78. A Novel Method of Cyanoethylation. Part IV.* Substitution Effects.

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Preparation of *N*-2-cyanoethylarylamines, by amine exchange from 2-diethylaminoethyl cyanide and the arylamine, has been found to depend on the basic strength of the arylamine and to be hindered by *o*-substitution and also by bulky *N*-substituents in the arylamine.

Instead of preformed 2-diethylaminoethyl cyanide, a mixture of vinyl cyanide and diethylamine may be used.

The effect of methyl substitution in the cyanoethyl group itself points to a substitution mechanism. The nature of the amine displaced also affects the yield, diethylamine giving optimum results.

The methiodides of dialkyl-2-cyanoethylamines undergo exchange with cyanide ion to give 1 : 2-dicyanoethane.

It has been shown [1] in Part I that *N*-2-cyanoethylarylamines are obtained by reaction of arylammonium salts with 2-diethylaminoethyl cyanide. Cyanoethylation of a variety of aromatic amines under standard conditions gave the results summarised in Table 1. Two conclusions emerge from this. The decreasing yield of cyanoethyl derivative as the basic strength of the amine falls is in accord with an S_N2 mechanism of the reaction (1), implying a nucleophilic attack by the arylamine nitrogen on the β-carbon atom of the cyanoethyl group, while the equivalent S_N1 mechanism, with the ionisation of 2-diethylaminoethyl cyanide as rate-determining step, would be expected to give yields independent of the nature of the arylamine.

Table 1.

Arylamine	pK_a (25°)	Yield (%) of	
		N-2-cyano-ethyl-arylamine	recovered arylamine
p-Anisidine	5·29	78	10
p-Phenetidine	5·25	70	5
p-Toluidine	5·07	67	11
m-Toluidine	4·69	61	15
Aniline	4·58	50	19
o-Anisidine	4·49	42	20
o-Toluidine	4·39	25	49
m-Anisidine	4·20	34	11
m-Chloroaniline	3·5	27·5	61
2 : 6-Dimethylaniline	3·42	7·6	72·5
m-Acetylaniline	—	0	20
p-Nitroaniline	1·11	0	90
N-Methylaniline	4·85	65	20
N-Ethylaniline	5·11	41	36
N-*n*-Propylaniline	5·02	17·5	40
N-*iso*Propylaniline	—	0·5	95

$$^{+}NHRR'\cdot CH_2\cdot CH_2\cdot CN + Ar\cdot NH_2 \longrightarrow NHRR' + {}^{+}NH_2Ar\cdot CH_2\cdot CH_2\cdot CN \quad . \quad . \quad (1)$$

The presence of a substituent *ortho* to the amino-group has already been reported to restrict cyanoethylation by the amine-exchange reaction [2] and by direct cyanoethylation; [3] comparison of the behaviour of *o*-toluidine and 2 : 6-dimethylaniline with that of *m*- and *p*-toluidine further illustrates this *ortho*-effect. Since the effect of lowered basic strength cannot be separated from the steric effect in these cases, several *N*-alkylanilines have been examined. Here the factor is a purely steric one, basicity being comparable throughout, and shows the increasing degree of steric hindrance with increase in size of the *N*-alkyl substituent.

It has been shown in Part III [4] that, whereas vinyl cyanide and *p*-anisidinium chloride did not react at 180°, reaction occurred readily in presence of diethylamine. Application of this method gave an improved yield of *m*-chloro-*N*-2-cyanoethylaniline, and led to the

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* Part III, *J.*, 1955, 3628.

[1] Bauer, Cymerman, and Sheldon, Part I, *J.*, 1951, 3311.

[2] Bates and Cymerman-Craig, *J.*, 1954, 1153.

[3] Braunholtz and Mann, *J.*, 1953, 1817.

[4] Cymerman-Craig, Moyle, Nicholson, and Werner, Part III, *J.*, 1955, 3628.

NN'-biscyanoethyl-*o*-phenylenediamine. *p*-Phenylenediamine, from which Braunholtz and Mann [3] obtained only the tetrakiscyanoethyl compound, gave the *NN'*-biscyanoethyl derivative, identified by the presence of a strong $>$NH band at 3345 cm.$^{-1}$ in its infrared spectrum (Nujol mull).

Attempted acid hydrolysis of *m*-chloro-*N*-2-cyanoethylaniline gave only *m*-chloroaniline; similar elimination of the cyanoethyl group has been reported by Johnson and De Acetis.[5]

The effect of substitution in the cyanoethyl group itself was investigated. *iso*Propenyl-cyanide did not react with diethylamine under a variety of conditions, but condensed readily with pyrrolidine and piperidine to give 1-2'-cyanopropyl-pyrrolidine and -piperidine respectively. The methiodide of the former underwent amine exchange smoothly with diethylamine to give the previously inaccessible 2-diethylamino-1-methylethyl cyanide.

Of these *iso*propyl cyanides only the first and last condensed satisfactorily with *p*-anisidinium chloride.

The dimethyl-substituted compound, $NEt_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CN$, which is incapable of undergoing an elimination reaction, was prepared by dehydration of 3-diethylamino-2 : 2-dimethylpropionaldoxime. It reacted with *p*-anisidinium chloride, giving only 0·1% of a product, presumably *N*-(2-cyano-2-methylpropyl)-*p*-anisidine, isolated as the unstable alkali-insoluble benzenesulphonamide.

The results agree with the effects predictable for an S_N2 mechanism. Increasing methyl-substitution in the 2-cyanoethyl group results in the carbon sleketon's being related in the same way as in the *n*-propyl, *iso*butyl, and *neo*pentyl group, for which the second-order rate constants [6] (*e.g.*, for the reaction RBr + OEt$^-$ in ethanol at 55°) lie in the order 0·82, 0·03, and 0·0000042, whereas the first-order rate constants for these substituents are of approximately equal magnitude.

