Quinolines and Uracils from Reactions of Isocyanates with Aliphatic Aldehydes

By **Iwao Yamamoto,* Takeshi Furukawa, Hiroshi Nakajima,** and **Haruo Gotoh,** Department of Chemistry, Shinshu University-Ueda, Ueda, Nagano 386, Japan

Reactions of phenyl isocyanate (1a) with n-alkanaldehydes (2a—c) afforded 3-alkyl-4-anilinoquinolines (3a—c), 5-alkyl-1,3-diphenyluracils (4a—c), and diphenylurea (5a). Upon treatment of (1a) with isobutyraldehyde (2d), the dihydrouracil derivative (13) was obtained. From the reactions of α-naphthyl isocyanate (1d) with n-alkanaldehydes (2a and b), 3-alkyl-4-α-naphthylaminobenzo[*h*]quinolines (21a and b) and 2,3-dialkylbenzo[*h*]quinolines (22a and b) were isolated. On the other hand, 2,3-dialkylbenzo[*f*]quinolines (28a and b), β-naphthylamine, and urea (5e) were isolated from the corresponding reactions of β-naphthyl isocyanate (1e). The routes to these products are discussed.

REACTIONS of aromatic carbonyl compounds with heterocumulenes are known to yield imines.[1] In the reaction between diphenylcarbodi-imide and n-alkanaldehydes [2] the intermediate imine (or its enamine tautomer), which reacts further with the carbodi-imide to form quinolines and pyrimidines, plays an important role. We report here reactions of isocyanates with aliphatic aldehydes, including other examples of the Conrad–Limpach quinoline synthesis.[3,4]

RESULTS AND DISCUSSION

Phenyl Isocyanate.—Reactions of phenyl isocyanate (1a) (2 mol. equiv.) with propionaldehyde (2a) or n-butyraldehyde (2b) at 200 °C in a sealed tube without solvent afforded the 3-alkyl-4-anilinoquinoline [(3a) 24%, (3b) 14%] and 5-alkyl-1,3-diphenyluracil [(4a) 14%, (4b) 38%] and diphenylurea (5a). Similar treatment of the isocyanate (1a) with the aldehyde (2b) in benzene at 200 °C led to compounds (3b), (4b), and (5a) in 65, 7, and 26% yields, respectively (Table). Structure

[1] H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes,' Academic Press, New York and London, 1974.

[2] I. Yamamoto, H. Gotoh, T. Minami, Y. Ohshiro, and T. Agawa, *J. Org. Chem.*, 1974, **39**, 3516.

[3] M. Conrad and L. Limpach, *Ber.*, 1887, **20**, 944.

[4] H. M. Blatter and H. Lukaszewski, *Tetrahedron Letters*, 1964, 855.

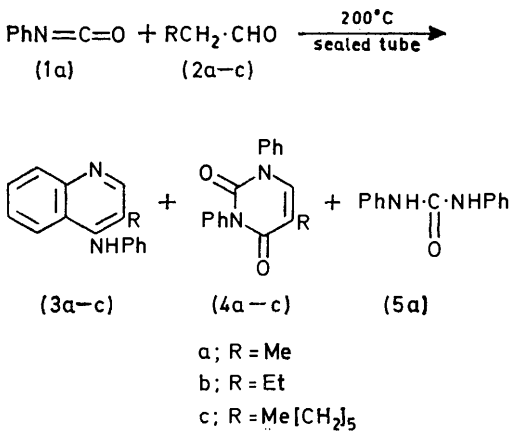
(3a) was confirmed by comparison with a sample prepared independently.[2] Structure (4a) was assigned from

Reactions of phenyl isocyanate (1a) with n-alkanaldehydes (2a—c)

R	Molar ratio of NCO to CHO	Reaction time (h)	Yields (%) [a] (3)	(4)	(5)
Me	2 : 1	3	24	14	28
Et	2 : 1	4	14	38	38
Et [b]	2 : 1	4	65	7	26
Et	3 : 1	4	23	27	39
n-C_6H_{13}	2 : 1	3	29	16	53
n-C_6H_{13}	4 : 1	3	35	14	42

[a] Based on phenyl isocyanate. [b] Reaction carried out in benzene.

i.r. [the spectrum was similar to that of the hexyl analogue (4c) [2]], n.m.r., and mass spectroscopic evidence.



Similar treatment of 2,6-xylyl isocyanate (1b) with the aldehyde (2b) gave the iminopyrimidone (6) and *NN'*-di-2,6-xylylurea in 32 and 60% yields, respectively. The identification of (6) is based on elemental analysis and i.r., n.m.r., and mass spectra.

