Tetrahedron, 1963, Vol. 19, pp. 1591 to 1601. Pergamon Press Ltd. Printed in Northern Ireland

ACTION OF HYDRAZOIC ACID AND ARYLAZIDES ON N-ARYLMALEIMIDES, WITH A SPECIAL NOTE ON THE PYROLYSIS OF THE RESULTING TRIAZOLINES

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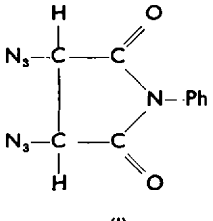
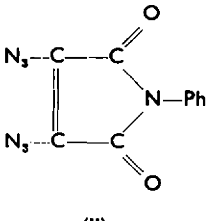
(*Received* 5 *April* 1963, *in revised form* 15 *May* 1963)

Abstract—Hydrazoic acid and arylazides add to N-arylmaleimides by fundamentally similar mechanisms to yield l-azido-succinimide derivative (V) and triazoline derivatives (VI) respectively. The constitution of these products has been studied by the use of I.R. and U.V. spectra. Pyrolysis of VI yields in some cases a mixture of aziridine (X) and anilino-N-arylmaleimide (XI), in contrast to that stated[1] previously. X is transformed to XI via the formation of XII followed by alkaline treatment or pyrolysis.

Mustafa *et al.*[1] claimed that sodium azide reacts with 2,3-dichloro-N-phenylmaleimide to give 2,3-diazido-N-phenylmaleimide in a similar manner to the reaction of sodium azide with 2,3-dichloro-1,4-naphthoquinone.[2] We believe that formula I assigned by these authors to the product is not correct and that it has formula II which was confirmed by its I.R. and U.V. spectra. Thus its I.R. spectrum showed the characteristic azido absorption band in the 4·7 μ region,[3-5] (cf. Fig. Ic). whereas its U.V. spectrum was very similar to that of N-phenylmaleimide[6] (cf. Fig. 2a) and is different from that of N-phenylsuccinimide[6]. The investigation was further extended to study the addition of hydrazoic acid to N-arylmaleimides. The products were found to be N-aryl-azido-succinimides. This type of addition is similar to that reported by Boyer[4] for the reaction of hydrazoic acid with conjugated systems.


(I)


(II)

The addition of aryl and alkylazides to N-arylmaleimides has been reported[1,7] (*inter alia*) to yield Δ^2-1,2,3-triazoline derivatives.

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[1] A. Mustafa, S. M. S. D. Zayed and S. Khatab, *J. Amer. Chem. Soc.* **78**, 145 (1956).
[2] K. Fries and P. O. Ochwat, *Ber., Dtsch. Chem. Ges.* **56**, 1291 (1923).
[3] E. H. Eyster and R. H. Gillets, *J. Chem. Phys.* **8**, 369 (1940).
[4] J. H. Boyer, *J. Amer. Chem. Soc.* **73**, 5248 (1951).
[5] Bellamy *The Infrared Spectra of Complex Molecules*, p. 273. Methuen, London (1960).
[6] W. I. Awad, S. M. A. R. Omran and M. Sobhy, *J. Org. Chem.* **26**, 4126 (1961).
[7] S. J. Davis and C. S. Rondesvedt jun., *Chem. & Ind.* 848 (1956)