Reaction of prop-1-enyl cyanide was also investigated. This condensed smoothly with pyrrolidine giving 1-(2-cyano-1-methylethyl)pyrrolidine, but not with diethylamine. 2-Diethylaminopropyl cyanide was however obtained by an exchange reaction between diethylamine and the pyrrolidine compound. Reaction of these cyanides with *p*-anisidinium chloride gave 40·5 and 50·5% respectively of *N*-(2-cyano-1-methylethyl)-*p*-anisidine. The increased yields compared with those of the isomers suggest that the mechanism of the reaction has changed from S_N2 to S_N1 for the compounds of structure $CN{\cdot}CH_2{\cdot}CHMeR$, which are analogous to secondary alkyl groups such as *iso*propyl or *sec.*-butyl. This change of mechanism is a common phenomenon on passing from the primary to the secondary alkyl series.[7]

The effect of change in the displaced amine was next examined. Reaction of 2-pyrrolidinoethyl cyanide, 2-diethylaminoethyl cyanide, 2-morpholinoethyl cyanide, and *N*-2-cyanoethyl-*N*-ethylbenzylamine with *p*-anisidinium chloride under standard conditions gave the results summarised in Table 2, each experiment being performed in duplicate.

TABLE 2. *Yield of* N-2-*cyanoethyl*-p-*anisidine.*

Starting material	Yield (%)	Recovered arylamine (%)
2-Pyrrolidinoethyl cyanide	26	59
2-Diethylaminoethyl cyanide	78	10
N-2-Cyanoethyl-*N*-ethylbenzylamine	56	30
2-Morpholinoethyl cyanide	45·5	40

The yields of *N*-2-cyanoethyl-*p*-anisidine vary considerably with the amine displaced, passing through a maximum when this is diethylamine. The dependence of the rate of S_N2 reactions on the nature of the displaced group is as yet only imperfectly understood; [8] our results are not explicable in terms of either the volatility or the basic strength of the displaced amine, and it appears likely that two opposing factors are involved. In this

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[5] Johnson and De Acetis, *J. Amer. Chem. Soc.*, 1953, **75**, 2766.
[6] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, p. 414.
[7] *Idem, op. cit.*, p. 318.
[8] *Idem, op. cit.*, p. 339.

connection it is interesting that Knott[9] reports that Mannich bases with aqueous potassium cyanide form the corresponding nitriles by reaction (2), but that the reaction fails when the group NRR′ is replaced by morpholine, piperidine, or pyrrolidine. We found that compounds of type $NC{\cdot}CH_2{\cdot}CH_2{\cdot}NMeRR'\}I$ reacted with aqueous potassium cyanide, forming 1 : 2-dicyanoethane, even when the amine displaced was 4-methylmorpholine or 1-methylpyrrolidine. Under the same conditions, 2-hydroxyethyl cyanide gave only 6% of 1 : 2-dicyanoethane; Tsai[10] reports a yield of 22% of succinic acid by hydrolysis during a similar reaction carried out for 4 hours. The conditions used and products obtained suggest either an S_N1 mechanism or fission followed by addition of cyanide ion.

$$R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NRR' + KCN + H_2O \longrightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CN + KOH + NHRR' \quad . \quad (2)$$

EXPERIMENTAL

Cyanoethylation by 2-*Diethylaminoethyl Cyanide.*—The arylamine hydrochloride or benzenesulphonate (1 mol.) and 2-diethylaminoethyl cyanide (1·25 mols.) were heated under reflux for 1 hr. at 180°. The cooled melt was treated in either of two ways: (*a*) addition of dry acetone precipitated the diethylammonium salt (70—90%), and the acetone filtrate was fractionally distilled; (*b*) addition of N-sodium hydroxide and extraction with chloroform, followed by fractional distillation of the dried (Na_2SO_4) chloroform extracts. Recovered arylamine in the mixture of arylamine and 2-diethylaminoethyl cyanide was estimated as the acetyl or benzenesulphonyl derivative. Only the isolation of the product is described below in those cases in which the above procedures were used.

N-2-*Cyanoethyl*-N-*methylaniline.* Distillation gave fractions: (*a*) b. p. 46—53°/0·4 mm., n_D^{23} 1·4973, containing 20% of recovered methylaniline; and (*b*) b. p. 127—128°/0·6 mm., $n_D^{23.5}$ 1·5590, *N*-2-cyanoethyl-*N*-methylaniline (65%) (Found: C, 75·3; H, 7·5. Calc. for $C_{10}H_{12}N_2$: C, 75·0; H, 7·55%). The picrate (yellow needles from alcohol) had m. p. 115° (Found: N, 18·2. Calc. for $C_{10}H_{12}N_2,C_6H_3O_7N_3$: N, 18·0%). Whitmore *et al.*[11] give b. p. 175—177°/20 mm., 25% yield, for the base, and m. p. 118° for the picrate, both without analytical figures.

N-2-*Cyanoethyl*-N-*ethylaniline.* Distillation gave fractions: (*a*) b. p. 50—55°/0·4 mm., n_D^{24} 1·5023, containing 36% of recovered *N*-ethylaniline, and (*b*) b. p. 126—127°/0·5 mm., n_D^{24} 1·5505, N-2-*cyanoethyl*-N-*ethylaniline* (41%) (Found: C, 75·9; H, 7·85; N, 15·85. $C_{11}H_{14}N_2$ requires C, 75·95; H, 8·1; N, 16·1%). The *picrate* (yellow needles from alcohol) had m. p. 109—111° (Found: N, 17·65. $C_{11}H_{14}N_2,C_6H_3O_7N_3$ requires N, 17·4%). Reaction with methyl toluene-*p*-sulphonate gave N-2-*cyanoethyl*-N-*ethyl*-N-*methylanilinium toluene*-p-*sulphonate,* needles (from ethyl acetate), m. p. 130—131° (Found: N, 8·1. $C_{19}H_{24}O_3N_2S$ requires N, 7·8%).

