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HETEROCYCLIC DERIVATIVES OF METHAZONIC ACID. FORMATION OF 5-NITRO-1,2,3,4-TETRAHYDROPYRIMIDINE DERIVATIVES

H. DABROWSKA-URBAŃSKA

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw 42, Poland

A. R. KATRITZKY

School of Chemical Sciences, University of East Anglia, Norwich, England

and

T. URBAŃSKI

Warsaw Institute of Technology (Politechnika), Warsaw 10, Poland.

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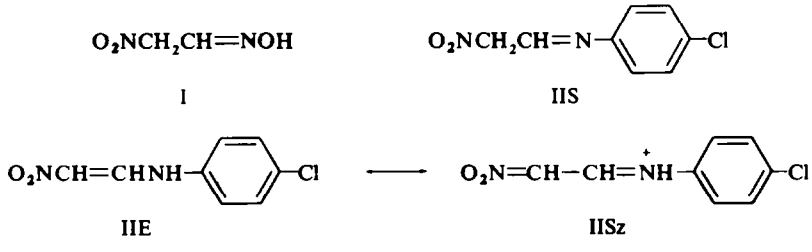
Abstract—The derivative produced by the reaction of methazonic acid with *p*-chloraniline reacts with formaldehyde and primary amines to form 1,3-disubstituted 5-nitro-1,2,3,4-tetrahydropyrimidines. These are readily transaminated at the 1- or 1,3-positions by warming with primary amines. Transamination involves (1) ring opening with loss of a mole of formaldehyde to form a Schiff's base zwitterion, (2) replacement of the amine forming the Schiff's base, and (3) reclosure of the ring by formaldehyde.

OUR researches on the formation of heterocyclic systems from primary nitroparaffins, formaldehyde and amines,[2] are now extended to methazonic acid (I).[3] Compound I is an oxime as well as a primary nitroparaffin which could lead to products more complicated than previously. To avoid the instability of methazonic acid, we used the derivative (II), obtained by reaction with *p*-chloroaniline.[4] Spectroscopic properties of related compounds[5a] suggest revision of the originally proposed Schiff's base structure (IIS) to a nitroenamine with (cf. also Ref. 5*b*) resonance structures IIE



I IIS IIE IISz

(enamine) and IISz (Schiff's base zwitterion), and this is confirmed by the NMR spectra, see below. Nitroolefins do not normally undergo aldol reactions with formaldehyde,[6] but the enamine function could modify this behaviour. Indeed, II reacted with formaldehyde in aqueous ethanol at pH of ca. 8 to yield the carbinol (IIIa) together with

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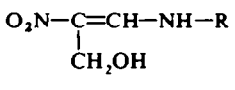
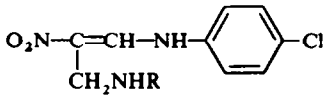
a little of the 1,2,3,4-tetrahydropyrimidine (Va). The origin of the cyclized product (Va) can be explained by partial hydrolysis of IIIa to give *p*-chloroaniline which then reacts with more IIIa and formaldehyde to yield Va. Although direct evidence is not available, diamine Va is probably an intermediate; the conversion (IIIa → IVa) may involve either dehydration followed by a Michael addition, or fission of IIIa back to II followed by a Mannich reaction.



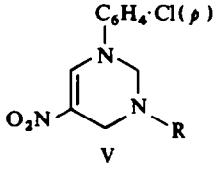
III

IIIa: R = *p*-Cl · C_6H_4
IIIb: R = Me



IV

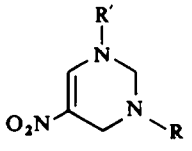
IVa: R = *p*-Cl · C_6H_4
IVb: R = Me
IVc: R = Et
IVd: R = CH_2Ph



V

Va: R = *p*-Cl · C_6H_4
Vb: R = Me
Vc: R = Et Vd: R = CH_2Ph

Treatment of the nitroolefin (II) with formaldehyde and the appropriate primary amine gave the four 5-nitro-1,2,3,4-tetrahydropyrimidines (Va–Vd). The yield was highest when the molar proportions of II, formaldehyde, and the amine were 1:3:2 These reactions may be of the Mannich type or they may involve the formation of the carbinol (IIIa). As expected IIIa also reacts with formaldehyde and the amine in the proportions 1:2:2 to give products of type V.



