Reissert Compound Chemistry. Part IV.[1] *N*-Acyl Pseudo-base Formation and Stereochemistry

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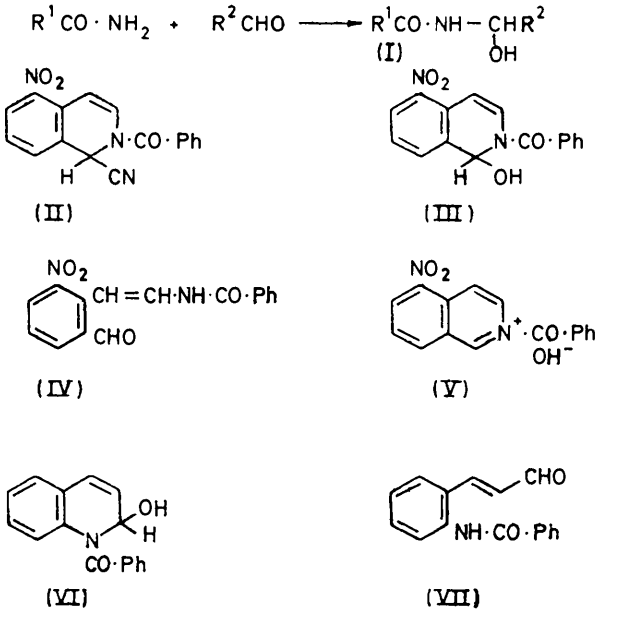
The formation is reported of a series of heterocyclic *N*-acyl pseudo-bases from 5-nitroisoquinoline, 3-methyl-5-nitroisoquinoline, and 6-nitroquinoline. The compounds were obtained under conditions for Reissert compound formation, only small yields of the latter being present in most cases. The *N*-acyl pseudo-bases appear to be covalent in character, and do not, in general, display tautomerism with an open chain or ionic form, in contrast to *N*-alkyl pseudo-bases. Long-range coupling observed in the n.m.r. of the *N*-acyl pseudo-bases and 1,2-dihydroisoquinolines and -quinolines of the Reissert type suggests the stereochemistry to be such that the substituent at the saturated carbon is adopting a quasi-axial position, analogous to substituted 1,2-dihydronaphthalenes. Characteristic resonance frequencies are indicated.

HETEROCYCLIC *N*-alkyl pseudo-bases are well known and their chemistry has been extensively investigated.[2] However, the analogous *N*-acyl structures are little known and we report the first examples of such systems in the isoquinoline and quinoline series. A few cases have been observed in other series, as mentioned below, and open-chain analogues (I) are known. The latter are formed from amides and aldehydes in the presence of base,[3] and are used in the Tscherniac–Einhorn reaction for α-amidomethylation at aromatic carbon [using (I; $R^2 = H$)].[3,4]

In an attempt to prepare the Reissert compound (II) [5] from 5-nitroisoquinoline by the standard procedure [6] we obtained a yellow compound (III), precipitated in high yield. The same product was formed when the reaction was carried out in the absence of cyanide. The structure (III) was supported by spectroscopic data, showing i.r. bands at 3385br (OH), 1663 (amide CO), and 1623 (C=C). The u.v. spectrum was closely similar to that of the authentic Reissert compound (II) [isolated in small yield from the mother liquors of the reaction after removal of (III)]. No aldehyde proton was observed in the n.m.r. nor was there any other evidence for the presence of the possible tautomeric forms (IV) or (V).

Unsubstituted quinoline was originally claimed by Reissert [7] to give the analogous *N*-acyl pseudo-base (VI) by treatment with benzoyl chloride and aqueous sodium hydroxide. However, it was subsequently shown [8] that the compound was the amido-aldehyde (VII). The equivalent reaction does not take place with isoquinoline.[8a] Benzimidazole on treatment with benzoyl chloride and aqueous alkali ring opens at 0 °C to give (X) [9] but by use of less basic conditions intermediates (VIII) and (IX) can be isolated.[10] Stable *N*-cyano pseudo-bases have been reported [11] (resulting from reaction of, *e.g.*, isoquinoline with cyanogen bromide) but a nearer analogy to our findings is given in an observation of Hull [12] that treatment of isoquinoline with thiophosgene in alkali gives products including (XI). This is considered as possibly being formed by dehydration of



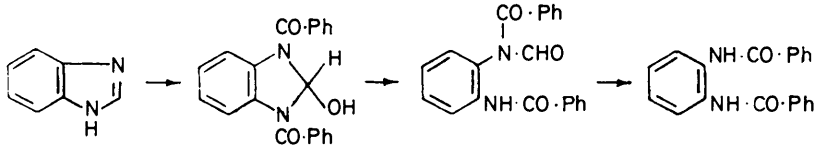
(XII) which was not isolated. An alternative mechanism not involving (XII) has also been advanced.[13]

Since our preliminary communication,[14] two other relevant analogues have been reported. The Reissert reaction of isoquinoline with (*p*-chlorophenylthio)thiocarbonyl chloride gives the cyclic form of the *N*-thioacyl pseudo-base (XIII) and none of the corresponding open chain form, and no Reissert compound.[15] 2-Phenyl-1,3,4-thiadiazole in the presence of benzoyl chloride and aqueous alkali or cyanide gives (XIV),[16] and again no evidence of ring–chain tautomerism was found.

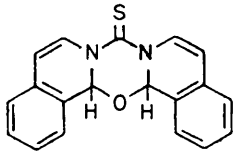
In order to establish the generality of *N*-acyl- pseudo-

[1] Part III, B. C. Uff, J. R. Kershaw, and S. R. Chhabra, *J.C.S. Perkin I*, 1972, 479.
[2] D. Beke, *Adv. Heterocyclic Chem.*, 1963, **1**, 167.
[3] H. E. Zaugg and W. B. Martin, *Org. Reactions*, 1965, **14**, 63.
[4] J. Tscherniac, G.P. 134,979/1901 (*J. Chem. Soc. Abs.*, 1903, **84** [i], 490); A. Einhorn, *Annalen*, 1905, **343**, 207; R. Ó. Cinnéide, *Nature*, 1955, **175**, 45.
[5] F. D. Popp and W. Blount, *J. Org. Chem.*, 1962, **27**, 297.
[6] F. D. Popp and W. Blount, *Chem. and Ind.*, 1961, 550.
[7] A. Reissert, *Ber.*, 1905, **38**, 1608.
[8] (*a*) A. Reissert, *Ber.*, 1905, **38**, 3415; (*b*) I. W. Elliott, *J. Org. Chem.*, 1964, **29**, 305; R. Bramley and M. D. Johnson, *J. Chem. Soc.*, 1964, 1372.
[9] E. Bamberger and B. Berlé, *Annalen*, 1892, **273**, 342.
[10] O. Gerngross, *Ber.*, 1913, **46**, 1913.
[11] M. D. Johnson, *J. Chem. Soc.*, 1962, 283; 1964, 200.
[12] R. Hull, *J. Chem. Soc.* (*C*), 1968, 1777.
[13] R. Hull, personal communication.
[14] B. C. Uff, J. R. Kershaw, and S. R. Chhabra, *Tetrahedron Letters*, 1969, 1687.
[15] F. D. Popp and C. W. Klinowski, *J. Chem. Soc.* (*C*), 1969, 741.
[16] A. Alemagna and T. Bacchetti, *Gazzetta*, 1972, **102**, 1068.