Based on these results, pathways for the reactions of the aromatic isocyanates (1a and b) with the aldehydes (2a—c) are shown in the Scheme. We consider that [2 + 2] cycloaddition of (1a) to the carbonyl group is followed by ring scission of the cycloadduct to give the imine (7). This imine (7) should be in equilibrium with the enamine (8), and the latter would react with the isocyanate (1a) to yield the enamide (9) (R' = H in the Scheme). This is followed by the formation of the iminoketen (10), with elimination of aniline. The replacement of a methylene or methyne hydrogen atom of enamines by isocyanates is analogous to known reactions of acetophenone anil,[5] and 1-morpholinocyclohexene.[6] The products (3a—c) and (4a—c) are presumably formed from the interaction of either the iminoketen (10) or the derived di-imine (11) [formed by the reaction of (10) with (1a)] with another molecule of isocyanate (1a). In the case of the 2,6-xylyl derivatives, intramolecular [4 + 2] cycloaddition cannot take place, because of substitution of both *ortho*-positions of the phenyl ring; therefore intermolecular [4 + 2] cycloaddition of (11) across the C=N bond of another molecule of (1b) occurs. The above consideration is compatible with the fact that the 4-anilinoquinolines (3a—c) were also obtained from reactions between diphenylcarbodi-imide and the aldehydes (2a—c).[2] Reactions involving a similar cyclization step [(9) ⟶ (10) ⟶ (4), (9) ⟶ (10) ⟶ (11) ⟶ (6), and (9) ⟶ (10) ⟶ (11) ⟶ (12) ⟶ (3)] have been reported recently,[7] and related intermediates were also discussed in reports on the Conrad–Limpach quinoline synthesis.[3,4]

In order to establish the pathways for the reaction between the isocyanate (1a) and the aldehydes (2a—c), we examined the reaction of (1a) with isobutyraldehyde (2d) at 200 °C for 4 h in a sealed tube. 5,5-Dimethyl-1,3-diphenyl-6-(*NN'*-diphenylureido)dihydrouracil (13), obtained in 37% yield, was identified by mass, n.m.r., and i.r. spectral data and chemical properties. Treatment with aqueous ethanol containing concentrated hydrochloric acid gave the known 6-hydroxydihydrouracil (14) [8] and diphenylurea in 87 and 90% yields, respectively.

For the formation of compound (13) either path A or B in the Scheme is considered possible; an ene reaction of the enamine (8) with (1a) must be excluded. In path A the isocyanate (1a) attacks the anilino NH of (8) to form the urea (15), which reacts further with (1a). In path B 2 : 1 cycloaddition of the isocyanate (1a) to the C=C bond is followed by addition of the isocyanate to the exocyclic NH. The formation of (13) from (1a) and (15) is compatible with reported reactions between isocyanates and enamines.[8]

Attempts to prepare the intermediate (9) and/or (10) were unsuccessful, but we obtained some further evidence for the above pathways. When a mixture of the isocyanate (1a) and cyclohexanone anil (17) was heated at 200 °C for 1.5 h without solvent, the quinazolinedione (18a), the cyclohexaquinoline (19), and diphenylurea (5a) were obtained in 26, 20, and 53% yields, respectively. The structure (18a) was determined by i.r. and n.m.r. spectral data and elemental analysis. The formation of these products can be accounted for in a similar way to the formation of (3a—c) and (4a—c); *i.e.* 2-phenyliminocyclohexanecarboxanilide (20a) is a key intermediate. We therefore studied reactions of isocyanates with the anilide (20a) prepared independently. Treatment of phenyl isocyanate (1a) with (20a) in a 2 : 1 molar ratio gave compounds (18a) and (5a) and an unidentified product (A) * in 49, 92, and 17% yields [based on (20a)], respectively. A reaction with *m*-tolyl isocyanate (1c) in place of (1a) gave the quinazolinedione (18c) and *N*-phenyl-*N'*-*m*-tolylurea (5c) in 42 and 69% yields, respectively, but did not give a 1,3-di-*m*-tolylquinazolinedione.

* Presumed to be 1,2,3,4-tetrahydro-5-(*NN'*-diphenylureido)-cyclohexa[*b*]quinoline, but confirmation was not obtained.

[5] J. Moszew and A. Inasinski, *Roczniki Chem.*, 1960, **34**, 1173 (*Chem. Abs.*, 1961, **55**, 15383).

[6] S. Hünig, K. Hübner, and E. Benzing, *Chem. Ber.*, 1962, **95**, 926.

