Studies of Oxazolobenzodiazepines.† Part 7.[1] Synthesis of 3-Methyloxazolo[3,2-*d*][1,4]benzodiazepines and Configurational Studies of their Ketimine Intermediates

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Some 3-substituted oxazolo[3,2-*d*][1,4]benzodiazepines have been synthesized by a novel double-cyclization reaction, and the geometrical configurations of their ketimine intermediates have been investigated by n.m.r. spectroscopy and *X*-ray analysis.

In an earlier paper,[2] we reported the synthesis and pharmacology of oxazolo[3,4-*d*][1,4]benzodiazepines (A). Among numerous oxazolobenzodiazepines which were synthesized in our laboratories, the compounds possessing a 3-methyl group on the oxazolidine ring showed greater antibemegride activity than the unsubstituted compounds. The methyl-substituted oxazolobenzodiazepines were, however, produced in poorer yields by a synthetic method [2] involving a double-cyclization reaction of 2-(2-hydroxy-1-methylethylamino)acetamidobenzophenone. With the aim of obtaining these compounds in better yields, we have investigated various synthetic methods and found an alternative novel double-cyclization reaction.

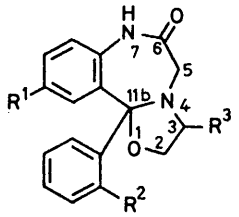
Treatment of 2-(2-bromoacetamido)-2′,5-dichlorobenzophenone (2a) with morpholine in methylene chloride at room temperature gave 2-(2-morpholinoacetamido)-2′,5-dichlorobenzophenone (3a). Heating of (3a) with an excess of 2-aminopropanol at 180—200 °C for 7 h followed by removal of the latter afforded the ketimine derivative (4a) as crystals of m.p. 174—175 °C, whose elemental analysis was consistent with the formula

† Formerly called benzo[6,7]-1,4-diazepino[5,4-*b*]oxazoles; I.U.P.A.C. nomenclature requires the name given in the title and text.

[1] Part 6, T. Miyadera, Y. Kawano, A. Terada, T. Kamioka, H. Takagi, and R. Tachikawa, *Ann. Rep. Sankyo Res. Lab.*, 1973, **25**, 69.

[2] T. Miyadera, A. Terada, M. Fukunaga, Y. Kawano, T. Kamioka, C. Tamura, H. Takagi, and R. Tachikawa, *J. Medicin. Chem.*, 1971, **14**, 520.

$C_{22}H_{25}Cl_2N_3O_3$. The i.r. spectrum exhibited the presence of the amide bond (1 700 cm^{-1}) and a C=N bond (1 610 cm^{-1}). The n.m.r. spectrum of (4a) showed two pairs of



(A)

doublets at δ 1.17 (J = 60 Hz) and 1.27 (J = 60 Hz) (nearly 1 : 1) due to the methyl protons, and overlapping peaks arising from the morpholino-, hydroxyethyl, and methylene protons adjacent to the amide bond. The n.m.r. and u.v. spectra [235 (ε 34 300), 268 (12 500), and 323 nm (4 600)] suggested that the ketimine (4a) might be a 1 : 1 mixture of *syn*- and *anti*-forms. The configurations of the ketimine isomers were investigated by correlating the u.v., i.r., and n.m.r. spectra with those of the corresponding oximes.[3a-c] Our attempts to separate a mixture of *syn*- and *anti*-forms of (4a) have so far been unsuccessful but some other compounds such as (10a—i) and (10l—n) were obtained as a single material as is described later.

Although there is a possibility that the condensation product (4a) might exist as the tautomer (8) the presence of the latter was not detected.[4] In contrast *syn*- and *anti*-configurational isomers were present as evidenced by the n.m.r. spectra of compounds (10i) and (10j) which show no hydroxy-group but, instead, two kinds of methylene proton due to the *syn*- and *anti*-isomers respectively (see Table 2).