N-2-*Cyanoethyl*-N-n-*propylaniline.* Distillation gave fractions: (*a*) b. p. 88—96°/1 mm., n_D^{23} 1·4853, containing 40% of recovered *N*-*n*-propylaniline, and (*b*) b. p. 122—123°/0·5 mm., n_D^{25} 1·5400, N-2-*cyanoethyl*-N-n-*propylaniline* (17·5%) (Found: C, 76·45; H, 8·65; N, 15·15. $C_{12}H_{16}N_2$ requires C, 76·5; H, 8·55; N, 14·9%).

N-iso*Propylaniline.* This base had b. p. 82—85°/0·5 mm., $n_D^{14.5}$ 1·5259, and gave a hygroscopic hydrochloride. N-iso*Propylbenzenesulphonanilide* had m. p. 71—72° (Found: N, 5·2. $C_{15}H_{17}O_2NS$ requires N, 5·1%).

N-2-*Cyanoethyl*-N-iso*propylaniline.* *N*-*iso*Propylaniline (25·2 g., 0·19 mole) and 2-cyanoethyldiethylmethylammonium iodide (67 g., 0·225 mole) were refluxed for 1 hr. at 180°. Working up as above gave fractions: (*a*) b. p. 60—100°/1 mm., recovered *N*-*iso*propylaniline (24 g., 95%); (*b*) b. p. 136°/1·5 mm. (0·19 g., 0·5%), *N*-2-cyanoethyl-*N*-*iso*propylaniline which gave a picrate, m. p. 142°, differing from that of *N*-*iso*propylaniline (m. p. 87—88°). Lack of material prevented further characterisation.

N-2-*Cyanoethyl*-p-*toluidine.* Working up by method (*b*) gave a distillate, b. p. 48—125°/0·3 mm., containing 11% of recovered *p*-toluidine. The residue crystallised from acetone to give *N*-2-cyanoethyl-*p*-toluidine (67%) as prismatic plates, m. p. 105—106° (Found: C, 75·3; H, 7·55; N, 17·65. Calc. for $C_{10}H_{12}N_2$: C, 75·0; H, 7·5; N, 17·5%). Braunholtz and Mann[12]

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[9] Knott, *J.*, 1947, 1190.

[10] Tsai, *J. Amer. Chem. Soc.*, 1951, **73**, 1886.

[11] Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Amer. Chem. Soc.*, 1944, **66**, 725.

[12] Braunholtz and Mann, *J.*, 1952, 3046.

give m. p. 103—104°. When the products were worked up by method (*a*), dry acetone precipitated a mixture of diethylammonium salt and *N*-2-cyanoethyl-*p*-toluidine. The *hydrochloride* crystallised from alcohol–ether as plates, m. p. 188·5—189·5° (Found : N, 14·6. $C_{10}H_{12}N_2$,HCl requires N, 14·25%).

N-2-*Cyanoethyl*-p-*phenetidine*. Distillation gave fractions: (*a*) b. p. 38—105°/0·6 mm., containing recovered *p*-phenetidine (5%) and (*b*) b. p. 136—138°/ 0·001 mm., N-2-*cyanoethyl*-p-*phenetidine* (70%), crystallising from chloroform–light petroleum (b. p. 40—60°) as plates, m. p. 75—76° (Found : C, 69·8; H, 7·25; N, 14·25. $C_{11}H_{14}ON_2$ requires C, 69·45; H, 7·4; N, 14·7%). The *hydrochloride* crystallised from alcohol–ether as needles, m. p. 136—137° (Found : N, 12·4. $C_{11}H_{14}ON_2$,HCl requires N, 12·4%).

N-2-*Cyanoethyl*-m-*toluidine*. Distillation gave fractions: (*a*) b. p. 46—110°/0·4 mm., containing 15% of recovered *m*-toluidine, and (*b*) b. p. 126—131°/0·4 mm., *N*-2-cyanoethyl-*m*-toluidine (61%), crystallising from chloroform–light petroleum (b. p. 40—60°) as plates, m. p. 47·5—49° (Found : C, 74·8; H, 7·8; N, 17·3. Calc. for $C_{10}H_{12}N_2$: C, 75·0; H, 7·5; N, 17·5%). Braunholtz and Mann [12] give m. p. 47·5—48·5°.

N-2-*Cyanoethyl*-m-*anisidine*. Distillation gave fractions : (*a*) b. p. 58—100°/1 mm., containing 11% of recovered *m*-anisidine, and (*b*) b. p. 180—184°/1 mm., N-2-*cyanoethyl*-m-*anisidine* (34%), crystallising from chloroform–light petroleum (b. p. 40—60°) as needles, m. p. 84—85° (Found : C, 68·0; H, 7·1. $C_{10}H_{12}ON_2$ requires C, 68·15; H, 6·9%).

