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REACTIONS OF TRIHALOGENOACETIC ACIDS—VII

DONOR–ACCEPTOR PROPERTIES OF α-(TRIHALOGENOMETHYL) AMINES

A. ŁUKASIEWICZ

Institute of Nuclear Research, Warsaw 91, Poland

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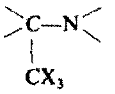
Abstract—α-(Trihalogenomethyl)amines, due to the presence in the molecule of both donor–amino and acceptor–CX_3 groups, form a wide range of the complexes with various electron–donor and donor–acceptor compounds.

COMPOUNDS with a α-(trihalogenomethyl)amino grouping (A) in the molecule, exhibit a virostatic and cytostatic action on cells and in a number of cases a stimulating activity was also observed.[1]



$\overset{\displaystyle >C-N<}{\underset{CX_3}{|}}$ (A) X = Cl or Br

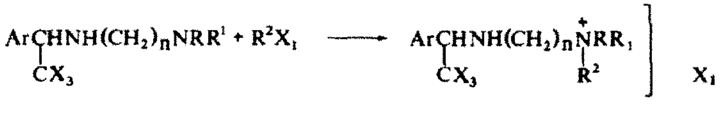
It has been suggested[2] that this biological activity may be caused by a chemical transformation of the group A initiated by the abstraction of an X^- anion from CX_3 group, but no relationship between activity of α-(trihalogenomethyl)amines and their ability to undergo these transformations was observed. Most of the compounds (I and II) are very stable and the abstraction of X^- does not occur easily (for X = Cl).

$\underset{CX_3}{ArCHNHR}$ I

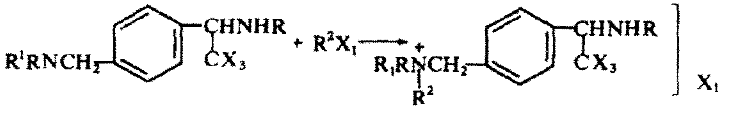
$\underset{CX_3}{ArCHNRR^1}$ II

Ar = aryl; R = alkyl; NRR^1 = pyrrolidine, piperidine or morpholine rest

Further, the amino group in derivatives I and II is chemically inert when compared with most aliphatic amines and, therefore, compounds III and IIIa can easily be obtained by the following reactions:[3]



III



IIIa

X_1 = Br or J

In these reactions the t-nitrogen is alkylated exclusively.

As the group A is chemically inactive the biological activity of α-(trihalogenomethyl)amines may result from the presence in the molecule of the electron-donating nitrogen and electronegative CX_3 group in α-position. The electron–acceptor ability of CX_3 group in some polyhalogenohydrocarbons (e.g. $CHCl_3$, $PhCCl_3$) is shown[4] by the formation of charge–transfer complexes with dimethylformamide and dimethylacetamide. It has been suggested that in these complexes an electron is transferred from nitrogen or the carbonyl group to the halogen. As the analogous fluorine derivatives do not form such complexes, it was suggested that the d-orbitals of the chlorine or bromine atom are involved in this electron-transfer.

In α-(trihalogenomethyl)amines, the neighbouring electronegative CX_3 group diminishes the donor ability of nitrogen (α-(trihalogenomethyl)amines are distinctly less basic than aliphatic and many aromatic amines). The amines of type I, II (without another amino group in the molecule) as well as aliphatic derivatives, e.g. IV[5] cannot be extracted from organic solvents with dilute (e.g. 1N) hydrochloric acid. The hydrochlorides obtained by using more concentrated HCl or in waterless medium undergo hydrolytic decomposition in the presence of water.[2,6]