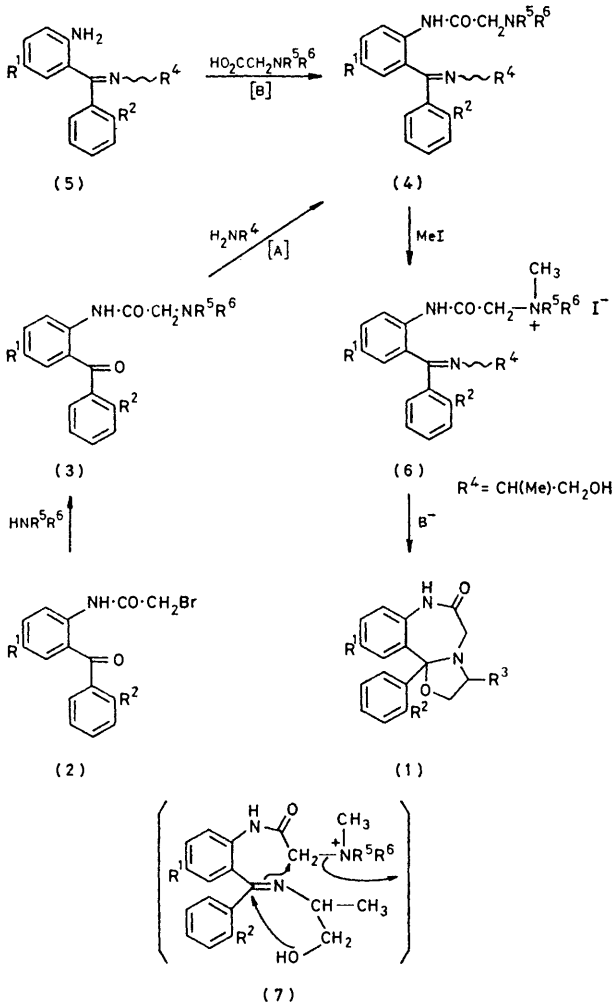
Although structure (4a) was consistent with the physical data of the product, structure (9) was also a possibility. In order to confirm the structure as (4a), an alternative synthesis from 2-[2-amino-5-chloro-α-(2-chlorophenyl)benzylidenamino]propanol (5a) [3c] and an X-ray crystallographic analysis of the relating analogues were carried out; on the basis of these results (4a) was shown conclusively to be 2-[2-morpholinoacetamido-5-chloro-α-(2-chlorophenyl)benzylideneamino]propanol.

Treatment of (5a) with morpholinoacetic acid in the presence of dicyclohexylcarbodi-imide gave (4a) which was identical in all respects with a sample obtained by the reaction of (3a) with 2-aminopropanol.

The ketimine (4a) was methylated with methyl iodide to give the quaternary salt (6a) in quantitative yield. It appears that (6a) also exists as a 1 : 1 mixture of *syn*- and *anti*-forms as is evident from the n.m.r. spectrum which exhibits two pairs of doublets at δ 1.19 and 1.23 (J = 6.0 Hz) assignable to the methyl group.

Similarly, several other derivatives, (3), (4), and (6), were synthesized; their physicochemical properties are summarized in the Tables.

The double-cyclization reaction of the quaternary salts (6a—d) leading to the oxazolobenzodiazepines (1a—d) was examined under a variety of conditions to find that most suitable for ring closure. Heating of the quaternary salt (5a) in dimethylformamide (DMF) in the presence



(3),(4),(5),(6),(1) (a): R^1 = R^2 = Cl, R^4 = CH(Me)·CH_2OH, R^5 = R^6 = ⬡O

(b): R^1 = Cl, R^2 = H, R^4 = CH(Me)·CH_2OH, R^5 = R^6 = ⬡

(c): R^1 = Br, R^2 = Cl, R^4 = CH(Me)·CH_2OH, R^5 = R^6 = ⬡

(d): R^1 = Br, R^2 = H, R^4 = CH(Me)·CH_2OH, R^5 = R^6 = ⬡

SCHEME

of $CaCO_3$ gave the desired product (1a) in 70% yield, together with *N*-methylmorpholine. The structure of (1a) was assigned on the basis of the mass, i.r., and n.m.r. spectra coupled with the elemental analysis; it

[3] (*a*) L. H. Sternbach, S. Kaiser, and E. Reeder, *J. Amer. Chem. Soc.*, 1960, **82**, 475; (*b*) S. C. Bell, G. L. Conklin, and A. J. Childress, *J. Org. Chem.*, 1964, **29**, 2368; (*c*) K. Meguro, H. Tawada, and Y. Kuwada, *J. Pharm. Soc. Japan*, 1973, **93**, 1253.

