Intramolecular Cyclisation of 2-Phenylethyl Isocyanates

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Cyclisations of 2-phenylethyl isocyanate (2), (+)-1-methyl-2-phenylethyl isocyanate (3), and 2,2-diphenylethyl isocyanate (4) have been studied using polyphosphoric acid, aluminium chloride, boron trifluoride–diethyl ether, and triethyloxonium tetrafluoroborate. Depending on the reaction conditions, triethyloxonium tetrafluoroborate, for example, not only gave the expected isoquinolones (14)—(16) and other expected products, but in two cases, also gave the 2-*N*-(2-phenylethyl)formamidyl-3,4-dihydroisoquinolin-1(2*H*)-ones (9) and (10). The isoquinolone (15) was alkylated with triethyloxonium tetrafluoroborate or methyl fluorosulphonate to give 1-ethoxy- (7) or 1-methoxy-3-methyl-3,4-dihydroisoquinoline (8), respectively.

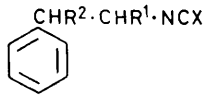
INTRAMOLECULAR cyclisation of isothiocyanates provides a useful synthesis of isoquinolines,[1] thienopyridines,[2] benzazepines,[3] and thieno[3,2-*c*]azepines.[3] Thus, for example, cyclisation of 2-phenylethyl isothiocyanate with triethyloxonium tetrafluoroborate gives 1-ethylthio-3,4-dihydroisoquinoline (5).[1] These results prompted us to study cyclisations of the corresponding isocyanates with triethyloxonium tetrafluoroborate and other reagents.

At the start of our work 6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (corydaldine) had been synthesised by cyclisation of homoveratryl isocyanate with phosphoryl chloride [4] and polyphosphoric acid [5] while the latter reagent had been used also to synthesise other 3,4-dihydroisoquinolin-1(2*H*)-ones.[6] Since then, polyphosphoric acid [7] and boron trifluoride–diethyl ether [8] have been used successfully to cyclise β-arylethyl isocyanates. A recently reported [9] two-stage treatment with phosphorus oxychloride and tin(IV) chloride appears to be advantageous, especially for the cyclisation of hindered β-arylethyl isocyanates.

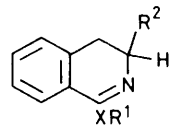
When 2-phenylethyl isocyanate (2) was heated with triethyloxonium tetrafluoroborate in methylene chloride under reflux there was no reaction. Consequently, the solvent was distilled off under reduced pressure and the residual mixture heated at 100 °C for 1 h prior to work-up.[1-3] This did not give the expected 1-ethoxy-3,4-dihydroisoquinoline (6) (see later). At 100 °C a gas was evolved which was collected and shown by ^{1}H n.m.r. and mass spectroscopy to be a mixture mainly of diethyl ether and other products one of which was probably ethyl fluoride. These obviously arise by breakdown of the reagent and it seemed likely that reaction had been promoted by the formation *in situ* of boron trifluoride–diethyl ether. Subsequently, it was shown that 2-phenylethyl isocyanate reacts with boron trifluoride–diethyl ether at 100 °C to give the same product (*cf.* ref. 8). This product was obtained also when the isocyanate (2) was treated with aluminium chloride. Mass

[1] M. W. Gittos, M. D. Robinson, J. P. Verge, R. V. Davies, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1976, 33.
[2] R. V. Davies, B. Iddon, T. McC. Paterson, M. W. Pickering, H. Suschitzky, and M. W. Gittos, *J.C.S. Perkin I*, 1976, 138.
[3] R. V. Davies, B. Iddon, M. W. Pickering, H. Suschitzky, P. T. Gallagher, M. W. Gittos, and M. D. Robinson, *J.C.S. Perkin I*, 1977, 2357.
[4] W. M. Whaley and T. R. Govindachari, *Org. Reactions*, 1951, **6**, ch. 2, p. 78; L. M. Mohunta and J. N. Rây, *J. Chem. Soc.*, 1934, 1263.
[5] R. Dran, F.P. 1 603 123/1971 (*Chem. Abs.*, 1972, **76**, 14779).
[6] G. Seidl, R. Kunstmann, and E. Granzer, German P., Offen. 2,143,745/1973 (*Chem. Abs.*, 1973, **78**, 147823).
[7] J. B. Hendrickson, T. L. Bogard, M. E. Fisch, S. Grossert, and N. Yoshimura, *J. Amer. Chem. Soc.*, 1974, **96**, 7781.
[8] S. Ohta and S. Kimoto, *Tetrahedron Letters*, 1975, 2279.
[9] Y. Tsuda, K. Isobe, J. Toda, and J. Taga, *Heterocycles*, 1976, **5**, 157.