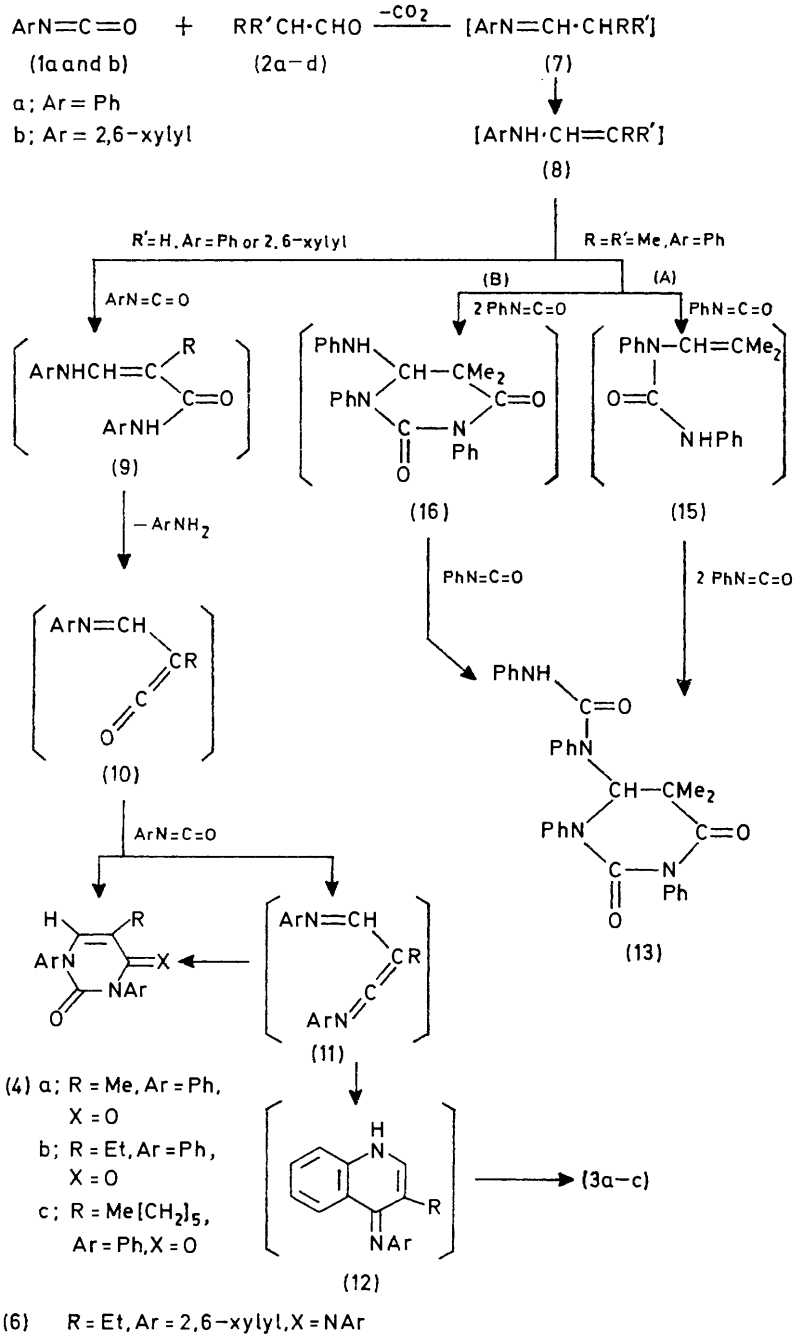
[7] R. Richter and H. Ulrich, *J. Org. Chem.*, 1973, **38**, 2614.

[8] A. K. Bose and G. Mina, *J. Org. Chem.*, 1965, **30**, 812.

These results suggest the elimination of aniline from (20) to form an iminoketen intermediate, and support the formation of various intermediates in the Scheme.

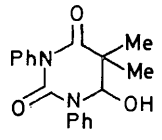
Naphthyl Isocyanates.—Treatment of α-naphthyl isocyanate (1d) with n-butyraldehyde (2b) at 200 °C in a sealed tube afforded 3-ethyl-4-α-naphthylaminobenzo[*h*]-quinoline (21b), 3-ethyl-2-n-propylbenzo[*h*]quinoline (22b), and *NN'*-di-α-naphthylurea (5d) in 36, 13, and 42% yields, respectively. Reaction with propionaldehyde (2a) in place of (2b) afforded the corresponding benzoquinolines (21a) and (22a) and the urea (5d) in 37, 11, and 26% yields, respectively.

The products (21a and b) and (22a and b) were characterized from spectral data and elemental analysis. The formation of (21a and b) could be explained by pathways similar to those discussed for the reactions between (1a) and (2a—c); *i.e.* the attack of the isocyanate (1d) on the imine (23) or its enamine tautomer (24) leading to an adduct (25). The formation of the products (22a and b) can be accounted for by aldol-type self-condensation of

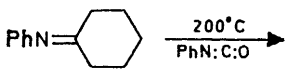


SCHEME

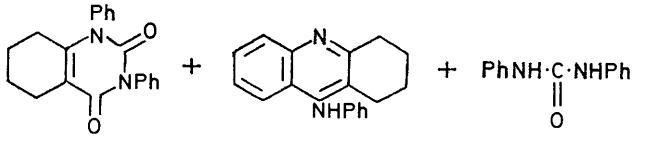
the imine (23) [leading to (26)], cyclization, and deamination to form the tetrahydrobenzoquinoline (27),



(14)

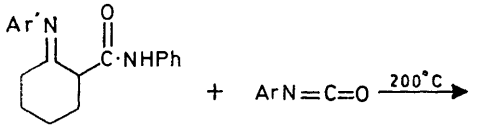


(17)