[4] T. Miyadera, A. Terada, C. Tamura, M. Yoshimoto, and R. Tachikawa, *Ann. Rep. Sankyo Res. Lab.*, 1976, **28**, 1.

was confirmed by comparison with an authentic sample prepared by the method reported previously.[2]

Likewise, several oxazolobenzodiazepine derivatives (1a—d) bearing various substituents in the phenyl group were synthesized and the results are summarized in Table 1.

TABLE 1

(1)	M.p. (°C)	Yield (%)	Formula	Analysis (%) Calc. (Found) C	H	N	Cl	Br
a	172—175	70	$C_{18}H_{16}Cl_2N_2O_2$	59.50 (59.5)	4.45 (4.51)	7.7 (7.63)	19.55 (19.27)	
b	126—127	31	$C_{18}H_{17}ClN_2O_2$	65.75 (65.49)	5.2 (5.22)	8.5 (8.50)	10.8 (10.62)	
c	182—184	36	$C_{18}H_{16}BrClN_2O_2$	53.0 (52.87)	3.95 (3.94)	6.85 (6.58)	8.7 (8.76)	19.6 (19.41)
d	126—128	56	$C_{18}H_{17}BrN_2O_2$	57.9 (57.99)	4.6 (4.50)	7.5 (7.32)		21.4 (21.18)

above. To determine the configuration (*syn* or *anti*), the n.m.r. and *X*-ray crystallographic analysis were performed. The methylene protons adjacent to the amide group showed a singlet and/or an AB type quartet, and the amide proton exhibited a broad singlet at low field indicating the existence of the hydrogen bond

TABLE 2

N.m.r. spectral data and configurations of the ketimine (10)

(10)	R^1	R^2	R^4	X *	N.m.r. δ values ($CDCl_3$) $COCH_2X$	(ratio)	NHCO	Config.†
(a)	Cl	Cl	$[CH_2]_2OH$	4-Mor	s (3.31)		13.40	*anti*
(b)	Cl	H	$[CH_2]_2OH$	Pip	s (3.29)		13.35	*anti*
(c)	Cl	Cl	$[CH_2]_2OH$	4-Mepz	s (3.31)		13.35	*anti*
(d)	Cl	Me	$[CH_2]_2OH$	NMe_2	s (3.26)		13.50	*anti*
(e)	Cl	H	$[CH_2]_2OH$	OH	s (4.28)		13.70	*anti*
(f)	Br	H	$[CH_2]_2OH$	OMe	s (4.20)		13.80	*anti*
(g)	Br	F	$[CH_2]_2OH$	NH_2	s (3.68)		13.34	*anti*
(h)	Br	H	$[CH_2]_3OH$	NMe_2	s (3.21)		13.35	*anti*
(i)	Cl	H		NMe_2	s (3.26), q (2.78, 3.13, *J* 18.0)	2 : 1	13.80	
(j)	Br	H	Ph	NHEt	s (3.43), q (3.04, 3.35, *J* 18.0)	2 : 3	13.00	
(k)	Cl	H	$[CH_2]_2OH$	SEt	s (3.45) q (3.00, 3.30, *J* 18.0)	5 : 1	13.70	
(l)	Cl	H	$[CH_2]_2OH$	4-Mepz	q (2.70, 3.10, *J* 18.0)		9.99	*syn*
(m)	Cl	H	$[CH_2]_2OMe$	4-Mor	q (2.76, 3.11, *J* 18.0)		9.15	*syn*
(n)	Br	—NHEt	Et	NMe_2	q (2.69, 2.91, *J* 18.0)		9.25	*syn*

s = Singlet and q = AB type quartet.

* 4-Mor = 4-morpholino, Pip = piperidyl, 4-Mepz = 4-methylpiperazinyl. † With respect to the amido-substituted phenyl group.

A plausible mechanism for the formation of oxazolobenzodiazepines (1) from the quaternary salts (6) is shown in (7).

As previously noted *cis*- and *trans*-isomers of (1) are possible and the n.m.r. spectrum of (1a) showed it to be one of these. An *X*-ray analysis confirmed that it was the *cis*-isomer.

