675. *Some Reactions of* 3-*Dimethylamino*-1 : 1-*diphenylbutyl Cyanide.*

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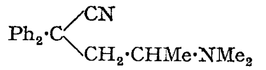
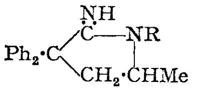
Reaction of 3-dimethylamino-1 : 1-diphenylbutyl cyanide (I) with ammonium benzenesulphonate has yielded 2-imino-1 : 5-dimethyl-3 : 3-diphenylpyrrolidine (II; R = Me). With a large excess of the ammonium compound (I) appears to give 2-imino-5-methyl-3 : 3-diphenylpyrrolidine (II; R = H). Ultra-violet absorption spectra of these and a number of related compounds have been determined.

The reaction of (±)-3-dimethylamino-1 : 1-diphenylbutyl cyanide (I) with ethylenediamine at 200° for 27·5 hours was reported by Wilson (*J.*, 1950, 2173) to give a base, m. p. 103°, believed to be 2-imino-1 : 5-dimethyl-3 : 3-diphenylpyrrolidine (II; R = Me). We have now examined the reaction of (I) with ammonium benzenesulphonate. Interaction of equimolecular quantities of (I) and ammonium benzenesulphonate at 255—260° for 4 hours gave, *via* a hydrochloride (50% yield), a crystalline base. Analyses and chemical properties indicated the structure (II; R = Me) for our base; however, a mixed m. p. (carried out by Dr. Wilson) with the product (m. p. 103°) described by Wilson (*loc. cit.*) showed a large depression in m. p. We now learn (Dr. W. Wilson, personal communication) that an independent synthesis of (II; R = Me) has given a base, m. p. 93·5—94° (hydrochloride, m. p. 277°). The identity of our base and Wilson's product of m. p. 93·5—94° was confirmed by a mixed m. p. determination for which we are indebted to Dr. Wilson. Professor R. H. Thorp kindly examined this compound for analgesic activity, but it was devoid of appreciable activity.

Reaction of (I) with ammonium benzenesulphonate (3 mols.) at 255—260° for 4 hours afforded, in addition to the hydrochloride of (II; R = Me), a small yield of a by-product, $C_{22}H_{22}N_2$, possessing 2 *N*-methyl groups. Its nature was not further investigated.

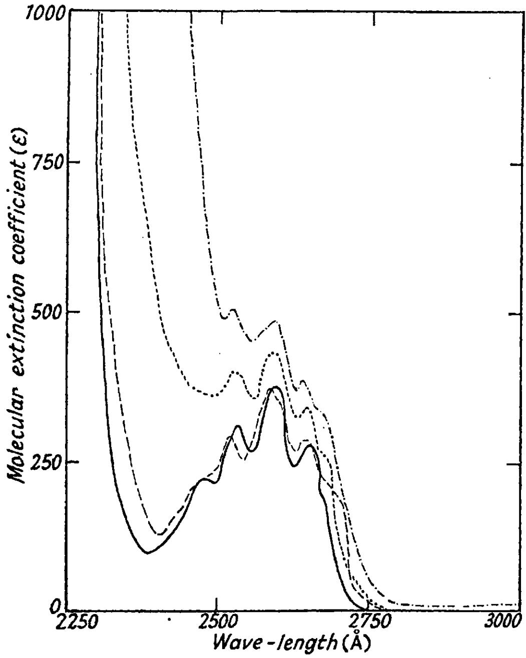
Treatment of (I) with 5 mols. of ammonium benzenesulphonate at 255—260° for 4 hours gave 34% of a base, $C_{17}H_{18}N_2$, m. p. 149·5—151·5°, which is believed to be 2-imino-5-methyl-3 : 3-diphenylpyrrolidine (II; R = H). It showed no evidence of unsaturation. Its formation would be accounted for by amine exchange with the large excess of ammonia present in the mixture, the intermediate (presumably 3-amino-1 : 1-diphenylbutyl cyanide) then cyclising to give (II; R = H) :

(I) 
$Ph_2C(CN)\cdot CH_2\cdot CHMe\cdot NMe_2$

 (II)

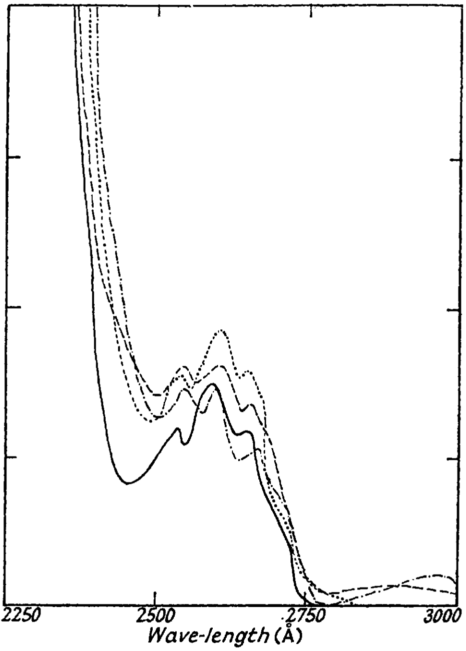
Attempted reaction of (I) with ammonia *via* the Pinner method (cf. Ashley, Barber, Ewins, Newbery, and Self, *J.*, 1942, 103) failed, no evidence of imino-ether formation being obtained; even after 2 weeks at 0° or after being heated at 60—65° for 6 hours, only unchanged (I) was recovered.

Fig. 1.