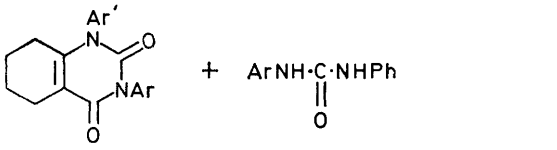


(18a) (19) (5a)

followed by oxidation. Similar aldol condensations of anils were reported by Knoevenagel for *N*-isopropylideneaniline.[9]

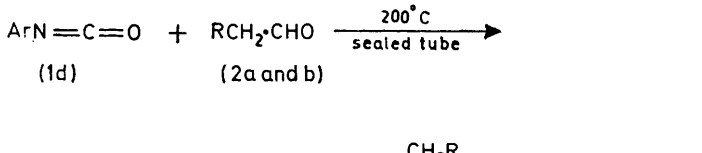


(20a and b) (1a and c)
a; Ar = Ph
c; Ar = *m* − MeC_6H_4



(18) a; Ar = Ph, Ar' = Ph (5) a; Ar = Ph
b; Ar = Ph, Ar' = *m* − MeC_6H_4 c; Ar = *m* − MeC_6H_4
c; Ar = *m* − MeC_6H_4, Ar' = Ph

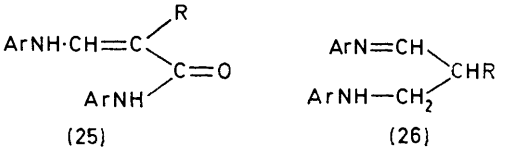
The reaction between β-naphthyl isocyanate (1e) and the aldehydes (2a and b) gave slightly different results. Heating a mixture of (1e) and (2a) at 200 °C in a sealed tube with benzene as solvent gave 3-ethyl-2-methylbenzo[*f*]quinoline (28a), β-naphthylamine, and *NN'*-di-β-naphthylurea (5e) in 36, 33, and 11% yields, respectively, but 2-methyl-1-β-naphthylaminobenzo[*f*]quinoline



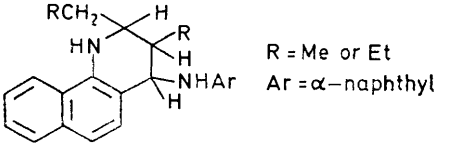
(21a and b) (22a and b) (5d)

a; R = Me
b; R = Et
Ar = α−naphthyl

(23) (24)



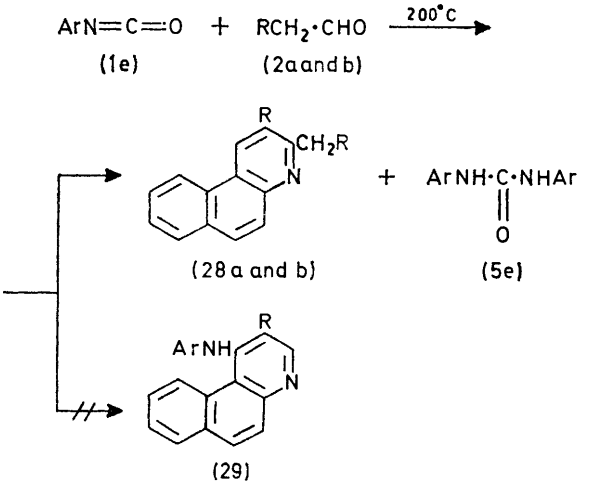
(25) (26)



(27)

(29a) was not obtained. The structures (28a and b) were determined from spectral data and elemental analysis. The benzoquinoline (28b) was also obtained by condensation between β-naphthylamine and (2b).

These observations confirm the initial formation of imines and the aldol condensation in the reactions of the isocyanates (1d and e) with the aldehydes (2a and b), and support the reaction paths illustrated in the Scheme. In the reactions between β-naphthyl isocyanate (1e) and the aldehydes (2a and b), one of the reasons for the absence of 1-β-naphthylaminobenzoquinolines (29) seems to be the reactivity of the isocyanate (1e).



(28a and b) (5e)

(29)

a; R = Me b; R = Et Ar = β−naphthyl

EXPERIMENTAL

I.r. spectra were recorded with a JASCO IRA 1 spectrometer, n.m.r. spectra with a JEOL JNM-C-60HL spectrometer (Me_4Si as internal standard), and mass spectra with a

[9] E. Knoevenagel, *Ber.*, 1922, **55**, 1923; R. W. Layer, *Chem. Rev.*, 1963, **63**, 489.

JEOL JMS 01SG-2 spectrometer on-line to a JEC-6 computer (16 k).