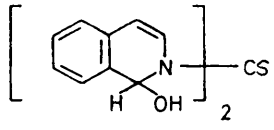
base formation with 5-nitroisoquinoline, other acid chlorides were used. In each case the pseudo-base precipitated from solution in high yield (Table 1) and only small amounts of the corresponding Reissert compounds were given, although their yields could be slightly increased (5—10%) by prolonged stirring. The *N*-acyl pseudo-bases could be converted into the corresponding alkyl ethers (XV) (Table 1) by heating with the appropriate alcohol, and the process reversed by stirring with



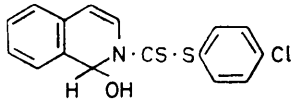
(VIII) (IX) (X)



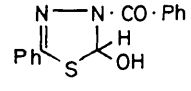
(XI)



(XII)



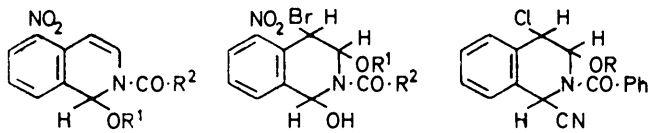
(XIII)



(XIV)

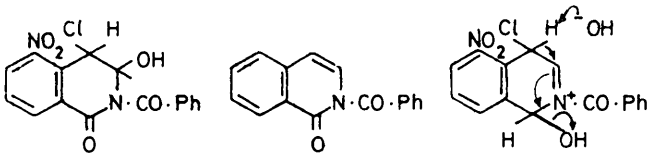
aqueous dioxan at room temperature. Ethers similar to (XV) have also been obtained in other series.[10,11,15-17] Use of conditions other than neutral (methanol–acetic acid, methanol–triethylamine) caused breakdown to 5-nitroisoquinoline. An attempt to open the hetero-ring of (III) by reductive cleavage of the carbinolamide system with borohydride also gave only 5-nitroisoquinoline. The amide i.r. absorption of the ethers (XV) appeared at *ca.* 1680 cm^{-1}, slightly higher than for the corresponding pseudo-bases (*ca.* 1660 cm^{-1}).

An attempt to modify the properties of the pseudo-base by introduction of a second carbinol function adjacent to the amide nitrogen was achieved by treating (III) with bromine in aqueous tetrahydrofuran, to give the bromohydrin (XVI; $R^1 = H$, $R^2 = Ph$). That the orientation of the addition had placed the OH at position 3 and not 4



(XV) (XVI) (XVII)

was indicated by the amide carbonyl absorption appearing at 1630 cm^{-1} (lowered by hydrogen bonding). Formation of the analogous ethers (XVI; $R^1 = Me$, $R^2 = Ph$ and $R^1 = R^2 = Me$) by use of bromine in methanol on the appropriate pseudo-base showed the absorption to be restored to 1663 cm^{-1} as in (III). Furthermore, in parallel studies in the Reissert series we have shown [18] by deuterium labelling at C-4 that the orientation of addition of hypochlorous acid to isoquinoline Reissert compound gives (XVII; R = H). The halogenation exclusively at C-4 may probably be related to the residual enamine character of the starting material. Use of hypochlorous acid with (III) or (XV; $R^1 = Me$, $R^2 = Ph$) results in addition to the 3,4-double bond being accompanied by oxidation at C-1 to give (XVIII). [In the case of (XV; $R^1 = Me$, $R^2 = Ph$) this must presumably proceed *via* the intermediacy of (III).] The *N*-benzoyl carbonyl group is now part of an imide system and shows i.r.



(XVIII) (XIX) (XX)

bands at 1665, 1682, and 1710 cm^{-1}, comparable with those shown by (XIX) [19] at 1660 (shoulder), 1680, and 1715 cm^{-1}. Interestingly, a minor product in the reaction of (III) with hypochlorous acid is 4-chloro-5-nitroisoquinoline, possibly arriving *via* intermediate (XX).

As with the simpler *N*-acyl pseudo-bases none of the halogenohydrin adducts described above showed the presence of ionic or open-chain isomers. We are, however, currently examining the effect of replacing the

[17] E. O. Snoke and F. D. Popp, *J. Heterocyclic Chem.*, 1973, **10**, 99.

[18] G. W. Kirby, S. L. Tan, and B. C. Uff, *Chem. Comm.*, 1970, 1138.

[19] M. M. Robinson and B. C. Robinson, *J. Org. Chem.*, 1956, **21**, 1337; S. L. Tan, unpublished work.

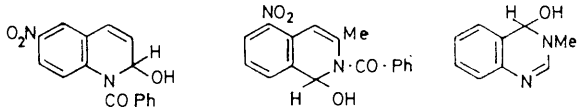
hydrogen at C-3 in (XVII; R = H) by more bulky substituents, and preliminary results [20] suggest that in such cases the open chain form of the carbinolamide system is preferred.

It is of interest that the introduction of the 5-nitro-group causes such a marked change of behaviour from the normal isoquinoline Reissert reaction. Possibly the increased positive character of the C-1 position is sufficient to result in loss of selectivity such that the nucleophile in excess (H_2O or OH^-) reacts predominantly. However, attempts to substantiate this by varying concentration proved inconclusive. In terms of the principle of ' hard ' and ' soft ' acids and bases [21] the effect of the 5-nitro-group is to enhance the ' hardness ' of the C-1 centre, thus favouring attack by the hard base H_2O (or OH^-) rather than the ' softer ' base CN^-. Hull also uses this principle in discussing the thiocarbonyl case cited above.[12] The effect of the 5-nitro-group has been noted in the *N*-alkyl pseudo-base situation. *N*-Methylisoquinolium salts on treatment with silver oxide give a strongly alkaline quaternary hydroxide which only slowly transforms to the covalent form, whereas a covalent pseudo-base is immediately provided when 5-nitroisoquinoline methiodide is subject to similar conditions.[22]

