Reactions of 1,2- and 1,3-Amino-alcohols with Imidate Salts and with Ortho Esters

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ω-Hydroxy-*N*-substituted amidines have been shown to be the intermediates in the formation of 2-oxazolines and 5,6-dihydro-4*H*-1,3-oxazines from the reactions of imidates and 1,2- and 1,3-amino-alcohols respectively. 1,2- and 1,3-Amino-alcohols also react with ortho esters to give 2-oxazolines and 5,6-dihydro-4*H*-1,3-oxazines, but *N*-acylamino-alcohols give rise to oxazolidines with ortho esters.

REACTIONS between imidates (or their salts) (1) and 1,2-amino-alcohols (2) could theoretically lead to different products (3)—(5) depending on the reaction conditions. Reactions of this type have, in the main, been used to synthesise 2-oxazolines [1] (5) but the isolation of one such amidine (3a) has been reported.[2,3] It has been claimed [4] that a *N*-substituted imidate (4a) is the intermediate in the formation of 2-phenyl-2-oxazoline (5a) from 2-aminoethanol (2a) and ethyl benzimidate (1a), but this claim is based on insufficient evidence. In this work attempts have been made to investigate routes to products of types (3) and (4).

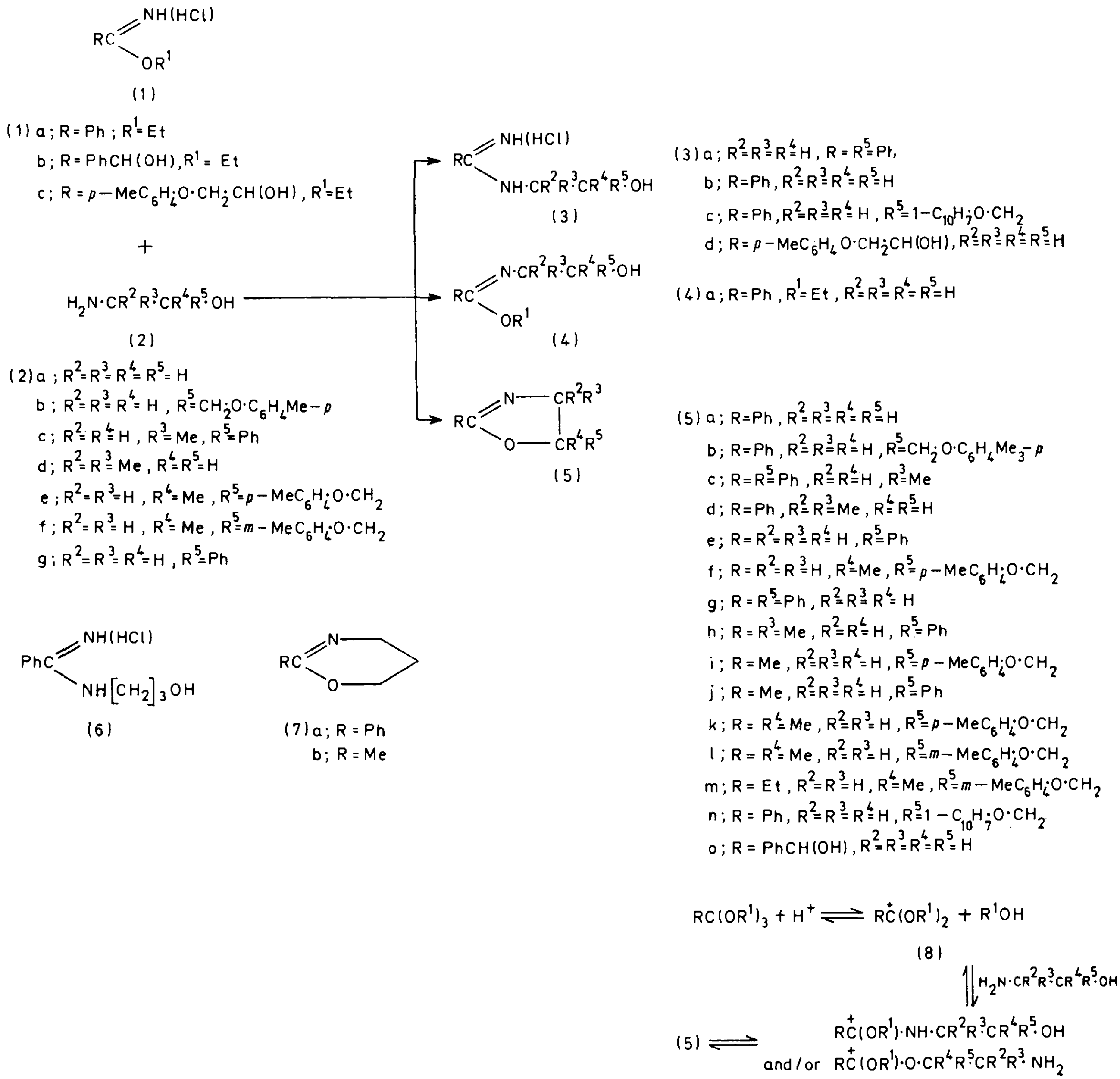
The amino-alcohols required (and not commercially available) were synthesised either by aluminium lithium hydride reduction of the corresponding cyanohydrins by the method of Nace and Smith [5] or by reduction of α-hydroxyamides prepared by thermal decomposition of imidate hydrochlorides.[1] Satoh and Suzuki [6] have suggested that an efficient way of producing an amino-alcohol possessing a primary amino-group is to reduce a cyanohydrin with a sodium borohydride cobaltous chloride system and report the reduction of mandelonitrile. In our hands, however, mandelonitrile yielded, in the main, benzyl alcohol and reduction of *p*-tolyloxyacetaldehyde cyanohydrin gave a mixture of primary (2b) and secondary amines [(*p*-$MeC_6H_4O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2)_2$-NH] in very poor yield.