Reactions of Phenyl Isocyanate (1a) *with Aldehydes* (2a—c).—(*a*) A mixture of the isocyanate (1a) (4.75 g, 40 mmol) and the aldehyde (2a) (1.16 g, 20 mmol) was heated at 200 °C for 3 h in a sealed tube without solvent. After cooling, the mixture was washed with benzene and filtered to give diphenylurea (1.2 g, 28%), m.p. 234—235° (lit.,[10] 253°). The benzene filtrate was chromatographed on alumina [benzene and benzene–ethanol (99 : 1) as eluants] to give 5-*methyl*-1,3-*diphenyluracil* (4a) (0.8 g, 14%) and 4-anilino-3-methylquinoline (3a) (1.1 g, 24%), m.p. 204—205° (lit.,[3] 204—205°). Compound (4a) had m.p. 172—174°; $\nu_{max.}$ (Nujol) 1 700 (C=O) and 1 650 cm^{-1} (C=O); δ ($CDCl_3$) 2.00 (3 H, d, *J* 2.5 Hz, CH_3) and 7.15—7.65 (11 H, m, vinylic and aromatic); *m/e* (75 eV) 278 (M^+), 159 (M^+ − PhNCO), 131, and 130 (Found: M^+, 278.104 0. $C_{17}H_{14}N_2O_2$ requires *M*, 278.105 7).

(*b*) A similar reaction (at 200 °C for 4 h) of the isocyanate (1a) (4.75 g, 40 mmol) with n-butyraldehyde (2b) (1.44 g, 20 mmol) gave *NN'*-diphenylurea (5a) (1.6 g, 38%), 5-*ethyl*-1,3-*diphenyluracil* (4b) (2.2 g, 38%), and 4-anilino-3-ethylquinoline (3b) (0.7 g, 14%), m.p. 177—178° (lit.,[2] 177—178°). Compound (4b) had m.p. 140—140.5°; $\nu_{max.}$ (Nujol) 1 720 and 1 665 cm^{-1}; δ ($CDCl_3$) 1.18 (3 H, t, CH_3), 2.45 (2 H, q, CH_2), 7.18 (1 H, s, CH), and 7.3—7.6 (11 H, m, aromatic); *m/e* 292 (M^+), 173, 144, and 130 (Found: C, 74.05; H, 5.4; N, 9.3. $C_{18}H_{16}N_2O_2$ requires C, 73.95; H, 5.5; N, 9.6%).

A reaction with (1a) (7.15 g, 60 mmol) and (2b) (1.44 g, 20 mmol) under similar conditions gave (3b), (4b), and (5a) in 23% (1.7 g), 27% (2.4 g), and 39% (2.5 g) yields, respectively.

A reaction of (1a) (4.75 g, 40 mmol) with (2b) (1.44 g, 20 mmol) in benzene (10 ml) at 200 °C in a sealed tube gave (5a) (1.1 g, 26%), (4b) (0.4 g, 7%), and (3b) (3.2 g, 65%).

(*c*) The reaction at 180—190 °C for 3 h under nitrogen of the isocyanate (1a) (7.2 g, 60 mmol) with n-octanal (2c) (3.84 g, 30 mmol) gave diphenylurea (5a) (3.4 g, 53%), 5-n-hexyl-1,3-diphenyluracil (4c) (1.7 g, 16%), m.p. 115.5—117° (lit.,[2] 116—117°), and 4-anilino-3-n-hexylquinoline (3c) (2.6 g, 29%), m.p. 140—141° (lit.,[2] 140—141°).

A reaction with (1a) (7.14 g, 60 mmol) and (2c) (1.8 g, 15 mmol) gave (3c), (4c), and (5c) in 35% (3.2 g), 14% (1.5 g), and 42% (2.7 g) yields, respectively.

Reaction of 2,6-*Xylyl Isocyanate* (1b) *with* n-*Butyraldehyde* (2b).—A mixture of the isocyanate (1b) (8.2 g, 60 mmol) and the aldehyde (2b) (2.16 g, 30 mmol) was heated for 4 h at 200 °C in a sealed tube without solvent. After cooling, the mixture was distilled under reduced pressure to afford unchanged (1b) (1.37 g, 15%). The residue was washed with benzene and the mixture filtered to give *NN'-di*-2,6-*xylylurea* (5b) (3.2 g, 60%); m.p. 324—325° (decomp.); $\nu_{max.}$ (Nujol) 3 280 (NH) and 1 620 cm^{-1} (C=O) (Found: C, 75.95; H, 7.7; N, 10.25. $C_{17}H_{20}N_2O$ requires C, 76.1; H, 7.5; N, 10.45%). The filtrate was chromatographed on alumina (benzene as eluant) to yield 5-*ethyl*-3,4-*dihydro*-1,3-*di*-2,6-*xylyl*-4-(2,6-*xylylimino*)*pyrimidin*-2(1H)-*one* (6) (2.9 g, 32%); m.p. 183—183.5°; $\nu_{max.}$ (Nujol) 1 695 (C=O) and 1 623 cm^{-1} (C=N); δ ($CDCl_3$) 0.75 (3 H, t, *J* 7.2 Hz, CH_3), 1.78 (2 H, q of d, *J* 7.2 and 1.5 Hz, CH_2), 2.0 (6 H, s, CH_3), 2.22 (6 H, s, CH_2), 2.6 (6 H, s, CH_3), 6.35 (1 H, t, *J* 1.5 Hz, CH), and 6.6—7.15 (9 H, m, aromatic); *m/e* 451 (M^+), 436, 422, 346, 331, and 289 (Found: C, 79.65; H, 7.15; N, 9.15. $C_{30}H_{33}N_3O$ requires C, 79.8; H, 7.35; N, 9.3%).

