731. *A Novel Method of Cyanoethylation.*

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2-Diethylaminoethyl cyanide (II) behaves as a Mannich base in undergoing both amine-elimination and amine-exchange reactions, the amine-exchange reaction with arylamines providing a convenient route to the difficultly accessible *N*-arylcyanoethylamines, *e.g.* *N*-2-cyanoethyl-*p*-anisidine. The reaction is shown to be acid-catalysed, and a mechanism is proposed which accounts satisfactorily for the experimental results.

Cyanoethylation of primary and secondary amines is usually achieved by addition of vinyl cyanide, often in the presence of an acidic or basic catalyst (Bruson, *Org. Reactions*, 1949, **5**, 79; Saunders, *Ann. Reports*, 1948, **45**, 124; Bayer, *Angew. Chem.*, 1949, **61**, 229). This method gives positive results with primary and secondary aliphatic and saturated cyclic amines, but is unsatisfactory for aromatic amines (Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Amer. Chem. Soc.*, 1944, **66**, 725; B.P. 466,316; Elderfield, Gensler, Bembry, Kremer, Brody, Hageman, and Head, *J. Amer. Chem. Soc.*, 1946, **68**, 1262; Cookson and Mann, *J.*, 1949, 67).

It is known that Mannich bases (Blicke, *Org. Reactions*, 1942, **1**, 303) such as (I) and their salts will readily undergo either amine elimination to give diethylamine and an ethylenic compound (reaction 1*a*, 1*b*) (Mannich and Honig, *Arch. Pharm.*, 1927, **265**, 598; Mannich and Heilner, *Ber.*, 1922, **55**, 356; Mannich, Koch, and Barkousky, *ibid.*, 1937, **70**, 355; cf. Du Feu, McQuillin, and Robinson, *J.*, 1937, 53; Snyder, Smith, and Stewart, *J. Amer. Chem. Soc.*, 1944, **66**, 200; Snyder and Speck, *ibid.*, 1939, **61**, 668) or amine exchange (reaction 2*a*, 2*b*) (Snyder and Brewster, *J. Amer. Chem. Soc.*, 1948, **70**, 4230; Snyder and Eliel, *ibid.*, 1948, **70**, 4233; Hultquist *et al.*, *ibid.*, 1948, **70**, 23; cf. Howe, Zambito, Snyder, and Tishler, *ibid.*, 1945, **67**, 38; von Braun, Kuhn, and Goll, *Ber.*, 1926, **59**, 2330).

2-Dialkylaminoethyl cyanides, such as (II), obtained in high yield by cyanoethylation of aliphatic amines, are known to dissociate into their precursors on prolonged heating (Whitmore *et al.*, *loc. cit.*; Hoffmann and Jacobi, U.S.P. 1,992,615) by an elimination reaction (reaction 3*a*, 3*b*), which is due to the easy removal of a hydrogen atom from the α-carbon atom as a

$$\mathrm{RCO{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2} \qquad \mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2} \qquad \mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}MeEt_2\}\overset{-}{I}}$$

(I) (II) (III)

proton by the influence of the neighbouring electron-attracting cyanide and carbonyl groups. It is known that, for example, an " onium " salt may undergo simultaneously both elimination and substitution reactions (Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 657); it was thought possible, therefore, that a corresponding amine-exchange reaction might occur also in the case of the dialkylaminoethyl cyanides (reaction 4*a*, 4*b*), and that, if R = aryl or substituted aryl, a means of obtaining the difficultly-accessible cyanoethylated aromatic amines would be at hand.

$$\mathrm{RCO{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2 \longrightarrow RCO{\cdot}CH{:}CH_2 + NHEt_2} \tag{1a}$$

$$\mathrm{RCO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2\}\overset{-}{X} \longrightarrow RCO{\cdot}CH{:}CH_2 + \overset{+}{N}H_2Et_2\}\overset{-}{X}} \tag{1b}$$

$$\mathrm{RCO{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2 + NHR_1R_2 \longrightarrow RCO{\cdot}CH_2{\cdot}CH_2{\cdot}NR_1R_2 + NHEt_2} \tag{2a}$$

$$\mathrm{RCO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2\}\overset{-}{X} + NHR_1R_2 \longrightarrow RCO{\cdot}CH_2{\cdot}CH_2{\cdot}NR_1R_2 + \overset{+}{N}H_2Et_2\}\overset{-}{X}} \tag{2b}$$