VI: R = R′
VIa: R = R′ = Me
VIb: R = R′ = CH_2Ph

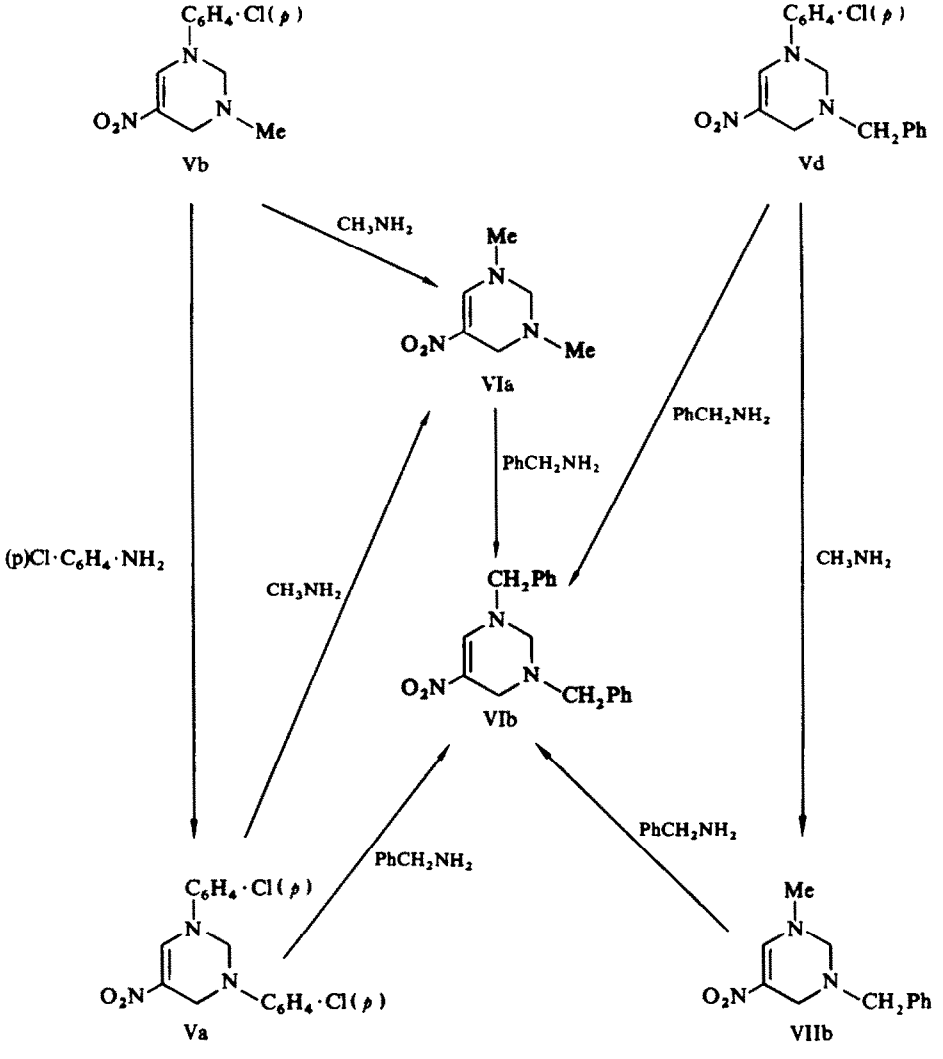
VII: R ≠ R′
VIIa: R = Et, R′ = Me
VIIb: R = CH_2Ph, R′ = Me

With amounts of the amine larger than 2 molar, transamination products (VI) were formed in addition to V; II with formaldehyde and benzylamine in boiling ethanol also gave both VIb and Vd.

Transmination of preformed 5-nitrotetrahydropyrimidines (V → VII) occured on treatment with various amines (see Scheme 1). The substituents at position 1 or at both positions 1 and 3 were changed depending on the amine used and the temperature: as a rule, both substituents were replaced in boiling ethanol. We did not examine closely the transaminating ability of amines, but the 1,3-dibenzyl derivative (VIb) was formed particularly readily when benzylamine was used. Transaminations also occur with the amines formed by fission of the original tetrahydropyrimidine

(V). Thus, heating Vb in boiling ethanol (basified with triethylamine to pH 8), rearranges Vb into Va (a type of "semi-disproportionation"). Boiling Vd in ethanol and methylamine gave some VIb by a similar "semi-disproportionation", although at 20° the intermediate product VIIb was formed.