When ethyl benzimidate (1a) and 2-aminoethanol (2a) were kept at 0 °C in ether, in accordance with the procedure in the reference [2] no reaction was observed and work-up yielded starting material quantitatively. However, when the imidate salt (1a)·HCl was stirred in methanol at room temperature with the amino-alcohol (2a) for 2 h, *N*-(2-hydroxyethyl)benzamidinium

[1] D. G. Neilson in 'The Chemistry of Amidines and Imidates,' ed. S. Patai, Wiley, New York, 1975, p. 385.
[2] A. Dornow and H. Theidel, *Ber.*, 1955, **88**, 1267.
[3] G. Drefahl and H.-H. Hörhold, *Ber.*, 1961, **94**, 1641.
[4] H. J. Barber, R. Slack, C. E. Stickings, and D. F. Elliot, Report 66 of Committee for Penicillin Synthesis, 1944.
[5] H. R. Nace and B. B. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 1861.
[6] T. Satoh and S. Suzuki, *Tetrahedron Letters*, 1969, **52**, 4555.

chloride (3b) was obtained in good yield although more prolonged reaction times decreased this yield and gave increasing quantities of 2-phenyl-2-oxazoline (5a). The related amidinium salts (3c and 6) were synthesised similarly. However, the amino-alcohols (2b, c, d) required either prolonged reaction times or more vigorous conditions and in each case the only product isolated was the cyclised compound (5b, c, d) respectively. The drug Inderal [$Pr^iNH\cdot CH_2\cdot CH(OH)\cdot CH_2O\cdot C_{10}H_7$-1] merely basified the imidate salt (1a) and was recovered unchanged as its hydrochloride.

α-Hydroxyimidate salts, *e.g.* ethyl mandelimidate hydrochloride (1b), tended to give intractable gums on reaction with amino-alcohols under varying conditions, but n.m.r. evidence pointed to the formation of an amidinium salt (3d) from the imidate salt (1c) and amino-alcohol (2a). Mandelamidinium chloride reacted similarly with 2-aminoethanol.