$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2 \longrightarrow CN{\cdot}CH{:}CH_2 + NHEt_2} \tag{3a}$$

$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2\}\overset{-}{X} \longrightarrow CN{\cdot}CH{:}CH_2 + \overset{+}{N}H_2Et_2\}\overset{-}{X}} \tag{3b}$$

$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2 + RNH_2 \longrightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}NHR + NHEt_2} \tag{4a}$$

$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2\}\overset{-}{X} + RNH_2 \longrightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}NHR + \overset{+}{N}H_2Et_2\}\overset{-}{X}} \tag{4b}$$

Reaction of anilinium benzenesulphonate with (II) at 180° for 1 hour gave 50% of the required 2-cyanoethylaniline (m. p. 51—52°) (Cookson and Mann, *loc. cit.*). However, reaction of (II) with aniline either at 180° or at 200° for 1 hour gave a quantitative recovery of the starting-materials. The reaction thus appears to be acid-catalysed. The benzenesulphonate of (II) was found to be extremely hygroscopic; however the action of methyl iodide on (II) readily gave the quaternary iodide (III); reaction of this with aniline at 180° for 1 hour gave 50% of 2-cyanoethylaniline.

Amine exchange in Mannich bases takes place with either the base (reaction 2*a*) or the salt (2*b*), and probably proceeds by amine elimination (reaction 1*a* or 1*b*) followed by a Michael addition to the activated ethylenic linkage (cf. Snyder and Brewster, *J. Amer. Chem. Soc.*, 1944, **66**, 200), since it is recorded only in the case of aliphatic and saturated cyclic bases which are known to add readily to vinyl cyanide under mild conditions (Whitmore *et al.*, *loc. cit.*) in contrast to aromatic amines. The occurrence of amine exchange in a substance which cannot react by amine elimination followed by amine addition has been reported by Snyder and Eliel (*loc. cit.*) for 1-methylgramine where it takes place readily if the salt (hydrochloride or methiodide) is used, but not with the free base alone under any conditions. The reaction is thus an acid-catalysed substitution reaction (cf. Snyder and Eliel, *J. Amer. Chem. Soc.*, 1948, **70**, 1703).

Boron trifluoride, a Lewis acid, was as effective as a proton for this reaction. In the present method of cyanoethylation of aromatic amines, the reaction was also found to be acid-catalysed, and the following mechanism is therefore put forward (reactions 5, 3*b*, 6, and 7).

$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2 + \overset{+}{N}H_3Ar\}\overset{-}{X} \longrightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2\}\overset{-}{X} + NH_2Ar} \quad . \; . \; . \quad (5)$$

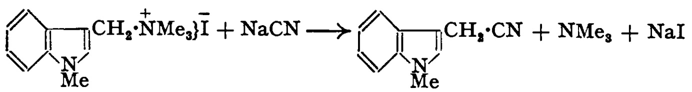
$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2\}\overset{-}{X} + NH_2Ar \longrightarrow NHEt_2 + CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}H_2Ar\}\overset{-}{X}} \quad . \; . \quad (6)$$

$$\mathrm{CN{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}H_2Ar\}\overset{-}{X} + NHEt_2 \longrightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}NHAr + \overset{+}{N}H_2Et_2\}\overset{-}{X}} \quad . \; . \quad (7)$$

Reaction (5) is a simple competition for the proton which is thereby transferred from the anilinium cation to the more strongly basic (II). The *N*-2-cyanoethyl-*NN*-diethylammonium ion is then able to react further by either reaction (3*b*), the elimination reaction, or with a molecule of arylamine (reaction 6), involving elimination of diethylamine and simultaneous reaction of arylamine to give the stable *N*-aryl-*N*-2-cyanoethylammonium ion. This then undergoes a further reaction (7) by which it loses its proton to the more basic diethylamine, giving the desired *N*-aryl-2-cyanoethylamine.