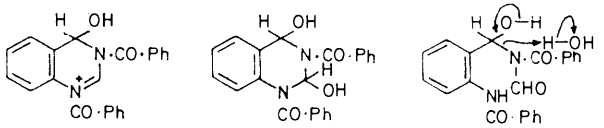
On examination of systems electronically analogous to 5-nitroisoquinoline for *N*-acyl pseudo-base behaviour it was disappointing to find that 4-nitro- and 7-nitro-isoquinoline, isoquinoline-5-sulphonic acid, and 8-nitroquinoline all failed to react. This may in part be a reflexion of their differing basicities and it can also be noted that 8-substituted quinolines have only rarely been found to undergo Reissert type reactions.[23]

Two cases which provided *N*-acyl pseudo-bases, though in a less pronounced manner than for 5-nitroisoquinoline, were 6-nitroquinoline and 3-methyl-5-nitroisoquinoline. In the former case, after 3 h reaction 43% of the quinoline *N*-acyl pseudo-base (XXI) was formed, based however on a high recovery of quinoline. The yield could not be improved by omitting cyanide. Prolonged stirring (8 h) resulted only in the Reissert compound being formed. Under the normal conditions 3-methyl-5-nitroisoquinoline gave 9% *N*-acyl pseudo-base (XXII) and 57% Reissert compound, the yield of (XXII) being augmented to 43% by omission of cyanide. The presence of the carbinolamides (XXI) and (XXII) was not reported in the earlier preparation of the two Reissert compounds.[5,23a] In common with the previous *N*-acyl-pseudo-bases neither (XXI) nor (XXII) showed any evidence of the presence of the open chain forms.

The behaviour of quinazoline was of interest since Reissert compound formation from diaza-heterocyclic systems has been little explored and with the nitrogen atoms at positions 1 and 3 quinazoline is electronically related to 4-nitroisoquinoline. Quinazoline is stable in cold dilute acid and alkaline solutions but is destroyed when these solutions are boiled, giving, in acid, *o*-aminobenzaldehyde.[24] Alkylation takes place at the 3-position



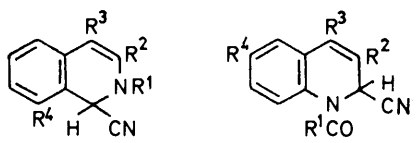
(XXI) (XXII) (XXIII)



(XXIV) (XXV) (XXVI)

and the normal pseudo-base (XXIII) is formed on treatment of the methiodide with aqueous potassium hydroxide.[25] We found that on subjection to the conditions for Reissert compound formation quinazoline gave neither a Reissert derivative nor *N*-acyl pseudo-base, the only product being *o*-formylbenzanilide. The same was the case in the absence of cyanide. It would, however, seem likely that the breakdown probably proceeds *via* (XXIV) and the bis-*N*-acyl pseudo-base (XXV), the ring opening at the 1,2-bond to give (XXVI) being analogous to the quinoline [8] and benzimidazole [9,10] cases mentioned above. The C-2 centre in (XXIV) will presumably be sufficiently ' hard ' to promote attack by H_2O or OH^- rather than by CN^-.

Our studies of Reissert intermediates have provided us with a representative number of 1,2-dihydroisoquinolines and 1,2-dihydroquinolines to permit some general conclusions to be drawn from their n.m.r. spectra regarding the stereochemistry of these systems as well as to indicate some characteristic absorptions useful in identification. Spectral assignments for the two series (XXVII) and (XXVIII) are shown in Tables 2 and 3, and *cf.* Table 1.



(XXVII) (XXVIII)

The observation of long-range coupling between the C-1 and C-3 protons in isoquinoline Reissert compounds [26] has made possible the unequivocal assignment of the

[20] G. W. Kirby, S. L. Tan, and B. C. Uff, International Congress of Pure and Applied Chemistry, Boston, 1971, Abstract 270, p. 113.

[21] R. G. Pearson in ' Hard and Soft Acids and Bases,' Dowden, Huchinson and Ross, Stroudsberg, Pennsylvania, 1973, pp. 40, 67, and 377.

[22] A. Claus and K. Hoffmann, *J. prakt. Chem.*, 1893, **47**, 252.

[23] (*a*) F. D. Popp, W. Blount, and P. Melvin, *J. Org. Chem.*, 1961, **26**, 4930; (*b*) Y. Hamada, *J. Pharm. Soc.* (*Japan*), 1960, **80**, 1573; (*c*) I. W. Elliott, *J. Amer. Chem. Soc.*, 1955, **77**, 4408.

[24] S. Gabriel, *Ber.*, 1903, **36**, 800; A. Albert and H. Yamamoto, *J. Chem. Soc.* (*B*), 1966, 956.

[25] A. Albert, W. L. F. Armarego, and E. Spinner, *J. Chem. Soc.*, 1961, 5267.

[26] S. R. Chhabra, J. R. Kershaw, and B. C. Uff, *Tetrahedron Letters*, 1967, 3199.

TABLE 1

N-Acyl pseudo-bases and ether derivatives (XV)

(XV)	R^1	R^2	Yield (%)	Chemical shift (τ) 1-H (d)	3-H (q)	4-H (d)	$J_{1,3}$* (Hz)	$J_{3,4}$* (Hz)	Other protons (τ)	Analogous Reissert cpd. yield (%)
a	H	Ph	90	†						1
b	Me	Ph	96	3·41	2·96	3·17	1·3	8·0	6·62 (3H, s, OMe)	
c	Et	Ph	68	3·31	2·94	3·14	1·3	8·0	6·29 (2H, q, CH_2) 8·84 (3H, t, Me)	
d	H	*p*-MeC_6H_4	67	†					7·71 (3H, s, Me)	4
e	Me	*p*-MeC_6H_4	96	3·42	2·93	3·19	1·3	8·0	6·53 (3H, s, OMe) 7·62 (3H, s, Me)	
f	Et	*p*-MeC_6H_4	99	3·33	2·96	3·17	1·3	8·0	6·28 (2H, q, Me) 7·60 (3H, s, ArMe) 8·83 (t, 3H, Me)	
g	H	*p*-ClC_6H_4	60	†						0·6
h	Me	*p*-ClC_6H_4	29	3·43	2·96	3·15	1·3	8·0	6·61 (3H, s, OMe)	
i	Et	*p*-ClC_6H_4	30	3·37	3·01	3·6	1·3	8·0	6·32 (2H, q, CH_2) 8·83 (3H, t, Me)	
j	H	*p*-$MeOC_6H_4$	70	†					6·17 (3H, s, OMe)	5
k	Me	*p*-$MeOC_6H_4$	98	3·44	2·91	3·18	1·3	8·0	6·15 (3H, s, ArOMe) 6·62 (3H, s, 1-OMe)	
l	Et	*p*-$MeOC_6H_4$	83	3·35	2·90	3·14	1·3	8·0	6·15 (3H, s, OMe) 6·28 (2H, q, CH_2) 8·83 (3H, t, Me)	
m	H	Me	74	†					7·61 (3H, s, Me)	2
(XXII)			9	3·43		3·11		1·5 ‡	5·30 (1H, d, $J_{1\text{-OH},\ 1\text{-H}}$ 6·0 Hz, 1-OH) 8·10 (3H, d, Me)	57

* Signs of coupling constants determined only when shown. † Proton signals partially obscured by aromatic envelope. ‡ C-Me allylic coupling.

