295. *Studies on Hydrogen Cyanide. Part X. The Tetrapolymer.*

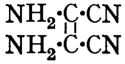
By L. E. Hinkel, G. O. Richards, and O. Thomas.

The previous evidence for the structure of the polymerised form of hydrogen cyanide is reviewed and further evidence is adduced for its quadrimolecular nature. The view that the polymer is diaminomaleic dinitrile is shown to be incorrect, and experiments now described indicate it to be aminoiminosuccinonitrile.

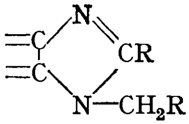
Lange (*Ber.*, 1873, **6**, 99) obtained a white crystalline compound from the black solid resulting from the polymerisation of liquid hydrogen cyanide. Since this compound yielded aminoacetic acid on hydrolysis, he considered it to be a tripolymer having the structure of aminomalononitrile. This structure was supported by later workers (Wippermann, *Ber.*, 1874, **7**, 167; Lescoeur and Rigaut, *Compt. rend.*, 1879, **69**, 310; Bamberger and Rudolf, *Ber.*, 1902, **35**, 1682). In order to confirm the structure of the polymer, Grischkevitsch-Trochimovski (*Rocz. Chem.*, 1921, **1**, 468; J., 1923, 1424) condensed it with benzaldehyde and claimed to have obtained a derivative of the type $\mathrm{R{\cdot}CH{:}N{\cdot}CH(CN)_2}$, without, however, confirming this result by analysis. Bedel (*Compt. rend.*, 1923, **176**, 168) in attempting to determine the molecular weight of the polymer ebullioscopically obtained values indicating it to be a tetrameride. He studied the hydrolysis of the polymer with dilute acids and alkalis, and found that, although its aqueous solution did not contain any free hydrogen cyanide, the addition of mineral acids eliminated one molecule of hydrogen cyanide. With alkali, only 3 instead of 4 mols. of ammonia were evolved, aminoacetic, oxalic, and carbonic acids being formed. He concluded from these results that the polymer was the hydrocyanide of aminomalononitrile. This and subsequent work are not mentioned by Taylor and Baker (Sidgwick's "Organic Chemistry of Nitrogen," 1937, 307), who still regard the polymer as aminomalononitrile.

The formation of oxalic and carbonic acids as hydrolytic products was a serious obstacle to this view. Bedel suggested that the oxalate was produced by the prolonged interaction between the formate and carbonate first produced during the hydrolysis. This view is, however, untenable since aqueous solutions of formates and carbonates do not react in this manner, and furthermore, it has since been found that the formation of oxalate is immediate, and the amount produced is not increased by prolonged boiling. Grischkevitsch-Trochimovski later (*Rocz. Chem.*, 1928, **8**, 165) assumed the compound to be a tetrameride, without explaining the discrepancies in his former paper, and claimed to have obtained dicyanopyrazine from its condensation with glyoxal. From this result he considered that the polymer must be diaminomaleinitrile (I), his claim, however, resting on the m. p. of the dicarboxylic acid obtained by the hydrolysis of the dicyanopyrazine; but the constitution of the acid was not proved. He also suggested the following scheme for the hydrolysis of the polymer :

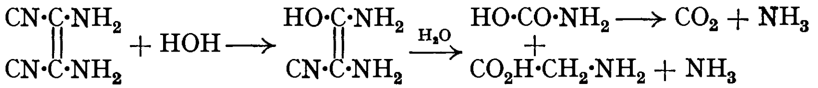
(I.)



$$\begin{array}{l}\mathrm{NH_2{\cdot}C{\cdot}CN}\\ \quad\;\|\\ \mathrm{NH_2{\cdot}C{\cdot}CN}\end{array}$$



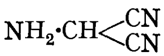
(II.)