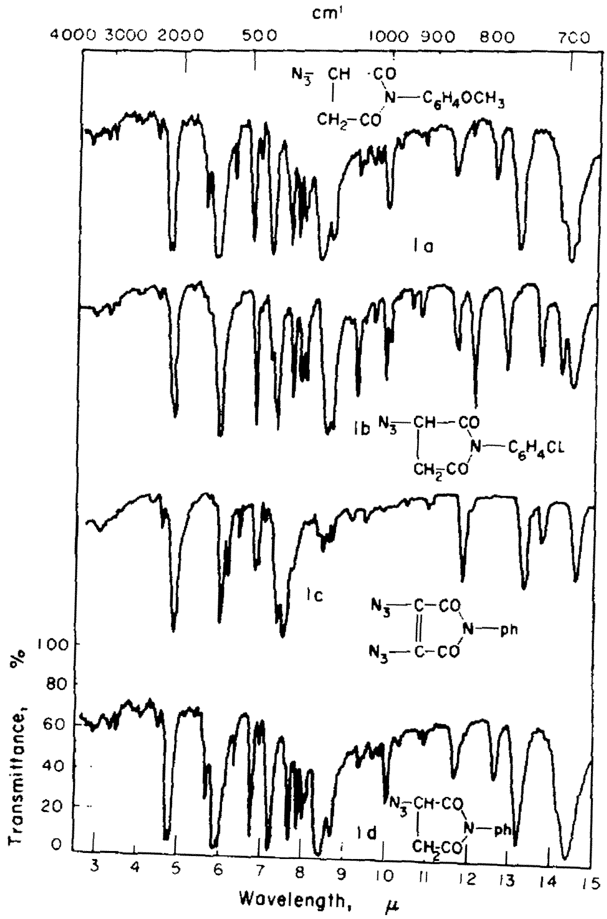

cm'
4000 3000 2000 500 1000 900 800 700
N3 CH CO N—C6H4OCH3 CH2—CO
1a
1b N3—CH—CO N—C6H4Cl CH2—CO
1c
N3—C—CO N—ph N3—C—CO
1d
N3-CH-CO N—ph CH2CO
Transmittance, %
100
80
60
40
20
0
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength, μ

FIG. 1

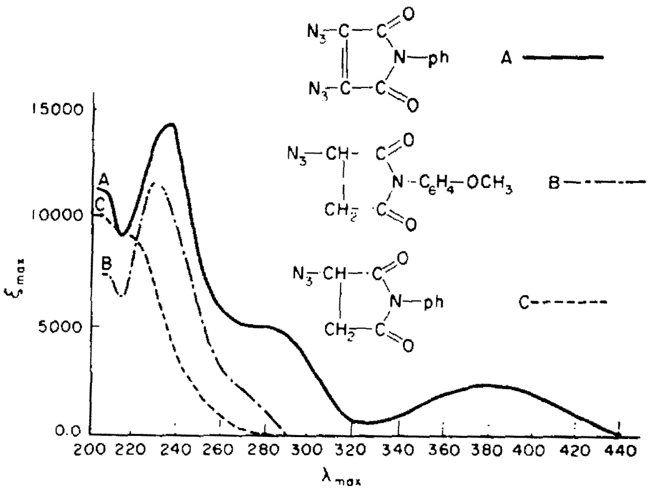
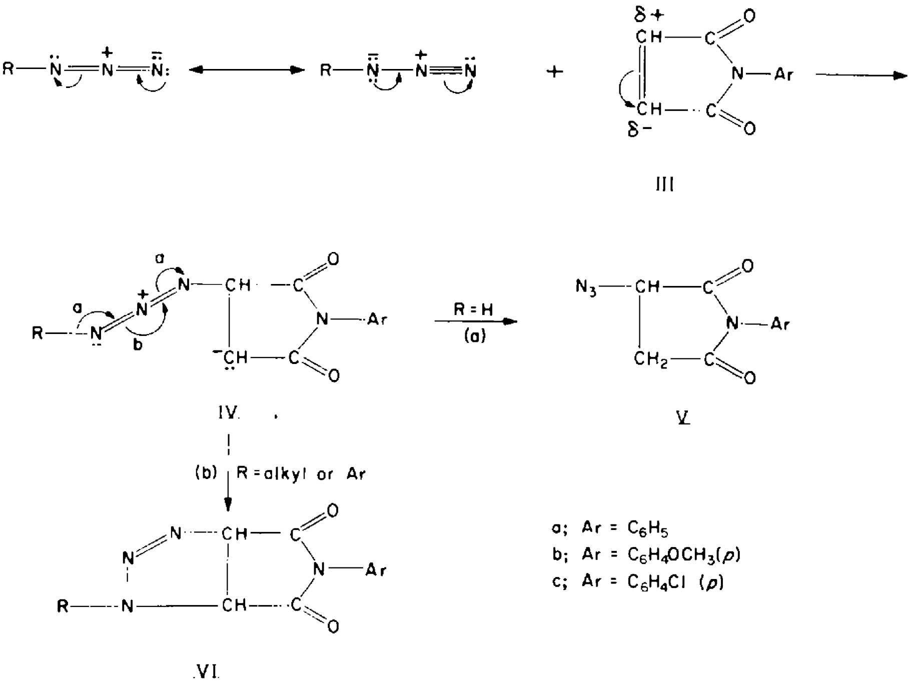

N3—C—C=O N—ph N3—C—C=O
A
N3—CH— C=O N-C6H4-OCH3 CH2 C=O
B
N3-CH—C=O N—ph CH2—C=O
C
15000
10000
5000
0.0
A
C
B
εmax
200 220 240 260 280 300 320 340 360 380 400 420 440
λmax

FIG. 2

We believe that the mechanism of the two reactions is fundamentally the same. (cf. Scheme A).



