml) were heated at 100° for 1·5 hr. The mixture was shaken with 1N HCl, washed with water, the excess of toluene removed under red. press. and ethanol 3:1 added, yielding 2·9 g (22 VII). After purification by precipitation from an organic liquid (a mixture of sec-butanol and ethanol) with water or by crystallization from benzine m.p. 85–86°. (Found: C, 38·7; H, 2·9; N, 3·7; $C_{14}H_{12}NBr_3$ requires: C, 38·7; H, 2·75; N, 3·25%). When stored the product became dark.

The reaction between benzylidene-p-ethoxyaniline with trichloroacetic acid

N-(1-phenyl-2,2,2-trichloroethyl)*p*-ethoxyaniline (23 VII)

Benzylidene-*p*-phenetidine (2·25 g), obtained by heating benzaldehyde with *p*-phenetidine in ethanol, m.p. 69–70°, and trichloroacetic acid (1·7 g) in toluene (20 ml) were heated at 100° for 2 hr. The mixture was shaken with 2N HCl, washed with water, the toluene distilled off, ethanol 2:1 added, yielding 1·98 g (23 VII), m.p. 81–82° (from ethanol). (Found: C, 55·85; H, 4·65; N, 4·4; $C_{16}H_{16}NCl_3$ requires: C, 55·8; H, 4·65; N, 4·05%).

Determination of the basicity of a certain derivative of trihalogenoaminoethane

The amine examined (0·1 g) was dissolved in an organic solvent (2 ml) (ether or benzene) and shaken with HCl (2 ml) for 15 min. The results are presented in Table 3.

The elementary analyses were carried out by the Department of Organic Chemistry, Warsaw University.

Acknowledgement—The author wishes to thank Professor T. Urbański for his perusal of the manuscript and valuable remarks.