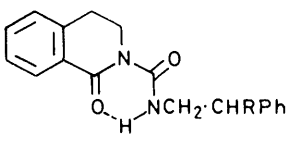
spectrometry and an ebullioscopic method gave the molecular weight 294 and the molecular formula $C_{18}H_{18}N_2O_2$, suggesting that it had been formed from two molecules of starting material. This, together with the i.r. evidence (see Experimental section) allowed us to



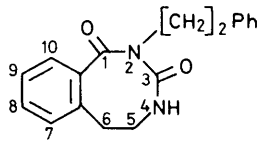
(1) X = S, $R^1 = R^2 = H$
(2) X = O, $R^1 = R^2 = H$
(3) X = O, R^1 = Me, $R^2 = H$
(4) X = O, $R^1 = H$, R^2 = Ph



(5) X = S, R^1 = Et, $R^2 = H$
(6) X = O, R^1 = Et, $R^2 = H$
(7) X = O, R^1 = Et, R^2 = Me
(8) X = O, $R^1 = R^2$ = Me



(9) R = H
(10) R = Ph



(11)

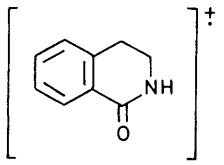
write the two possible structures (9) and (11). A prominant fragment ion in the mass spectrum at *m/e* 147 is probably due to the formation of ion (12) (C_9H_9NO), but the ^1H n.m.r. and other spectroscopic evidence did not allow us to distinguish conclusively between these two structures.

Hydrolysis of the unidentified compound with dilute sodium hydroxide gave the urea derivative (13), which cyclised in dilute hydrochloric acid to give back the starting material in quantitative yield. While the urea derivative (13) may arise by hydrolysis of either of the proposed structures, (9) or (11), it is unlikely that its cyclisation would yield the eight-membered ring structure (11) in preference to the 3,4-dihydroisoquinolin-1(2*H*)-one derivative (9). Further support for the latter structure was obtained by hydrolysis of the new compound with 70% sulphuric acid, which gave 3,4-dihydroisoquinolin-1(2*H*)-one (14), identical with samples prepared unambiguously by cyclisation of ethyl *N*-(2-phenylethyl)carbamate (17) or the corresponding thiocarbamate (18).

It seemed surprising, however, that compound (9) was not ethylated in the experiment involving triethyloxonium tetrafluoroborate After its isolation we showed that it was unreactive towards both this reagent and methyl fluorosulphonate. In the ^1H n.m.r. spectrum of compound (9) the NH proton signal at τ 0.55 disappeared extremely slowly on addition of deuterium oxide, which suggests that the compound may exist, as shown, with a strongly hydrogen bonded NH proton. This may also account for the fact that we failed to alkylate it.

When 2-phenylethyl isocyanate (2) was heated with triethyloxonium tetrafluoroborate at 160 °C without the initial addition of reactants in a hot solvent, different products were obtained, namely 3,4-dihydroisoquinolin-1(2*H*)-one (14) (40% yield), *NN'*-bis-(2-phenylethyl)-urea (31%), and ethyl *N*-(2-phenylethyl)carbamate (17) (15%), all identical with samples prepared unambiguously. With polyphosphoric acid, 2-phenylethyl isocyanate (2) gave a high yield of the expected 3,4-dihydroisoquinol-1(2*H*)-one (14).

(+)-1-Methyl-2-phenylethyl isocyanate (dexamphetamine isocyanate) (3) gave only 3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (15) when heated at 100 °C with triethyloxonium tetrafluoroborate. The same product was obtained with aluminium chloride or boron trifluoride–diethyl ether as the reagent. It was alkylated with triethyloxonium tetrafluoroborate and methyl fluorosulphonate to give 1-ethoxy- (7) or 1-methoxy-3-methyl-3,4-dihydroisoquinoline (8), respectively. With methyl fluorosulphonate (+)-1-methyl-2-phenylethyl isocyanate (3) gave the 1-methoxy-derivative (8) directly, in low yield.