N-2-*Cyanoethyl*-o-*toluidine*. Distillation gave fractions: (*a*) b. p. 66—71°/1 mm., containing 49% of recovered *o*-toluidine, and (*b*) b. p. 120—121°/0·7 mm., n_D^{26} 1·5530, *N*-2-cyanoethyl-*o*-toluidine (25%) (Found : C, 74·75; H, 7·55; N, 17·2. Calc. for $C_{10}H_{12}N_2$: C, 75·0; H, 7·5; N, 17·5%). Braunholtz and Mann [3] give b. p. 125—126°/0·2 mm. The *picrate* crystallised from methanol as solvated needles, m. p. 205—206° (Found : N, 16·75. $C_{10}H_{12}N_2,C_6H_3O_7N_3,CH_3{\cdot}OH$ requires N, 16·65%); the solvent was removed only at 140° (Found: N, 17·65. $C_{10}H_{12}N_2,C_6H_3O_7$ requires N, 18·0%). The *benzenesulphonate* formed prismatic needles, m. p. 176—177°, from acetone (Found : N, 9·1. $C_{10}H_{12}N_2,C_6H_6O_3S$ requires N, 8·8%).

N-2-*Cyanoethyl*-o-*anisidine*. Distillation gave fractions : (*a*) b. p. 60—81°/0·6 mm., containing 20% of recovered *o*-anisidine, and (*b*) b. p. 165—167°/0·6 mm., n_D^{24} 1·5600, N-2-*cyanoethyl*-o-*anisidine* (42%) (Found : C, 68·3; H, 6·7; N, 16·15. $C_{10}H_{12}ON_2$ requires C, 68·15; H, 6·9; N, 15·9%).

N-2′-*Cyanoethyl*-2 : 6-*dimethylaniline*. Distillation gave fractions: (*a*) b. p. 49—110°/0·5 mm., containing 72·5% of 2 : 6-dimethylaniline, and (*b*) b. p. 122°/0·5 mm., n_D^{16} 1·5400, which solidified on cooling to a low-melting solid (7·6%), N-2′-*cyanoethyl*-2 : 6-*dimethylaniline* (Found : N, 15·95. $C_{11}H_{14}N_2$ requires N, 16·05%). The *benzenesulphonate* formed needles, m. p. 199—200°, from alcohol–ether (Found : C, 61·5; H, 6·1; S, 9·5. $C_{11}H_{14}N_2,C_6H_6O_3S$ requires C, 61·45; H, 6·1; S, 9·6%).

N-2-*Cyanoethyl*-m-*chloroaniline*. (i) A mixture of *m*-chloroanilinium chloride (32·8 g., 0·2 mole) and 2-diethylaminoethyl cyanide (31·5 g., 0·25 mole) was refluxed at 180° for 1·5 hr. Working up by method (*b*) gave fractions (1) b. p. 70—110°/0·5 mm., containing recovered *m*-chloroaniline (61%), and (2) b. p. 152—162°/0·4 mm., n_D^{19} 1·5733 (9·85 g., 27·5%), *N*-2-cyanoethyl-*m*-chloroaniline, solidifying to needles, m. p. 44—47°. An identical experiment at 180° for 1 hr. gave 23% of *N*-2-cyanoethyl-*m*-chloroaniline. Bekhli [13] gives m. p. 48°, b. p. 184—185°/4—5 mm.

Reaction with toluene-*p*-sulphonyl chloride in pyridine gave N-m-*chlorophenyl*-N-2′-*cyanoethyltoluene*-p-*sulphonamide*, needles (from aqueous alcohol), m. p. 95—96° (Found : N, 8·3; S, 9·35. $C_{16}H_{15}O_2N_2SCl$ requires N, 8·35; S, 9·55%).

(ii) *m*-Chloroanilinium chloride (16·4 g., 1 mol.), vinyl cyanide (6·6 g., 1·25 mol.), and diethylamine (9·1 g., 1·25 mols.) were refluxed at 180° for 2·5 hr. Working up by method (*a*) gave fractions: (1) b. p. 70—94°/1·5 mm., containing 7·3 g. (57%) of *m*-chloroaniline and 2·9 g. of *N*-2-cyanoethyldiethylamine, and (2) b. p. 123—128°/0·001 mm., solidifying to needles, m. p. 44—46°, *m*-chloro-*N*-2-cyanoethylaniline (7·6 g., 42·5%).

Attempted Preparation of β-(m-*Chloro*-N-*toluene*-p-*sulphonylanilino*)*propionic Acid*.—*m*-Chloro-*N*-2-cyanoethylaniline (3 g.) and sulphuric acid (70 c.c.; 65% v/v) were refluxed for 2 hr. and the cold mixture was extracted with ether at pH 5. The residue (2·26 g.; m. p. 70—75°) left on evaporation of the dried (Na_2SO_4) ethereal extracts gave, with toluene-*p*-sulphonyl chloride in pyridine, *N*-*m*-chlorophenyltoluene-*p*-sulphonamide, m. p. and mixed m. p. 135—137°.

NN′-*Bis*-2-*cyanoethyl*-o-*phenylenediamine*.—*o*-Phenylenediammonium dibenzenesulphonate

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[13] Bekhli, *J. Gen. Chem.* (*U.S.S.R.*), 1951, **21**, 86.

(42·4 g., 1 mol.), diethylamine (18·25 g., 2·5 mols.), and vinyl cyanide (13·25 g., 2·5 mols.) were refluxed at 180° for 2·5 hr. Working up by method (*a*) gave fractions (1) b. p. 58—66°/1·5 mm., n_D^{19} 1·4330, *N*-2-cyanoethyldiethylamine (5·6 g.), and (2) b. p. 190—200°/ 0·001 mm., needles, m. p. 116—118°, *NN'*-bis-2-cyanoethyl-*o*-phenylenediamine (15 g., 70%). Braunholtz and Mann[3] give m. p. 118·5—119°.