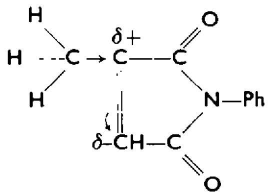
Scheme A

	R	Ar
a	C_6H_5	C_6H_5
b	C_6H_5	$C_6H_4Cl(p)$
c	C_6H_5	$C_6H_4OCH_3(p)$
d	C_6H_5	$C_6H_4CH_3(p)$
e	$C_6H_4NO_2$	C_6H_5
f	$C_6H_4NO_2$	$C_6H_4CH_3(p)$
g	$C_6H_4NO_2$	$C_6H_4OCH_3(p)$
h	$C_6H_4NO_2$	$C_6H_4Cl(p)$

The constitution of the azidosuccinimide derivatives (V) is confirmed by its I.R. spectrum which shows the azido stretching frequency in the 4·7 μ region[3–5] and a carbonyl stretching frequency at 5·85–5·9 μ (cf. Fig. 1a, 1b and 1d). Its U.V. spectrum is similar to that of N-phenylsuccinimide and cyclopropane-2,3-(N-phenyl)-dicarboximide[6] (cf. Fig. 2b and 2c).

The I.R. spectra of the triazolines under investigation do not show the stretching frequency of the azido group.

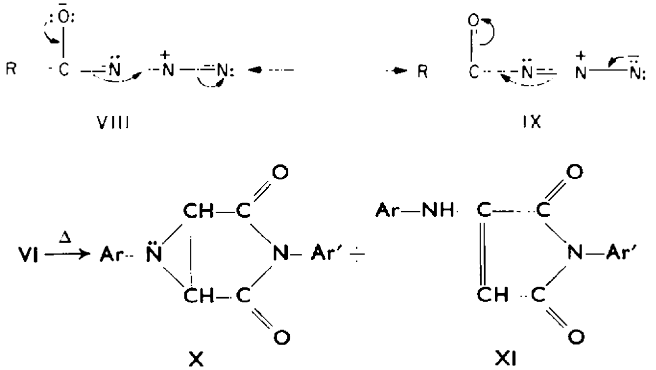
The above mechanism is supported by the fact that N-phenyl-citraconimide was recovered unchanged under similar conditions. A fact which can be attributed to +I effect of Me group which practically neutralizes the partial positive charge that can be formed on the N-arylmaleimide (cf. VII). Maleamic acid is also found to be inactive towards this reagent. Furthermore, benzazide failed to react with the arylmaleimides investigated and instead it gave together with the recovered maleimide a compound of molecular formula $(PhNH)_2CO$[8] which is also obtained when benzazide is heated alone. A fact which can be explained by considering the canonical structures (VIII and IX) as strongly contributing to the actual state of the acylazide resonance hybrid:



(VII)

Mustafa *et al.*[1] and Davis and Rondesvedt jun.[7] claimed that pyrolysis of VI yields only the corresponding aziridine.

By comparison with the pyrolysis products of the isoteric pyrazolines,[6,9] which yield both cyclic and unsaturated compounds, it is expected that VI on pyrolysis would give similar results (cf. Scheme B)



Scheme B

	Ar	Ar'	Ar	Ar'
a	C_6H_5	C_6H_5	C_6H_5	C_6H_5
b	C_6H_5	$C_6H_4Cl(p)$	C_6H_5	$C_6H_4Cl(p)$
c	C_6H_5	$C_6H_4OCH_3(p)$		
d	C_6H_5	$C_6H_4CH_3(p)$		
e	$C_6H_4NO_2(p)$	C_6H_5		
f	$C_6H_4NO_2(p)$	$C_6H_4CH_3(p)$		
g	$C_6H_4NO_2(p)$	$C_6H_4OCH_3(p)$		
h	$C_6H_4NO_2(p)$	$C_6H_4Cl(p)$		

This was proved to be the case only with VIa and VIb where mixtures of Xa, XIa and Xb, XIb were isolated respectively.