(1)
(1) a; R = Ph; R¹ = Et
b; R = PhCH(OH), R¹ = Et
c; R = p-MeC6H4O·CH2·CH(OH), R¹ = Et
(2)
(2) a; R² = R³ = R⁴ = R⁵ = H
b; R² = R³ = R⁴ = H, R⁵ = CH2O·C6H4Me-p
c; R² = R⁴ = H, R³ = Me, R⁵ = Ph
d; R² = R³ = Me, R⁴ = R⁵ = H
e; R² = R³ = H, R⁴ = Me, R⁵ = p-MeC6H4O·CH2
f; R² = R³ = H, R⁴ = Me, R⁵ = m-MeC6H4O·CH2
g; R² = R³ = R⁴ = H, R⁵ = Ph
(3)
(3) a; R² = R³ = R⁴ = H, R = R⁵ = Ph
b; R = Ph, R² = R³ = R⁴ = R⁵ = H
c; R = Ph, R² = R³ = R⁴ = H, R⁵ = 1-C10H7O·CH2
d; R = p-MeC6H4O·CH2CH(OH), R² = R³ = R⁴ = R⁵ = H
(4)
(4) a; R = Ph, R¹ = Et, R² = R³ = R⁴ = R⁵ = H
(5)
(5) a; R = Ph, R² = R³ = R⁴ = R⁵ = H
b; R = Ph, R² = R³ = R⁴ = H, R⁵ = CH2O·C6H4Me-p
c; R = R⁵ = Ph, R² = R⁴ = H, R³ = Me
d; R = Ph, R² = R³ = Me, R⁴ = R⁵ = H
e; R = R² = R³ = R⁴ = H, R⁵ = Ph
f; R = R² = R³ = H, R⁴ = Me, R⁵ = p-MeC6H4O·CH2
g; R = R⁵ = Ph, R² = R³ = R⁴ = H
h; R = R³ = Me, R² = R⁴ = H, R⁵ = Ph
i; R = Me, R² = R³ = R⁴ = H, R⁵ = p-MeC6H4O·CH2
j; R = Me, R² = R³ = R⁴ = H, R⁵ = Ph
k; R = R⁴ = Me, R² = R³ = H, R⁵ = p-MeC6H4O·CH2
l; R = R⁴ = Me, R² = R³ = H, R⁵ = m-MeC6H4O·CH2
m; R = Et, R² = R³ = H, R⁴ = Me, R⁵ = m-MeC6H4O·CH2
n; R = Ph, R² = R³ = R⁴ = H, R⁵ = 1-C10H7O·CH2
o; R = PhCH(OH), R² = R³ = R⁴ = R⁵ = H
(6)
(7) a; R = Ph
b; R = Me
(8)
and/or

When the amidinium salt (3b), or its free base, was heated in the presence of triethyl orthoformate, no reaction between these compounds was observed, but the ortho ester acted merely as a high-boiling solvent allowing cyclisation of compound (3b) to the oxazoline (5a). The amidine (6) yielded similarly 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (7a). Thus the *N*-substituted amidines (3) and (6) and not, as suggested in the literature,[4] the *N*-substituted imidates (4) are the intermediates[2] in the formation of 2-oxazolines and

5,6-dihydro-4*H*-1,3-oxazines from the reaction of imidate salts with 1,2- and 1,3-amino-alcohols respectively.

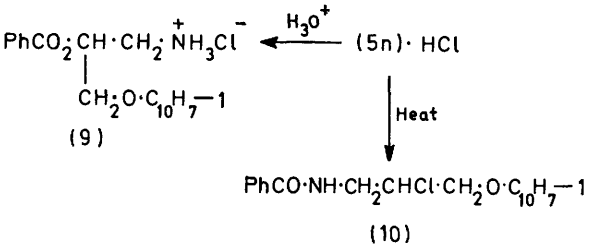
Despite extensive work on ortho esters,[7] there appears to be little, if any, work reported on their interaction with amino-alcohols. In our hands, 2-amino-alcohols were readily converted, by interaction with ortho esters in the presence of catalytic amounts of hydrogen chloride, into 2-oxazolines (Table). This reaction most likely proceeds *via* a carbocation intermediate (8) to give the cyclised product (5)—the yields of the product pointing to the stability of the carbocation (8; R = alkyl) as against (8; R = H). The lower yields from the ion (8; R = Ph) may be explained on the basis that it has been suggested for this cation (8; R = Ph) that the phenyl group does not exhibit its usual stabilising effect due to steric factors.[8]