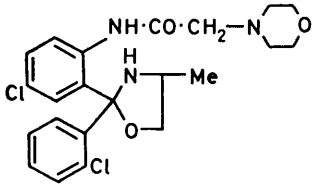
Since some of the ketimines (3) possessed excellent tranquilizing activity comparable to that of the oxazolobenzodiazepines (1) it appeared of interest to test the pharmacology of these and investigate the configuration of the *syn*- and *anti*-forms.

The ketimine derivatives were prepared by the usual method mentioned above (A and B in the Scheme) and the results are summarized in Tables 2 and 6. Of these compounds, (10g) showed excellent tranquilizing activity and the details of the pharmacology of the ketimines will be described elsewhere.

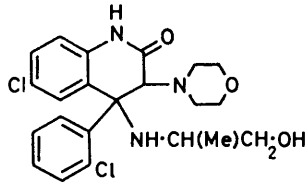
The ketimines would also have *syn*- and/or *anti*-configuration with respect to —C=N bond as described in deuteriated chloroform, methanol, benzene, or dimethyl sulphoxide (DMSO) in the n.m.r. spectra. For example, the methylene protons of (10 h) showed a singlet at δ 3.21 in $CDCl_3$ and the amide proton revealed a broad singlet at δ 13.35. When a $CDCl_3$ solution of *anti*-(10h) was set aside for 24 h at room temperature there was a decrease of the singlet at δ 3.21 due to the methylene protons and the concurrent appearance of a new AB type quartet at δ 2.70 and 3.06 (J = 18.0 Hz) (nearly 1 : 1); this was ascribed to the formation of an equilibrium mixture of *anti*- and *syn*-forms. In contrast, the n.m.r. spectrum of *syn*-(10l) showed a broad singlet at δ 9.99 due to the amide proton and an AB type quartet at δ 2.70 and 3.10 (J = 18.0 Hz) for the methylene protons; this decreased with the appearance of new singlet at δ 3.05 due to the *anti*-form (*syn*/*anti* *ca.* 1 : 1) when the solution was set aside at room temperature in $CDCl_3$ for 24 h.

It is noteworthy that the methylene protons of (10h) and (10l) appeared as a singlet and an AB type quartet,

respectively, immediately upon their dissolution in $CDCl_3$. This suggests that (10h) and (10l) exist either



(8)



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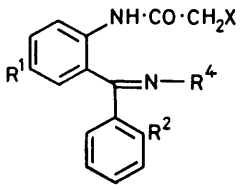
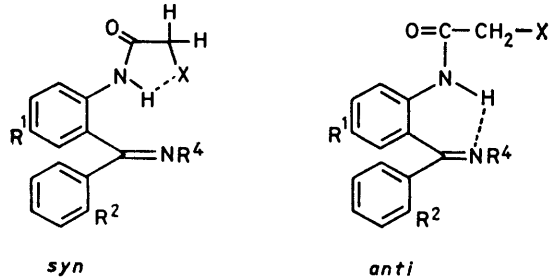


(10)

as the *anti*- or *syn*-form in the solid and as an equilibrium mixture in solution. Based on the spectral data of the methylene protons and the amide proton forming the hydrogen bond, (10h) and (10l) were assumed to be *anti*- and *syn*-forms respectively. Since hydrogen bonding between the amide hydrogen and nitrogen atom of CN bond is more likely in (10h) it is reasonable that the methylene peak should show a singlet in the n.m.r. spectrum. On the other hand, whilst hydrogen bonding in *syn*-(10l) may be disfavoured the formation of a five-membered ring with the substituted-amino nitrogen



syn *anti*

X = NR_2, OR, SR

atom may be easier; this would explain the AB type quartet for the methylene protons on the five-membered ring.

To confirm the structure of (10h) and (10l), an *X*-ray crystallographic study was carried out and their structures were unambiguously determined to be *anti* and *syn*, respectively, as shown in Figures 1 and 2.

EXPERIMENTAL

^1H N.m.r. spectra were recorded with a Varian T60 spectrometer with $SiMe_4$ as internal standard. I.r. and u.v. spectra were taken with Hitachi 215 and Cary 14 spectrophotometers, respectively.

General Procedure for the Preparation of 2-[(N-*Substituted-amino*)*acetamido*]*benzophenones* (3).—To a solution of 2-bromoacetamidobenzophenone (2) (33.0 mmol) in CH_2Cl_2 (70 ml) the appropriate amine (80 mmol) was added with ice cooling. After being stirred for 30 min at 3—5 °C and then for 5 h at room temperature, the reaction mixture was poured into ice–water and extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were washed with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure to give a solid. Recrystallization from ethanol gave the product (Table 3).