Compounds of type XI were differentiated from X by the appearance of an NH stretching frequency in their I.R. spectra (cf, Fig. 3). The U.V. spectrum of XIa is similar to that of N-phenylmaleimide[6] (cf. Fig. 4). Furthermore X(a-c) react with HCl to give the corresponding XII. This is a well known reaction for aziridines.[10] Compounds of structure XII are known to give the aziridines or the corresponding dimer

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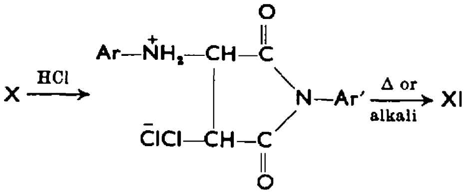
[8] L. Horner, E. Spietschka, and A. Gross, *Liebigs Ann.* **573**, 17, 1951, cf. *Chem. Abstr.* **46**, 3977 (1952).

[9] W. I. Awad, S. M. A. R. Omran and M. Sobhy, Part (II), *J. Chem. Soc., U.A.R.* in press.

(piperazine derivative) by the action of NaOH.[10] However it was found in the present investigation that XII yields XI and not X either by boiling in toluene or when treated with NaOH (cf. Scheme C).



XII

Scheme C

	Ar	Ar'
a	C_6H_5	C_6H_5
b	C_6H_5	$C_6H_4Cl(p)$
c	C_6H_5	$C_6H_4CH_3(p)$

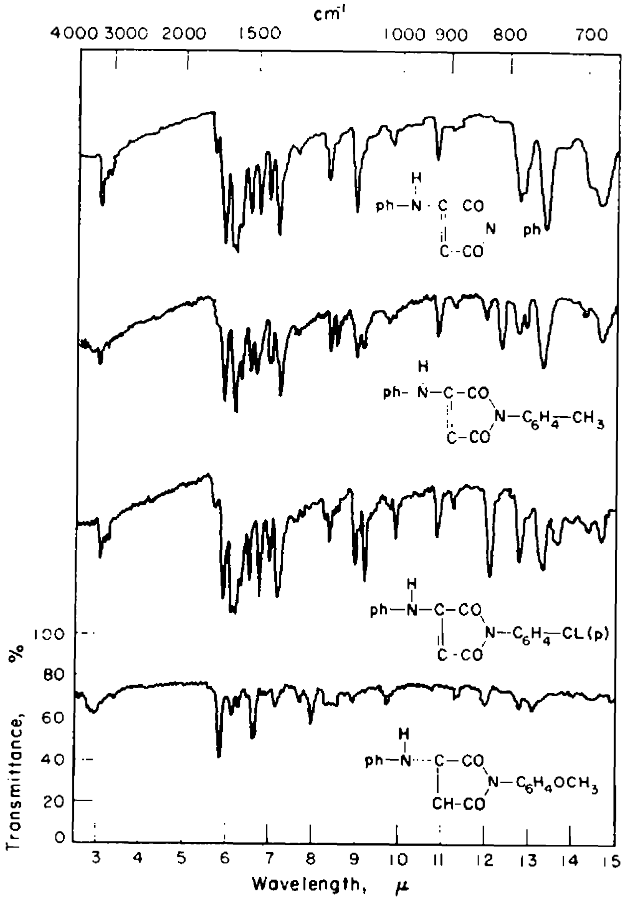


FIG. 3

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[10] R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds" Interscience Publishers Ltd., London, 1960, pp. 8 and 9.

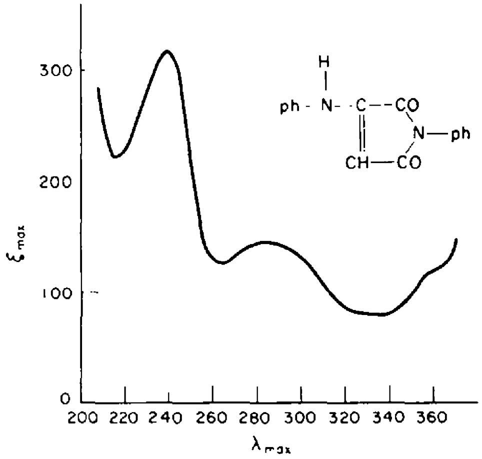
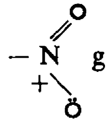


FIG. 4

The aziridines (XIe-h) are recovered unchanged when treated with HCl. This fact can be attributed to the -I and -T effect of the  $-\mathrm{N}^{+}(=\mathrm{O})\mathrm{O}^{-}$ group which minimizes the availability of the lone pair of electron on the aziridine nitrogen atom.