SCHEME 1

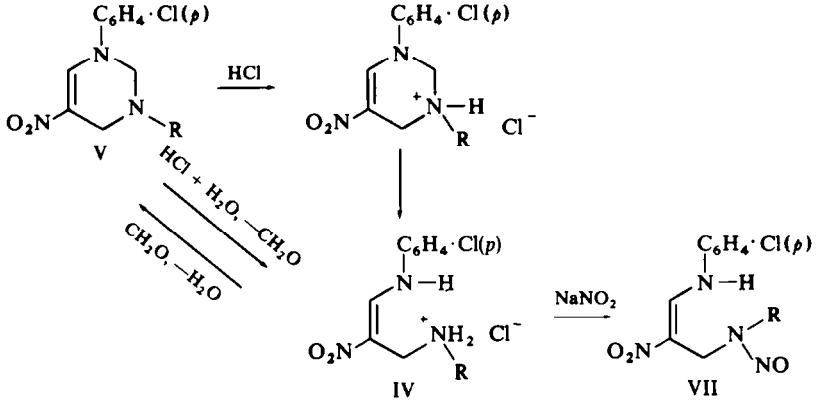


Reaction mechanisms. Carbinol IIIa was transaminated by heating with ethanolic methylamine to give *p*-chloroaniline and the new carbinol IIIb which reacted with formaldehyde and various primary amines to form 5-nitro-1,2,3,4-tetrahydropyrimidines (VI). We did not succeed in transaminating compound II by any of the methods successful with compounds V–VII. Transaminations of carbinols of type III are analogous to the well-known properties of Schiff's bases.[7] Compound III is mesomeric with enamine (IIIE) and Schiff's base zwitterion (IIISz) canonical forms.

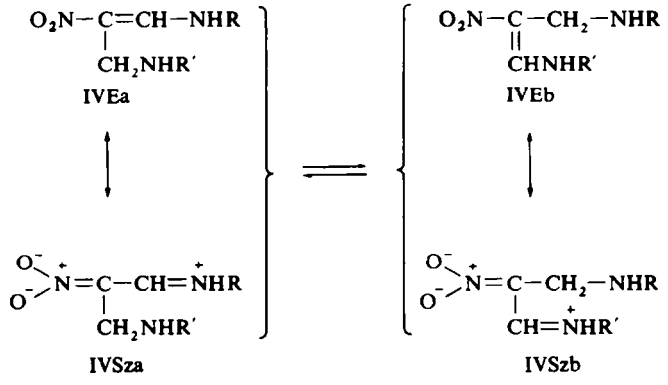
IIIE IIISz

In anhydrous media, the tetrahydropyrimidines (V) form hydrochlorides, these are readily hydrolyzed by water to formaldehyde and the diamine hydrochlorides (IV). The latter reform the tetrahydropyrimidines by treatment with formaldehyde at pH 8 (cf. Scheme 2). The hydrochloride (IV) gives an N-nitroso compound (VIII) with sodium nitrite.

SCHEME 2



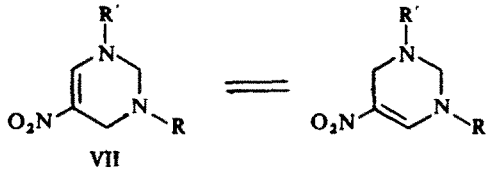
The novel transaminations of the hydropyrimidine derivatives (V–VII) probably involve preliminary ring opening of these tautomeric N-*p*-chlorophenyl-N′-alkyl (or aralkyl)-2-nitro-1,3-diaminopropenes, where each of the two enamine forms (IVEa, b) is mesomeric with a Schiff's base zwitterion (IVSza, b) contributing to the resonance hybrid. Each tautomer can react with amines at the C=N$^+$HR group and thus transamination can occur successively at both positions 1 and 3. The formulae (IVEa, b and IVSza, b) also illustrate the possible formation of potentially tautomeric cyclic products (VII); the double bond shift in VII is of a different type from the known tautomerism of enamines.[8]



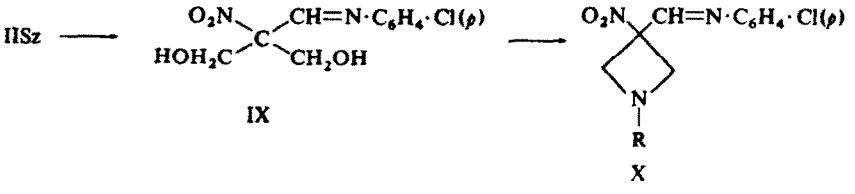
IVEa IVEb

IVSza IVSzb

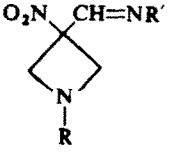
Spectroscopic proof of structure. Nitroolefins do not normally undergo aldol reactions with formaldehyde[6] which seemed originally to indicate addition to the primary nitro group of IISz to give the hypothetical diol (IX) converted by a primary amine to an azetidine (X), which was transaminated by $R'NH_2$ to yield compounds of type XI and XII. However, the diol (IX) could not be isolated, and firm evidence for the tetrahydropyrimidine structure was later obtained from ultraviolet and NMR spectra.