$\underset{CX_3}{R^1\underset{|}{C}HNHR}$ IV R^1 and R = alkyl

It was found, however, that amines I show a much greater ability to form salts with certain mineral and organic acids, such as HNO_3, HJ, HBr, CX_3COOH (X = F, Cl, Br), $(COOH)_2$ than with HCl. Crystalline salts are precipitated in good yields on mixing the amines I with dilute aqueous solutions of those acids in equimolar proportions (or with slight excess of the acid). The hydrochlorides (I HCl) are not formed under these conditions (the amines remain in the free state in the presence of dilute HCl), but the nitrates, hydroiodides, hydrobromides, trihalogenoacetates (I CX_3COOH or I $2CX_3COOH$) and oxalates precipitate also in the presence of HCl or some other mineral acids (e.g. H_2SO_4). The nitrates (I HNO_3), hydroiodides (I HJ) and trihalogenoacetates (I CX_3COOH) are selectively precipitated from an aqueous medium when the hydrochlorides (I HCl) are added to dilute (e.g. 1%) neutral solutions of $NaNO_3$, NaJ or CX_3COONa in the presence of a manifold excess of some other mineral anions (e.g. Cl^-, $SO_4^=$). The hydroiodides (I HJ) precipitate selectively in the presence of Br^- from neutral solutions, whereas the hydrobromides precipitate in the presence of Cl^- from an acidic medium. A high affinity of the amines I for HNO_3 was demonstrated also by extraction of the amines from hexane. The amines I combine with HNO_3 when extracted from hexane solution by dilute HNO_3 (0·25–0·5N, Table 1), whereas extraction with HCl requires 2·0N or even more concentrated acid (e.g. the amine 6-I is not extracted by 2·0N HCl from hexane). However, if benzene is used instead of hexane, then extraction of the amines I by HNO_3 requires the more concentrated acid (Table 1). This effect of solvents is demonstrated in Table 2, when some compounds were added to hexane solutions of the amine 6-I. The addition of certain ketones, phosphate esters (dibutylphosphate -DBP and tributylphosphate-TBP) and benzene retarded the extraction of the amine (6-I) from hexane when 0·5N HNO_3 was used. The influence of phosphate esters was the greatest, while the effect of aliphatic ketones (except acetone and methyl vinyl ketone), formates and acetates was the smallest.

An enhanced affinity towards NO_3^- anion as compared with chloride anion was found also for the diamines V, which form diastereoisomers (DL and meso) differing in their basicity towards HCl (the forms A and B[2,6]).

V

$$\mathrm{Ar\underset{\displaystyle CX_3}{\underset{|}{C}}HNHCH_2CH_2NH\underset{\displaystyle CX_3}{\underset{|}{C}}HAr}$$

In Table 3 the extraction of the forms A and B with HNO_3 and HCl is compared. The difference in "basicity" of the two forms disappears when HNO_3 is used for extraction of these amines from benzene and this indicates the greater affinity for NO_3^- anion of the form B (less basic towards HCl) than A (more basic). The form A is extracted more easily from ether (with HNO_3) than from benzene; for B this difference is less marked. As the diamines V (A and B) are poorly soluble in hexane, it was impossible to compare the extraction from hexane and benzene. From previous work[6] it follows that both forms A and B are more easily extracted by HCl from ether than from benzene and this difference is greater for B rather than A (Table 3).

This selective affinity of the amines I and V for anions as well as the retarding influence exerted by some compounds on extraction of the amines with HNO_3 shows that α-(trihalogenomethyl)amines form complexes with a wide range of electron–donors and donor–acceptors. The acidity of the strong mineral acids in water is the same, but the acidity of the carboxylic acids such as $(COOH)_2$ and CBr_3COOH is distinctly lower. Therefore, a higher affinity of the amines I and V for certain mineral and organic acids must be due to complex binding of these anions in salts formed. As NO_3^-, J^-, Br^- and carboxylate anions are electron–donors a high affinity of α-(trihalogenomethyl)amines for these anions is defined by the acceptor ability of the amines. The affinity of the amines I for the halogenide anions increases according to the electron-donating ability of these anions: $Cl^- < Br^- < J^-$.* The affinity of the compounds I for HCl is defined by their basicity (ability towards proton), for HJ—by their acceptor ability (affinity for J^-). The retarding effect of some compounds on extraction of the amines I by HNO_3 indicates a complex-binding of the amines with the organic phase. Benzene, phosphate esters and carbonyl compounds (ketones) are the electron–donors. Therefore, they can compete with the NO_3^- anion in complex-binding of the α-(trihalogenomethyl)amines. As the carbonyl group of the ketones possesses also the acceptor properties it seems possible that in an interaction with α-(trihalogenomethyl)amines (acceptor–donors) both the donor and acceptor properties of this group are involved. As follows from Table 2 the steric conditions exert a distinct influence on stability of these complexes. Extraction of the amine (6-I) was retarded by cyclic ketones (5–7 carbons), but in the group of aliphatic ketones (saturated) this effect was observed for acetone only. Evidently, a steric hindrance due to rotations of the alkyls of aliphatic ketones makes impossible the formation of a stable complex with the amine.