TABLE

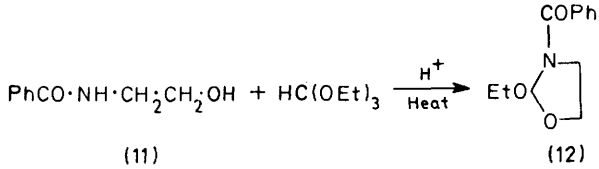
2-Oxazolines

Product (5)	Ortho ester	Amino-alcohol (2)	Time (h)	B.p. or m.p. (θ_c/°C)	Yield (%)	Found C	Found H	Found N	Required C	Required H	Required N
e *	$HC(OEt)_3$	g	19	62/1 mmHg	56						
f	$HC(OEt)_3$	e	15	146/10 mmHg	50	70.3	7.5	6.8	70.2	7.4	6.8
g †	$PhC(OEt)_3$	g	14	148/1.5 mmHg	31						
h ‡	$MeC(OEt)_3$	c	16	64/0.5 mmHg	78						
i	$MeC(OEt)_3$	b	20	77—78 (m.p.)	55	70.2	7.2	6.6	70.2	7.3	6.8
j	$MeC(OEt)_3$	g	20	60/0.5 mmHg	76	74.5	7.0	8.8	74.5	6.9	8.7
k	$MeC(OEt)_3$	e	24	132—134/2 mmHg	82	70.9	8.1	6.6	71.2	7.8	6.4
l	$MeC(OEt)_3$	f	24	126—128/2 mmHg	67	71.3	8.0	6.6	71.2	7.8	6.4
m	$EtC(OEt)_3$	f	24	132/2 mmHg	77	71.8	8.5	5.9	72.1	8.2	6.0

* Lit.,[17] b.p. 85°/2 mm. † Lit.,[2] 202—203°/15 mm. ‡ Picrate m.p. 158 °C (m.p. 158 °C recorded by R. Kornhann and A. Funke, *Compt. rend.*, 1955, **240**, 321).

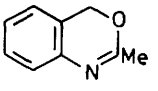


2-Oxazolines are typical cyclic imidates[1] and their salts decompose on hydrolysis and on heating. Thus compound (5n) yielded the ester (9) and amide (10) under appropriate conditions.



In an earlier report[9] on the interaction between amides and orthoformates, we confirmed that, apart from mandelamide, the products of these reactions were of the general type $(RCONH)_3CH$. However, when the *N*-substituted amide (11) was treated with triethyl orthoformate the product proved to be the oxazolidine (12)—two similar but isolated oxazolidine syntheses have been noted in the literature[10,11] and it would appear, in view of the differing conditions employed that this reaction could have wide applicability.

Triethyl orthoacetate reacted similarly with 1,3-amino-alcohols to give, for example, the 5,6-dihydro-4*H*-1,3-oxazine (7b) from 3-aminopropan-1-ol, and the benzoxazine (13) from *o*-aminobenzyl alcohol.



(13)

EXPERIMENTAL

p-Tolyloxyacetaldehyde Cyanohydrin.—Sodium (23 g) was dissolved in dry methanol (250 ml), *p*-cresol (108 g) was then added and the mixture stirred for 1 h. Bromoacetaldehyde diethyl acetal (197 g), previously kept over powdered potassium iodide (2 g) for 24 h, was dropped slowly into the stirred mixture during 2 h. Excess of methanol was evaporated off, toluene (300 ml) was added, and the mixture heated under reflux for 4 days. After filtration, distillation of the filtrate yielded *p*-tolyloxyacetaldehyde diethyl acetal [(152 g), b.p. 145—150 °C/12 mmHg] which was then stirred with hydrochloric acid (8M; 600 ml) for 24 h at room temperature. The free aldehyde was extracted with ether, the ether removed, and the aldehyde stirred with aqueous sodium hydrogen sulphite (140 ml; 40% w/w) at room temperature for 12 h. The resultant solid was filtered off, washed with ether, and stirred with sodium cyanide (23 g) in water (200 ml) at 0 °C until a clear solution resulted. The solution was extracted with ether, which, after drying and evaporation *in vacuo*, gave the cyanohydrin (72 g) which was used without further purification.

m- *and* p-*Tolyloxyacetone Cyanohydrins.*—Prepared by literature methods, *m*-tolyloxyacetone had b.p. 115—

[7] R. H. De Wolfe, 'Carboxylic Ortho Acid Derivatives,' Academic Press, New York, 1970.
[8] Y. Chiang, A. J. Kresge, P. Salomaa, and C. I. Young, *J. Amer. Chem. Soc.*, 1974, **96**, 4494.
[9] J. K. Fraser, D. G. Neilson, L. R. Newlands, K. M. Watson and, in part, M. I. Butt, *J.C.S. Perkin I*, 1975, 2280.
[10] R. Vince and R. G. Isakson, *J. Medicin. Chem.*, 1973, **16**, 37.
[11] G. Crank and F. W. Eastwood, *Austral. J. Chem.*, 1965, **18**, 1967.