$$\begin{array}{l}\mathrm{CN{\cdot}C{\cdot}NH_2}\\ \quad\;\|\\ \mathrm{CN{\cdot}C{\cdot}NH_2}\end{array} + \mathrm{HOH} \longrightarrow \begin{array}{l}\mathrm{HO{\cdot}C{\cdot}NH_2}\\ \quad\;\|\\ \mathrm{CN{\cdot}C{\cdot}NH_2}\end{array} \xrightarrow{\mathrm{H_2O}} \begin{array}{l}\mathrm{HO{\cdot}CO{\cdot}NH_2} \longrightarrow \mathrm{CO_2} + \mathrm{NH_3}\\ \qquad +\\ \mathrm{CO_2H{\cdot}CH_2{\cdot}NH_2} + \mathrm{NH_3}\end{array}$$

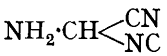
In this scheme Grischkevitsch-Trochimovski considers the double bond as the initial point of attack, which is contrary to the general behaviour of methyl-, amino-, and hydroxy-maleic acids, all of which are stable to boiling alkalis; furthermore, he overlooks the formation of oxalic acid. Another serious objection to the diamino-structure for the polymer lies in its behaviour with aldehydes. It has been shown (Ladenburg, *Ber.*, 1878, **11**, 590, 1648; Weil and Marcinkowska, *Rocz. Chem.*, 1934, **14**, 1312) that *o*-diamines react with two molecules of an aldehyde forming a heterocyclic product (II), yet according to Grischkevitsch-Trochimovski (*loc. cit.*) the polymer gives rise to an open-chain derivative of a tripolymer.

Although the mechanism of the polymerisation of hydrogen cyanide is not yet fully understood, it would appear to proceed in stages through the final addition of a hydrogen cyanide molecule to an intermediate tripolymer which can be either (III) or (IV) (cf. Wippermann, *loc. cit.*). The tetrapolymer could therefore have the structure (V) or (VI).



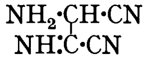
$$\mathrm{NH_2{\cdot}CH}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}$$

(III.)



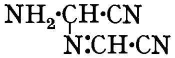
$$\mathrm{NH_2{\cdot}CH}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{NC}\end{smallmatrix}$$

(IV.)



$$\begin{array}{l}\mathrm{NH_2{\cdot}CH{\cdot}CN}\\ \quad\;\;|\\ \mathrm{NH{:}C{\cdot}CN}\end{array}$$

(V.)



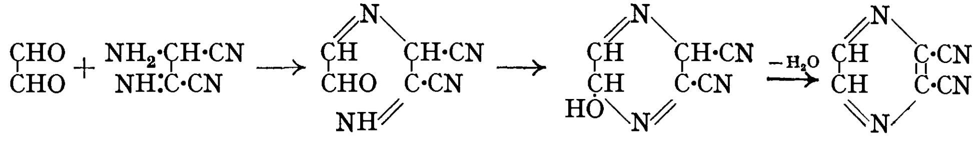
$$\begin{array}{l}\mathrm{NH_2{\cdot}CH{\cdot}CN}\\ \qquad\;|\\ \qquad\mathrm{N{:}CH{\cdot}CN}\end{array}$$

(VI.)

The diaminomaleinitrile structure (I) cannot be considered as a possibility in this connection since it necessitates the migration of a hydrogen atom during the addition of the last molecule of hydrogen cyanide, and there seems no valid reason for this supposition, nor is there any evidence that the polymer acts tautomerically.

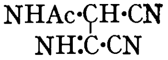
Although the aminoiminosuccinonitrile (V) formula seemed the more probable, that represented by (VI), which contains the N·C·N·C— chain, could not be disregarded since it has been shown (Hinkel and Dunn, J., 1930, 1834) that when hydrogen chloride reacts with hydrogen cyanide, a compound is formed which also possesses the alternating carbon and nitrogen structure. Differentiation between these two structures should be readily achieved from a study of the condensation of the polymer with glyoxal, since a structure represented by (V) should give rise to a pyrazine derivative whereas the compound (VI) containing the N·C·N·C— chain could only give rise to pyrimidine derivatives.