TABLE 2

1,2-Dihydroisoquinolines (XXVII)

(XXVII)	R^1	R^2	R^3	R^4	Chemical shift (τ) 1-H	3-H	4-H	$J_{1,3}$* (Hz)	$J_{3,4}$* (Hz)	Other protons (τ)
a [a]	Bz	H	H	H	3·42d	3·36q	3·94d	0·80	8·0	
b	*p*-MeC_6H_4CO	H	H	H	3·46d	3·33q	3·96d	0·80	8·0	7·60 (3H, s, Me)
c	*o*-$NO_2{\cdot}C_6H_4CO$	H	H	H	3·19d	3·76q	4·02d	0·85	8·0	
d [b]	*p*-MeC_6H_4CO	H	H	OBz	3·33d	3·27q	3·95d	0·80	8·0	7·62 (3H, s, Me)
e [c]	PhCH=CH·CO	H	H	H	3·31d	3·04q	3·83d	0·90	8·0	2·12 (1H, d, =CH·Ph) 3·31 (1H, d, CO·CH=)
f [d]	Ac	H	H	H	3·35d	3·28q	3·96d	0·80	8·0	7·80 (3H, s, Me)
g	CH_2=CH·CO	H	H	H	3·40d	3·16q	3·46d	0·85	8·0	3·38 (1H, m, CO·CH=) 3·90 (2H, m, =CH_2)
h	$MeCH_\beta$=CH_α·CO	H	H	H	3·38d	3·12q	3·88d	0·85	8·0	β proton obscured 3·72 (1H, m, CO·CH=)
i	$MeCH_\beta$=CH_α·CO	Me	H	H	3·38s		3·69q		1·5 [e]	β proton obscured 3·96 (1H, m, CO·CH=) 7·73 (3H, d, Ar*Me*) 8·13 (3H, dd, Me)
j	Me_2C=CH·CO	H	H	H	3·43d	3·21q	4·03d	0·80	8·0	4·10 (1H, m, CO·CH=) 7·96 (3H, d, Me) 8·13 (3H, d, Me)
k [f]	*p*-MeC_6H_4CO	Me	H	H	3·50s		3·67q		1·5 [e]	7·61 (3H, s, Ar*Me*) 8·19 (3H, e, 3-Me)
l [g]	Bz	H	Br	H	3·44d	3·00d		0·90		
m [h]	$MeOCH_2$	H	H	H	4·54d	3·79q	4·38d	0·95	8·0	5·53 (2H, ABq, CH_2) 6·70 (3H, s, Me)
n	Me	H	H	H	4·36d	3·96q	4·82d	0·80	8·0	7·13 (3H, s, Me)

* Signs of coupling constants determined only when shown.

[a] B. C. Uff and J. Kershaw, *J. Chem. Soc.* (*C*), 1969, 666. [b] Ref. 1. [c] V Boekelheide and J. Weinstock, *J. Amer. Chem. Soc.*, 1952, **74**, 660. [d] F. D. Popp and A. Soto, *J. Chem. Soc.*, 1963, 1760. [e] C-Me allylic coupling. [f] H. W. Gibson, *J. Heterocyclic Chem.*, 1970, **7**, 1169. [g] Ref. 5. [h] H. Böhme and R. Schweitzer, *Chem. Ber.*, 1969, **102**, 3606.

chemical shifts of the C-3 and C-4 protons, which had not previously been certain.[27] Absorption of the C-4 proton at τ *ca.* 3·7—4·0 and the C-3 proton at 3·1—3·3 is in general characteristic of the isoquinoline Reissert structures (Table 2). In the quinoline analogues (Table 3) the C-4 proton signal is usually partially obscured by the aromatic multiplet but the C-3 proton resonates at a higher field, τ *ca.* 3·9, presumably reflecting the more remote *N*-benzoyl group. ABX analyses [28] were required in cases (XXVIIIa, f, and g) in which the quinoline

[27] R. Bramley and M. D. Johnson, *J. Chem. Soc.*, 1965, 1372.

[28] C. N. Banwell, 'N.m.r. for Organic Chemists,' ed. D. W. Mathieson, Academic Press, London, 1967, p. 85, and references therein.

Reissert compounds carry a proton at each of the 2-, 3- and 4-positions, and designation of the C-2 proton signal (*ca.* τ 3·8) was in some instances confirmed by replacement with deuterium.

The calculated values for the allylic coupling, $J_{2,4}$, fall between −1·0 and −0·5 Hz (Table 3). Assuming that this coupling relates principally to the geometric arrangements of the bonds joining the atoms involved, known correlations of transoid allylic coupling with stereochemistry [29] suggest that the C-2 proton is occupying, on average, a position weighted towards a quasi-equatorial environment. Thus, as for the 1,2-dihydroisoquinoline cases,[26] the substituent at the saturated carbon is preferring the quasi-axial situation. Although electrostatic interactions are probably not minimised in this environment, the situation is relatively free from non-bonded steric interactions particularly of the 1,3-type (and also with the amidic phenyl ring), a situation similar to that reported for alicyclic analogues of the cyclohexa-1,3-diene type, the 1,2-dihydronaphthalenes,[30a] and 9,9′,10,10′-tetrahydro-9,9′-biphenanthryls [30b] in particular. Some $J_{2,4}$ values of 1,2-disubstituted 1,2-dihydroquinolines of the non-Reissert type have been reported [27] and also fall within the same areas shown above, suggesting similar stereochemistry.

A report [31] published concurrently with the preparation of this paper, complements these findings. Gibson [31] has studied the stereochemistry of 1-alkyl substituted isoquinoline Reissert compounds where, of course, long range coupling ($J_{1,3}$) is no longer available. By the inclusion of diastereotopic groups in the 1-substituent the resulting anisochronism observed has enabled the deduction to be made that, as our cases show, the more bulky substituent at C-1 prefers to adopt the quasi-axial environment.