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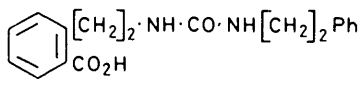
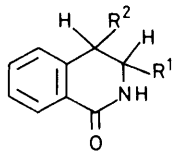
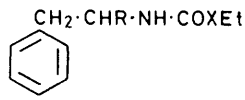


(13)



(14) $R^1 = R^2 = H$
(15) R^1 = Me, $R^2 = H$
(16) $R^1 = H$, R^2 = Ph



(17) X = O, R = H
(18) X = S, R = H
(19) X = O, R = Me

2,2-Diphenylethyl isocyanate (4) reacted with triethyloxonium tetrafluoroborate at 150 °C to give 4-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (16) (67% yield) together with 4-phenyl-2-*N*-(2,2-diphenylethyl)formamidyl-3,4-dihydroisoquinolin-1(2*H*)-one (10) (20%).

EXPERIMENTAL (With P. T. Gallagher)

General comments (spectroscopic instruments used, etc.) are as given previously.[1]

The isocyanates (2)—(4) and ethyl *N*-(2-phenylethyl)-monothiocarbamate (18) were synthesised as described elsewhere.[10]

Light petroleum had b.p. 60—80 °C unless stated otherwise.

Ethyl N-(2-*Phenylethyl*)*carbamate* (17).—A solution of ethyl chloroformate (22 g, 0.21 mol) in chloroform (100 ml)

[10] M. W. Gittos, R. V. Davies, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1976, 141.

was added dropwise to a stirred mixture of 2-phenylethylamine (24 g, 0.20 mol), triethylamine (20 g), and chloroform (50 ml) at ambient temperature, and the resulting mixture was stirred for a further 1 h. The solvent was distilled off under reduced pressure and addition of anhydrous ether (500 ml) to the residue left a precipitate of triethylamine hydrochloride, which was filtered off. Distillation of the filtrate gave the product (27.3 g, 71%), b.p. 114 °C at 0.6 mmHg, m.p. 38 °C (lit.,[11] 35—35.5 °C), $\nu_{max.}$ (Nujol) 1 720 (C:O) and 3 320 cm^{-1} (NH).

Ethyl N-(1-Methyl-2-phenylethyl)carbamate (19).—Ethyl chloroformate (10.8 g, 0.1 mol) was added dropwise to a stirred mixture of (+)-1-methyl-2-phenylethylamine (13.5 g, 0.1 mol), triethylamine (10.1 g, 0.1 mol), and ethanol (100 ml) at ambient temperature. The temperature of the mixture rose to 60 °C. After 30 min, when the mixture had cooled, it was worked up as described in the preceding experiment to give the product (18.3 g, 88%), b.p. (Kugelrohr apparatus) 100 °C at 2.0 mmHg (lit.,[11] 110—120 °C at 3.0 mmHg), m.p. 23—23.5 °C, $\nu_{max.}$ (film) 1 700 (C:O) and 3 330 cm^{-1} (NH); *m/e* 207 (M^+).

3,4-Dihydroisoquinolin-1(2H)-one (14).—(*a*) A stirred mixture of ethyl *N*-(2-phenylethyl)carbamate (17) (10 g, 54 mmol) and polyphosphoric acid (100 g) was heated at 120 °C for 1 h, and was then poured into water. Extraction with chloroform and distillation gave 3,4-dihydroisoquinolin-1-(2*H*)-one (6.0 g, 60%), b.p. (Kugelrohr apparatus) 150 °C at 0.4 mmHg, m.p. 58 °C (from aqueous methanol) (lit.,[12] 58 °C), $\nu_{max.}$ (Nujol) 1 665 (C:O) and 3 225 cm^{-1} (NH), with satisfactory n.m.r. and mass spectra.

(*b*) Ethyl *N*-(2-phenylethyl)monothiocarbamate (18) (5.0 g, 25 mmol), cyclised as described in the preceding experiment for the corresponding carbamate (17), gave 3,4-dihydroisoquinolin-1(2*H*)-one (3.02 g, 85%) identical (i.r.) with that prepared as described in (*a*).