The affinity of aliphatic derivatives IV for HNO_3 is low in comparison with the amines I (Table 1). The crystalline nitrates can be obtained by using more concentrated acid or by removal of water from equimolar quantities of HNO_3 and IV. In water–medium these nitrates easily undergo hydrolytic decomposition. This low

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* This selective affinity of α-(trihalogenomethyl)amines for anions may be of practical importance, e.g. they can be used for the separation of J^- in the presence of Br^- and Cl^-, or Br^- in the presence of Cl^- (in preparation).

affinity for HNO_3 of the aliphatic derivatives IV in comparison with aromatic derivatives I suggests that the aromatic nucleus of the amines I is involved in this complex-formation. The t-amines II also form nitrates less easily than secamines I (Table 1). This difference in affinity for HNO_3 between aliphatic (IV), aromatic tertiary (II) and aromatic secondary (I) derivatives of α-(trihalogenomethyl)amines may be due to difference in their acceptor ability (affinity for NO_3^-) as well as, at least partially, to difference in their basicity, i.e. donor-ability of nitrogen towards proton. The tertiary amines are usually less basic than analogous secondary amines. It was found also that the aliphatic amine 11-IV is less basic than analogous aromatic derivative 1-I.

$$\mathrm{Me_2CH}\underset{\underset{\displaystyle \mathrm{CCl_3}}{|}}{\mathrm{C}}\mathrm{HNHCH_2CHMe_2}$$

11-IV

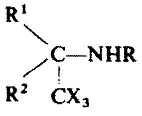
$$\mathrm{Ph}\underset{\underset{\displaystyle \mathrm{CCl_3}}{|}}{\mathrm{C}}\mathrm{HNHCH_2CHMe_2}$$

1-I

When the hydrochloride (11-IV) HCl and the free amine 1-I were shaken in hexane, the amine 11-IV was quantitatively replaced by 1-I in the hydrochloride (solid phase). The same result was obtained for the *para*-F derivative (p-F—$C_6H_4 \cdot CH)CCl_3(NHC_4H_9)$ and the hydrochloride (11-IV) HCl.

This difference in basicity of the amines of IV and of I type cannot be caused by inductive effect, as this should act in reverse. Evidently, there is an intramolecular steric interaction between the halogens of the CX_3 group and unshared electrons of the nitrogen. A lower basicity of the amine 11-IV than amines of type I indicates that this interaction must be lower in I than in IV. This effect can be explained by assuming that in aromatic derivatives I an intramolecular interaction between halogens and nucleus occurs. The acceptor ability of the CX_3 group is evidently directed intramolecularly towards both unshared electrons of nitrogen and the π-electrons of the nucleus. The greater interaction between halogens and nucleus the weaker should be steric the influence of the CX_3 group on nitrogen. Steric hindrance should decrease the possibility of nucleus to interact with halogens of CX_3 group, and this should then increase the influence of halogens on nitrogen. The influence of an ortho-Me group on the affinity of α-(trihalogenomethyl)amines for HNO_3 seems to be very characteristic (Table 1).

This explanation may account for the stabilizing influence of the aromatic nucleus on the stability of the amines VI[7] (R^2 = aryl):



VI

R^1 and R = alkyl

R^2 = alkyl or aryl

The compounds of type VI, when R^2 = alkyl, easily undergo transformations initiated by abstraction of X^-. Under steric conditions when a halogen atom approaches the nitrogen the intramolecular transfer of an electron from the unshared pair of nitrogen to halogen can occur with simultaneous abstraction of the X^- anion and formation of the new bond between N and C of the CX_2 group

The interaction between halogens and nucleus both decreases "electron capacity" and limits free rotation of the CX_3 group and the probability of electron transfer from nitrogen to halogen becomes less. The binding of the electron pair on nitrogen by a proton attachment makes such electron transfer impossible; indeed, the hydrochlorides are stable, even if the amines A are very unstable in the free state. The low basicity of α-(trihalogenomethyl)amines and their chemical inactivity, e.g. in reaction of alkylation can be explained in a similar way: beside an inductive effect of the CX_3 group the interaction between halogens and nitrogen occurs, causing a partial transfer of electron from nitrogen to halogen (a partial binding of the unshared electron pair).