Reaction of Phenyl Isocyanate (1a) *with Isobutyraldehyde* (1d).—The reaction of the isocyanate (1a) (3.6 g, 30 mmol) with the aldehyde (2d) (1.08 g, 15 mmol) was carried out as before for 4 h at 200 °C. After cooling, the mixture was dissolved in benzene, and chromatographed on neutral alumina to afford 5,5-*dimethyl*-6-(*NN'-diphenylureido*)-1,3-*diphenyldihydrouracil* (13) (1. 4 g, 37%) as the only product isolated; m.p. 177—177.5°; $\nu_{max.}$ (Nujol) 3 420 (NH), 1 740 (C=O), and 1 680 cm^{-1} (C=O); δ ($CDCl_3$) 1.68 (6 H, s, CH_3), 5.88 (1 H, s, NH), 6.75 (1 H, s, CH), and 7.0—7.7 (20 H, m, aromatic); *m/e* 504.217 8 ($C_{31}H_{28}N_4O_3$ requires 504.216 1), 293.129 0 ($C_{18}H_{17}N_2O_2$ requires 293.129 0), 174.090 9 ($C_{11}H_{12}NO$ requires 174.091 8), 146.096 8 ($C_{10}H_{12}N$), and 131.073 8 (C_9H_9N).

Acid-catalysed Hydrolysis of the Dihydrouracil (13).—A solution of compound (13) (1.6 g, 3.3 mmol) in 95% ethanol (20 ml) containing concentrated hydrochloric acid (0.5 ml) was refluxed for 2 h. The solvent was removed *in vacuo*, and the residue was washed with benzene. Filtration afforded diphenylurea (5a) (0.60 g, 90%). On concentrating the benzene filtrate, 6-hydroxy-5,5-dimethyl-1,3-diphenyldihydrouracil (14) was obtained in 87% (0.85 g) yield; m.p. 231—232° (lit.,[8] 228—231°).

Reaction of Phenyl Isocyanate (1a) *with Cyclohexanone Anil* (17).—A mixture of the isocyanate (1a) (6.25 g, 50 mmol) and the anil (17) (4.3 g, 25 mmol) was heated at 200 °C without solvent under nitrogen. After cooling, the mixture was washed with benzene and filtered to afford diphenylurea (5a) (2.8 g, 53%). The filtrate was chromatographed on alumina [benzene and benzene–ethanol (99 : 1) as eluants] to afford 5,6,7,8-*tetrahydro*-1,3-*diphenylquinazoline*-2,4-(1H,3H)-*dione* (18a) and 5-anilino-1,2,3,4-tetrahydrocyclohexa[*b*]quinoline (19) in 26% (2.1 g) and 20% (1.3 g) yields, respectively. Compound (18a) had m.p. 187—188°; $\nu_{max.}$ (Nujol) 1 700 and 1 650 cm^{-1}; δ ($CDCl_3$) 1.4—3.0 (8 H, m, C_4H_8), and 7.17—7.6 (10 H, m, aromatic); *m/e* 318 (M^+), 198, and 77 (Found: C, 75.55; H, 5.6; N, 8.85. $C_{20}H_{18}N_2O_2$ requires C, 75.45; H, 5.7; N, 8.8%).

2-*Phenyliminocyclohexanecarboxanilide* (20a).—A solution of 2-oxocyclohexanecarboxanilide [6] (3.25 g, 15 mmol) and aniline (1.4 g, 15 mmol) in benzene was refluxed for 7 h in the presence of toluene-*p*-sulphonic acid (0.1 g) (Dean–Stark trap). Solvent was removed *in vacuo* and the residue was washed with ether to afford the *anil* (20a) (4.3 g, 98%); m.p. 89—89.5°; $\nu_{max.}$ (Nujol) 3 470, 1 635, and 1 595 cm^{-1}; δ($CDCl_3$) 1.35—2.60 (8 H, m, C_6H_8), 6.7—7.7 (11 H, m, CH and aromatic), and 10.7—11.1br (1 H, NH); *m/e* (75 eV) 292 (M^+), 200, 173, 145, 130, 93, and 77 (Found: C, 77.95; H, 7.05; N, 9.4. $C_{19}H_{20}N_2O$ requires C, 78.05; H, 6.9; N, 9.6%).