TABLE 3

1,2-Dihydroquinolines (XXVIII)

(XXVIII)	R¹	R²	R³	R⁴	Chemical shift (τ) 2-H	Chemical shift (τ) 3-H	$J_{2,3}$ * (Hz)	$J_{3,4}$ * (Hz)	$J_{2,4}$ * (Hz)	Other protons (τ)	Ref. to preparation
a	Ph	H	H	H	3·82	3·92	6·3	9·3	−1·01		9
b	Ph	Br	H	H	3·76d				0·4		23*a*
c	*p*-MeC$_6$H$_4$	NH·Bz	H	H	obscured				obscured	0·79br (1H, s, NH) 7·70 (3H, s, Me)	
d	*p*-MeC$_6$H$_4$	OBz	H	H	3·63br,s				†	7·65 (3H, s, Me)	
e	Ph	H	Me	H	3·86d	4·10m	6·4	1·7 ‡		7·78 (3H, d, Me)	23*a*
f	Ph	H	H	Me	3·84	3·95	6·3	9·2	−0·7	7·78 (3H, s, Me)	23*c*
g	Ph	H	H	NO_2	3·87	3·73	6·5	9·4	−0·5		23*a*
h	Me	H	H	Me	3·54q	3·99q	6·3	9·3	0·7	3·32 (1H, q, 4-H) 7·64 (3H, s, CO·Me) 7·78 (3H, s, 6-Me)	

* Signs of coupling constants determined only when shown. † Not resolved. ‡ C-Me allylic coupling.

EXPERIMENTAL

N.m.r. spectra were recorded with $CDCl_3$ as solvent at 60 MHz on a Perkin-Elmer R10 instrument and at 100 MHz [compounds (XXVIIIa, f, and g)] on a Varian HA-100F instrument with tetramethylsilane as internal standard.

Reaction of 5-Nitroisoquinoline with Acid Chlorides and Potassium Cyanide.—General procedure. The acid chloride (0·032 mol) was added over 2 h to a stirred mixture of 5-nitroisoquinoline [32] (0·016 mol) in methylene chloride (20 ml) and potassium cyanide (0·048 mol) in water (8 ml). Immediately a yellow precipitate appeared which increased with the continued addition of acid chloride. The stirring was continued for an additional 2 h and the yellow precipitate of *N*-acyl pseudo-base, *N*-acyl-1-hydroxy-5-nitro-1,2-dihydroisoquinoline (XV; R¹ = H) was filtered off at the pump, washed with water, and dried. Compound (XVa) crystallised from ethanol–ethyl acetate, (XVd) from acetone, and the remainder from ethanol, all as yellow needles. Other details, including analytical data, are in Tables 1 and 4. From the filtrate, the organic layer was washed with water, 2N-hydrochloric acid, water, 2N-sodium hydroxide, and finally with water again. The solution was dried (Na_2SO_4) and evaporation of the solvent gave a residue which was chromatographed on alumina in benzene–ethyl acetate (4 : 1) to give the Reissert compound, *N*-acyl-5-nitro-1,2-dihydroisoquinoline-1-carbonitrile. The yields obtained are recorded in Table 1.

By this procedure the following Reissert compounds were obtained. *5-Nitro-*N*-p-toluoyl-1,2-dihydroisoquinoline-1-carbonitrile*, fine yellow needles (from 95% ethanol), m.p. 198—200° (Found: C, 67·65; H, 4·1; N, 13·3. $C_{18}H_{13}N_3O_3$ requires C, 67·7; H, 4·1; N, 13·15%), $\nu_{max.}$ 1688 (N–C=O) and 1623 cm^{-1} (C=C), τ 1·8—3·4 (10H, m, aromatic, H-1, -3, and -4) and 7·60 (3H, s, CH_3), *m/e* 319. *N-p-Chlorobenzoyl-5-nitro-1,2-dihydroisoquinoline-1-carbonitrile*, deep yellow plates (from ethyl acetate), m.p. 199—200° (Found: C, 60·0; H, 3·15; N, 12·4. $C_{17}H_{10}ClN_3O_3$ requires C, 60·1; H, 2·95; N, 12·35%), $\nu_{max.}$ 2245w (CN), 1673 (N–C=O), 1620 (C=C), and 1520 cm^{-1} (NO_2), τ 1·7—2·8 (7H, m, aromatic protons), 3·12 (2H, s), and 3·36 (1H, s). *N-Anisoyl-5-nitro-1,2-dihydroisoquinoline-1-carbonitrile*, deep yellow plates (from ethyl acetate), m.p. 209—210° (Found: C, 64·3; H, 3·8; N, 12·65. $C_{18}H_{13}N_3O_4$ requires C, 64·45; H, 3·9; N, 12·55%), $\nu_{max.}$ 2245w (CN), 1663 (N–C=O), and 1630 cm^{-1} (C=C), τ 1·7—3·0 (7H, m, aromatic protons), 3·10br (2H, s), 3·40 (1H, s), and 6·10 (3H, s, OMe). *N-Acetyl-5-nitro-1,2-dihydroisoquinoline-1-carbonitrile*, yellow needles (from ethyl acetate), m.p. 186—187° (Found: C, 59·3; H, 3·9; N, 17·4. $C_{12}H_9N_3O_3$ requires C, 59·25; H, 3·75; N, 17·3%), $\nu_{max.}$ 2250w (CN), 1653 (N–C=O), and 1620 cm^{-1} (C=C), τ 1·8—3·3 (6H, m, aromatic, H-1, -3, and -4), and 7·69, (3H, s, Me).

By the inclusion of diastereotopic groups in the 1-substituent the resulting anisochronism observed has enabled the deduction to be made that, as our cases show, the more bulky substituent at C-1 prefers to adopt the quasi-axial environment.

[29] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

[30] (*a*) M. J. Cook, A. R. Katritzky, F. C. Pennington, and B. M. Semple, *J. Chem. Soc.* (*B*), 1969, 23; (*b*) D. Cohen, I. T. Millar, H. Heaney, P. R. Constantine, A. R. Katritzky, B. M. Semple, and M. J. Sewell, *ibid.*, 1967, 1248.

[31] H. W. Gibson, *J. Org. Chem.*, 1973, **38**, 2851.

[32] M. J. S. Dewar and P. M. Maitlis, *J. Chem. Soc.*, 1957, 2521.

Preparation of N-*Acyl-1-alkoxy-5-nitro-1,2-dihydroisoquinolines.—General procedure.* The *N*-acyl pseudo-base (0·5 g) was heated in methanol (50 ml) at 45—50 °C, or in ethanol (40 ml) at reflux, for several hours (Table 4). After cooling, the solvent was evaporated and the residue chromatographed on neutral alumina in benzene and ethyl acetate to give the 1-*methoxy*- or 1-*ethoxy*-N-*acyl-5-nitro-1,2-dihydroisoquinoline.* 1-Methoxy-compounds were recrystallised from methanol to give yellow needles; 1-ethoxy-compounds crystallised as yellow needles from ethanol, (XVf) giving yellow plates. Other details, including analytical data, are in Tables 1 and 4.