NN'-*Bis*-2-*cyanoethyl*-p-*phenylenediamine*.—Repetition of the previous experiment, but with *p*-phenylenediammonium dibenzenesulphonate (42·4 g., 1 mol.), gave *N*-2-cyanoethyldiethylamine (5·8 g.), b. p. 60—66°/1·5 mm., n_D^{19} 1·4340. The residue crystallised from ethanol as plates, m. p. 138—139°, of NN'-*bis*-2-*cyanoethyl*-p-*phenylenediamine* (5 g., 22%) (Found: C, 66·9; H, 6·65. $C_{12}H_{14}N_4$ requires C, 67·2; H, 6·6%). A mixed m. p. with *p*-phenylenediamine was depressed. The substance did not distil even at 260°/0·001 mm. A patent[14] claims m. p. 140°.

2-*Diethylamino*-1 : 1-*dimethylpropionaldehyde*.—*iso*Butyraldehyde (51 g., 0·72 mol.), diethylammonium chloride (63 g., 0·47 mol.), and paraformaldehyde (21·6 g., 0·72 mol.) were refluxed for 1 hr. with vigorous stirring; paraformaldehyde (21·6 g.) and 10N-hydrochloric acid (1 c.c.) were then added, and refluxing and stirring continued for a further hour. After addition of 10N-hydrochloric acid (1 c.c.) the viscous cooled mixture was extracted with cold ethanol (300 c.c.), and the Mannich base hydrochloride obtained on evaporation of the alcoholic extracts was basified and extracted into ether. Distillation of the dried (Na_2SO_4) extracts gave the aldehyde (18·05 g., 68%), b. p. 42—45°/1·5 mm., 38—40°/1 mm., $n_D^{16·5}$ 1·4360 (Found: C, 68·75; H, 11·75; N, 8·95. Calc. for $C_9H_{19}ON$: C, 68·75; H, 12·15; N, 8·95%). The semicarbazone (plates from water) had m. p. 125—126° (Found: C, 56·5; H, 10·35. Calc. for $C_{10}H_{22}ON_4$: C, 56·1; H, 10·35%). Mannich *et al.*[15] give b. p. 175—177° for the aldehyde and m. p. 124—125° for the semicarbazone, neither analyses nor yields being reported. NN-*Diethyl*-N-2'-*formyl*-2'-*methylpropyl*-N-*methylammonium iodide* (needles from ethanol) had m. p. 161—162° (Found: C, 40·35; H, 7·2. $C_{10}H_{22}ONI$ requires C, 40·15; H, 7·4%). The *oxime*, obtained by shaking the aldehyde and hydroxylamine acetate for 6 hr. at pH 10—11, was a mobile oil (45%), b. p. 88—90°/0·6 mm., $n_D^{18·5}$ 1·4659 (Found: C, 62·65; H, 11·7; N, 15·9. $C_9H_{20}ON_2$ requires C, 62·75; H, 11·7; N, 16·25%). The oxime gave a negative test with Schiff's reagent.

2-*Diethylamino*-1 : 1-*dimethylethyl Cyanide*.—The preceding oxime (9 g.) and acetic anhydride (90 g.) were refluxed for 2 hr., and the cooled mixture was basified and extracted with ether. Distillation gave the *cyanide* (6·17 g., 59%), b. p. 56—57°/1 mm., $n_D^{15·5}$ 1·4310 (Found: C, 70·05; H, 11·75; N, 18·0. $C_9H_{18}N_2$ requires C, 70·05; H, 11·75; N, 18·15%). The *methiodide* crystallised from ethanol as needles, m. p. 147—148° (Found: C, 41·05; H, 7·2; N, 8·5. $C_{10}H_{21}N_2I,\frac{1}{2}C_2H_5{\cdot}OH$ requires C, 41·35; H, 7·55; N, 8·75%).

N-(2-*Cyano*-2-*methylpropyl*)-p-*anisidine*.—Reaction of *p*-anisidinium chloride (5·3 g., 1 mol.) and 2-diethylamino-1 : 1-dimethylethyl cyanide (6·4 g., 1·25 mols.) at 180° for 1·5 hr. and working up by method (*a*) gave fractions (1) b. p. 65—130°/3 mm., containing recovered cyanide (3·8 g.) and *p*-anisidine (2·7 g., 66%), and (2) 90—150°/0·001 mm., converted into the benzenesulphonyl derivative. This was washed with aqueous ammonia, sodium hydroxide, hydrochloric acid, and sodium hydrogen carbonate, and the alkali-insoluble derivative (0·03 g., 0·1%) crystallised from aqueous methanol as unstable plates, m. p. 55—57°. Lack of material and the instability of the compound precluded further identification.

1-2'-*Cyanoethylpyrrolidine*.—Obtained from pyrrolidine (10 g., 1 mol.) and vinyl cyanide (10 g., 1·3 mols.) refluxed at 100° for 0·5 hr., this cyanide (15·2 g., 86%) had b. p. 78—80°/2 mm., n_D^{15} 1·4670. Corse *et al.*[16] give 81% after 12 hr. at 100°. N-2-*Cyanoethyl*-N-*methylpyrrolidinium iodide* had m. p. 121—122° (needles from ethanol) (Found: C, 35·9; H, 5·45. $C_8H_{15}N_2I$ requires C, 36·1; H, 5·65%).

4-2'-*Cyanoethyl*-4-*methylmorpholinium Iodide*.—Obtained from 2-morpholinoethyl cyanide,[11] the *methiodide* crystallised from aqueous alcohol as needles, m. p. 178—179° (Found: C, 34·1; H, 5·4. $C_8H_{15}ON_2I$ requires C, 34·05; H, 5·4%).