Reactions of 2-Phenylethyl Isocyanate (2).—(*a*) *With triethyloxonium tetrafluoroborate.* (i) A stirred mixture of the isocyanate (7.4 g, 50 mmol), the reagent (9.5 g, 50 mmol), and methylene chloride (100 ml) was heated under reflux for 2 h. I.r. spectroscopy showed that considerable isocyanate was unchanged. Therefore, the solvent was distilled off under reduced pressure and the residue was heated at 100 °C for 1 h. It was then poured into 1M-sodium hydroxide to give 2-N-(*2-phenylethyl)formamidyl-3,4-dihydroisoquinolin-1(2H)-one* (9) (4.1 g, 56%), m.p. 101 °C (from aqueous methanol), $\nu_{max.}$ (Nujol) 1 640 (C:O), 1 690 (C:O), and 3 270 cm^{-1} (NH); τ($CDCl_3$) 0.55br (1 H, t, exchangeable with difficulty, NH), 2.08 (1 H, m, Ar), 2.50—3.00 (8 H, m, Ar), 5.95 (2 H, t, *J* 6.5 Hz, CH_2), 6.48 (2 H, m which collapsed to a t, *J* 6.5 Hz, on irradiation at the NH proton frequency, $NHCH_2$), and 7.00—7.28 (4 H, m, 2 × CH_2); *m/e* 294 (M^+), 203 (M − $PhCH_2$), 174 (M − $PhCH_2$ − CHO), 147 ($C_9H_9NO^+$) (probably the ion 12), 130 ($C_9H_8N^+$), 118 ($C_8H_8N^+$), 104 ($C_8H_8^+$), 91 ($PhCH_2^+$), and 77 (Ph^+); M (ebullioscopic method) 299 (Found: C, 73.3; H, 6.3; N, 9.5%; M^+, 294.137 2. $C_{18}H_{18}N_2O_2$ requires C, 73.4; H, 6.2; N, 9.5%; M, 294.136 9).

At 100 °C a gas was evolved (1.1 l) which did not decolourise bromine water and which burnt with a pale blue, smoky flame. ^1H N.m.r. and mass spectroscopy showed that this was a mixture containing predominantly diethyl ether together with a number of other compounds.

(ii) When the reaction described in (i) was repeated but with heating of the residual mixture after distillation of the solvent at 100 °C for 4 h, the yield of product (9) increased to 67%.

(iii) A stirred mixture of the isocyanate (14.7 g, 0.1 mol) and the reagent (19.0 g, 0.1 mol) was heated at 160 °C for 3 h. Work-up as described in (i) gave an oil (16.3 g) which was distilled to yield two fractions: (i) a 70 : 30 mixture (8.3 g) (i.r., mass, and ^1H n.m.r. spectroscopy), b.p. 140—150 °C at 1.0 mmHg, of 3,4-dihydroisoquinolin-1(2*H*)-one (14) and ethyl *N*-(2-phenylethyl)carbamate (17); and (ii) *NN'*-bis-(2-phenylethyl)urea (4.1 g, 34%), b.p. 150—190 °C at 1.0 mmHg, m.p. 139 °C (from ethanol) (lit.,[13] 137—138 °C), identical with a sample prepared (91% yield) by reaction of the isocyanate (2) with sodium hydroxide.

(iv) The reaction described in (i) was repeated on half the scale but the mixture was heated under reflux for 1 h and the solvent was not distilled off. Instead the mixture was poured into 2M-sodium hydroxide. Extraction with chloroform gave an oil (3.5 g) which was shown by i.r. and n.m.r. spectroscopy to be mainly starting material containing a trace of another compound.

(*b*) *With boron trifluoride–diethyl ether.* A mixture of the isocyanate (7.4 g, 50 mmol) and the reagent (15 ml) was stirred at 100 °C for 2 h, and then kept at ambient temperature for 10 h prior to being poured into 2M-sodium hydroxide. The precipitate was filtered off to give 2-*N*-(2-phenylethyl)formamidyl-3,4-dihydroisoquinolin-1(2*H*)-one (9) (2.8 g, 38%), m.p. 100 °C (from aqueous methanol), identical (i.r.) with the sample prepared as described before.