Displacements showing close similarity to reaction (6) have been reported; thus Snyder and Speck (*J. Amer. Chem. Soc.*, 1939, **61**, 668, 2895) and Snyder and Eliel (*ibid.*, 1948, **70**, 1703) respectively record that reactions (8) and (9) took place very readily.

$$\mathrm{2Ph{\cdot}CH_2{\cdot}\overset{+}{N}Me_2Ph\}\overset{-}{Cl} + Na_2S \longrightarrow (Ph{\cdot}CH_2)_2S + 2NaCl + 2Ph{\cdot}NMe_2} \quad . \; . \; . \quad (8)$$



. . . (9)

It is seen that, whatever the relative rates of reactions (3*b*) and (6), there is formed one mol. of diethylammonium salt. That the reaction is a substitution and not an elimination followed by an addition reaction was also shown by the following experiment. Vinyl cyanide (1·5 mols.), diethylamine (1·5 mols.), and anilinium benzenesulphonate (1 mol.), heated at 180° for 1 hour, gave 77% of diethylammonium salt, evidently formed by the proton-exchange reaction (10), but only 2·5% of 2-cyanoethylaniline. The formation of this product must be ascribed to the formation, *in situ*, of some (II) (cf. Whitmore *et al.*, *loc. cit.*) from the amount of diethylamine (0·5 mol.) not consumed in reaction (10) followed, by the reaction (5) of (II) with such anilinium ion as had not undergone reaction (10), to give the *N*-2-cyanoethyl-*NN*-diethylammonium ion, which could then react further by either reaction (3*b*) or (6). Since a 50% yield of 2-cyanoethylaniline is normally obtained by this method, it follows that probably not more than about 5% of *N*-2-cyanoethyl-*NN*-diethylammonium ion was formed in the first instance, *i.e.* that about 95% of anilinium salt had reacted according to reaction (10).

$$\mathrm{Ph{\cdot}\overset{+}{N}H_3\}\overset{-}{X} + NHEt_2 \longrightarrow Ph{\cdot}NH_2 + \overset{+}{N}H_2Et_2\}\overset{-}{X}} \quad . \; . \; . \; . \; . \quad (10)$$

In view of Snyder aud Eliel's findings (*loc. cit.*) that boron trifluoride was effective as an acid catalyst in the amine-exchange reaction of 1-methylgramine, a mixture of aniline and (II) was treated with boron trifluoride (1 mol.) at 180° for 1 hour, but this gave almost quantitative reovery of starting-materials. In view of the well-known tendency of boron trifluoride to co-ordinate with the cyanide group (cf. its use as a Friedel–Crafts catalyst), a similar experiment using 2 mols. of boron trifluoride was carried out, with the same negative result. This failure of boron trifluoride to function as an acid catalyst in the present reaction may possibly be ascribed to the much more electron-attracting nature of the aryl group in aniline, and of the 2-cyanoethyl group in (II), compared with the alkyl residues in dimethylamine and piperidine, the two bases concerned in Snyder and Eliel's work (*loc. cit.*). This greater electron-attracting power may result in a reduced availability of the free electron-pair on the amino-nitrogen for co-ordination with boron trifluoride.

The extension of the present cyanoethylation reaction to other aromatic amines was next investigated. Reaction of (II) with 4-diphenylylammonium benzenesulphonate (Bauer and Cymerman, *J.*, 1950, 1826) at 200° for 1 hour gave 68% of diethylammonium salt and 50% of the required 4-2'-cyanoethylaminodiphenyl (m. p. 146°); some 4-aminodiphenyl was also formed in the reaction. Treatment of 4-diphenylylammonium benzenesulphonate with 2-morpholinoethyl cyanide at 200° for 1 hour similarly gave morpholinium benzenesulphonate, and a smaller yield of 4-2'-cyanoethylaminodiphenyl. This compound was also obtained by direct reaction of 4-aminodiphenyl and vinyl cyanide. Although treatment of 4-aminodiphenyl with vinyl cyanide in acetic acid at 170° for 4—6 hours under pressure, with and without copper acetate and/or copper powder catalysts, gave only 4-acetamidodiphenyl, repetition of the experiment in an autoclave at 150° for 4 hours, a reduced amount of acetic acid being used, gave a 13% yield of 4-2'-cyanoethylaminodiphenyl, isolated as the hydrochloride, identical with that of the sample prepared as described above.