EXPERIMENTAL

All m.p. are not corrected. Analysis were carried out by Alfred Bernhardt, im Max-Plank Institute, Mulheim, Germany. I.R. spectra were measured on a Perkin-Elmer, Infracord Model 137 spectrophotometer using KBr Wafer technique. U.V. spectra were measured on a Perkin-Elmer, spectracord Model 4000A, spectrophotometer for ethyl alcohol solutions except in the case of (Xa) where cyclohexane was used as a solvent.

2,3-*Diazido*-N-*phenylmaleimide* (II). This was prepared as previously described,[1] yellow crystals m.p. 100°.

Azido-N-*arylsuccinimides* (V). To a solution of N-aryl-maleimide (1 g in the least amount of glacial acetic acid); was added a solution of NaN_3 (0·7 g in 2 ml water). The reaction mixture was heated (70–80°) (water bath) for 30–45 min. A remarkable change in colour was observed. Upon cooling and diluting with water a colourless product deposited, which was filtered off and crystallized from a suitable solvent (cf. Table 1).

On repeating the above experiment using N-phenylcitraconimide or maleamic acid no reaction took place as indicated by the recovery of the starting materials (m.p. and mixture m.ps).

Action of phenylazide,[11] and p-*nitrophenylazide*[12] on N-*arylmaleimides*. A solution of the azide (0·005 mole) in ethyl acetate was added to the maleimide (0·005 mole) solution in the same solvent. The mixture was refluxed for 4 hr, and the solvent was then removed under red. press. The residue was washed several times with light petroleum (b.p. 60–80°) and then with little cold ethanol. The colourless product so obtained was recrystallized from a suitable solvent. (cf. Table 2).

On repeating the above experiment using N-phenylcitraconimide, or *p*-nitrophenylmaleimide no reaction took place as indicated by the recovery of the starting materials (m.p. and mixture m.ps).

Thermal decomposition of VI. Triazolines (VI) in Table 2 were heated *in vaccuo* (0·4 mm) just above the m.p. (oil bath) for 30 min. The cold residue was then extracted several times with light petroleum (b.p. 70–80°) and the product was recrystallized from a suitable solvent (cf. Table 3).

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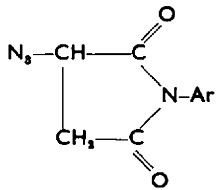
[11] R. O. Lindsay and C. F. H. Allen, *Organic Synthesis* Coll. Vol. III p. 710.

[12] P. A. S. Smith and J. H. Boyer, *Organic Synthesis* **31,** 14 (1953).

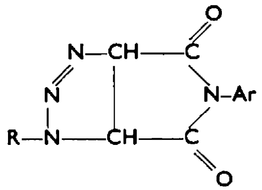
TABLE 1



Compound		Crystallization solvent	Yield %	m.p.	Formula	Carbon %		Hydrogen %		Nitrogen %		Chlorine %	
						req.	found	req.	found	req.	found	req.	found
V	a	A	80	85–86°	$C_{10}H_8N_4O_2$	55·5	54·95	3·73	3·69	25·92	25·32		
	b	B	80	102–103°	$C_{11}H_{10}N_4O_3$	53·66	54·28	4·09	4·25	22·76	22·45		
	c	C	70	110–111°	$C_{10}H_7N_4O_2Cl$	47·9	48·2	2·79	2·55	22·35	22·20	14·17	14·42

A. Light petroleum (b.p. 60–80°).
B. Benzene–light petroleum (b.p. 80–100°).
C. Benzene–light petroleum (b.p. 60–80°).

Table 2

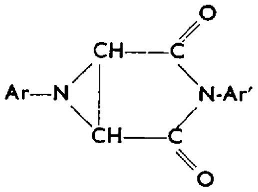


Compound	Crystallization solvent	m.p.	yield (%)	Formula	Carbon %		Hydrogen %		Nitrogen %		Chlorine %	
					calcd	found	calcd	found	calcd	found	calcd	found
VI a	A	156°	77	$C_{16}H_{18}N_4O_2$	65·75	65·28	4·14	4·17	19·17	18·30		
					*		*		*		*	
b	A	175°	91	$C_{16}H_{11}N_4O_2Cl$	58·80	58·89	3·30	3·43	17·10	16·89	10·87	11·11
c	B	150°	91	$C_{17}H_{14}N_4O_3$	63·35	63·26	4·38	4·68	17·38	16·78		
d	A	159°	83	$C_{17}H_{14}N_4O_2$					18·29	17·57		
e	C	191°	87	$C_{16}H_{11}N_5O_4$	56·97	56·91	3·29	3·44	20·77	20·30		
f†	B	185°	81	$C_{17}H_{13}N_5O_4$	58·12	58·37	3·73	3·78	19·94	19·74		
g	A	182°	75	$C_{17}H_{13}N_5O_5$	55·59	56·52	5·57	3·77	19·07	18·69		
					*		*		*		*	
h	A	184°	86	$C_{16}H_{10}N_5O_4Cl$	51·68	52·47	2·69	2·96	18·80	18·25	9·55	9·64