(*c*) *With alumimium chloride.* A mixture of the isocyanate (2) (7.4 g, 50 mmol), aluminium chloride (6.7 g, 50 mmol), and tetrachloroethane (20 ml) was stirred at 100 °C for 3 h. The solvent was distilled off under reduced pressure and the residue was dissolved in ethanol. Dropwise addition of 2M-sodium hydroxide gave a precipitate of 2-*N*-(2-phenylethyl)formamidyl-3,4-dihydroisoquinolin-1(2*H*)-one (9) (2.4 g, 32%), m.p. 101 °C (from aqueous methanol), identical (i.r.) with the samples prepared as described before.

(*d*) *With polyphosphoric acid.* The isocyanate (2) (10.0 g, 68 mmol) was added dropwise to polyphosphoric acid (100 g) stirred and heated at 100 °C. The temperature was allowed to rise to 180 °C during 2 h after the initial reaction had subsided. Then the mixture was poured into cold (0 °C) water, and ammonium hydroxide was added to make the mixture alkaline. Extraction with chloroform gave 3,4-dihydroisoquinolin-1(2*H*)-one (14) (7.0 g, 70%), b.p. (Kugelrohr apparatus) 150 °C at 13.0 mmHg, m.p. 58 °C (from aqueous methanol), identical with the samples prepared as described before.

Hydrolysis of 2-N-(2-Phenylethyl)formamidyl-3,4-dihydroisoquinol-1(2H)-one (9).—(*a*) *With 2M-sodium hydroxide.* A stirred mixture of compound (9) (2.0 g, 6.8 mmol) and 2M-sodium hydroxide (50 ml) was heated under reflux for 3 h. Then the mixture was kept overnight at ambient temperature, filtered, and the filtrate was adjusted to pH 6 by addition of 2M-hydrochloric acid. The precipitate was filtered off and washed with water, to give N-[2-(*o-carboxyphenyl)ethyl*]-N'-(*2-phenylethyl)urea* (13) (1.4 g, 67%), m.p. 145 °C, $\nu_{max.}$ (Nujol) 1 700 (C:O), 2 400—3 400br (OH), and 3 340 cm^{-1} (NH); τ($CDCl_3$) 0.25—1.75br (1 H, s, exchangeable, OH), 1.80—2.10 (1 H, m, Ar), 2.40—2.80

[11] R. L. Shriner and R. G. Child, *J. Amer. Chem. Soc.*, 1952, **74**, 549.

[12] W. Schneider and B. Müller, *Arch. Pharm.*, 1958, **291/63**, 560.

[13] T. Hayashi and M. Kuyama, *Nat. Sci, Rept. Ochanomizu Univ.*, 1951, **2**, 79 (*Chem. Abs.*, 1954, **48**, 1274).

(8 H, m, Ar), 4.30br (2 H, s, exchangeable, 2 × NH), 6.30—6.80 (6 H, m, 3 × CH_2), and 7.16 (2 H, t, *J* 7.0 Hz, CH_2) (Found: C, 68.7; H, 6.2; N, 9.1%; M^+, 312.148 1. $C_{18}H_{20}N_2O_3$ requires C, 69.2; H, 6.45; N, 9.0%; *M*, 312.147 4).

Acidification of the filtrate to pH 1 gave a second crop (0.3 g, 14%) of the same product.

(*b*) *With 70% sulphuric acid.* A stirred mixture of compound (9) (1.5 g, 5.1 mmol) and 70% sulphuric acid was heated under reflux for 2 h, and was then stirred at ambient temperature for a further 3 days. The resulting solution was adjusted to pH 6 by addition of 4M-sodium hydroxide, and extraction with chloroform gave 3,4-dihydroisoquinolin-1(2*H*)-one (0.73 g, 97%), m.p. 58 °C, identical (i.r.) with the samples prepared as described previously.

Cyclisation of N-[2-(o-*carboxyphenyl*)*ethyl*]-N′-(2-*phenylethyl*)*urea* (13).—A stirred mixture of the urea (13) (0.4 g, 1.28 mmol) and 4M-hydrochloric acid (25 ml) was heated under reflux for 4 h to give a precipitate (0.35 g, 87.5%) of 2-*N*-(2-phenylethyl)formamidyl-3,4-dihydroisoquinolin-1-(2*H*)-one (9), identical in all respects (mixed m.p., and i.r., n.m.r., and mass spectra) with the samples prepared as described before.