The interactions between amines and polyhalogenohydrocarbons ($CHCl_3$, CCl_4),[8] leading to abstraction of an halogenide anion[9] are known.

The suggestion was advanced[6] that the difference in basicity of two forms (A and B) of the amines V is due to intramolecular hydrogen bonding N–H ... X, depending on steric condition of the two optical isomers (DL and meso). In view of the new data this hypothesis requires modification. Although the possibility of such a hydrogen bonding cannot be excluded, the decisive cause of this difference in basicity should be ascribed rather to interactions between halogens and electrons of nucleus and nitrogen, depending on their conformation. Determination of the conformation of

TABLE 1. COMPARISON OF THE EXTRACTION OF SOME AMINES I, II AND IV FROM ORGANIC SOLVENTS WITH HNO_3

$$\text{I—Ar}\underset{CX_3}{\underset{|}{C}}\text{HNHR; II—Ar}\underset{CX_3}{\underset{|}{C}}\text{HNRR}^1\text{; IV—R}^2\underset{CX_3}{\underset{|}{C}}\text{HNHR}$$

Amine					Conc. of HNO_3 (moles per litre) and solvent used				
No.	Type I, II, IV	Ar(R^2)	R(NRR^1)	X	0·25	0·5		1·0	
					hexane	hexane	benzene	hexane	benzene
1	I	C_6H_5	iso-C_4H_9	Cl	+*	+ +	−		+ +
2	I	C_6H_5	n-C_5H_{11}	Cl	+ −	+ +	−		−
3	I	C_6H_5	cyclohexyl	Cl	+	+ +	−		+ +
4	I	p-MeO—C_6H_4	cyclohexyl	Cl	+ +		−		+ +
5	I	p-MeO—C_6H_4	cyclohexyl	Br	+	+ +	−		+
6	I	p-Cl—C_6H_4	cyclohexyl	Cl		+ +	−		+ +
7	I	m-Cl—C_6H_4	cyclohexyl	Cl		−		+ +	−
8	I	o-Me—C_6H_4	cyclohexyl	Cl	−	+			−
9	II	Ph	piperidine	Cl				−	
10	II	p-MeO—C_6H_4	piperidine	Cl		−		+ +	
11	IV	iso-Pr	iso-C_4H_9	Cl				−	(ether −)
12	IV	iso-Pr	cyclohexyl	Cl				−	(ether −)

* The nitrate precipitates slowly; + + precipitation of the nitrate occurs quickly; − no ppt is formed after 15 min; + − a very small amount of the ppt is formed after 15 min.

both forms A and B should indicate the difference in their basicity (ability towards proton) and ability towards NO_3^- (acceptor ability).

The problem of complex-ability of α-(trihalogenomethyl)amines towards various electron donors and donor–acceptors as well as of the structures of these complexes requires further study.

TABLE 2. INFLUENCE OF ADDITION OF SOME COMPOUNDS ON EXTRACTION OF THE AMINE 6-I WITH HNO_3 FROM HEXANE*

No.	Compound added to hexane solution of 6-I	Conc. of HNO_3	
		0·5N	1·0N
1	n-Hexane	+	
2	Acetone	−	+
3	Methyl vinyl ketone	−	+
4	Ethyl-n-propyl ketone	+	
5	2-Heptanone	+	
6	Methyl-n-nonyl ketone	+	
7	Cyclopentanone	−	+
8	Cyclohexanone	−	+
9	Cycloheptanone	−	+
10	Cyclooctanone	+†	
11	n-Amylformate	+	
12	n-Butylacetate	+	
13	DBP (+ ether)	−	+†
14	TBP	−	+†
15	Ether	+	
16	Benzene	+†	

* This effect of some compounds on equilibrium of the extraction of α-(trihalogenomethyl)amines is being investigated quantitatively using radiometric methods.