VII



IX X



XI: $R \neq R'$
XII: $R = R'$

TABLE 1. UV SPECTRA OF DIOXAN SOLUTIONS

Compound	λ_{max} 1		λ_{max} 2	
	mμ	ε	mμ	ε
II	245	21,500	370	25,500
IIIa	245	58,300	385	23,750
IVa[a]	240	17,900	380	22,700
VIII	245	20,200	380	21,250
Va	250	24,500	385	22,100
Vb	250	20,750	385	26,500
Vd	250	15,000	385	23,750
VIa	220[b]	[c]	365	20,210
VIb	220[b]	[c]	365	22,900

[a] Hydrochloride
[b] In n-hexane
[c] Not determined owing to the low solubility in n-hexane.

UV spectral data are recorded in Table 1. Compounds II, IIIa, IVa and VIII, which all contain the *p*-chlorophenyl group, show two band spectra almost identical with those of the ring compounds (Va–d) containing the same substituent in position 1 (or both 1 and 3) (Fig. 1). The bands are hypsochromically shifted in VIa and VIb which do not contain conjugated aromatic rings.

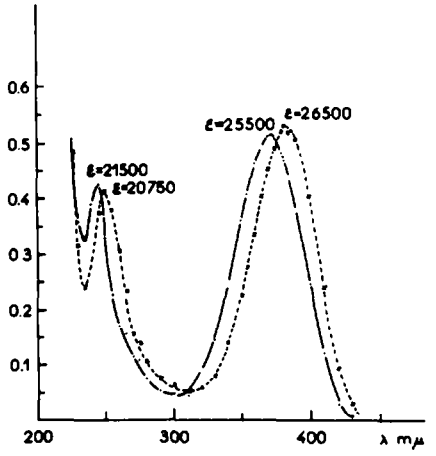


FIG. 1 UV spectra of dioxan solutions of II (— · — · —) and Vb (× – – × – – ×).

In the infrared spectra (Table 2), the heterocyclic compounds V, VI and VII show two characteristic bands in the region 1325–1180 cm^{-1} which do not appear in the ring opened derivatives IV and VIII, nor the acyclic starting materials. We assigned these bands to tetrahydropyrimidine ring stretching modes. The other bands agree with the suggested structures. The nitro symmetric and asymmetric modes occur at the lower frequencies characteristic for conjugated systems.

The NMR spectrum of II (Fig. 2) clearly indicates the olefinic structure. The tetrahydropyrimidine spectra (Figs 3–5) show the signals from the CH_2 groups as singlets: this is a result of rapid inversion of the rings (deformed chair ⇌ deformed chair).

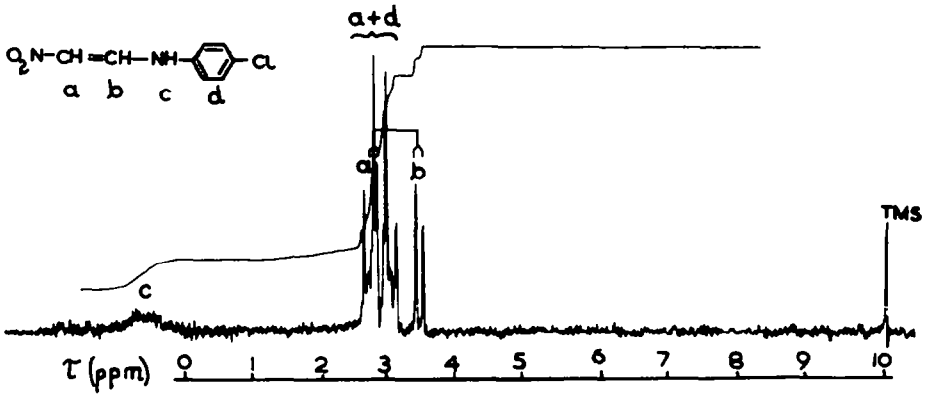


FIG. 2 NMR spectrum of II in deuteriochloroform: a, 2·72 τ; b, 3·31 τ; c, 0·60 τ; d, 2·51–3·02 τ; $J \simeq 6{\cdot}5$ c/s.

TABLE 2. WAVE NUMBERS OF IR ABSORPTION BANDS[a]