Reaction of 4-chloroanilinium toluene-*p*-sulphonate, 2-naphthylammonium benzenesulphonate, *p*-methoxyanilinium benzenesulphonate, and diphenylammonium benzenesulphonate with (II) at 180—200° for 0·5—1 hour gave the required *N*-aryl-2-cyanoethylamine, recovered arylamine, and diethylammonium salt in the yields shown in the Table.

		% Yield of		
Arylammonium salt used	pK_a at 25° of arylamine	*N*-aryl-2-cyano-ethylamine	arylamine	diethylammonium salt
p-Methoxyanilinium	5·29	69	21	78·5
Anilinium	4·58	50	19	77
4-Diphenylylammonium	4·27	50	—	68
2-Naphthylammonium	4·11	20·5	49	70·5
p-Chloroanilinium	4·0	20	25	49
Diphenylammonium	0·85	0, 0	62, 79	85, 73·5

A connection between the yields of 2-cyanoethylamines and the basic strengths (pK_a) of the parent amines (Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469) is immediately apparent, and may indicate that reaction (6) involves co-ordination of the amino-nitrogen of the arylamine with the electron-deficient β-carbon atom of a carbonium cation. An increase in the electron-attracting properties of the aryl nucleus would then reduce the availability of the electron-pair for this co-ordination step, thus lowering the rate of reaction (6). Further work is in progress to confirm this hypothesis.

In one experiment with 2-naphthylammonium benzenesulphonate and (II), 3 : 4-6 : 7-dibenzacridine was obtained in 14% yield. The formation of this compound from 2-naphthylamine and formaldehyde is well known (Mohlau and Haase, *Ber.*, 1902, **35**, 4164; Ullmann and Fetvadjian, *ibid.*, 1903, **36**, 1027), and its isolation here presupposes the existence of formaldehyde in the reaction mixture; this can only have arisen from the decomposition of (II) into methyl cyanide, formaldehyde, and diethylamine—equivalent to the reversibility of the formation of certain Mannich bases (Mannich and Kather, *Arch. Pharm.*, 1919, **257**, 18; Mannich and Dannehl, *ibid.*, 1938, **276**, 206). Such an explanation may be feasible. This, and other implications of this cyanoethylation reaction, are receiving further investigation.

EXPERIMENTAL.

N-2-*Cyanoethyl*-NN-*diethyl*-N-*methylammonium Iodide*.—From the exothermic reaction of 2-diethylaminoethyl cyanide (6·3 g.) and methyl iodide (14 g., 2 mols.) in dry ether (25 c.c.) the quaternary *iodide* (9·5 g., 71%) was obtained as white crystals, m. p. 165° (decomp.) (Found : N, 10·05. $C_8H_{17}N_2I$ requires N, 10·4%).

2-*Cyanoethylaniline*.—(*a*) A mixture of anilinium benzenesulphonate (10 g.) and 2-diethylaminoethyl cyanide (8·5 g., 1·5 mols.) was heated at 180° for 1 hour. The cooled mixture was treated with ether, and the precipitate recrystallised from acetone, giving white needles (7 g., 77%) of diethylammonium benzenesulphonate, m. p. and mixed m. p. 138—139°.

Distillation of the ethereal filtrate afforded two fractions : (1) 2 g., b. p. 40—42°/0·05 mm., n_D^{19} 1·5072, a mixture of aniline and 2-diethylaminoethyl cyanide, which when boiled with acetic anhydride gave acetanilide (1 g.), m. p. 114° [corresponding to 0·7 g. (19%) of aniline]; (2) 2·85 g. (50%), b. p. 122—125°/0·05 mm., white needles, m. p. 51—52°, of 2-cyanoethylaniline (Cookson and Mann, *loc. cit.*, give b. p. 178—186°/16 mm., m. p. 51·5°).

(*b*) A mixture of *N*-2-cyanoethyl-*NN*-diethyl-*N*-methylammonium iodide (6·7 g.) and aniline (2·8 g., 1·2 mols.) was heated under reflux at 180° for 1 hour. Distillation gave two fractions : (1) 0·4 g.

(0·2 mol.), b. p. 45°/0·07 mm., recovered aniline; (2) 1·8 g. (50%), b. p. 126—130°/0·07 mm., prismatic needles, m. p. 50—52°, of 2-cyanoethylaniline.