Conversion of N-*Benzoyl-1-methoxy-5-nitro-1,2-dihydroisoquinoline into* N-*Benzoyl Pseudo-base.*—*N*-Benzoyl-1-methoxy-5-nitro-1,2-dihydroisoquinoline (0·5 g) in aqueous dioxan (40 ml; *ca.* 25%) was stirred at room temperature. A yellow precipitate appeared and precipitation was complete after 20 min (by t.l.c., no starting material present). The dried precipitate had an identical i.r. spectrum with that of authentic *N*-benzoyl-1-hydroxy-5-nitro-1,2-dihydroisoquinoline prepared previously.

Bromohydrin Formation.—To a solution of *N*-benzoyl-1-hydroxy-5-nitro-1,2-dihydroisoquinoline (1·0 g, 3 mmol) in aqueous tetrahydrofuran (100 ml; 66%) was added bromine (0·5 g, 3 mmol). The bromine colour disappeared immediately. The solution was poured into water (300 ml) and extracted with ether; the extract was dried (Na_2SO_4) and evaporated to give a brown viscous oil (1·4 g). Chromatography on silica in ethyl acetate–methanol (95 : 5) gave N-*benzoyl-4-bromo-1,3-dihydroxy-5-nitro-1,2,3,4-tetrahydroisoquinoline* as an oil (1·2 g, 92%). Recrystallisation from methanol gave stout needles, m.p. 153—154° (Found: C, 49·05; H, 3·45; N, 7·2. $C_{16}H_{13}BrN_2O_5$ requires C, 48·85; H, 3·35; N, 7·15%), $\nu_{max.}$ 3340br (OH) and 1630 cm^{-1} (N–C=O), τ 1·8—2·8 (8H, m, aromatic protons), 3·55br (1H, s, H-1), 4·23 (2H, d, H-3 and -4), 4·50br (2H, s, exchangeable, 2OH), $\lambda_{max.}$ 225 nm, *m/e* 394/392 (1 : 1).

O-*Methylbromohydrin Formation.*—*N*-Benzoyl-1-hydroxy-5-nitro-1,2-dihydroisoquinoline (0·5 g, 1·5 mmol) in methanol (40 ml) containing acetic acid (1 ml) was heated for 15 min and cooled. Bromine (0·25 g, 1·5 mmol) was added and the bromine colour disappeared immediately. The solution was poured in water and extracted with ether, and the extract was dried (Na_2SO_4) and evaporated to give N-*benzoyl-4-bromo-1-hydroxy-3-methoxy-5-nitro-1,2,3,4-tetrahydroisoquinoline* (0·4 g, 59%). Recrystallisation from methanol gave long fine needles, m.p. 148—150° (Found: C, 50·45; H, 3·95; N, 7·35. $C_{17}H_{15}BrN_2O_5$ requires C, 50·15; H, 3·7; N, 6·9%), $\nu_{max.}$ 3460br (OH), 1663 (N–C=O), and 1050 cm^{-1} (ether), τ 1·6—2·6 (10H, m), 3·85 (1H, d), 4·61br (1H, s, exchangeable, OH), and 6·52 (3H, s, OMe), *m/e* 408/406 (1 : 1).

Preparation of N-*Acetyl-4-bromo-3-methoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile.*— *N*-Acetyl-1,2-dihydroisoquinoline-1-carbonitrile (1·0 g, 5 mmol) on treatment with bromine (0·8 g, 5 mmol) in methanol (80 ml) by the same method as described for the last experiment gave a thick brown syrup (1·2 g, 80%). Recrystallisation from methanol gave N-*acetyl-4-bromo-3-methoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile* as rhombs, m.p. 155—156° (Found: C, 50·55; H, 4·3); N, 9·15. $C_{13}H_{13}BrN_2O_2$ requires C, 50·5; H, 4·25; N, 9·05%), $\nu_{max.}$ 2240w (CN), 1663 (N–C=O), and 1055 cm^{-1} (ether), τ [$(CD_3)_2SO$] 2·2—2·7 (4H, m, aromatic protons), 3·95 (1H, s, 1-H), 4·20 (1H, d, $J_{3,4}$ 3·0 Hz, 3-H), 4·30 (1H, d, $J_{4,3}$ 3·0 Hz, 4-H), 6·71 (3H, s, OMe), and 7·66 (3H, s, Me), *m/e* 310/308 (1 : 1).

TABLE 4

N-Acyl pseudo-bases and ether derivatives (XV)

(XV)	Reaction time (h)	M.p. (°C)	Molecular formula	Required (%) C	H	N	Found (%) C	H	N
a	4	189—190	$C_{16}H_{12}N_2O_4$	64·85	4·1	9·45	65·0	4·1	9·5
b	12	115—115·5	$C_{17}H_{14}N_2O_4$	65·8	4·55	9·05	65·65	4·65	8·95
c	3	108—109	$C_{18}H_{16}N_2O_4$	66·65	4·95	8·65	66·65	5·05	8·6
d	4	183—184	$C_{17}H_{14}N_2O_4$	65·8	4·55	9·05	65·85	4·55	9·15
e	22	128—128·5	$C_{18}H_{16}N_2O_4$	66·65	4·95	8·65	66·56	5·05	8·75
f	*	118—119	$C_{19}H_{18}N_2O_4$	67·45	5·35	8·3	67·4	5·5	8·4
g	4	179—180	$C_{16}H_{11}ClN_2O_4$	58·1	3·35	8·45	58·05	3·6	8·45
h	20	173—174	$C_{17}H_{13}ClN_2O_4$	59·2	3·8	8·15	59·45	3·85	7·95
i	4	150—151	$C_{18}H_{15}ClN_2O_4$	60·25	4·2	7·8	60·45	4·3	7·75
j	4	167—169	$C_{17}H_{14}N_2O_5$	62·55	4·3	8·6	62·95	4·3	8·6
k	20	186—187	$C_{18}H_{16}N_2O_5$	63·5	4·75	8·25	63·55	4·6	8·2
l	1	137—138	$C_{19}H_{18}N_2O_5$	64·4	5·1	7·9	64·55	4·95	7·8
m	4	174—176	$C_{11}H_{10}N_2O_4$	56·4	4·3	11·95	56·7	4·3	12·05

* Product obtained directly on attempted recrystallisation of 1-hydroxy-5-nitro-*N*-*p*-toluoyl-1,2-dihydroisoquinoline from ethanol.

Reaction of N-*Benzoyl-1-hydroxy-5-nitro-1,2-dihydroisoquinoline with Hypochlorous Acid.*—Hypochlorous acid was prepared by the addition of a solution of sodium hypochlorite (12% w/v available chlorine) (50 ml) to 2N-nitric acid (50 ml). The strength was determined as 0·57% hypochlorous acid by titration with sodium thiosulphate, using potassium iodide–starch solution as indicator.