General Procedure for the Preparation of the Ketimines (4).—*Method A*. A mixture of 2-[(*N*-substituted amino)-acetamido]benzophenone (3) (10 mmol) and 2-amino-propanol (40 mmol) was heated at 180—200 °C for 4 h, after which excess of the latter was removed slowly under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure to give a solid. Recrystallization from benzene gave the product (Table 4).

Method B. To a solution of 2-amino-α-phenylbenzyl-ideneaminopropanol (5) (10 mmol) and the appropriate *N*-substituted aminoacetic acid (10 mmol) in tetrahydrofuran (THF) (60 ml) was added dicyclohexylcarbodi-imide (11 mmol) with ice cooling. Stirring of the reaction mixture was continued for 2 h at 3—5 °C after which it was poured

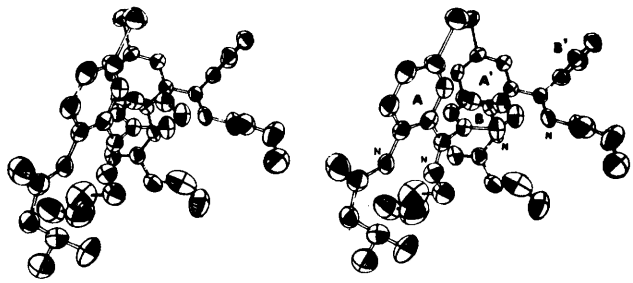


FIGURE 1

into saturated aqueous NaCl and THF layer separated. THF was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 layer was washed with H_2O, dried (Na_2SO_4), and evaporated to give a solid which was recrystallized from benzene to give the product (Table 4).

General Procedure for the Preparation of the Quaternary

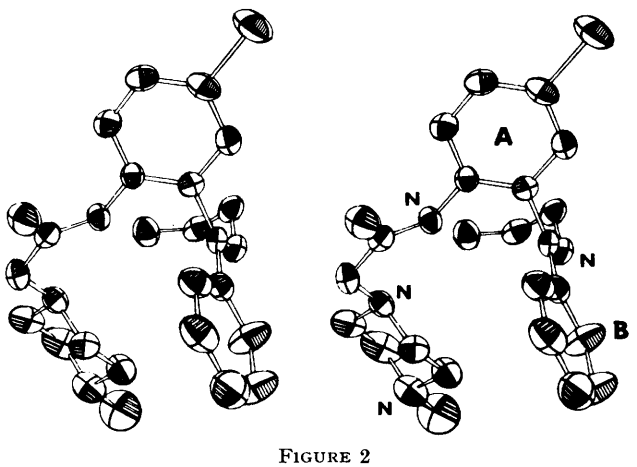


FIGURE 2

Salts (6).—To a solution of the ketimine (4) (4.5 mmol) in CH_2Cl_2 (20 ml) was added methyl iodide (10.0 g) at room

temperature. The reaction mixture was refluxed for 15 h, and then CH_2Cl_2 and excess of methyl iodide were distilled off under reduced pressure to give a solid; recrystallization of this from ethanol afforded the product (Table 5).

General Procedure for the Preparation of Oxazolo[3,4-d]-[1,4]*benzodiazepines* (1).—A mixture of the quaternary salt (6) (2.0 mmol), $CaCO_3$ (2.3 mmol), and dimethylformamide (DMF) (10 ml) was heated at 105—110 °C with stirring for 24 h. After cooling of the mixture the solvent was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2 and H_2O. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were washed with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure to give a solid. Recrystallization from ethanol gave the product (Table 1).

General Procedure for the Preparation of the Ketimines (10).—*Method A*. A mixture of 2-(2-substituted)acetamidobenzophenone (10 mmol) and the appropriate substituted amine (20—40 mmol) was heated at 170—200 °C for 4 h, and the excess substituted amine was then removed slowly under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure to give a solid. Recrystallization from the suitable solvent gave the product (Table 6).