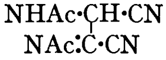
The properties of the dicarboxylic acids of pyrazine and pyrimidine are similar in many respects, and the m. p. upon which Grischkevitsch-Trochimovski relied is not sufficient evidence to decide between the two constitutions, especially as pyrimidine-2 : 4-dicarboxylic acid, which could result from (VI), is not known. The condensation of the polymer with glyoxal has therefore been re-investigated. Glyoxal in aqueous or alcoholic solution condenses readily with the polymer at ordinary temperatures to an orange-coloured product, $C_6H_4ON_4$ (Grischkevitsch-Trochimovski could not have employed pure polymer since he obtained a dark mass which he did not analyse). The primary reaction may be regarded as condensation of the amino-group with one aldehyde group, followed by ring formation, the first product being probably *6-hydroxy-2 : 3-dicyanodihydropyrazine* (VIII). This compound cannot be the open-chain compound (VII) with a free aldehyde group, since it does not react with phenylhydrazine. It can, however, be readily converted into a compound identical with the cyanopyrazine described by Grischkevitsch-Trochimovski, which has now been definitely characterised as 2 : 3-dicyanopyrazine by conversion into the corresponding dicarboxylic acid and into the parent base through its mercuric chloride salt. All these derivatives have been identified through authentic specimens prepared from quinoxaline (Gabriel and Sohn, *Ber.*, 1907, **40**, 4850). These results, which definitely dispose of the possible structure (VI), give strong support for the aminoiminosuccinonitrile structure (V) for the polymer, and this structure has been confirmed by a further study of the properties and reactions. The polymer unites with only one molecule of hydrogen chloride, a reaction which affords evidence, not only that the polymer is a tetrameride, but also that it does not possess two amino-groups, since all aliphatic diamines are strongly dibasic and yield dihydrochlorides. Moreover, the polymer readily condenses with one molecule of monoaldehydes, yielding open-chain *compounds* of the type $R\cdot CH:N_4C_4H_2$, contrary to Grischkevitsch-Trochimovski's observations (*loc. cit.*). In no circumstances has it been found possible to obtain a heterocyclic product characteristic of *o*-diamines (Ladenburg, *loc. cit.*).

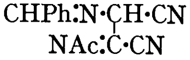


(VII.) (VIII.) (IX.)

With acetic anhydride the polymer first yields a *monoacetyl* derivative (X), which on more vigorous acetylation is converted into a *diacetyl* derivative (XI). In this reaction also, no evidence has been found for the formation of heterocyclic ring compounds characteristic of *o*-diamines (cf. Hübner, *Annalen*, 1881, **208**, 278).

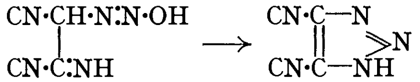

$$\begin{array}{l} NHAc\cdot CH\cdot CN \\ \quad NH:C\cdot CN \end{array}$$
(X.)


$$\begin{array}{l} NHAc\cdot CH\cdot CN \\ \quad NAc:C\cdot CN \end{array}$$
(XI.)


$$\begin{array}{l} CHPh:N\cdot CH\cdot CN \\ \qquad NAc:C\cdot CN \end{array}$$
(XII.)

Although the *benzylidene* derivative does not unite with a second molecule of benzaldehyde, yet on vigorous acetylation it yields an *acetyl* derivative (XII). The polymer condenses readily with *o*-diketones such as diacetyl and benzil, yielding *2 : 3-dicyano-5 : 6-dimethyl-* and *-diphenyl-pyrazine* respectively. In these two cases in which ring formation is possible, the pyrazine derivatives are formed without the intermediate stage (compare glyoxal). The constitution of the former compound was established by hydrolysis to dimethylpyrazinedicarboxylic acid (Gabriel and Sohn, *loc. cit.*).