A stirred solution of *N*-benzoyl-1-hydroxy-5-nitro-1,2-dihydroisoquinoline (1·0 g, 3·0 mmol) in dioxan (50 ml) was treated with the freshly prepared hypochlorous acid solution (30 ml, 3·2 mmol) dropwise at room temperature until a slight excess was present (tested by potassium iodide–starch paper). The solution was stirred for a further 1 h and the solvent was evaporated off. The residue was washed with water and recrystallised from methanol to give N-*benzoyl-4-chloro-3-hydroxy-5-nitro-3,4-dihydroisoquinol-1(2H)-one* (XVIII) (0·4 g, 36%) as rhombs, m.p. 226—227° (Found: C, 55·35; H, 3·5; N, 8·25. $C_{16}H_{11}ClN_2O_5$ requires C, 55·4; H, 3·2; N, 8·1%), $\nu_{max.}$ 3440 (OH), 1710, 1682, and 1665 cm^{-1} (CO–N–CO), τ [$(CD_3)_2SO$] 1·4—2·6 (8H, m, aromatic protons), 3·90 (1H, d, $J_{3,4}$ 3·0 Hz, 3- or 4-H), 3·9br (1H, s, exchangeable, 3-OH), and 4·07 (1H, d, 4- or 3-H), *m/e* 348/346 (3 : 1).

The mother liquor was concentrated and chromatographed on alumina in benzene–ethyl acetate to afford 4-*chloro-5-nitroisoquinoline* (15 mg, 2%). Recrystallisation

from 95% ethanol gave pale yellow needles, m.p. 180—182° (Found: C, 52·05; H, 2·5; N, 13·25. $C_9H_5ClN_2O_2$ requires C, 51·8; H, 2·4; N, 13·45%), $\nu_{max.}$ 1625 (C=N) and 1575 cm^{-1} (NO_2), τ 0·53 (1H, s, 1-H), 1·26 (1H, s, 3-H), 1·46 (1H, dd, $J_{6,7}$ 7·7, $J_{6,8}$ 2·5 Hz, 6-H), 1·65 (1H, dd, $J_{8,7}$ 7·7, $J_{8,6}$ 2·5 Hz, 8-H), and 2·10 (unsymmetrical t, $J_{7,6} = J_{7,8}$ 7·7 Hz, 7-H), *m/e* 210/208 (3 : 1).

Reaction of N-*Benzoyl*-1-*methoxy*-5-*nitro*-1,2-*dihydroisoquinoline with Hypochlorous Acid.*—*N*-Benzoyl-1-methoxy-5-nitro-1,2-dihydroisoquinoline (0·2 g) was treated with freshly prepared hypochlorous acid (6 ml) by the same method as described in the previous experiment. Recrystallisation from methanol gave rhombs, m.p. 226—227°. The compound, N-*benzoyl*-4-*chloro*-3-*hydroxy*-5-*nitro*-1,2,3,4-*tetrahydroisoquinolone* (XVIII) (95 mg, 42%), had identical i.r. and n.m.r. spectra as the sample prepared above, and the mixed m.p. was undepressed.

The mother liquor was concentrated and chromatographed on silica plates in benzene–ethyl acetate (4 : 1) to afford 5-nitroisoquinoline (65 mg, 58%). Recrystallisation in benzene–ethyl acetate gave *N*-benzoyl-2-hydroxy-6-nitro-1,2-dihydroquinoline [0·15 g, 43% based on recovered starting material (1·8 g, 90%)]. Recrystallisation from ethyl acetate gave rhombs, m.p. 189—190°. The compound had an identical i.r. spectrum with that obtained above and the mixed m.p. was undepressed.

Reissert Reaction with 3-*Methyl*-5-*nitroisoquinoline.*—Benzoyl chloride (2·5 ml, 2·2 mmol) was added over 2 h to a stirred mixture of 3-methyl-5-nitroisoquinoline [33] (2·0 g, 1·1 mmol) in methylene chloride (20 ml) and potassium cyanide (2·0 g, 3·3 mmol) in water (5 ml). After an additional 2 h stirring, the layers were separated. The methylene chloride solution was washed with water, 2N-hydrochloric acid, water, 2N-sodium hydroxide, and water, dried, and evaporated to give a deep yellow oil. Chromatography on alumina in benzene–ethyl acetate (4 : 1) gave *N*-benzoyl-3-methyl-5-nitro-1,2-dihydroisoquinoline-1-carbonitrile (0·8 g, 57% based on recovered starting material); yellow needles (from 95% ethanol), m.p. 159—160° (lit.,[5] 159°). Also obtained was N-*benzoyl*-1-*hydroxy*-3-*methyl*-5-*nitro*-1,2-*dihydroisoquinoline* (XXII) (0·12 g, 9% based on recovered starting material), yellow needles (from aq. acetone), m.p. 151—152° (Found: C, 65·95; H, 4·55; N, 9·0. $C_{17}H_{14}N_2O_4$ requires C, 65·8; H, 4·55; N, 9·05%), $\nu_{max.}$ 3430 (OH) and 1650 cm^{-1} (N–C=O), *m/e* 310. Unchanged 3-methyl-5-nitroisoquinoline was recovered from the acidic washings (1·2 g, 60%).

The foregoing procedure was repeated twice; (*a*) using potassium hydroxide (2·0 g) when the pseudo-base, *N*-benzoyl-1-hydroxy-3-methyl-5-nitro-1,2-dihydroisoquinoline [0·45 g, 40% based on recovered starting material (1·0 g, 50%)] was obtained, and (*b*) using water alone when the pseudo-base [0·72 g, 37% based on recovered starting material (1·1 g, 55%)] was obtained.

Reissert Reaction with Quinazoline.—Benzoyl chloride (1·8 ml, 8 mmol) was added over 2 h to a stirred mixture of quinazoline (0·52 g, 4 mmol) in methylene chlorine (10 ml) and potassium cyanide (1·6 g, 12 mmol) in water (4 ml). After stirring for an additional 2 h, the reaction was worked up and an oily product obtained. Chromatography on alumina in benzene gave *o*-formylbenzanilide as a low melting solid (0·25 g, 31%). Recrystallisation from light petroleum (b.p. 40—60°) gave needles, m.p. 73° (lit.,[34] 73°), undepressed on admixture with an authentic sample.