Compound	ν_{OH}	ν_{H_2O}	ν_{NH}	ν_{NH} in hydrochlorides	$\nu_{C=C}$ Benzene ring	ν_{CH} Benzene ring or olefin	ν_{CH} in CH_2 or CH_3	$\nu_{C=C}$	ν_{NO_2} assym.	ν_{NO_2} symm.	CH_2	Tetrahydro-pyrimidine ring
II			3280 w		1590 m	3020 w		1650 vs	1490 vs	1370 vs		
IIIa	3550 w		3280 w		1590 m	3020 vw	2920 vw	1650 vs	1500 vs	1380 vs	1450 m	
IIIb	3500 m		3250 m			3020 vw	2920 vw	1650 vs	1470 m	1380 vs	1450 m	
IVb			3220 w	2700 s	1595 m			1660 vs	1500 s	1370 vs		
IVc		3400 m	3220 w	2700 s	1620 w			1650 vs	1500 m	1380 s		
IVd		3390 vs	3250 w	2750 w 2550 w	1590 m			1650 vs	1495 s	1370 vs		
Va					1590 s	3085 vw	2900 vw	1610 vs	1500 s	1360 s	1470 m	1230 vs 1220 vs
Vb					1590 s	3090 vw	2976 vw 2917 vw	1615 vs	1500 s	1360 s	1476 s	1262 vs 1226 vs
Vb · HCl				2200 s 2350 s	1590 m	3010 vw		1630 vs	1500 vs	1370 m		1280 vs 1300 vs
Vc					1585 s	3086 vw	2950 vw 2900 vw 2840 vw	1620 vs	1500 s	1360 m	1470 m	1245 vs 1222 vs
Vc · HCl				2400 s 2450 s	1590 m	3020 w		1645 vs	1505 s	1350 m		1270 vs 1300 vs
Vd					1590 m	3050 vw	2900 vw 2850 vw	1615 vs	1500 s	1360 m	1475 s	1240 vs 1210 vs
VIa						3061 w	2967 w 2915 w 2880 w 2835 w	1615 vs	1500 s	1370 s	1460 s	1291 vs 1278 vs
VIa · HCl				2400 s 2480 s				1630 vs	1510 s	1380 s		1305 vs 1325 vs
VIb						3050 m	2950 vw 2820 vw	1622 vs	1500 m	1360 vs		1300 vs 1275 vs
VIIa						3024 m	2993 m 2953 m 2906 m 2868 m	1615 vs	1500 m	1360 s	1474 m	1200 vs 1180 vs
VIII			3297 m		1596 m			1655 vs	1500 s	1377 vs		

[a] Measured in KBr discs.

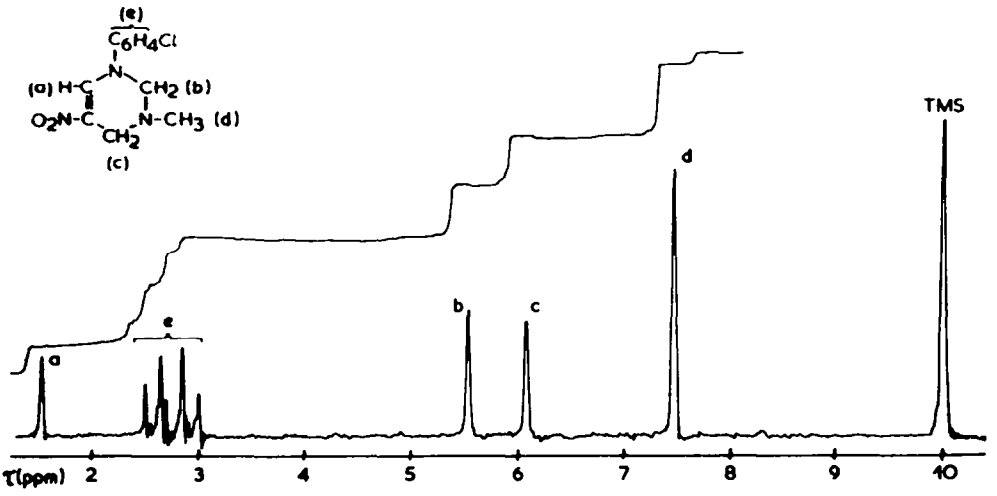


FIG. 3 NMR spectrum of Vb in deuteriochloroform: a, 1·57 τ; b, 5·55 τ; c, 6·09 τ; d, 7·47 τ; e, 3·1–2·55 τ.