A. Benzene.
B. Ethanol.
C. Ethyl acetate.
* Required.

† In Reference 1 this compound was crystallized from chlorobenzene, but we found that crystallization from such a solvent lead to the formation of the corresponding aziridine.

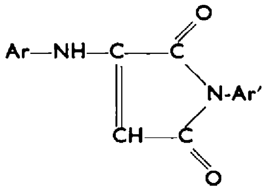
TABLE 3



Compound		Crystallization solvent	m.p.	Yield %	Formula	Carbon %		Hydrogen %		Nitrogen %		Chlorine %	
						calcd	found	calcd	found	calcd	found	calcd	found
X	a†	A	120°	91	$C_{16}H_{12}H_2O_2$	72·73	72·92	4·55	4·65	10·60	10·60		
						*		*		*		*	
	b‡	A	121°	94	$C_{16}H_{11}N_2O_2Cl$	64·40	64·27	3·63	3·63	9·38	9·16	11·89	12·11
	c	A	112°	80	$C_{17}H_{14}N_2O_3$	69·64	69·37	4·70	4·80	9·50	9·52		
	d	A	138°	83	$C_{17}H_{14}N_2O_2$	73·38	73·27	5·03	5·06	10·07	10·09		
	e§	A	150°	73	$C_{16}H_{11}N_3O_4$	62·13	62·07	3·55	3·40	13·59	13·32		
	f	A	190°	90	$C_{17}H_{13}N_3O_4$	63·15	63·27	4·05	4·04	13·00	13·18		
	g	B	178°	91	$C_{17}H_{13}N_3O_5$	60·17	60·16	3·86	3·85	12·39	12·00		
						*		*		*		*	
	h	B	180°	90	$C_{16}H_{10}N_3O_4Cl$	55·89	56·78	2·90	2·94	12·20	12·19	10·30	10·23

A. Light petroleum (b.p. 70–80°)
B. Benzene.
* Required.
† The corresponding anilino compound XIa, m.p. 230° was also isolated in 5·5% yield.
‡ XIb m.p. 238° was also isolated in 5·5% yield.
§ In Reference 1 m.p. 240°.

TABLE 4



Compound		Crystallization solvent	m.p.	Formula	Carbon %		Hydrogen %		Nitrogen %		Chlorine %	
					req.	found	req.	found	req.	found	req.	found
XI	a	A	230°	$C_{16}H_{12}N_2O_2$	72·73	72·61	4·55	4·58	10·60	10·60		
	b	A	238°	$C_{16}H_{11}N_2O_2Cl$	64·40	64·42	3·63	3·73	9·38	9·10	11·89	12·10
	c	A	219°–220	$C_{17}H_{14}N_2O_2$	73·38	73·77	5·03	4·78	10·07	10·01		

A. Toluene.

In the case of VIa and VId a residue remains after extraction with light petroleum. It was dissolved in hot benzene and concentrated to yield the corresponding anilino compounds (XIa and b).

Action of HCl *on* Xa. Compound Xa (0·5 g) was dissolved in ethanol (20 ml) and dry HCl gas was bubbled in this solution for few min. A colourless product (XIIa) separated out which was filtered off and washed several times with ethyl alcohol m.p. 194–195: (Found: N, 8·1; Cl, 19·5. $C_{16}H_{13}N_3Cl_2O_2$ requires: N, 8·3; Cl, 21·1%).

In a similar manner Xb was treated to give a colourless product (XIIb) m.p. 199–200: (Found: N, 8·1; Cl, 20·3. $C_{17}H_{15}N_3O_2Cl_2$ requires: N, 8·0; Cl, 20·7%).

These compounds could not be recrystallized since they loose HCl by this treatment. (*inter alia*).

Conversion of X to XI. Compound X was converted first to XII as described in the previous experiment. When XII was treated with cold KOH solution (10%), it was quantitatively converted to XI. When XII was boiled in toluene it was also converted to the corresponding XI (cf. Table 4).