120 °C/15 mmHg (lit.,[12] 110—111 °C/5 mmHg) and *p*-tolyloxyacetone had b.p. 125—130 °C/20 mmHg (lit.,[12] 108—112 °C/6 mmHg). The cyanohydrins were prepared as described above and used without purification.

Imidate Salts.—These compounds were prepared by standard Pinner syntheses[1] from the nitriles or cyanohydrins and then stored *in vacuo* and used without further purification. Ethyl benzimidate hydrochloride, m.p. 119—120 °C (decomp.) (lit.,[13] 118—120 °C); ethyl mandelimidate hydrochloride, m.p. 122—123 °C (decomp.) (lit.,[14] 124—125 °C); ethyl 3-*p*-tolyloxylactimidate hydrochloride, m.p. 152—153 °C (decomp.); ethyl 2-*m*-tolyloxymethyl-lactimidate hydrochloride, m.p. 138—139 °C (decomp.); ethyl 2-*p*-tolyloxymethyl-lactimidate hydrochloride, m.p. 153—154 °C (decomp.); ethyl 2-hydroxy-2-methylbutyrimidate hydrochloride, m.p. 93 °C (decomp.) (lit.,[15] 98 °C).

Amino-alcohols.—(a) *By reduction of cyanohydrins with aluminium lithium hydride.* To aluminium lithium hydride (12 g) in anhydrous ether (200 ml) was added slowly, with stirring, *p*-tolyloxyacetaldehyde cyanohydrin (17.7 g) in dry ether (100 ml). The mixture was then heated under reflux for 24 h, after which time excess of reagent was destroyed and the mixture made strongly alkaline with aqueous sodium hydroxide (8M). The ether layer was separated and the aqueous layer extracted a further three times. The combined, dried extract yielded 1-*amino*-3-p-*tolyloxypropan*-2-*ol* (2b) (7.2 g), m.p. 102—103 °C from cyclohexane–ethanol (Found: C, 66.0; H, 8.6; N, 7.6. $C_{10}H_{15}NO_2$ requires C, 66.2; H, 8.3; N, 7.7%).

Prepared similarly from the corresponding cyanohydrins were 1-amino-2-(*p*-tolyloxymethyl)propan-2-ol hydrochloride (2e)·HCl (70%), m.p. 122—123 °C from ethyl acetate–methanol (Found: C, 57.2; H, 7.9; N, 6.1. $C_{11}H_{18}ClNO_2$ requires C, 57.0; H, 7.8; N, 6.0%) and 1-amino-2-(*m*-tolyloxymethyl)propan-2-ol hydrochloride (2f)·HCl (70%), m.p. 131—132 °C (Found: C, 57.2; H, 7.7; N, 6.0%).

(b) *By reduction of α-hydroxy-amide with aluminium lithium hydride.* 2-*p*-Tolyloxymethyl-lactamide (5.2 g), obtained by heating ethyl 2-*p*-tolyloxymethyl-lactimidate hydrochloride (6.8 g) at 165 °C for 5 min, was placed in a Soxhlet connected to a flask containing aluminium lithium hydride (2 g) in ether (250 ml). The reaction mixture was heated under reflux for 3 days. Work-up as above yielded the product (3.5 g) identical with compound (2e) above.

(c) *By reduction of cyanohydrins by the method of Satoh and Suzuki.*[6] Sodium borohydride (38 g) was added in portions to a stirred mixture of *p*-tolyloxyacetaldehyde cyanohydrin (17.7 g) and cobaltous chloride hexahydrate (47.6 g) in methanol (600 ml) at 0 °C. After reaction, addition of hydrochloric acid (300 ml; 3M) failed to dissolve all the black precipitate and this caused problems on work-up. However, methanol was removed *in vacuo*, excess of cyanohydrin was extracted with ether and the residue made alkaline with aqueous ammonia. Extraction of the solution yielded 1,1′-*bis*-(p-*tolyloxymethyl*)-2,2′-*iminodiethanol* (0.7 g), m.p. 121—122 °C from cyclohexane–ethanol (Found: C, 69.4; H, 7.9; N, 4.0. $C_{20}H_{27}NO_4$ requires C, 69.6; H, 7.8; N, 4.1%) and compound (2b) (1 g) identical with that described above.