(*c*) A mixture of 2-diethylaminoethyl cyanide (12·6 g.) and aniline (18·6 g., 2 mols.) was heated under reflux at 180° (200° in a second experiment) for 1 hour. Distillation gave only one fraction, b. p. 35—40°/0·05 mm. (30 g.). No residue remained.

(*d*) Similar results were obtained on addition of boron trifluoride–ether complex (1 or 2 mols.) to the reaction mixture

(*e*) Vinyl cyanide (3·2 g., 0·06 mol.), diethylamine (4·4 g., 0·06 mol.), and anilinium benzenesulphonate (10 g., 0·04 mol.) were heated under reflux at 180° for 1 hour. The cooled mixture on trituration with acetone gave white needles (6 g., 66%) of diethylammonium benzenesulphonate, m. p. and mixed m. p. 139°. The acetone filtrate on distillation gave two fractions: (1) 3·2 g., b. p. 35—40°/0·07 mm., n_D^{19} 1·4841, a mixture of aniline and 2-diethylaminoethyl cyanide, which when treated with acetic anhydride gave acetanilide (1 g.) [corresponding to 0·7 g. (19%) of aniline]; (2) 0·15 g. (2·5%), b. p. 120—125°/0·07 mm., m. p. 51—52°, of 2-cyanoethylaniline. The residue (2·8 g.) solidified, and on crystallisation from acetone gave white needles (1 g., 11%) of diethylammonium benzenesulphonate, m. p. and mixed m. p. 139°. A buff residue (1·5 g.) remained, m. p. 220—230°, insoluble in acetone, methanol, pyridine, chloroform, 2-ethoxyethanol, and nitrobenzene; this was not further investigated.

4-2′-*Cyanoethylaminodiphenyl.*—(*a*) A mixture of 2-diethylaminoethyl cyanide (6·3 g., 1·5 mols.) and 4-diphenylylammonium benzenesulphonate (11 g., 1 mol.) (Bauer and Cymerman, *J.*, 1950, 1826) was heated at 200° for 1 hour. The cooled mixture was dissolved in alcohol (charcoal); on cooling there separated 4-2′-*cyanoethylaminodiphenyl* (3·5 g., 50%), m. p. 143—144°, which gave, on recrystallisation from alcohol or benzene, shining plates, m. p. 146° (Found: C, 80·5, 81·3; H, 6·4, 6·3; N, 12·3, 12·4, 12·6. $C_{15}H_{14}N_2$ requires C, 81·1; H, 6·4; N, 12·6%). The hydrated *hydrochloride* crystallised from ethanol–ether in fine needles, m. p. 177—178° (Found: N, 10·1. $C_{15}H_{15}N_2Cl,H_2O$ requires N, 10·1%).

On dilution of the alcoholic filtrate from the reaction mixture with ether, diethylammonium benzenesulphonate (5·2 g., 68%), m. p. 135—137°, separated; it crystallised from acetone in needles, m. p. and mixed m. p. 138—139°. Treatment of the alcoholic–ethereal solution with benzenesulphonic acid gave 4-diphenylylammonium benzenesulphonate, crystallising from water in buff plates, m. p. and mixed m. p. 276—278°; the base, 4-aminodiphenyl, had m. p. 48—50°, mixed m. p. 50—52°.

(*b*) 2-Morpholinoethyl cyanide (7 g.) and 4-diphenylylammonium benzenesulphonate (11 g.) were heated at 200° for 1 hour. Extraction of the cooled mixture with *iso*propanol, dilution of the extract with ether, and crystallisation of the precipitate from acetone, gave *morpholinium benzenesulphonate*, m. p. 110—111° (undepressed on admixture with an authentic specimen), in lustrous scales (Found: C, 49·0; H, 6·2. $C_{10}H_{15}O_4NS$ requires C, 49·0; H, 6·1%).

A solution of 4-diphenylylammonium toluene-*p*-sulphonate (7 g., 1 mol.) in 2-morpholinoethyl cyanide (5·6 g., 2 mols.) was maintained at 134° for 2·25 hours, then at 160° for 0·25 and finally at 180° for 0·25 hour. The mixture was diluted with methanol, basified, and then extracted with chloroform. The residue obtained on removal of solvent was kept at 100°/20 mm. for several hours and then crystallised from carbon tetrachloride; it formed white plates, m. p. 140—142° undepressed on admixture with the material (m. p. 146°) obtained in (*a*).