TABLE 5

Reissert compounds; physical and analytical data

Reissert compound	Yield (%)	M.p. (°C)	Molecular formula	Required (%) C	Required (%) H	Required (%) N	Found (%) C	Found (%) H	Found (%) N
(XXVIIb)	74	132—133 [e]	$C_{18}H_{14}N_2O$	78·8	5·15	10·2	78·5	5·1	10·25
(XXVIIc)	2 [a]	154—155 [d]	$C_{17}H_{11}N_3O_3$	66·9	3·65	13·75	66·65	3·55	13·9
(XXVIIg)	12	151—152 [d]	$C_{13}H_{10}N_2O$	74·25	4·8	13·35	74·5	5·0	13·35
(XXVIIh)	55	141—141·5 [e]	$C_{14}H_{12}N_2O$	75·0	5·4	12·5	75·1	5·5	12·3
(XXVIIi)	70	117—118 [d]	$C_{15}H_{14}N_2O$	75·6	5·9	11·75	75·7	5·8	11·7
(XXVIIj)	98	110—110·5 [d]	$C_{15}H_{14}N_2O$	75·6	5·9	11·75	75·5	5·95	11·85
(XXVIIIc)	76	170—171 [c]	$C_{25}H_{19}N_3O_2$	76·3	4·85	10·7	76·55	4·95	10·55
(XXVIIId)	58 [b]	111—112 [e]	$C_{25}H_{18}N_2O_3$	76·15	4·6	7·1	76·4	4·8	7·4
(XXVIIIh)	27	80—81 [c, e]	$C_{13}H_{12}N_2O$	73·55	5·7	13·2	73·75	5·8	13·3

[a] The *o*-nitrobenzoyl chloride was not distilled prior to use in view of the possible explosion hazard (A. I. Vogel, ' Practical Organic Chemistry,' Longmans, London, 3rd edn., 1959, p. 792). [b] Prepared from 3-hydroxyquinoline (A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1956, 1294; R. A. Abramovitch, *ibid.*, 1954, 3839) *via* 3-benzoyloxyquinoline (C. J. Cavallito and T. H. Haskell, *J. Amer. Chem. Soc.*, 1944, **66**, 1166). [c] From ether–light petroleum (b.p. 40—60°). [d] From ethyl acetate. [e] From 95% ethanol.

from aqueous ethanol gave yellow needles, m.p. 109—110° (lit.,[32] 110°).

Reissert Reaction with 6-*Nitroquinoline.*—Use of 6-nitroquinoline (2·0 g, 11·2 mmol), benzoyl chloride (2·6 ml, 22·4 mmol), and potassium cyanide (2·2 g, 33·6 mmol) in the general procedure with stirring for 8 h gave *N*-benzoyl-6-nitro-1,2-dihydroquinoline-1-carbonitrile (0·78 g, 23%). Recrystallisation from ethyl acetate gave pale yellow needles, m.p. 204—206° (reported [23a] 201—202°), $\nu_{max.}$ 2245w (CN), 1664 (N–C=O), 1614 (C=C), and 1516 cm^{-1} (NO_2).

The foregoing reaction was repeated using potassium hydroxide (2·2 g). The usual work-up and chromatography on alumina gave N-*benzoyl*-2-*hydroxy*-6-*nitro*-1,2-*dihydroquinoline* (XXI) [0·11 g, 32% based on recovered starting material (1·8 g, 90%)], as rhombs (from ethyl acetate), m.p. 189—190° (Found: C, 65·05; H, 4·25; N, 9·6. $C_{16}H_{12}N_2O_4$ requires C, 64·85; H, 4·1; N, 9·45%), $\nu_{max.}$ 3320 (OH) and 1643 cm^{-1} (N–C=O), τ [$(CD_3)_2SO$] 1·64 (1H, d, $J_{5,7}$ 2·5 Hz, 5-H), 2·04 (1H, dd, $J_{5,7}$ 2·5, $J_{7,8}$ 8·8 Hz, 7-H), 2·47 (5H, s, Ph), 2·72 (1H, d, $J_{8,7}$ 8·8 Hz, 8-H), 2·93 (1H, d, $J_{4,3}$ 9·0 Hz, 4-H), 3·50br (1H, s, exchangeable, 2-OH), 3·53 (1H, q, $J_{3,4}$ 9·0, $J_{3,2}$ 5·1 Hz, 3-H), and 4·03 (1H, q, $J_{2,3}$ 5·1, $J_{H,OH}$ 1·7 Hz, 2-H), *m/e* 296.

The Reissert reaction using potassium cyanide was repeated and monitored by t.l.c. After 3 h, the reaction was worked up in the usual manner. Chromatography on alumina

[33] R. C. Elderfield, J. M. Lagowski, O. L. McCurdy, and S. L. Wythe, *J. Org. Chem.*, 1958, **23**, 435.

[34] A. Bischler and M. Lang, *Ber.*, 1895, **28**, 287.

On repeating the above reaction using potassium hydroxide or water alone the same product was isolated in 73 and 83% yields respectively.

Preparation of Reissert Compounds.—The general procedure of Popp and Blount [6] was used. Table 5 contains physical and analytical data for Reissert compounds not reported elsewhere.

Monodeuterio-Reissert Compounds.—The isoquinoline and quinoline Reissert compounds deuteriated at the 1- and 2-positions respectively were prepared by dissolving the Reissert compound (0·3 g) in dry dimethylformamide (5 ml) and adding the solution to a stirred suspension of sodium hydride (0·2 g) in dry dimethylformamide (10 ml) at −5 to 0° under nitrogen. After 1 min deuterium oxide (2 ml) was added and after stirring for a further 2 min the mixture was neutralised with solid carbon dioxide. The solution was poured onto ice and the precipitated solid filtered off. A chloroform solution of the product was then washed with water, 2N-hydrochloric acid, and water, dried, and evaporated to give the monodeuteriated Reissert compound.

3-*Benzoylaminoquinoline.*—Sodium hydroxide (1·2 g) in water (30 ml) was added to a cooled chloroform solution of 3-aminoquinoline (4·3 g) and benzoyl chloride (7·0 ml) and the red mixture was shaken until almost colourless. The product was filtered off and crystallisation from 95% ethanol gave 3-*benzoylaminoquinoline* as needles, m.p. 199—199·5° (4·6 g, 62%) (Found: C, 77·45; H, 5·05; N, 11·5. $C_{16}H_{12}N_2O$ requires C, 77·4; H, 4·85; N, 11·3%), $\nu_{max.}$ 3300 (NH) and 1675 cm^{-1} (CO), τ [$(CD_3)_2SO$] 0·67 (1H, d, $J_{2,4}$ 2·5 Hz, 2- or 4-H), 1·02 (1H, d, 4- or 2-H), and 1·6—2·6 (10H, m, aromatic and NH).

N-*Methyl*-1,2-*dihydroisoquinoline*-1-*carbonitrile* (XXVIIn) —Potassium cyanide (12 g) in water (50 ml) was added to isoquinoline methiodide (10 g) in water (80 ml). The mixture was stirred vigorously for 30 min, and the precipitate was filtered off and recrystallised from ethyl acetate to give the *carbonitrile* (3·9 g, 58%) as plates, m.p. 93—94° (Found: C, 77·4; H, 6·2; N, 16·2. $C_{11}H_{10}N_2$ requires C, 77·6; H, 5·9; N, 16·5%), $\nu_{max.}$ 2230 (CN) and 1630 cm^{-1} (C=C).

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