It has been shown (Grischkevitsch-Trochimovski, *Rocz. Chem.*, 1921, **1**, 469) that the polymer readily reacts with nitrous acid, yielding a triazole in the manner of *o*-diamines (cf. Ladenburg, *loc. cit.*). The formation of a triazole can be equally well explained on the aminoiminosuccinonitrile structure, diazotisation of the amino-group being followed by ring closure (XIII) :

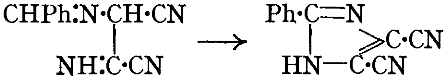


(XIII.)

The constitution of the triazole has been established by hydrolysis into 1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (Bladin, *Ber.*, 1893, **26**, 545, 2737).

Grischkevitsch-Trochimovski (*J. Soc. Phys. Chim. Russ. Univ. Leningrad*, 1924, **55**, 548) and Fialkoff (*Bull. Soc. chim.*, 1927, **41**, 1209) claim to have obtained a yellow and a colourless variety of the dicyanotriazole possessing different crystallographic forms, and different electrical conductivities in aqueous solution. We have found that when the pure colourless polymer is diazotised under diverse conditions only one variety of the triazole is obtained, which is colourless; when, however, a slightly coloured specimen of the polymer was employed, a coloured triazole was obtained, from which the colour could not entirely be removed by crystallisation. We are forced to conclude that both the above authors employed impure polymer in their investigations.

Conclusive evidence for the existence of only one amino-group in the polymer is furnished through the benzylidene derivative. This compound is unaffected by nitrous acid, but with nitrous fumes it is readily oxidised with ring closure into 4 : 5-*dicyano*-2-*phenyliminazole* (XIV), the constitution of which was determined by hydrolysis into the corresponding dicarboxylic acid and subsequent decarboxylation to 2-phenyliminazole (Maquenne, *Compt. rend.*, 1890, **111**, 742; *Ann. Chim.*, 1891, **24**, 542).



(XIV.)

In marked contrast to the benzylidene derivative, the monoacetyl compound readily reacts with nitrous acid, yielding a mixture of dicyanotriazole and 4(or 5)*cyano*-1 : 2 : 3-*triazole*-5(or 4)-*carboxyamide*, both of these compounds being identified by hydrolysis into 1 : 2 : 3-triazole-4 : 5-dicarboxylic acid. In this reaction the mineral acid employed eliminates the acetyl group, and the liberated polymer then reacts with the nitrous acid with the formation of the triazole ring. During this reaction partial hydrolysis of a cyano-group is induced by the liberated acetic acid in conjunction with the hydrochloric acid, since the polymer does not yield any cyano-amide when diazotised under the same conditions.

EXPERIMENTAL.

The black product resulting from the polymerisation of dry liquid hydrogen cyanide with either ammonium or potassium cyanide was repeatedly extracted with ether. The crude, dark solid so obtained was purified from boiling water after decolorisation with animal charcoal. After repeated recrystallisation from water, the polymer was obtained as colourless needles, m. p. 181° (decomp.).

6-*Hydroxy*-2 : 3-*dicyanodihydropyrazine*.—Glyoxal (1·2 g.; 1 mol.), dissolved in warm water (20 c.c.), was added to the polymer (2 g.; 1 mol.) dissolved in hot water (50 c.c.), and the mixture gently warmed on the water-bath for 5 minutes; a red powder separated, which was purified by means of alcohol, separating as a red amorphous powder, decomposing at 240° without melting (Found: C, 48·5; H, 3·0; N, 37·2. $C_6H_4ON_4$ requires C, 48·7; H, 2·7; N, 37·7%). The *substance* is very slowly decomposed by boiling water, but readily dissolves in boiling water containing a little oxalic acid to a yellow solution from which, on cooling, dicyanopyrazine separates as colourless needles, m. p. 132° (Found: C, 55·7; H, 1·5; N, 42·8. Calc.: C, 55·4; H, 1·3; N, 43·0%).