(*c*) (Experiment by Mr. W. J. SHELDON.) A mixture of 4-aminodiphenyl (20 g.), vinyl cyanide (9 c.c.), and acetic acid (8 c.c.) was heated with copper powder (2 g.) and copper acetate (1 g.) in an autoclave for 4 hours at 150° (bath temp.). Distillation of the mixture gave a product (20·7 g.), b. p. 120—180°/0·085 mm., the ethereal extracts of which were saturated with dry hydrogen chloride; the precipitate obtained, on recrystallisation from alcohol–ether, gave white crystals of 4-2′-cyanoethylaminodiphenyl hydrochloride, m. p. 174—177° (4 g., 13%) undepressed on admixture with the material obtained in (*a*).

p-*Chloro*-N-2-*cyanoethylaniline.*—2-Diethylaminoethyl cyanide (9·5 g., 1·5 mols.) and *p*-chloroanilinium toluene-*p*-sulphonate (15 g., 1 mol.) were heated at 180° for 1 hour. The cooled mixture was treated with ether, and the precipitated solid crystallised from acetone, giving diethylammonium toluene-*p*-sulphonate (6·0 g., 49%), m. p. 88° undepressed on admixture with an authentic specimen. Distillation of the ethereal filtrate afforded three fractions: (1) b. p. 53°/0·05 mm., unchanged 2-diethylaminoethyl cyanide (2·5 g., 0·4 mols.); (2) b. p. 75°/0·05 mm., *p*-chloroaniline (1·5 g., 25%), m. p. and mixed m. p. 70—71°; (3) 1·8 g. (20%), b. p. 155—160°/0·05 mm., m. p. 70—71°. Crystallisation from light petroleum (b. p. 90—100°) gave white prismatic needles, m. p. 75·5—76°, of p-*chloro*-N-2-*cyanoethylaniline* (Found: C, 60·2; H, 5·3. $C_9H_9N_2Cl$ requires C, 59·8; H, 5·0%).

N-2′-*Cyanoethvl*-2-*naphthylamine.*—(*a*) 2-Diethylaminoethyl cyanide (12·6 g., 2 mols.) and 2-naphthylammonium benzenesulphonate (15 g., 1 mol.) were heated under reflux at 200° for 0·5 hour. The cooled mixture, on treatment with acetone, gave diethylammonium benzenesulphonate (8·1 g., 70·5%), m. p. and mixed m. p. 137—139°. The acetone filtrate on distillation afforded 2-diethylaminoethyl cyanide (6·3 g., 1 mol.), b. p. 100°/22 mm. The residue on trituration with 95% alcohol gave a pale yellow solid (2 g., 20·5%), m. p. 95—96°, which on crystallisation from light petroleum (b. p. 90—100°) afforded white hexagonal plates, m. p. 102°, of N-2′-*cyanoethyl*-2-*naphthylamine* (Found: C, 79·9; H, 6·3. $C_{13}H_{12}N_2$ requires C, 79·5; H, 6·15%). The residue (m. p. 90—92°) left on evaporation of the 95%-alcoholic filtrate crystallised from light petroleum (b. p. 60—90°), giving 2-naphthylamine (3·5 g., 49%), identified by m. p. and mixed m. p.

(*b*) 2-Diethylaminoethyl cyanide (9·5 g., 1·5 mols.) and 2-naphthylammonium benzenesulphonate (15 g., 1 mol.) were heated at 180° for 1 hour. Trituration of the cooled mixture with acetone gave diethylammonium benzenesulphonate (7·7 g., 69%), m. p. and mixed m. p. 138—139°. The residue left by evaporation of the acetone filtrate gave, on trituration with ether, 3 : 4-

6 : 7-dibenzacridine, m. p. 215—216° (1 g., 14%), as pale yellow needles, from chloroform–alcohol or aqueous acetone (Found : C, 89·6; H, 4·6; N, 5·3. Calc. for $C_{21}H_{13}N$: C, 90·25; H, 4·65; N, 5·05%). The m. p. was undepressed on admixture of the material with an authentic specimen (m. p. 215—215·5°), prepared by Senier and Goodwin's method (*J.*, 1902, 280). Both samples dissolved in sulphuric acid to a greenish-yellow solution with a strong blue fluorescence.