Reactions of (+)-1-*Methyl*-2-*phenylethyl Isocyanate* (3).—(*a*) *With triethyloxonium tetrafluoroborate.* A stirred mixture of the isocyanate (8 g, 50 mmol), the reagent (9.5 g, 50 mmol), and methylene chloride (150 ml) was heated under reflux for 2 h. The solvent was distilled off under reduced pressure and the residue was then heated at 100 °C for 2 h, and finally poured into 2M-sodium hydroxide (100 ml). The precipitate was filtered off and washed with water to give 3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (15) (7.5 g, 94%), m.p. 147 °C (from aqueous methanol) (lit.,[14] 130—132 °C), $\nu_{max.}$ (Nujol) 1 665 (C:O) and 3 170 cm^{-1} (NH); τ($CDCl_3$) 1.71—1.91 (1 H, m, 8-H), 2.39—2.83 (3 H, m, 5-, 6-, and 7-H), 2.97br (1 H, s, exchangeable, NH), 5.84—6.40 (1 H, m, CH), 7.00—7.28 (2 H, m, 4-CH_2), and 8.60 (3 H, d, *J* 7.0 Hz, Me) (Found: C, 75.0; H, 6.9; N, 9.0%; M^+, 161. $C_{10}H_{11}NO$ requires C, 74.5; H, 6.9; N, 8.7%; *M*, 161).

(*b*) *With boron trifluoride–diethyl ether.* A stirred mixture of the isocyanate (4 g, 25 mmol) and an excess of the reagent (10 ml) was heated at 100 °C for 36 h. Work-up as described before gave 3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (15) (3.7 g, 93%), identical (m.p., i.r., *etc.*) with the sample prepared as described in (*a*).

(*c*) *With aluminium chloride.* The isocyanate (4 g, 25 mmol) was added dropwise to a stirred mixture of aluminium chloride (3.35 g, 25 mmol) in carbon tetrachloride (50 ml) at ambient temperature, when a vigorous reaction occurred and the solvent boiled. After the reaction had subsided the mixture was worked-up as described before, to give 3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (15) (1.3 g, 33%), identical (m.p., i.r., *etc.*) with the samples prepared as described before.

(*d*) *With methyl fluorosulphonate.* A stirred mixture of the isocyanate (3) (8.0 g, 50 mmol), methyl fluorosulphonate (5.7 g, 50 mmol), and chloroform (10 ml) was heated under reflux for 1 h, and was then kept overnight at ambient temperature. Since isocyanate was still present (i.r.) more methyl fluorosulphonate (11.4 g, 100 mmol) was added and the mixture was heated under reflux for a further 4 h. Distillation of the solvent under reduced pressure gave a dark, water-soluble oil (8.4 g). This was dissolved in water, the solution was made alkaline with 2M-sodium hydroxide, and extraction with ether followed by distillation have 1-*methoxy*-3-*methyl*-3,4-*dihydroisoquinoline* (8) (3.0 g, 34%), b.p. 150 °C at 1.0 mmHg, τ($CDCl_3$) 2.20—2.45 (1 H, m, 8-H), 2.70—3.00 (3 H, m, 5-, 6-, and 7-H), 6.10—6.50 (1 H, m, CH), 6.20 (3 H, s, Me), 6.86—7.93 (2 H, m, CH_2), and 8.72 (3 H, d, *J* 7.0 Hz, Me) (Found: C, 75.2; H, 7.5; N, 7.8. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.5; N, 8.0%).

Alkylation of 3-*Methyl*-3,4-*dihydroisoquinolin*-1(2H)-*one* (15).—(*a*) *With methyl fluorosulphonate.* A stirred mixture of 3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (15) (1 g, 6.25 mmol) and the reagent (1.71 g, 15 mmol) in chloroform (4 ml was heated under reflux for 5 h, and was then poured into 4M-sodium hydroxide (50 ml). The organic layer was separated and the aqueous layer was extracted with chloroform. The chloroform layer and extracts were combined, washed with water, and dried ($MgSO_4$). Distillation gave 1-methoxy-3-methyl-3,4-dihydroisoquinoline (8) (0.51 g, 47%), b.p. 70—72 °C at 0.2 mmHg, identical (i.r.) with the sample prepared as described in the preceding experiment.