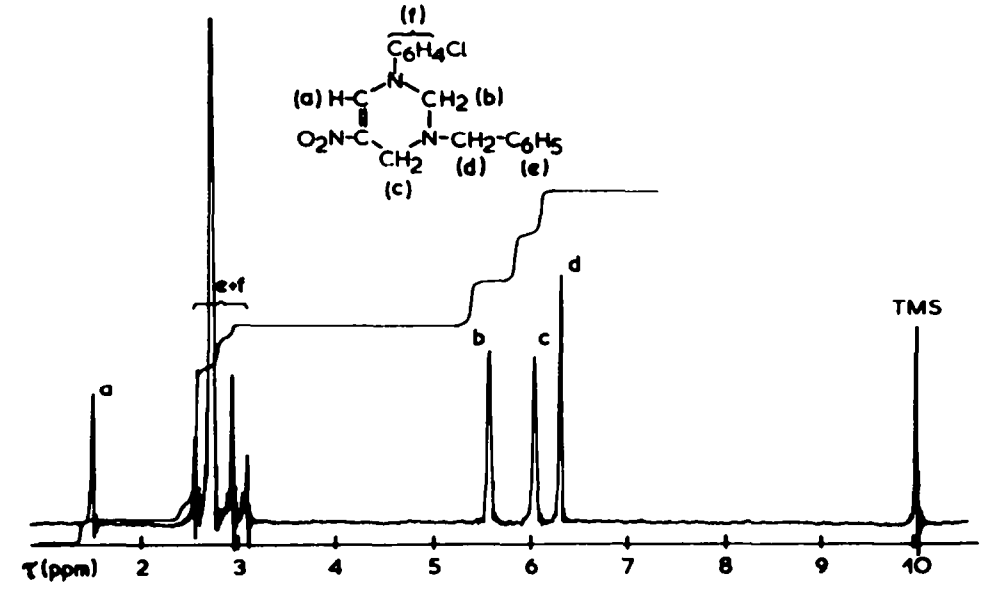


FIG. 4 NMR spectrum of Vd in deuteriochloroform: a, 1·55 τ; b, 5·62 τ; c, 6·06 τ; d, 6·32 τ; e, 2·73 τ; f, 3·12–2·55 τ.

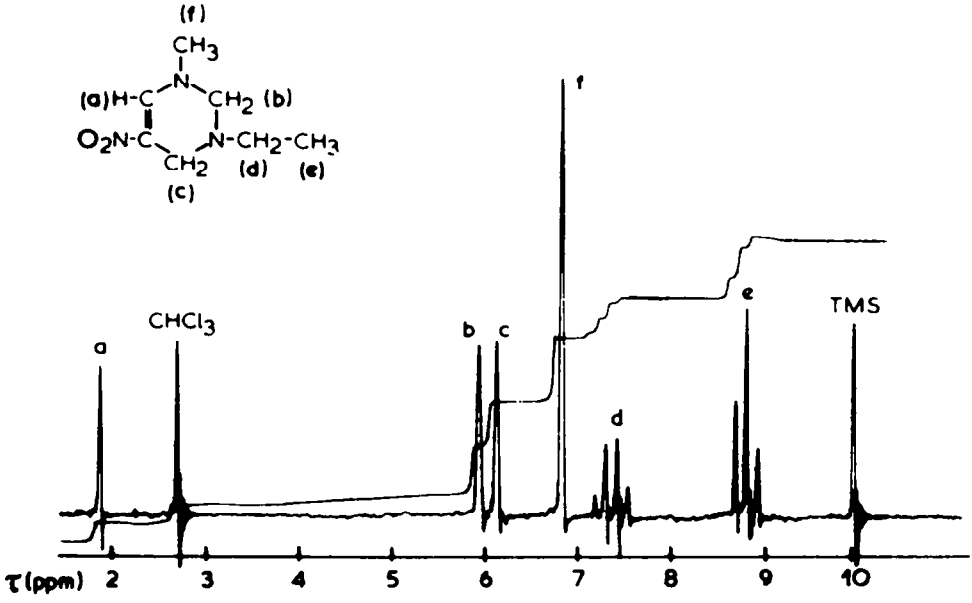


FIG. 5 NMR spectrum of VIIa in deuteriochloroform: a, 1·91 τ; b, 5·92 τ; c, 6·15 τ; d, 7·39 τ; e, 8.84 τ; f, 6·88 τ.

EXPERIMENTAL

M.ps, crystal shapes and analytical data are collected in Table 3. Mol wts were determined by the ebulliometric method of Swietoslawski in benzene or dioxan as solvents. Water of crystallization was determined by the Karl Fischer reagent.

Spectroscopy. UV spectra were obtained with a Unicam SP-700 spectrophotometer in cuvettes of 1 cm with dioxan or n-hexane as solvents. IR spectra were recorded for nujol mulls or KBr discs with Unicam SP-200 and Hilger 800 spectrophotometers fitted with a NaCl prism.

NMR spectra were recorded on a Varian 4300-C (generator frequency 60 MHz) in deuteriochloroform or deuterioacetone with TMS as internal standard.

1-N-(p-*Chlorophenyl*)*amino*-2-*hydroxy*-2-*nitromethylethylene* (IIIa)

Compound IIa was obtained from methazonic acid and *p*-chloroaniline,[4] m.p. 162–163° (lit.[4] 165°). Compound IIa (3·9 g, 0·02 mol), EtOH (60 ml), and aqueous 27% formaldehyde (20·4 ml, 0·2 mol), were mixed and brought to pH ca. 8, with Et_3N or 2% NaOH aq. After 12 hr the *nitroenamine* IIIa (3·8 g, 84%) separated. It crystallized from EtOH or nitromethane and is soluble also in acetone and (sparingly) in water. After 24 hr the by-product Va (0·04 g, 1%) crystallized, see below.