TABLE 3

2-[(*N*-Substituted amino)acetamido]benzophenone (3)

(3)	R^1	R^2	R^5,R^6	M.p. (°C)	Yield (%)	Formula	Analysis (%) Calc. (Found) C	H	N	Cl	Br
(a)	Cl	Cl	$[CH_2]_2O[CH_2]_2$	133	96	$C_{19}H_{18}Cl_2N_2O_3$	58.02 (58.0)	4.58 (4.7)	7.12 (7.1)	18.06 (18.5)	
(b)	Cl	H	$[CH_2]_4$	90—91	90	$C_{19}H_{19}ClN_2O_2$	66.57 (66.3)	5.55 (5.7)	8.17 (7.85)	10.34 (10.5)	
(c)	Br	Cl	$[CH_2]_5$	141—142	93	$C_{20}H_{20}BrClN_2O_2$	55.13 (55.0)	4.63 (4.7)	6.43 (6.4)	8.14 (8.15)	18.34 (18.15)
(d)	Br	H	$[CH_2]_5$	88—89	91	$C_{20}H_{21}BrN_2O_2$	65.04 (65.1)	5.73 (5.7)	7.58 (7.5)		21.63 (21.7)

Method B. To a solution of *N*-substituted-(2-amino-α-phenyl)benzylidene)amine (10 mmol) and the appropriate substituted acetic acid (10 mmol) in THF (60 ml) was added dicyclohexylcarbodi-imide (11 mmol) with ice–water cooling; stirring was continued for 2 h at 3—5 °C. The reaction mixture was then poured into saturated aqueous NaCl and the THF layer separated. The solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 layer was washed with H_2O, dried (Na_2SO_4), and evaporated to give a solid, recrystallization of which from a suitable solvent gave the product (Table 6).

TABLE 4

2-[(2-Substituted amino)acetamido-α-phenylbenzylideneamino]propanol (4)

(4)	R^1	R^2	R^5,R^6	Method	M.p. (°C)	Yield (%)	Formula	Analysis (%) Calc. (Found) C	H	N	Cl	Br
(a)	Cl	Cl	$[CH_2]_2O[CH_2]_2$	A	174—175	61.4	$C_{22}H_{25}Cl_2N_3O_3$	58.66 (58.95)	5.55 (5.75)	9.33 (9.1)	15.77 (15.85)	
(a)	Cl	Cl	$[CH_2]_2O[CH_2]_2$	B	174—175	57.0						
(b)	Cl	H	$[CH_2]_5$	A	156—157	79.3	$C_{22}H_{26}ClN_3O_3$	66.10 (66.25)	6.50 (6.5)	10.50 (10.65)	8.89 (9.05)	
(c)	Br	Cl	$[CH_2]_5$	A	194—195	52.8	$C_{23}H_{27}BrClN_3O_2$	56.05 (56.25)	5.52 (5.45)	8.53 (8.5)	7.19 (7.2)	16.22 (16.05)
(d)	Br	H	$[CH_2]_5$	A	139—140	63.0	$C_{23}H_{28}BrN_3O_2$	60.26 (60.75)	6.15 (6.1)	9.16 (9.05)		17.43 (17.4)

TABLE 5

Quaternary salt (6) of 2-[(2-substituted amino)acetamido-α-phenylbenzylideneamino]propanol

(6)	R^1	R^2	R^5,R^6	M.p. (°C)	Yield (%)	Formula	Analysis (%) Calc. (Found) C	H	N	Cl	Br	I
(a)	Cl	Cl	O	209—211	98	$C_{23}H_{28}Cl_2IN_3O_3$	46.62 (46.55)	4.73 (4.8)	7.09 (7.0)	11.99 (12.0)		24.45 (24.65)
(b)	Cl	H	O	207—210	97	$C_{23}H_{29}ClIN_3O_2$	50.97 (50.95)	5.35 (5.35)	7.76 (7.8)	6.55 (6.1)		23.46 (24.05)
(c)	Br	Cl	O	208—209	97	$C_{24}H_{30}BrClIN_3O_2$	45.41 (45.15)	4.76 (4.8)	6.62 (6.6)	5.58 (5.55)	12.59 (12.7)	19.99 (19.75)
(d)	Br	H	O	199—200	95	$C_{24}H_{31}BrIN_3O_2$	48.01 (47.9)	5.20 (5.3)	7.00 (6.7)		13.31 (13.5)	21.14 (21.15)

Crystallographic Analyses of the Ketimine (10h) *and* (10l).—The ketimine (10h) was recrystallized from isopropyl ether to give colourless prisms of m.p. 105—107 °C.