(*b*) *With triethyloxonium tetrafluoroborate.* A stirred mixture of 3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (15) (4 g, 25 mmol), the reagent (9.5 g, 50 mmol), and chloroform (50 ml) was heated under reflux for 3 h, and then kept at ambient temperature for 3 days. The solvent was removed under reduced pressure, anhydrous ether (100 ml) was added to the stirred residue, and the precipitate was filtered off and washed with ether, to give 1-*ethoxy*-3-*methyl*-3,4-*dihydroisoquinoline hydrotetrafluoroborate* (3.9 g, 56%), m.p. 165 °C (from propan-2-ol–ether), $\nu_{max.}$ (Nujol) 9 500—1 150br ($\bar{B}F_4$), 1 645 (C=$\overset{+}{N}$H), and 3 100—3 400br ($\overset{+}{N}$H), τ[$(CD_3)_2SO$] 2.10—2.80 (4 H, m, Ar), 5.45 (2 H, q, *J* 6.5 Hz, CH_2), 5.90 (1 H, sym. sextet, CH), 6.65—7.30 (2 H, sym. octet, 4-CH_2), 8.51 (3 H, t, *J* 6.5 Hz, Me), and 8.70 (3 H, d, *J* 7.0 Hz, Me) (Found: C, 52.3; H, 5.8; N, 5.1%; *M*, 189).

Treatment of the salt (0.5 g) with 2M-sodium hydroxide in the usual way gave 1-*ethoxy*-3-*methyl*-3,4-*dihydroisoquinoline* (7) (0.32 g, 94%), $\nu_{max.}$ (film) 1 650 cm^{-1} (C=N); τ($CDCl_3$) 2.20—2.40 (1 H, m, 8-H), 2.50—3.00 (3 H, m, 5-, 6-, and 7-H), 5.70 (2 H, q, *J* 6.5 Hz, CH_2), 6.00—6.60 (1 H, m, CH), 7.00—7.80 (2 H, m, 4-CH_2), 8.65 (3 H, t, *J* 6.5 Hz, Me), and 8.75 (3 H, d, *J* 7.0 Hz, 3-Me).

Reactions of 2,2-*Diphenylethyl Isocyanate* (4).—(*a*) *With triethyloxonium tetrafluoroborate.* A stirred mixture of the isocyanate (4) (2.5 g, 11.2 mmol) and the reagent (2.5 g, 13.1 mmol) was heated at 150 °C for 1 h with gas evolution. A 50 : 50 mixture of ether and propan-2-ol was added to the residue and the mixture was stirred at ambient temperature for 24 h. Filtration gave 2-N-(2,2-*diphenyl*)*formamidyl*-4-*phenyl*-3,4-*dihydroisoquinolin*-1(2H)-*one* (10) (0.5 g, 20%), m.p. 176 °C (from ether–propan-2-ol), $\nu_{max.}$ (Nujol) 1 650 (C:O), 1 700 (C:O), and 3 290 cm^{-1} (NH), τ[$(CD_3)_2SO$] 0.73br (1 H, t, exchangeable, NH), 2.05—2.20 (1 H, m, 8-H), 2.50—3.20 (8 H, m, Ar), 5.50—6.80 (6 H, m, aliphatic) (Found: M^+, 446.198 7. $C_{30}H_{26}N_2O_2$ requires 446.199 4). The filtrate was poured into 2M-sodium hydroxide and the precipitate was filtered off and washed with water, to give 4-*phenyl*-3,4-*dihydroisoquinolin*-1(2H)-*one* (16) (1.7 g, 68%), m.p. 158—160 °C (from aqueous ethanol), $\nu_{max.}$ (Nujol) 1 670 (C:O) and 3 200 cm^{-1} (NH); τ($CDCl_3$) 1.70—2.00 (1 H, m, 8-H), 2.35—3.20 (8 H, m, Ar), 5.50—5.85 (1 H, m,

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CH), 6.15—6.45 (2 H, m, CH_2), and 7.10br (1 H, t, exchangeable, NH) (Found: C, 80.4; H, 5.8; N, 6.1%; M^+, 223.100 3. $C_{15}H_{13}NO$ requires C, 80.7; H, 5.9; N, 6.3%; M, 223.099 7).

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