† Precipitation of the nitrate occurs distinctly slower than for hexane alone (in exp. No. 1).

EXPERIMENTAL

Materials. α-(Trihalogenomethyl)amines used were described in publications: I[2,6], II[10] (Table 1), V[6] (Table 3). The aliphatic derivatives IV (Table 1) were prepared by the reaction of corresponding imines with CCl_3COOH.[5] The amine 14-I (Table 4) was obtained by reaction of an imine from benzaldehyde and t-butylamine with CCl_3COOH according to general procedure described in the work,[2] and isolated as the hydrochloride, m.p. 172–176° dec. (Found: C, 45·8; H, 5·45; N, 4·5. $C_{12}H_{17}NCl_4$ requires: C, 45·45; H, 5·35; N, 4·4%.) The *para*-F derivative (p-F—$C_6H_4 \cdot CH(CCl_3)NHC_4H_9$) was prepared as above (analytical data will be given elsewhere). As solvents (Tables 1–3) the commercial products of chemical or analytical grade of purity were used (n-hexane, methylvinyl ketone, ethyl-n-propyl ketone of Fluka; cyclopentanone and n-amylformate of B.B.H.; cycloheptanone and cyclooctanone of Schuchardt). D.B.P. and T.B.P. were purified (T.B.P. by distillation in vacuum).

Extraction of the amines I, II and IV with HNO_3 from hexane and benzene alone

General procedure. The hydrochloride (200 mg) of the amine (I, II or IV) was decomposed by shaking with a mixture of water (4 ml) and organic solvent (hexane or benzene, 4 ml), the organic layer was separated and shaken with 2 ml HNO_3 (0·25; 0·5 or 1·0N) for 15 min. The results are given in Table 1. If no precipitate was formed, the acidic layer was made alkaline and from organic phase the hydrochloride was reprecipitated. In all such cases the amines remained almost quantitatively in organic layer (no extraction occurred).

TABLE 3. COMPARISON OF THE EXTRACTION OF A AND B FORMS OF THE DIAMINES V ($ArCH(CX_3)NHCH_2CH_2NH(CX_3)CHAr$) WITH HNO_3 AND HCl FROM ORGANIC SOLVENTS

Compound V			HNO_3			HCl*			
Ar	X	Form	Conc. (N)	Solvent		Conc. (N)	Solvent		
				ether	benzene		ether	benzene	toluene
Ph	Cl	A	0·25	+†	–	0·5	+†	–	
			0·5		+	1·0		+	
		B	0·25	–		0·5	–		
			0·5	+	+	1·0	+	–	
						2·0		–	+
p-MeO—C_6H_4	Cl	A	0·25	+	–	0·5	+	–	
			0·5		–	1·0		+	
			0·75		+				
		B	0·25	–		0·5	–		
			0·5	+	–	1·0	+	–	
			0·75		+	2·0		–	+

* These data for extraction with HCl were taken from publication.[6]

† The amine is extracted from solution (the nitrate or hydrochloride is precipitated); – the amine is not extracted.

Extraction of the amines I *with* HNO_3 *from hexane with addition of another component*

The 6-I hydrochloride (5·0 g) was decomposed by shaking with water + hexane and the hexane layer was separated (45 ml). To 1·5 ml of this hexane solution 0·5 ml of another component was added, then 1 ml HNO_3 (0·5 or 1·0N) and the mixture was shaken for 15 min. The results are given in Table 2. In Example 1 (Control) 0·5 ml hexane was added and in Ex. 13 0·5 ml DBP + 0·5 ml ether. For the control (1) a complete precipitation of the nitrate after about 5 min occurred. Most of the experiments were repeated and the same results were obtained.

Extraction of A and B forms of the diamines V *with* HNO_3 *from ether and benzene*

The diamine V (A or B, 100 mg) was dissolved in benzene (2 ml) or ether (8 ml; the forms B are badly soluble in ether) and shaken with 2 ml HNO_3 for 15 min (the experiments were repeated). The results are presented in Table 3.