N-*Ethylbenzylamine*.—Reduction of *N*-acetylbenzylamine by lithium aluminium hydride in boiling ether gave *N*-ethylbenzylamine (60% overall yield from benzylamine), b. p. 62—64°/2 mm., n_D^{14} 1·5180. Parvatiker and McEwen[17] give n_D^{30} 1·5058.

N-*Ethylbenzylammonium chloride* crystallised from ethanol–ether as plates, m. p. 182—183° (Found: C, 63·2; H, 7·9. $C_9H_{13}N,HCl$ requires C, 63·0; H, 8·2%).

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[14] Lincoln, Ellis, and Richardson, B.P. 613,807; *Chem. Abs.*, 1949, **43**, 5414.

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N-2-*Cyanoethyl*-N-*ethylbenzylamine*.—*N*-Ethylbenzylamine (33·75 g., 1 mol.) and vinyl cyanide (17 g., 1·25 mols.) were refluxed for 10 hr. at 110°. Distillation gave *N*-ethylbenzylamine (10·6 g.), b. p. 68—70°/3 mm., n_{D}^{16} 1·5170 and N-2-*cyanoethyl*-N-*ethylbenzylamine* (30·2 g., 94% on reacted amine), b. p. 148°/3 mm., n_{D}^{16} 1·5170 (Found : C, 76·7; H, 8·4. $C_{12}H_{16}N_2$ requires C, 76·5 ; H, 8·5%). The *methiodide* crystallised from ethanol as needles, m. p. 125—126° (Found : C, 47·4 ; H, 5·7. $C_{13}H_{19}N_2I$ requires C, 47·31 ; H, 5·8%).

1-2′-*Cyanopropylpyrrolidine*.—Pyrrolidine (7·2 g., 1 mol.) and *iso*propenyl cyanide (6·7 g., 1 mol.) were refluxed at 110° for 8 hr. Distillation gave unchanged material (1·0 g.), b. p. 38—40°/60 mm., and 1-2′-*cyanopropylpyrrolidine* (12·15 g., 88%), b. p. 132—136°/60 mm., 58°/0·8 mm., n_{D}^{19} 1·4560 (Found : C, 69·7 ; H, 10·25. $C_8H_{14}N_2$ requires C, 69·55 ; H, 10·2%). The *methiodide* crystallised from ethanol–ether as needles, m. p. 100—101° (Found : C, 38·55 ; H, 6·0. $C_9H_{17}N_2I$ requires C, 38·5 ; H, 6·1%). Treatment of this methiodide with lithium picrate gave 1-2′-*cyanopropyl*-1-*methylpyrrolidinium picrate* as yellow plates (from ethyl acetate), m. p. 130—131° (Found: C, 47·3; H, 4·9. $C_{15}H_{19}O_7N_5$ requires C, 47·25; H, 5·0%).

1-2′-*Cyanopropylpiperidine*.—Reaction of piperidine (17 g., 0·2 mole) and *iso*propenyl cyanide (10 g., 0·15 mole) at 110° for 10 hr. under reflux gave unchanged material (5 g.), b. p. 80—104°/760 mm., and the new *cyanide* (14·8 g., 72% on reacted cyanide), b. p. 70—72°/2 mm., $n_{\mathrm{D}}^{17\cdot5}$ 1·4662 (Found : C, 71·1 ; H, 10·25. $C_9H_{16}N_2$ requires C, 71·0 ; H, 10·55%). The *methiodide* crystallised from ethanol–ether as needles, m. p. 144—145° (Found: C, 40·7; H, 6·35. $C_{10}H_{19}N_2I$ requires C, 40·8 ; H, 6·5%).

Preparation of 2-*Diethylamino*-1-*methylethyl Cyanide*.—(*A*) Molar quantities of diethylamine and *iso*propenyl cyanide failed to react when refluxed for 5 hr. with or without benzyltrimethylammonium hydroxide or heated at 175° for 2 hr. or at 215° for 3 hr.

(*B*) 1-2′-Cyanopropyl-1-methylpyrrolidinium iodide (44·0 g.) and diethylamine (60·0 g., 5 mols.) were heated at 100° for 8 hr. Ether-extraction of the residue after removal of diethylamine gave 2-*diethylamino*-1-*methylethyl cyanide* (13·2 g., 60%), b. p. 92°/20 mm., n_{D}^{15} 1·4350 (Found : C, 68·4 ; H, 11·5. $C_8H_{16}N_2$ requires C, 68·5 ; H, 11·5%). The *methiodide* crystallised from alcohol–ether as needles, m. p. 166—168° (decomp.) (Found : C, 37·8 ; H, 6·55. $C_9H_{19}N_2I$ requires C, 38·3 ; H, 6·8%).

1-(2-*Cyano*-1-*methylethyl*)*pyrrolidine*.—Pyrrolidine (14·2 g., 0·2 mole) and prop-1-enyl cyanide (17 g., 0·2 mole) were refluxed at 130° for 3 hr. Distillation gave the new *cyanide* (24·6 g., 89%), b. p. 121—122°/25 mm., n_{D}^{25} 1·4660 (Found : C, 69·4 ; H, 10·3. $C_8H_{14}N_2$ requires C, 69·5 ; H, 10·2%). The hygroscopic methiodide on treatment with lithium picrate gave *N*-methylpyrrolidinium picrate, crystallising from ethyl acetate as yellow plates, m. p. 222° (lit., m. p. 222°) (Found: C, 42·1; H, 4·5; N, 17·75. Calc. for $C_{11}H_{14}O_7N_4$: C, 42·0; H, 4·5; N, 17·85%).

