103. *Imidochlorides. Part IV. Condensation of Anilide Imidochlorides with Urethanes. A New Synthesis of 4-Hydroxy-2-phenylquinazolines.*

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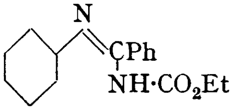
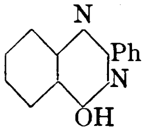
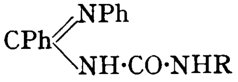
THERE are but few recorded observations on the synthesis of heterocyclic nitrogen compounds from anilide imidochlorides (see Just, *Ber.*, 1885, **18**, 2623, 2632; 1909, **42**, 3360; preceding paper). The formation of 3-chloro-4-anilino-2-chloromethylquinolines from chloroacetanilides and phosphorus pentachloride takes place through the intermediately formed imidochlorides (*Ber.*, 1930, **63**, 3191).

As part of a comprehensive study of the problem, we have investigated the condensation of anilide imidochlorides with urethanes. The direct condensation of benzanilide imidochloride and urethane is a complex reaction, but a smooth condensation took place when the sodium derivative of urethane was used. The product, (*phenyliminobenzyl*)*urethane* (I), was feebly basic and formed a crystalline hydrochloride. As amidines of this type are not known, its characteristic reactions were examined. The action of heat led to 4-hydroxy-2-phenylquinazoline (II) (Bischler and Lang, *Ber.*, 1895, **28**, 289; Bhattacharya, Bose, and Ray, *J. Indian Chem. Soc.*, 1929, **6**, 286), the constitution of (I) being thus confirmed. The amidine (I) was easily decomposed by hydrolysis with the formation of benzanilide. The action of bromine gave benzo-*p*-bromoanilide, probably through the dibromo-additive product initially formed (cf. Hantzsch, *Ber.*, 1890, **23**, 2774). The action of α- and β-naphthylamine afforded crystalline *ureas* (III, R = α- or β-naphthyl).


(I.)


(II.)


$\mathrm{CPh}\begin{matrix}{=}\mathrm{NPh}\\ {-}\mathrm{NH{\cdot}CO{\cdot}NHR}\end{matrix}$

(III.)

Benzanilide imidochloride condensed similarly with methyl carbamate and with acetylurethane. *Acetyl*(*phenyliminobenzyl*)*urethane*, a crystalline solid, was cyclised by heating to 3-*acetyl*-2-*phenyl*-4-*quinazolone*, which could not be obtained by acetylation of (II).

Benzo-α- and -β-naphthalide imidochlorides on condensation with urethane yielded (α- and β-*naphthyliminobenzyl*)*urethanes*, which underwent cyclisation on heating, giving 4-*hydroxy*-2-*phenyl*-1 : 3-*naphtha*iso*diazine* and 1-*hydroxy*-3-*phenyl*-2 : 4-*naphtha*iso*diazine* respectively; the ring closure in the latter case is assumed to take place in the α-position with the production of the angular compound (cf. Lindner and Staufer, *Monatsh.*, 1925, **46**, 231).

EXPERIMENTAL.

Condensation of Benzanilide Imidochloride with Urethane.—A mixture of pulverised sodium (1 g., 1 atom.) and dry ether (80 c.c.) was treated with a solution of urethane (12·2 g., 3 mols.) in dry ether (80 c.c.), added drop by drop, and the whole was kept over-night, the sodium compound separating, and then refluxed for 12 hours with an ethereal solution of benzanilide imidochloride (10 g., 1 mol.). Water was added, and benzanilide (1·5 g.) removed by filtration. The residue obtained from the ethereal solution was washed with water, redissolved in ether (benzanilide separated), dried, and recovered as a turbid yellow oil containing a trace of benzanilide. By repeated solution in warm light petroleum (b. p. 60—70°) and recovery, (*phenyliminobenzyl*)-*urethane* (I) was obtained as a clear yellow, viscous oil (8 g.), which could not be distilled without conversion into the quinazoline. For analysis, it was purified through the hydrochloride (Found: C, 71·0; H, 6·3; N, 9·7. $C_{16}H_{16}O_2N_2$ requires C, 71·7; H, 6·0; N, 10·4%). The *hydrochloride* separated in colourless needles, m. p. 215—217°, on addition of dry ether to a solution of the substance in methyl-alcoholic hydrogen chloride (Found: Cl, 11·9. $C_{16}H_{16}O_2N_2,HCl$ requires Cl, 11·7%).