Formation of the nitrates, oxalates and trichloroacetates of the amines* I *in water medium*

General procedure. The hydrochloride I (0·6 g) was decomposed (ether + water with some alkali), ether layer was washed with water, ether distilled off and the residue (free amine) in 3 ml EtOH dissolved. To 1 ml of the EtOH soln 3 ml (a), 7 ml (b) water or 3 ml water + 1 ml 1·0N HCl (c) were added. In all the cases (a), (b) and (c) the oil free amine was precipitated. To the mixtures (a), (b) and (c) 1 ml of the acid (HNO_3, $(COOH)_2$ or CCl_3COOH) soln in water (1 mol/l) were added. In all the experiments (a), (b) and (c) the oil completely disappeared after adding the acid and a ppt formed. Formation of the ppt occurred very quickly for nitrates and relatively slower for oxalates and trichloroacetates (especially in Exp. b). The ppt formed was filtered off, washed with hexane or ether and dried. The yields were on the average above 80% for the nitrates and trichloroacetates and about 50% for the oxalates (more soluble in water). In Table 4 the m.ps (uncorrected) and analytical data are given (the oxalates for analysis were washed after filtering with EtOH–water mixture containing some HCl, and then with hexane).

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* Other salts of the amines I will be described in a subsequent publication.

TABLE 4. ANALYTICAL DATA AND M.PS OF SOME NITRATES (I HNO_3) OXALATES I $(COOH)_2$ AND TRICHLOROACETATES I CCl_3COOH AND I $2CCl_3COOH$

Amine	Acid	M.p§ °C	Found			Formula	Requires		
			C	H	N		C	H	N%
13-I*	HNO_3	167–168	42·1	4·95	8·5	$C_{12}H_{17}O_3N_2Cl_3$	42·0	4·95	8·15
	$(COOH)_2$	152·5–153·5	45·4	4·8	4·1	$C_{14}H_{18}O_4NCl_3$	45·4	4·85	3·8
	CCl_3COOH	115·5–116	37·85	3·9	3·35	$C_{14}H_{17}O_2NCl_6$	37·85	3·85	3·15
1-I	HNO_3	165–165·5	41·95	5·0	8·25	$C_{12}H_{17}O_3N_2Cl_3$	42·0	4·95	8·15
14-I†	$(COOH)_2$	156–157	45·4	4·85	4·2	$C_{14}H_{18}O_4NCl_3$	45·4	4·85	3·8
	$2CCl_3COOH$‡	148·5–149	32·1	2·9	2·65	$C_{16}H_{18}O_4NCl_9$	31·65	2·95	2·3
2-I	HNO_3	147–148	43·9	5·25	8·15	$C_{13}H_{19}O_3N_2Cl_3$	43·7	5·3	7·85
4-I	HNO_3	151–151·5	45·4	5·2	7·2	$C_{15}H_{21}O_4N_2Cl_3$	45·1	5·25	7·0
5-I	HNO_3	186	34·05	4·05	5·5	$C_{15}H_{21}O_4N_2Br_3$	33·75	3·95	5·25
6-I	HNO_3	156–156·5	41·9	4·4	7·3	$C_{14}H_{18}O_3N_2Cl_3$	41·6	4·45	6·95

* See formula I: Ar = Ph; X = Cl; R = n-Bu.

† Ar = Ph; X = Cl; R = CMe_3.

‡ Analytical data indicate on the formula (14-I)·$2CCl_3COOH$.

§ All the compounds melted with decomposition; in the case of (5-I)·HNO_3 a partial decomposition occurred above 140° already (a brown colour appeared). All m.ps are uncorrected.

A comparison of the basicity of the amines I *and* IV

The hydrochloride 11-IV (0·5 g) and the free amine 1-I (0·35 g) were shaken in hexane (5 ml) for 1 hr. The solid phase (hydrochloride) was filtered off and decomposed by shaking with water–ether (with some alkali), the ether-layer was shaken with 1·0N HNO_3 (3 ml), the nitrate (1-I) formed was filtered off and dried (0·32 g). The hexane phase was shaken with 1·0N HNO_3 (3 ml)—no ppt was formed. By adding ether soln of HCl the 11-IV hydrochloride was precipitated from hexane layer. The same result was obtained for *p*-F derivative (p-F—$C_6H_4\cdot CH(CCl_3)NHC_4H_9$, 0·35 g) and 11-IV hydrochloride (0·5 g).

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