3-*Substituted* 1,2,3,4-*tetrahydro*-1-(p-*chlorophenyl*)-5-*nitropyrimidines* (V).

Method 1, *from* IIa. Aqueous (27%) formaldehyde (15·4 ml, 0·15 mol) and the appropriate primary amine (0·1 mol) (methylamine, ethylamine, *p*-chloroaniline or benzylamine) was added to IIa (9·9 g, 0·05 mol) suspended in EtOH (120 ml) (or MeOH for the preparation of Vc). For Va and Vd it was necessary to basify the mixture with Et_3N to pH ca. 8. The soln was stirred for 1 hr, left for 10 hr, and the resulting ppt recrystallized; Vb and Vd from EtOH, Vc from MeOH and Va from benzene. The yields were 81–84%.

Method 2, *from* IIIa. To a suspension of IIIa (1·14 g, 0·005 mol) in EtOH (15 ml) aqueous (27%) formaldehyde (1·02 ml, 0·01 mol) and a primary amine (0·01 mol) as in method 1, were added. The mixture was heated on a steam-bath until the solid dissolved, and was kept 10 hr at 20°. The ppts were crystallized as in method 1. The yields were 60–75%.

Compound	Formula	Crystalline shape[a]	m.p.	Molecular Weight		Analysis %								Water of crystallization	
				Found	Required	Found				Required				Found	Required
						C	H	N	Cl	C	H	N	Cl		
IIIa	$C_9H_9ClN_2O_3$	N	173–174°	204	228·5	47·8	4·1	12·4	15·9	47·3	3·9	12·25	15·5		
IIIb	$C_4H_8N_2O_3$	P	132			36·8	6·0	21·3		36·3	6·1	21·1			
IVb	$C_{10}H_{12}ClN_3O_2 \cdot HCl$	N	180			43·1	4·8	14·7		43·2	4·7	15·1			
IVc	$C_{11}H_{14}ClN_3O_2 \cdot HCl \cdot \frac{1}{2}H_2O$	N	181			44·3	5·2	14·1		44·1	5·3	13·9		3·5	3·0
IVd	$C_{16}H_{16}ClN_3O_2 \cdot HCl \cdot H_2O$	N	170			52·5	4·9	11·3	19·2	51·9	5·0	11·3	19·1	4·95	4·8
Va	$C_{16}H_{13}Cl_2N_3O_2$	P	165–166	355	350	54·65	3·7	12·6	19·9	54·85	3·7	12·0	20·3		
Vb	$C_{11}H_{12}ClN_3O_2$	N	117	251	253·5	52·15	4·7	16·9	14·3	52·1	4·7	16·9	14·0		
Vb · HCl	$C_{11}H_{12}ClN_3O_2 \cdot HCl$	P	183			46·3	4·4	14·6		45·7	4·5	14·4			
Vc	$C_{12}H_{14}ClN_3O_2$	P	127–128	272	267·7	53·5	5·3	15·3	13·4	53·5	5·2	15·6	13·1		
Vc · HCl	$C_{12}H_{14}ClN_3O_2 \cdot HCl$	P	181			47·9	4·6	14·4		47·4	4·6	13·8			
Vd	$C_{17}H_{16}ClN_3O_2$	P	118			61·8	4·75	12·9		61·9	4·85	12·75			
VIa	$C_6H_{11}N_3O_2$	P	161–162	168	157	46·35	7·1	26·8		45·9	7·0	26·75			
VIa · HCl	$C_6H_{11}N_3O_2 \cdot HCl$	N	188–189			37·9	6·2	21·0	18·1	37·45	6·2	21·6	18·3		
VIb	$C_{18}H_{19}N_3O_2$	P	148–149			69·7	6·0	13·7		69·9	6·1	13·9			
VIIa	$C_7H_{13}N_3O_2$	P	98–99	177	171	49·25	7·6	24·7		49·1	7·6	24·6			
VIIb	$C_{12}H_{15}N_3O_2$	P	127–128			62·1	6·2	18·2		61·8	6·4	18·0			
VIII	$C_{10}H_{11}ClN_4O_3$	P	166–168			43·9	4·3	21·1		44·1	4·1	20·7			

[a] N = needles, P = prisms.

The tetrahydropyrimidines V form bright yellow crystals, readily soluble in benzene, chloroform and dioxan, and sparingly soluble in water.

2-Hydroxymethyl-1-N-methylamine-2-nitroethylene (IIIb)

Aqueous $MeNH_2$ (40%, 1·5 g, 0·02 mol) was added to a suspension of IIIa (2·28 g, 0·01 mol) in EtOH (15 mol). The yellow *enamine* IIIb (1·2 g, 90%) soon crystallized.