Hydrolysis of Dicyanopyrazine.—The finely powdered dicyanopyrazine (0·5 g.) was suspended in water (50 c.c.), and sodium peroxide (9 g.) slowly added with shaking until complete solution was obtained. After being heated on a water-bath for 2 hours, the mixture was acidified with nitric acid, and excess of silver nitrate added. The collected silver salt was decomposed with slight excess of hydrochloric acid, and the filtrate from the silver chloride evaporated to dryness under reduced pressure. The dark mass was dissolved in water, and the solution decolorised (charcoal) and concentrated; pyrazinedicarboxylic acid crystallised in colourless plates, m. p. 182—184° (decomp.), unchanged by admixture with an authentic specimen; the anhydrous acid melted at 193° (Gabriel and Sohn, *loc. cit.*, give for hydrated acid m. p. 186°, for anhydrous acid m. p. 193°).

Isolation of Base.—The above acid was decarboxylated with acetic anhydride, according to Gabriel and Sohn (*loc. cit.*). The resulting liquid, after being made alkaline with sodium hydroxide, was distilled into an aqueous solution of mercuric chloride. The resulting white mercurichloride of the base, after being washed with alcohol and ether, melted at 272° (cf. Stoehr, *J. pr. Chem.*, 1895, **51**, 457), unchanged by admixture with an authentic specimen prepared according to Gabriel and Sohn. The mercuric salt (2 g.) was added to saturated solution of sodium sulphide (4 c.c.), and the mixture distilled. The distillate (2 c.c.) was cooled in ice and salt, and solid sodium hydroxide added to precipitate the free base, which was then extracted with the minimum amount of ether. From the dried ethereal solution the base was obtained by rapid evaporation of the ether on a water-bath; the cooled residue solidified, m. p. 52°, unchanged when admixed with an authentic specimen of pyrazine prepared from quinoxaline according to Gabriel and Sohn (*loc. cit.*).

Aminoiminosuccinonitrile Hydrochloride.—The powdered polymer was dissolved in dry ether, and the solution saturated with dry hydrogen chloride. The white *hydrochloride* which was deposited was washed with ether and dried in a vacuum over sulphuric acid; decomp. 135° (Found : C, 33·15; H, 3·5; N, 38·1; Cl, 24·5. $C_4H_4N_4,HCl$ requires C, 33·3; H, 3·4; N, 38·8; Cl, 24·5%).

Compounds of Aminoiminosuccinonitrile with Aldehydes.—Molecular proportions of the polymer and the aldehydes in alcohol were heated under reflux for 30 minutes. The condensation products crystallised on cooling, and were purified by crystallisation from alcohol. *Benzylideneaminoiminosuccinonitrile*, yellow needles, m. p. 191° (decomp.) (Found : C, 67·1; H, 4·1; N, 28·5. $C_{11}H_8N_4$ requires C, 67·3; H, 4·1; N, 28·6%). *Salicylideneaminoiminosuccinonitrile*, yellow needles with a greenish tinge, m. p. 234° (decomp.) (Found : N, 26·7. $C_{11}H_8N_4$ requires N, 26·4%). m-*Bromosalicylideneaminoiminosuccinonitrile*, yellow needles, m. p. above 250° (Found : N, 28·5; Br, 27·5. $C_{11}H_7ON_4Br$ requires N, 28·6; Br, 27·5%). *Anisylideneaminoiminosuccinonitrile*, yellow needles, m. p. 227° (decomp.) (Found : N, 24·9. $C_{12}H_{10}ON_4$ requires N, 24·8%). iso*Butylideneaminoiminosuccinonitrile*, colourless laminæ, m. p. 91° (decomp.) (Found : C, 58·1; H, 6·15. $C_8H_{10}N_4$ requires C, 58·4; H, 6·17%). In none of the above condensations was it possible to cause reaction with a second molecule of aldehyde.