2-m-*Tolyliminocyclohexanecarboxanilide* (20b).—This material was prepared (99%) above from 2-oxocyclohexanecarboxanilide (3.25 g, 15 mmol) and *m*-toluidine (1.8 g, 15 mmol), and had m.p. 87—88.5°; $\nu_{max.}$ 3 450, 1 620, 1 598, and 1 520 cm^{-1}; *m/e* (75 eV) 306, 214, 213, 187, 186, 125, and 119 (Found: C, 78.1; H, 7.45; N, 8.95%; M^+, 306.172 4. $C_{20}H_{22}H_2O$ requires C, 78.4; H, 7.25; N, 9.1%; M^+, 306.173 3).

Reaction of Phenyl Isocyanate (1a) *with the Carboxanilides* (20a *and* b).—(*a*) A mixture of the isocyanate (1a) (4.3 g, 36 mmol) and the anilide (20a) (5.25 g, 18 mmol) was heated at 200 °C without solvent under nitrogen. After cooling, the mixture was washed with benzene and filtered to afford

[10] T. L. Davis and K. C. Blanchard, *Org. Synth.*, Coll. Vol. I, 1967, p. 453.

diphenylurea (5a) (3.5 g, 92%). The filtrate was chromatographed on alumina [benzene, benzene–ethanol (99 : 1), and ethanol as eluants] to afford the quinazolinedione (18a) (2.8 g, 49%) and an unidentified product (A) (1.2 g), m.p. 186—188°; $\nu_{max.}$ 3 300, 1 650, and 1 600 cm^{-1}; *m/e* (75 eV) 393 (M^+), 275, 274, 273, 271, and 259.

(*b*) A similar reaction with (1a) (4.3 g, 36 mmol) and (20b) (5.5 g, 18 mmol) gave diphenylurea (2.8 g, 74%) and *5,6,7,8-tetrahydro-3-phenyl-1-m-tolylquinazoline-2,4(1H,3H)-dione* (18b) (2.2 g, 37%), m.p. 175—176°; $\nu_{max.}$ 1 710 and 1 660 cm^{-1}; δ ($CDCl_3$) 1.48—2.75 (11 H, m, CH_3 and C_6H_8) and 7.05—7.80 (9 H, m, aromatic); *m/e* (75 eV) 332 (M^+), 319, 318, 289, 288, and 199 (Found: C, 75.75; H, 6.1, N, 8.4. $C_{21}H_{20}N_2O_2$ requires C, 75.9; H, 6.05; N, 8.45%).

Reaction of m-*Tolyl Isocyanate* (1c) *with the Carboxanilide* (20a).—The reaction was carried out as above with (1c) (4.7 g, 36 mmol) and (20a) (5.3 g, 18 mmol). The yields of *N*-phenyl-*N'*-*m*-tolylurea (5c) and *5,6,7,8-tetrahydro-1-phenyl-3-m-tolylquinazoline-2,4(1H,3H)-dione* (18c) were 69% (2.8 g) and 42% (2.5 g), respectively. The urea (5c) had m.p. 175—176°; a mixed m.p. of (5c) and an authentic sample prepared from phenyl isocyanate (1a) and *m*-toluidine was 174—175.5°. Compound (18c) had m.p. 173.5—174.4°; $\nu_{max.}$ 1 710 and 1 660 cm^{-1}; *m/e* (75 eV) 332 (M^+), 255, 240, and 199 (Found: C, 80.0; H, 6.25; N, 8.7. $C_{21}H_{20}N_2O_2$ requires C, 75.9; H, 6.05; N, 8.45%).

Reactions of α-Naphthyl Isocyanate (1d) *with the Aldehydes* (2a *and* b).—(*a*) A mixture of the isocyanate (1d) (13.5 g, 80 mmol) and the aldehyde (2a) (2.32 g, 40 mmol) was heated at 200 °C for 4 h in a sealed tube. After cooling, the mixture was washed with benzene and filtered to afford *NN'*-di-α-naphthylurea (5d) (3.3 g, 26%), m.p. 283—284° (lit.,[11] 280—292°). The filtrate was chromatographed on alumina to afford *2-ethyl-3-methylbenzo*[h]*quinoline* (22a) (2.0 g, 11%) and *3-methyl-4-α-naphthylaminobenzo*[h]*quinoline* (21a) (5.0 g, 37%), m.p. 172.5—173°; $\nu_{max.}$ 3 390, 1 610, 1 585, and 1 560 cm^{-1}; δ($CDCl_3$) 2.27 (3 H, s, CH_3), 6.22 (1 H, s, NH, D_2O-exchangeable), 6.3—6.5 (1 H, m, aromatic), 7.0—8.3 (11 H, m, aromatic), 8.83 (1 H, s, aromatic), and 9.2—9.4 (1 H, m, aromatic); *m/e* (75 eV) 334 (M^+), 319, 207, 192, and 178 (Found: C, 85.95; H, 5.5; N, 8.5. $C_{24}H_{18}N_2$ requires C, 86.2; H, 5.45; N, 8.4%). Compound (22a) had m.p. 79—80°; $\nu_{max.}$ 1 613, 1 605, and 1 598 cm^{-1} (Found: C, 86.75; H, 6.9; N, 6.3. $C_{16}H_{15}N$ requires C, 86.85; H, 6.85; N, 6.35%).