Reactions of (*Phenyliminobenzyl*)*urethane.*—(1) By 2 hours' heating at 180—190°, the urethane (2 g.) was converted into 4-hydroxy-2-phenylquinazoline, which crystallised from alcohol in colourless needles (0·6 g.), m. p. 230—232° (Found: N, 12·7. Calc. for $C_{14}H_{10}ON_2$: N, 12·6%)

undepressed by a specimen prepared by the method of Bhattacharya, Bose, and Ray (*loc. cit.*), who give m. p. 222—223°.

(2) The urethane (2 g.), heated with water (20 c.c.) at 140—150° for 5 hours or with concentrated hydrochloric acid (10 c.c.) at 70—80° for ½ hour, gave benzanilide, m. p. 158—160° after crystallisation from alcohol.

(3) Bromine (0·6 g.) and the urethane (1 g.) in chloroform gave benzo-*p*-bromoanilide, m. p. (after crystallisation from alcohol) and mixed m. p. 202—203° (Found : Br, 29·4. Calc. : Br, 29·0%).

(4) A mixture of the urethane (2 g.) and α-naphthylamine (1·5 mols.) was heated at 100—110° for 4 hours; the product solidified on cooling, and on crystallisation from boiling alcohol gave colourless needles of s.-(*phenyliminobenzyl*)-α-*naphthylurea* (III, R = α-naphthyl), m. p. 258—260° (Found : N, 11·4. $C_{24}H_{19}ON_3$ requires N, 11·5%). The corresponding β-naphthylamine *derivative* had m. p. 273—278° (Found : N, 11·3%).

Methyl (Phenyliminobenzyl)carbamate.—When methyl carbamate was substituted for urethane in the above condensation, the product was *methyl (phenyliminobenzyl)carbamate*, a yellow oil easily soluble in the common organic solvents (Found : N, 10·5. $C_{15}H_{14}O_2N_2$ requires N, 11·0%). The action of heat, hydrolysis, the action of α-naphthylamine, and bromination gave products identical with those obtained from (I).

Acetyl(phenyliminobenzyl)urethane.—This *compound* (7 g.), obtained from acetylurethane (18 g.), pulverised sodium (1·6 g.), and benzanilide imidochloride (10 g.) by the procedure described for the condensation with urethane, solidified after long standing and then crystallised from alcohol in fine colourless needles, m. p. 85—88° (Found : C, 69·2; H, 6·1; N, 9·4. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8; N, 9·0%).

3-*Acetyl*-2-*phenyl*-4-*quinazolone.*—The foregoing compound was heated at 210—220° for 1 hour. The reddish-brown viscous product solidified when washed with cold alcohol and then crystallised from hot alcohol in pale yellow needles of the *quinazolone*, m. p. 233°, depressed by (II) (Found : N, 10·3. $C_{16}H_{12}O_2N_2$ requires N, 10·6%).

(α-*Naphthyliminobenzyl*)*urethane.*—Benzo-α-naphthalide imidochloride (Just, *Ber.*, 1886, **19**, 984) (22 g.) on condensation with the sodium derivative of urethane by the usual method gave (α-*naphthyliminobenzyl*)*urethane* (15 g.) as a yellow viscous oil (Found : N, 8·8. $C_{20}H_{18}O_2N_2$ requires N, 8·8%). Cyclisation by heating at 200—205° for 2 hours gave 4-*hydroxy*-2-*phenyl*-1 : 3-*naphtha*iso*diazine* which crystallised from alcohol in colourless needles, m. p. 300° (Found : N, 10·0. $C_{18}H_{12}ON_2$ requires N, 10·3%).

(β-*Naphthyliminobenzyl*)*urethane*, prepared from benzo-β-naphthalide imidochloride (Just, *loc. cit.*) (15 g.), was obtained as a yellow oil (8 g.) (Found : N, 9·0%). Heated at 190° for 1½ hours, it gave 1-*hydroxy*-3-*phenyl*-2 : 4-*naphtha*iso*diazine*, which formed colourless prismatic needles, m. p. 295—298°, from alcohol (Found : N, 10·0%).

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