————	*Diphenylmethyl cyanide.*
— — — —	3-*Dimethylamino*-1 : 1-*diphenylbutyl cyanide hydrochloride.*
- - - - - - -	3-*Dimethylamino*-1 : 1-*diphenylbutyl cyanide.*
— · — · —	2-*Imino*-1 : 5-*dimethyl*-3 : 3-*diphenylpyrrolidine.*

Fig. 2.



————	2-*Imino*-1 : 5-*dimethyl*-3 : 3-*diphenylpyrrolidinium chloride.*
— — — —	6-*Dimethylamino*-4 : 4-*diphenylheptan*-3-*one.*
- - - - - - -	2-*Imino*-5-*methyl*-3 : 3-*diphenylpyrrolidine.*
— · — · —	6-*Dimethylamino*-4 : 4-*diphenylheptan*-3-*one hydrochloride.*

The ultra-violet absorption spectra of (I), (II; R = Me), and a number of related compounds in 95% alcoholic solution were determined, a Beckman quartz spectrophotometer, model DU, being used. The spectra of diphenylmethyl cyanide, of (I) and its hydrochloride, of (II; R = Me) and its hydrochloride, of (II; R = H), and of 6-dimethylamino-4 : 4-diphenylheptan-3-one (amidone) and its hydrochloride all showed similar absorption curves (Figs. 1 and 2) with intense end-absorption below 2400 Å, and three characteristic maxima at 2540, 2600, and 2650 Å with molecular extinction coefficients of about 400.

The curve obtained for amidone hydrochloride is in good agreement with that reported by Kumler, Strait, and Alpen (*J. Amer. Chem. Soc.*, 1950, **72**, 1463) but our curve for amidone does not correspond well with Ofner and Walton's absorption curve (*J.*, 1950, 2160) which shows no evidence of the characteristic fine structure in the 2600-Å region. The by-product (m. p. 212°) gave an entirely different absorption curve (see Experimental).

EXPERIMENTAL

*2-Imino-*1 : 5*-dimethyl-*3 : 3*-diphenylpyrrolidine.*—A mixture of 3-dimethylamino-1 : 1-diphenylbutyl cyanide (5·6 g., 0·02 mol.) and ammonium benzenesulphonate (3·6 g., 0·02 mol.) was heated at 255—260° for 4 hours. The reaction mixture was dissolved in warm 2N-hydrochloric acid and filtered, and the cooled filtrate made alkaline with aqueous sodium hydroxide. The oily base was taken up in chloroform, and the dried (Na_2SO_4) solution treated with dry hydrogen chloride, affording on evaporation and trituration with acetone, *2-imino-*1 : 5*-dimethyl-*3 : 3*-diphenylpyrrolidinium chloride* (3·0 g., 50%; m. p. 275·5—277°), crystallising from methyl cyanide–acetone in cubes, m. p. 279—281° [Found : C, 71·4, 71·8, 72·25; H, 7·15, 7·15, 7·1; N, 9·25, 9·1, 9·1; Cl, 11·15; *N*-Me, 9·45%; equiv. (by titration), 294; *M* (Niederl, Kasanov, Kisch, and Rao, *Mikrochem.*, 1949, **34**, 132), 311. $C_{18}H_{20}N_2,HCl$ requires C, 71·9; H, 6·7; N, 9·3; Cl, 12·1; *N*-Me, 9·65%; equiv. and *M*, 300·5].

Vacuum distillation of the oily base obtained from the pure hydrochloride gave a viscous oil, b. p. 170°/0·9 mm., which solidified to a white solid (m. p. 90—92·5°); a mixed m. p. with (I) (m. p. 92·5°) gave m. p. 70—75°. Crystallisation from light petroleum (b. p. 60—90°) gave bipyramids of the *base*, m. p. 93—94·5° (Found : C, 81·95; H, 7·7; N, 10·25, 10·5; *N*-Me, 11·5, 12·0, 8·1. $C_{18}H_{20}N_2$ requires C, 81·9; H, 7·6; N, 10·6; *N*-Me, 11·0%); the mixed m. p. with the base of m. p. 103° (Wilson, *J.*, 1950, 2173) was 77—81°.

*2-Imino-5-methyl-*3 : 3*-diphenylpyrrolidine.*—A mixture of (I) (5·6 g., 0·02 mol.) and ammonium benzenesulphonate (17·5 g., 0·1 mol.) was heated at 255—260° for 4 hours. Working up of the reaction mixture as described above gave an oil which solidified on trituration with ether; the *base* (1·8 g., 34%), m. p. 129—139°, on crystallisation from aqueous alcohol, formed plates, m. p. 149·5—151·5° (Found : C, 80·95; H, 6·9; N, 10·9, 11·55. $C_{17}H_{18}N_2$ requires C, 81·55; H, 7·25; N, 11·2%).

By-product (*m. p.* 211—212°).—A 4-hour fusion similar to the above with (I) (14 g., 0·05 mol.) and ammonium benzenesulphonate (44 g., 0·15 mol.) at 255—260° gave, apart from the hydrochloride (m. p. 275—277°) described above, a *by-product* (0·3 g.), m. p. 205—210°, insoluble in methanol, water, hydrochloric acid, or aqueous sodium hydroxide. Crystallisation from alcohol afforded white plates, m. p. 211—212° (Found : C, 83·75, 83·7; H, 6·7, 6·9; N, 8·6, 8·75, 8·75; *N*-Me, 18·75. $C_{22}H_{22}N_2$ requires C, 84·1; H, 7·0; N, 8·9; *N*-Me, 18·5%). Light absorption : Maximum at 2700—2720 Å, $E^{1\%}_{1\,\mathrm{cm.}} = 215$; minimum at 2400 Å, $E^{1\%}_{1\,\mathrm{cm.}} = 115$; intense end-absorption below 2400 Å.

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