(*b*) The reaction was carried out as above with (1d) (13.5 g, 80 mmol) and (2b) (2.88 g, 40 mmol) for 4 h. The yield of the urea (5d) was 5.2 g (42%), that of *3-ethyl-2-n-propylbenzo*[h]*quinoline* (22b) was 2.6 g (13%), and that of *3-ethyl-4-α-naphthylaminobenzo*[h]*quinoline* (21b) was 5.0 g (35%). Compound (21b) had m.p. 137—138°; $\nu_{max.}$ 3 320, 1,605, 1 590, 1 575, and 1 520 cm^{-1}; δ($CDCl_3$) 1.28 (3 H, t, CH_3), 2.76 (2 H, q, CH_2), 6.2 (1 H, s, NH, D_2O-exchangeable), 6.3—6.42 (1 H, m, aromatic), 7.1—8.35 (11 H, m, aromatic), 8.90 (1 H, s, aromatic), 9.2—9.4 (1 H, m, aromatic); *m/e* (75 eV) 348 (M^+), 333, 319, and 220 (Found: C, 85.9; H, 5.45; N, 7.85. $C_{25}H_{20}N_2$ requires C, 86.15; H, 5.8; N, 8.05%). Compound (22b) had m.p. 70—71°; $\nu_{max.}$ 1 615, 1 605, and 1 595 cm^{-1}; δ 1.08 (3 H, t, CH_3), 1.27 (3 H, t, CH_3), 1.68—2.28 (2 H, m, CH_2), 2.57—3.08 (4 H, m, 2 CH_2), and 7.35—7.80 (7 H, m, aromatic); *m/e* (75 eV) 249 (M^+), 234, 220, 206, and 193 (Found: C, 86.6; H, 7.6; N, 5.75. $C_{18}H_{19}N$ requires C, 86.7; H, 7.7; N, 5.6%).

Reactions of β-*Naphthyl Isocyanate* (1e) *with the Aldehydes* (2a *and* b).—(*a*) A mixture of the isocyanate (1e) (6.76 g, 40 mmol) and the aldehyde (2a) (2.32 g, 40 mmol) in benzene (5 ml) was heated at 200 °C for 5 h in a sealed tube. After cooling, the benzene solution was filtered and the residue washed with benzene (10 ml) to afford *NN'*-di-β-naphthylurea (0.67 g, 11%); m.p. 286° (lit.,[11] 288—295°). The filtrate was chromatographed on alumina [benzene and benzene–ethanol (98 : 2) as eluants] to give β-naphthylamine (1.86 g, 33%) and *2-methyl-3-ethylbenzo*[f]*quinoline* (28a) (3.4 g, 36%); m.p. 90—91°; $\nu_{max.}$ 1 610 and 1 595 cm^{-1}; δ($CDCl_3$) 1.43 (3 H, t, CH_3), 2.61 (3 H, s, CH_3), 3.09 (2 H, q, CH_2), and 7.59—8.75 (7 H, m, aromatic) (Found: C, 86.85; H, 6.75; N, 6.3. $C_{16}H_{15}N$ requires C, 86.85; H, 6.85; N, 6.5%).

(*b*) The reaction was carried out as above with (1e) (8.45 g, 50 mmol) and (2b) (3.6 g, 50 mmol) for 5 h to give the urea (5e) (0.92 g, 12%), β-naphthylamine (2.7 g, 38%), and *2-ethyl-3-n-propylbenzo*[f]*quinoline* (28b) (3.64 g, 29%); m.p. 60—62°; $\nu_{max.}$ 1 610 and 1 595 cm^{-1}; δ($CDCl_3$) 1.08 (3 H, t, CH_3), 1.18 (2 H, m, CH_2), 1.75 (3 H, t, CH_3), 2.6—3.15 (4 H, m, 2 CH_2), and 7.47—8.7 (7 H, m, aromatic); *m/e* (75 eV) 249 (M^+), 235, and 206 (Found: C, 86.35; H, 7.65; N, 5.9. $C_{18}H_{19}N$ requires C, 86.7; H, 7.7; N, 5.6%).

Reaction of β-*Naphthylamine with the Aldehyde* (2b).—A solution of β-naphthylamine (20 g, 138 mmol) and the aldehyde (2b) (18.8 g, 261 mmol) in benzene was refluxed for 15 h. Concentration *in vacuo* gave the crude benzo[*f*]-quinoline (28b) in 90% (15.4 g) yield.

[6/167 *Received*, 26*th January*, 1976]

[11] R. A. Franz, F. Applegath, F. V. Morriss, F. Baiocchi, and C. Bolze, *J. Org. Chem.*, 1961, **25**, 3311.