1,2,3,4-Tetrahydro-1,3-dimethyl-5-nitropyrimidine (VIa). Aqueous formaldehyde (27%, 0·4 ml, 0·004 mol) and aqueous $MeNH_2$ (40%, 0·3 ml, 0·004 mol) were added to a suspension of IIIb (0·26 g, 0·002 mol) in EtOH (5 ml). The mixture was heated on a steam-bath until the solid dissolved, then left at room temp for a few hr. The product VIa separated and was recrystallized from MeOH or EtOH, m.p. 161–162° (0·1 g, 30%).

Transamination of the tetrahydropyrimidines V, VI *and* VII

1. *Reaction of* Vb *or* Vd *with methylamine.* Aqueous $MeNH_2$ (40%, 1·5 ml, 0·02 mol) was added to a suspension of Vb or Vd (0·01 mol; 2·5 g or 3·3 g, respectively) in EtOH (30 ml). The solid dissolved rapidly and immediately a yellow product, VIa (1·5 g, 90%) or VIIb (1·95 g, 85%) precipitated.

2. *Reaction of* Vc *or* Va *with methylamine.* Aqueous $MeNH_2$ (40%, 1·5 ml, 0·02 mol) was added to a suspension of Vc or Va (2·67 g, and 3·5 g respectively, 0·01 mol) in MeOH (30 ml). For Va the mixture was refluxed for 45 min. When the solid had dissolved, the solvent was evaporated at 20° and ether was added. Yellow crystals of VIIa (1·2 g, 70%) or VIa (0·4 g, 50%) resulted.

3. *Reaction of* Vb *with p-chloraniline. p*-Chloroaniline (1·27 g, 0·01 mol) was added to a suspension of Vb (1·26 g, 0·005 mol) in EtOH (15 ml) and the whole made alkaline with Et_3N to pH ca. 8, and refluxed for 30 min. Two products (Vb and Va) were detected by TLC; the latter was isolated by its lower solubility.

4. *Reaction of* Va, Vd, VIa *or* VIIb *with benzylamine.* Benzylamine (0·02 mol) was added to a suspension of Va, Vd, VIa or VIIb (0·01 mol) in EtOH. With Va, VIa and VIIb, the mixture was refluxed for 30 min, but with Vd the reaction occurred at room temp. After cooling, yellow crystals of Va, Vd, VIIb (70–90%) or VIa (15%) were collected.

5. *Reaction of* Vb *in basic medium.* A suspension of Vb (1 g) in EtOH was brought by Et_3N to pH ca. 8 and refluxed for 40 min. After cooling, the product (0·8 g) was collected and identified as Vb with a smaller amount of Va by TLC.

6. *Reaction of* Vd *with an excess of methylamine.* A suspension of Vd (0·66 g, 0·002 mol) in MeOH and aqueous $MeNH_2$ (40%, 1·5 ml, 0·02 mol) were refluxed for 1½ hr. The product, VIb (0·05 g, 25%) was collected.

Hydrochlorides of the tetrahydropyrimidines V *and* VI

Compounds Vb, Vc or VIa (1 g) were kept overnight in anhyd EtOH and ethereal HCl (5 ml). Light yellow hydrochlorides of Vb or Vc, or the colourless hydrochloride of VIa were collected (yields 1·1 g, 1·1 g and 1·2 g respectively). The hydrochloride of VIa was recrystallized from MeOH, the others could not be purified by crystallization because of low solubility, rapid decomposition when heated, and easy hydrolysis. To the suspension of hydrochloride Vb, Vc or VIa (0·0025 mol) in EtOH, $NHCO_3$ aq (0·005 mol) was added, slightly warmed and filtered: Vb, Vc or VIa precipitated.

Hydrolysis of the tetrahydropyrimidines V

Compound Vb, Vc or Vd (1 g), EtOH (15 ml) and conc HCl (0·3 ml) were boiled until the solid dissolved. The hydrochlorides IVb, IVc or IVd resulted (yields 0·7 g, 64%; 0·8 g, 75%; 0·6 g, 53%, respectively), and were crystallized from EtOH.

Reaction of the diamine hydrochloride IVb *with sodium nitrite*

Saturated $NaNO_2$ aq (0·5 g) was added to the soln of IVb (0·9 g) in water (30 ml). A crystalline yellow ppt of VIII (0·7 g) was collected. It gave a positive Liebermann test.

Reaction of the diamine hydrochlorides IV *with formaldehyde*

Aqueous formaldehyde (27%, 1·02 ml, 0·01 mol) was added to a suspension of hydrochlorides IVb, IVc or IVd (0·005 mol, 1·4 g and 1·85 g respectively) in EtOH, and $NaHCO_3$ aq or Et_3N was added to pH ca. 8. The products were identified as Vb, Vc or Vd (yields 1 g, 1·1 g and 1·4 g, respectively; ca. 85%).

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