Crystal Data.—Ketimine (10h). Triclinic. Space group $P_{\bar{1}}$; $a = 12.91$, $b = 19.57$, $c = 10.11$, $\alpha = 92.96$, $\beta = 66.42$, $\gamma = 116.44$, $D_c = 1.341$ ($Z = 4$), $D_o = 1.370$; number of reflections 3 537.

Ketimine (10l) was recrystallized from isopropyl ether to afford colourless prisms of m.p. 115—116 °C.

Crystal Data.—Ketimine (10l). Monoclinic. Space group $P2_1/c$; $a = 9.94$, $b = 17.78$, $c = 12.67$, $\alpha = 90.0$, $\beta = 104.76$, $\gamma = 90.0$, $D_c = 1.271$ ($Z = 4$), $D_o = 1.30$; number of reflections 2 659.

Intensity data were collected on an automated Rigaku four-circle diffractometer with Mo-K_α radiation. The structures were solved by a heavy-atom technique and refined by block-diagonal least-squares procedure. The conventional R values of (10h) and (10l) were reduced to 0.10 and 0.087, respectively.

TABLE 6

(10) *	Method	M.p. (°C)	Yield (%)	Formula	Analysis (%) Calc. (Found) C	H	N	Cl	Br	F	S
(a)	A	125—126	85	$C_{21}H_{23}Cl_2N_3O_3$	57.78	5.31	9.62	16.25			
					(57.65)	(5.1)	(9.8)	(15.95)			
(b)	A	111—112	78	$C_{22}H_{26}ClN_3O_2$	66.05	6.55	10.50	8.87			
					(65.9)	(6.7)	(10.6)	(8.8)			
(c)	A	119—123	73	$C_{22}H_{26}Cl_2N_4O_2$	63.82	6.33	13.53	8.57			
					(63.85)	(6.1)	(13.8)	(8.45)			
(d)	A	100—102	66	$C_{20}H_{24}ClN_3O_2$	64.24	6.46	11.23	9.49			
					(64.5)	(6.5)	(11.2)	(9.4)			
(e)	A	156—157	46	$C_{17}H_{17}ClN_2O_3$	61.84	5.14	8.41	10.66			
					(61.6)	(5.15)	(8.55)	(10.55)			
(f)	A	103—105	67	$C_{18}H_{19}BrN_2O_3$	55.25	4.89	7.16		20.42		
	B		74		(55.35)	(4.8)	(7.0)		(20.15)		
(g)	B	167—168	47	$C_{17}H_{17}BrFN_3O_2$	51.79	4.34	10.65		20.26	4.81	
					(51.5)	(4.45)	(10.45)		(20.3)	(4.6)	
(h)	A	105—107	75	$C_{20}H_{24}BrN_3O_3$	57.42	5.78	10.04		19.10		
	B		64		(57.15)	(5.75)	(10.4)		(19.0)		
(i)	A	110—111	35	$C_{19}H_{22}ClN_3O$	63.40	6.16	11.67	9.85			
					(63.7)	(6.0)	(11.65)	(9.75)			
(j)	A	125—127	47	$C_{23}H_{22}BrN_3O$	61.06	4.90	9.28		17.66		
					(60.85)	(5.0)	(9.25)		(17.6)		
(k)	A	78—79	64	$C_{19}H_{21}ClN_2OS$	63.23	5.86	7.76	9.83			8.86
					(63.4)	(5.75)	(7.8)	(9.65)			(8.6)
(l)	A	115—116	66	$C_{22}H_{27}ClN_4O_2$	63.67	6.55	13.50	8.55			
	B		48		(63.5)	(6.35)	(13.5)	(8.6)			
(m)	A	Oil	73	$C_{22}H_{26}ClN_3O_3$	63.52	6.30	10.10	8.53			
					(63.45)	(6.3)	(10.25)	(8.8)			
(n)	A	158—159	15	$C_{21}H_{27}BrN_4O$	56.37	6.08	12.52		17.86		
					(56.25)	(6.15)	(12.65)		(17.6)		

* R^1, R^2, R^4 and X: see Table 2.

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