Mandelonitrile, treated similarly, yielded benzyl alcohol (25%) and 2-amino-1-phenylethanol (5%), both characterised by comparison of their i.r. and n.m.r. spectra with those of authentic materials.

Preparation of N-*Substituted Benzamidinium Chlorides* (3).—(a) N-2-*Hydroxyethylbenzamidinium chloride* (3b) (3.2 g) prepared by stirring together 2-aminoethanol (1.22 g) and ethyl benzimidate hydrochloride (3.7 g) in dry methanol (20 ml) at room temperature for 2 h and precipitating the product with dry ether, had m.p. 146—147 °C from ethyl acetate–methanol (Found: C, 53.5; H, 6.9; N, 14.0. $C_9H_{13}ClN_2O$ requires C, 53.9; H, 6.5; N, 14.0%).

(b) N-3-*Hydroxypropylbenzamidinium chloride* (6a) (66%) prepared similarly from 3-aminopropan-1-ol during 4 h had m.p. 149—150 °C (Found: C, 55.4; H, 7.0; N, 13.1. $C_{10}H_{15}ClN_2O$ requires C, 55.9; H, 7.0; N, 13.1%).

(c) N-[2-*Hydroxy*-3-(1-*naphthyloxy*)*propyl*]*benzamidinium chloride* (3c) (33%) prepared similarly from 1-amino-3-(1-naphthyloxy)propan-2-ol during 22 h had m.p. 185—186 °C (Found: C, 67.1; H, 6.0; N, 7.7. $C_{20}H_{21}ClN_2O_2$ requires C, 67.3; H, 5.9; N, 7.9%). The filtrate from this experiment, after solvent removal, yielded 5-(1-naphthyloxymethyl)-2-phenyl-2-oxazoline (5n) which was converted by the action of anhydrous hydrogen chloride in ether into its hydrochloride (5n)·HCl. The salt (5n) was kept molten at 150 °C for 5 min and on cooling the resultant N-[2-*chloro*-3-(1-*naphthyloxy*)]*propylbenzamide* (10) (94%) had m.p. 121—122 °C from cyclohexane (Found: C, 70.8; H, 5.5; N, 4.0. $C_{20}H_{18}ClNO_2$ requires C, 70.7; C, 5.3; N, 4.1%).

The salt (5n) after refluxing in ethanol for 15 min and removal of solvent gave 2-*amino*-1-(1-*naphthyloxymethyl*)-*ethyl benzoate hydrochloride* (9) (88%), m.p. 190—191 °C from methanol–ethyl acetate (Found: C, 66.9; H, 5.6; N, 3.9. $C_{20}H_{20}ClNO_2$ requires C, 67.1; H, 5.6; N, 3.9%).

(d) *Reaction of* 1-(1-*naphthyloxy*)-3-*isopropylaminopropan*-2-*ol* (*Inderal*) *and ethyl benzimidate hydrochloride.* Equimolar proportions of these reagents were heated together in dry ethanol for 24 h. After removal of most of the ethanol and trituration of the residue with ether, solid identified as the Inderal hydrochloride (98%) was recovered.

Attempted Preparation of N-*Substituted Amidines from α-Hydroxy-imidates.*—(a) Ethyl mandelimidate hydrochloride (1b), or mandelamidinium chloride, and an equimolar proportion of 2-aminoethanol when heated in dry methanol for 2 h yielded, in each case on removal of solvent, the same hygroscopic gum, i.r. 1 690 and 1 650 cm^{-1} (amidine bands), but which gave *m/e* 177 corresponding to M^+ for the 2-α-hydroxybenzyloxazoline (5o).