2-*Diethylaminopropyl Cyanide*.—(*a*) A mixture of 1-(2-cyano-1-methylethyl)-1-methylpyrrolidinium iodide (21·5 g.) and diethylamine (36·5 g., 6 mols.) was refluxed at 100° for 6 hr. Removal of diethylamine and ether-extraction of the residue gave 2-*diethylaminopropyl cyanide* (9·7 g., 91%), b. p. 101—102°/25 mm., n_{D}^{24} 1·4380 (Found : C, 68·05 ; H, 11·5. $C_8H_{16}N_2$ requires C, 68·5; H, 11·5%). The *methiodide* crystallised from alcohol as needles, m. p. 172—174° (decomp.) (Found : C, 38·0 ; H, 6·6. $C_9H_{19}N_2I$ requires C, 38·3; H, 6·8%). (*b*) Prop-1-enyl cyanide was recovered quantitatively after 6 hours' refluxing with diethylamine at 100°.

2-*Methylprop*-1-*enyl Cyanide*.—Decarboxylation of α-cyano-β-methylcrotonic acid[18] in presence of a catalytic amount of copper bronze commenced at 180—190°, giving 2-methyprop-1-enyl cyanide (76%), b. p. 140—143°/760 mm., n_{D}^{20} 1·4232 (lit., b. p. 140—142°).

Attempted Preparation of 2-*Diethylamino*-2-*methylpropyl Cyanide*.—No reaction occurred between diethylamine and 2-methylprop-1-enyl cyanide even in the presence of benzyltrimethylammonium hydroxide or potassium carbonate.

N-2-*Cyanoethyl*-p-*anisidine*.—This had b. p. 136—145°/0·001 mm., m. p. and mixed m. p. 62—64°. Each of the following experiments was performed in duplicate. (*A*) *N*-2-Cyanoethylpyrrolidine (12·4 g., 1·5 mols.) and *p*-anisidinium chloride (10·65 g., 1 mol.) were refluxed at 180° for 1·5 hr. Working up by method (*b*) gave fractions (1) b. p. 84—100°/1 mm., containing 59% of recovered *p*-anisidine, and (2) *N*-2-cyanoethyl-*p*-anisidine (3 g., 26%). (*B*) *N*-2-Cyanoethylmorpholine (14 g., 1·5 mols.) by the same method afforded fractions (1) b. p. 112°/4 mm. to 120°/0·001 mm., containing 40% of recovered *p*-anisidine, and (2) *N*-2-cyanoethyl-*p*-anisidine (5·3 g., 45·5%). (*C*) *N*-2-Cyanoethyl-*N*-ethylbenzylamine (14·1 g., 1·5 mols.) by the same method

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[18] Knoevenagel, G.P. 162,181.

gave fractions (1) b. p. 96—150°/3 mm., containing 30% of *p*-anisidine, and (2) *N*-2-cyanoethyl-*p*-anisidine (4·9 g., 56%). (*D*) Morpholine (9·7 g., 1·5 mols.), vinyl cyanide (5·3 g., 1·5 mols.), and *p*-anisidinium chloride (10·65 g., 1 mol.) were refluxed at 180° for 1·5 hr. Working up by method (*b*) gave fractions: (1) b. p. 94—100°/1 mm., containing 49% of *p*-anisidine and *N*-2-cyanoethylmorpholine(4·3 g.), and (2) *N*-2-cyanoethyl-*p*-anisidine (4·35 g., 37%).

N-2-*Cyanopropyl*-p-*anisidine*.—(*A*) 1-2′-Cyanopropylpyrrolidine (15 g., 1·25 mols.) and *p*-anisidinium chloride (15 g., 1 mol.) were refluxed at 180° for 1·5 hr. Working up by method (*b*) gave fractions (1) b. p. 60°/0·5 mm. to 120°/0·001 mm., containing 80% of *p*-anisidine, and (2) b. p. 120—130°/0·001 mm., converted into the alkali-insoluble N-*benzenesulphonyl*-N-2′-*cyanopropyl*-p-*anisidine* (2·4 g., 8% yield), crystallising from benzene–light petroleum (b. p. 60—90°) as needles, m. p. 56—57° (Found: C, 61·5; H, 5·3. $C_{17}H_{18}O_3N_2S$ requires C, 61·8; H, 5·5%).

(*B*) Repetition of this experiment gave a second form of this *benzenesulphonamide*, crystallising from chloroform–light petroleum as needles, m. p. 91—92° (Found: C, 61·5; H, 5·4%).

(*C*) 1-2′-Cyanopropylpiperidine (12·7 g., 1·25 mols.) and *p*-anisidinium chloride (10·6 g., 1 mol.) were refluxed at 180° for 1·5 hr. Working up by method (*a*) gave piperidinium chloride (7·2 g., 89%), m. p. and mixed m. p. 230—232°. Distillation of the acetone filtrate gave fractions of b. p. 70—98°/0·7 mm. and b. p. 100—130°/0·001 mm.; together these contained 69% of recovered *p*-anisidine. No alkali-insoluble benzenesulphonamide was obtained.

(*D*) 2-Diethylamino-1-methylethyl cyanide (3·5 g.) and *p*-anisidinium chloride (4 g., 1 mol.) were treated as in (*A*) above. Working up gave *p*-anisidine (84%), and a residue which was converted into the alkali-insoluble benzenesulphonamide (0·85 g., 10%), m. p. 88—90°, undepressed on admixture with the product obtained as in (*B*).