The dibenzacridine gave a *picrate*, which crystallised from 2-ethoxyethanol in yellow needles, m. p. 326° (decomp.) (Found : C, 62·2; H, 3·3; N, 11·15. $C_{21}H_{13}N,C_6H_3O_7N_3$ requires C, 62·8; H, 3·2; N, 11·2%) ; the methosulphate, prepared by the method described by Kermack, Slater, and Spragg (*Proc. Roy. Soc. Edinburgh*, 1930, **50**, 258), crystallised from 95% alcohol in yellow needles, m. p. 308° (decomp.) (Found : N, 3·7. Calc. for $C_{21}H_{13}N,C_{12}H_6O_4S$: N, 3·5%) (Kermack *et al.*, *loc. cit.*, give m. p. >300°).

The ethereal filtrate from the trituration of the product, on treatment with light petroleum, gave 2-naphthylamine (3 g., 20%), identified by m. p. and mixed m. p.

N-2-*Cyanoethyl*-p-*anisidine*.—A mixture of *p*-methoxyanilinium benzenesulphonate (14 g.) (Partridge, *J.*, 1949, 2686) and 2-diethylaminoethyl cyanide (9·5 g., 1·5 mols.) was heated under reflux at 180° for 1 hour. Treatment of the cooled melt with acetone gave diethylammonium benzenesulphonate (9·0 g., 78·5%), m. p. and mixed m. p. 138—139°. The acetone filtrate on distillation afforded three fractions : (1) b. p. 41—42°/0·05 mm., unchanged 2-diethylaminoethyl cyanide (1·8 g., 0·22 mol.), n_D^{19} 1·4407; (2) b. p. 45—55°/0·05 mm., *p*-anisidine (1·4 g., 21%), as an oil, n_D^{19} 1·5450, solidifying to white crystals, m. p. 52—56° undepressed on admixture with an authentic specimen ; (3) b. p. 170—180°/0·05 mm., white needles (6·0 g., 69%) of *N*-2-cyanoethyl-*p*-anisidine, m. p. 56—60°. Crystallisation from chloroform–light petroleum (b. p. 60—90°) afforded white nacreous plates, m. p. 63·5—64·5° (Found : N, 15·5. Calc. for $C_{10}H_{12}ON_2$: N, 15·9%). This compound is described by Elderfield *et al.* (*loc. cit.*) as a liquid, b. p. 247°/0·7 mm.

Diphenylammonium Benzenesulphonate.—This *salt* crystallised from alcohol–ether in white prisms, m. p. 124°, which became pink on exposure to light and air (Found : C, 65·6; H, 5·35; S, 10·15, 10·25. $C_{18}H_{17}O_3NS$ requires C, 66·05; H, 5·2; S, 9·8%).

Attempted Preparation of N-2-*Cyanoethyldiphenylamine*.—(*a*) Addition of diphenylammonium benzenesulphonate (13 g.) to 2-diethylaminoethyl cyanide (10 g., 2 mols.) gave an exothermic reaction, and a homogeneous melt was obtained immediately. The mixture was heated under reflux at 180° for 0·5 hour, cooled, and triturated with acetone, giving white needles (7·8 g., 85%) of diethylammonium benzenesulphonate, m. p. and mixed m. p. 139°. The acetone filtrate on distillation gave two fractions : (1) b. p. 120°/25 mm., recovered 2-diethylaminoethyl cyanide (3 g.); (2) b. p. 95—100°/0·05 mm., m. p. 54°, diphenylamine (mixed m. p.) (4·1 g., 61%). The residue from the distillation gave more diphenylamine (0·5 g., 7%).

(*b*) The same experiment was repeated at 200° for 1 hour. Trituration with acetone gave diethylammonium benzenesulphonate (6·7 g., 73·5%), m. p. and mixed m. p. 137—139°. Distillation of the acetone filtrate gave only two fractions : (1) b. p. 40—45°/0·05 mm., 2-diethylaminoethyl cyanide (5 g., 1 mol.) ; (2) b. p. 94—100°/0·05 mm., m. p. 52—54°, diphenylamine (5·3 g., 79%).

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