(b) Ethyl 3-*p*-tolyloxyacetimidate hydrochloride (1c) (2.6 g) and 2-aminoethanol (0.67 g) were stirred in dry ethanol for 16 h without any apparent reaction. The mixture was then heated for 1 h. Solid (0.3 g), obtained by precipitation with ether, had m.p. 107—108 °C from methanol–ethyl acetate. The compound (3d) gave unsatisfactory analytical results but showed i.r. absorption at 1 690 and 1 640 cm^{-1} (amidine bands); the n.m.r. signals in $(CD_3)_2SO$ were δ 2.29 (s, CH_3), 3.27—3.91 (m, NCH_2 + 2 × OH), 4.27—4.50 (d, $CHCH_2$), 4.9—5.2 (t, CH), 6.9—7.3 (dd, C_6H_4), and 9.0—9.8 (s, NH_2).

Preparation of 2-*Oxazolines.*—(a) *From amino-alcohols and imidate salts.* 1-Amino-3-*p*-tolyloxypropan-2-ol (2b) (2.4 g) and the benzimidate salt (1a) (2.5 g) were stirred

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[13] A. Pinner, *Ber.*, 1883, **16**, 1655.

[14] H. Beyer, *J. prakt. Chem.*, 1885, **31**, 382.

[15] A. B. Sen and K. Shanker, *J. prakt. Chem.*, 1965, **29**, 309.

together in dry ethanol (25 ml) for 20 h at room temperature. Addition of dry ether precipitated ammonium chloride. Removal of the solvent then gave 2-*phenyl*-5-p-*tolyloxymethyl*-2-*oxazoline* (5b) (2.4 g), m.p. 99—100 °C from cyclohexane (Found: C, 76.3; H, 6.3; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.3%).

4,4-Dimethyl-2-phenyl-2-oxazoline (5d) prepared similarly from the amino-alcohol (2d) and imidate salt (1a) had b.p. 115 °C/2 mmHg (lit.,[16] 105—110 °C/1 mmHg).

(b) *From amino-alcohols and ortho esters.* The amino-alcohols (1 mol. equiv.) were heated under reflux with the appropriate ortho ester (1—2 mol equiv.) for periods of 14—24 h using hydrogen chloride or hydrochloric acid (conc.) as catalyst. Low-boiling material was removed *in vacuo* and the resultant product was recrystallised (light petroleum, b.p. 40—60 °C) or distilled *in vacuo* (see Table).

(c) *From* N-2-*hydroxyethylbenzamidinium chloride* (3a). Amidinium salt (3a) (2.0 g) was heated under reflux for 2 h [with or without the presence of sodium carbonate (1g)] with triethyl orthoformate. Distillation of the product yielded the 2-oxazoline (5a) (1.4 g), b.p. 85 °C/2 mmHg (lit.,[17] 75 °C/1 mmHg).

5,6-*Dihydro*-4H-1,3-*oxazines*.—Amidinium salt (6) under similar conditions over a period of 6 h yielded 5,6-dihydro-4*H*-1,3-oxazine (7a) (94%), b.p. 110—112 °C/1 mmHg (lit.,[17] 115 °C/1.5 mmHg).

The 5,6-dihydro-4*H*-1,3-oxazine (7b) was prepared by refluxing 3-aminopropan-1-ol (1.5 g) and ethyl orthoacetate (3.5 g) for 20 h in the presence of hydrogen chloride. Distillation *in vacuo* yielded the product (7b) (1.3 g), b.p. 132 °C, identified as its picrate, m.p. 103 °C (lit.,[18] 103—104 °C).

o-Aminobenzyl alcohol and triethyl orthoacetate yielded similarly 2-methyl-6*H*-4,5-benzoxazine (13) (70%), b.p. 104—106 °C/10 mmHg characterised as its picrate, m.p. 148—149 °C (lit.,[19] 148—149 °C).

Preparation of 3-*Benzoyl*-2-*ethoxyoxazolidine* (12).—*N*-Benzoyl-2-aminoethanol [20] (3.3 g) was refluxed for 20 h with triethyl orthoformate (17.8 g) in the presence of a catalytic amount of dry hydrogen chloride. *Compound* (12) (2.2 g), b.p. 128—130 °C/1 mmHg, was obtained by distillation of the resultant mixture (Found: C, 65.3; H, 6.8; N, 6.5. $C_{12}H_{15}NO_3$ requires C, 65.2; H, 6.8; N, 6.3%).

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