N-(2-*Cyano*-1-*methylethyl*)-p-*anisidine*.—(*A*) *p*-Anisidinium chloride (10 g., 1 mol.) and 1-(2-cyano-1-methylethyl)pyrrolidine (10·2 g., 1·25 mols.) were refluxed at 180° for 1·5 hr. Working up by method (*b*) gave fractions (1) b. p. 80—100°/1 mm., containing 20% of *p*-anisidine, (2) b. p. 100—120°/0·001 mm., converted into the benzenesulphonamide [the alkali-soluble portion corresponded to a further 20% of recovered *p*-anisidine; the alkali-insoluble portion (5·5 g., 28%) crystallised from ethanol as needles of N-*benzenesulphonyl*-N-2-*cyano*-1-*methylethyl*-p-*anisidine*, m. p. 81—82° (Found: C, 61·6; H, 5·5. $C_{17}H_{18}O_3N_2S$ requires C, 61·8; H, 5·5%)], and (3) b. p. 122—125°/0·001 mm., needles, m. p. 91—92° (from ethanol), N-(2-*cyano*-1-*methylethyl*)-p-*anisidine* (1·45 g., 12·5%) (Found: C, 69·2; H, 7·4. $C_{11}H_{14}ON_2$ requires C, 69·45; H, 7·4%). (*B*) Reaction of *p*-anisidinium chloride (8 g., 1 mol.) and 2-diethylaminopropyl cyanide (7 g., 1 mol.), as described in (*A*), gave *p*-anisidine (42·5%), b. p. 80—90°/0·5 mm., and *N*-(2-cyano-1-methylethyl)-*p*-anisidine (4·8 g., 50·5%), b. p. 126—132°/0·001 mm., needles, m. p. and mixed m. p. 88—90°.

NN-*Dibenzenesulphonyl*-p-*anisidine*.—Treatment of *p*-anisidine in pyridine with excess of benzenesulphonyl chloride at 100°, and working up with ammonia, sodium hydroxide solution, dilute hydrochloric acid, and sodium hydrogen carbonate solution gave the stable NN-*dibenzenesulphonyl*-p-*anisidine*, crystallising from alcohol as plates, m. p. 139—140° (Found: C, 56·75; H, 4·25; N, 3·3; S, 16·0. $C_{19}H_{17}O_5NS_2$ requires C, 56·55; H, 4·25; N, 3·45; S, 15·9%).

1 : 2-*Dicyanoethane*.—The reactants were added to gently boiling water and refluxed for 35 min.; the cold solution was extracted with chloroform. All experiments were performed in duplicate. All samples of 1 : 2-dicyanoethane had m. p. and mixed m. p. 52—54°.

(*a*) Reaction of 2-cyanoethyldiethylmethylammonium iodide (2·7 g., 1 mol.), potassium cyanide (1·3 g., 2 mols.), and water (5 c.c.) gave 1 : 2-dicyanoethane (0·5 g., 62·5%).

(*b*) Benzyl-2-cyanoethylethylmethylammonium iodide (3·3 g., 1 mol.), potassium cyanide (1·3 g., 2 mols.), and water (5 c.c.) were treated as above. The chloroform extract was washed with 2N-hydrochloric acid. The neutral fraction gave 1 : 2-dicyanoethane (0·45 g., 56%), and the basic fraction gave *N*-ethyl-*N*-methylbenzylamine (0·85 g., 57%) [picrate, m. p. 113—114° (lit., m. p. 113°)].

(*c*) 1-2′-Cyanoethyl-1-methylpyrrolidinium iodide (5·32 g., 1 mol.), potassium cyanide (2·6 g., 2 mols.), and water (10 c.c.) gave 1 : 2-dicyanoethane (0·8 g., 50%).

(*d*) 4-2′-Cyanoethyl-4-methylmorpholinium iodide (16·9 g., 1 mol.), potassium cyanide (7·8 g., 2 mols.), and water (30 c.c.), worked up as in (*b*), gave 1 : 2-dicyanoethane (1·35 g., 28%). The basic portion (3·3 g., 54%) was 4-methylmorpholine (picrate, m. p. 225°; methiodide, m. p. 246°; lit., 225° and 246° respectively).

(*e*) 2-Hydroxyethyl cyanide (2·15 g., 1 mol.), potassium cyanide (3·9 g., 2 mols.), and water (15 c.c.) gave 1 : 2-dicyanoethane (0·15 g., 6%).

Various.—Some additional salts are recorded in Table 3.

TABLE 3. *Arylammonium benzenesulphonates.*

Benzenesulphonate	Formula	M. p.	Found (%) C	Found (%) H	Required (%) C	Required (%) H
p-*Nitroanilinium* [a, b]	$C_6H_6O_2N_2,C_6H_6O_3S$	235—236°	48·9	4·3	48·7	4·1
m-*Acetylanilinium* [a, b]	$C_8H_9ON_2,C_6H_6O_3S$	163—164	57·4	5·0	57·3	5·1
o-*Anisidinium* [d]	$C_7H_9ON,C_6H_6O_3S$	200—201	55·5	5·25	55·5	5·35
m-*Anisidinium* [c]	$C_7H_9ON,C_6H_6O_3S$ [e]	170—171	—	—	—	—
2 : 6-*Dimethylanilinium* [b]	$C_8H_{11}N,C_6H_6O_3S$ [f]	183—184	—	—	—	—
o-*Phenylenediammonium* [c]	$C_6H_8N_2,2C_6H_6O_3S$	245 *	50·65	4·65	50·9	4·7
p-*Phenylenediammonium* [c] ...	$C_6H_8N_2,2C_6H_6O_3S$	340—345 *	50·75	4·75	50·9	4·7

* With decomp. [a] Yellow. [b] From MeOH. [c] From EtOH. [d] From H_2O. [e] Found : N, 5·3. Reqd. : N, 5·0%. [f] Found : N, 4·9; S, 11·5. Reqd. : N, 5·0; S, 11·5%.

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