Acetamidoiminosuccinonitrile.—The polymer (1 g.) was gently warmed with acetic anhydride (2 c.c.), in which it dissolved. On cooling, crystals slowly separated (1·4 g.) which, after being decolorised with charcoal, crystallised from alcohol in colourless needles, m. p. 164° (decomp.) (Found : C, 47·8; H, 3·9; N, 36·6. $C_6H_6ON_4$ requires C, 48·0; H, 4·0; N, 37·3%).

Acetamidoacetimidosuccinonitrile.—The polymer (1 g.) and acetic anhydride (5 c.c.) were heated on a water-bath for 30 minutes. The excess of anhydride was removed at 100° under reduced pressure. The product (1·8 g.), after being decolorised, crystallised from alcohol in colourless needles, m. p. 224° (decomp.) (Found : C, 50·0; H, 4·2; N, 30·0. $C_8H_8O_2N_4$ requires C, 50·0; H, 4·2; N, 29·2%).

Benzylideneaminoacetimidosuccinonitrile.—A mixture of the benzylidene derivative of the polymer (2 g.) and acetic anhydride (10 c.c.) was heated to boiling for 45 minutes, and the excess of anhydride removed under reduced pressure. The residue (1·8 g.), after being decolorised, separated from alcohol as a colourless crystalline powder, m. p. 227° (decomp.) (Found : C, 65·9; H, 4·37; N, 23·6. $C_{13}H_{10}ON_4$ requires C, 65·55; H, 4·2; N, 23·5%).

2 : 3-*Dicyano*-5 : 6-*dimethylpyrazine.*—Molecular proportions of diacetyl and of the polymer in alcohol were heated for 2 hours on a water-bath. The solid which separated crystallised from alcohol–acetone and yielded 2 : 3-*dicyano*-5 : 6-*dimethylpyrazine* in large white laminæ, m. p. 171° (Found : C, 60·5; H, 3·8. $C_8H_6N_4$ requires C, 60·7; H, 3·8%).

2 : 3-*Dicyano*-5 : 6-*diphenylpyrazine.*—The condensation of benzil with the poylmer was carried out as above. The product, crystallised from alcohol–benzene, gave 2 : 3-*dicyano*-5 : 6-

diphenylpyrazine as colourless prisms, m. p. 246° (Found : C, 76·3; H, 3·6; N, 19·5. $C_{18}H_{10}N_4$ requires C, 76·6; H, 3·5; N, 19·9%).

Hydrolysis of 2 : 3-*Dicyano*-5 : 6-*dimethylpyrazine*.—The powdered substance (12 g.) was suspended in water (120 c.c.), and sodium peroxide (24 g.) gradually added with shaking until complete solution was effected. The mixture was then heated on a water-bath for 3 hours until evolution of ammonia ceased; it was then acidified with glacial acetic acid and concentrated to 50 c.c. Addition of barium chloride precipitated the barium salt, which was washed and dried; the powdered salt (20 g.) was made into a paste with water (45 c.c.), and sulphuric acid monohydrate (6 g.) added, the mixture being heated on a water-bath for 1 hour. The filtered solution was evaporated to dryness under reduced pressure. The residue (9 g.) crystallised from hot water, yielding 2 : 3-dimethylpyrazine-5 : 6-dicarboxylic acid in colourless needles, m. p. (anhydrous acid) 200° (Found : C, 48·0; H, 4·2. Calc. : C, 48·9; H, 4·1%).

Action of Nitrous Acid on Aminoiminosuccinonitrile.—Pure colourless polymer (2·16 g.) was suspended in water (50 c.c.), in which sodium nitrite (1·38 g.) was dissolved, and cooled in ice; 4*N*-hydrochloric acid (5 c.c.) was then gradually added with stirring. The polymer readily dissolved, and the reaction was completed by warming on a water-bath. The cooled solution was extracted with ether. Removal of the ether yielded 4 : 5-dicyano-1 : 2 : 3-triazole entirely devoid of any yellow tinge; it crystallised from alcohol in transparent prisms, m. p. 145°.

Hydrolysis of 4 : 5 *Dicyano*-1 : 2 : 3-*triazole*.—The powdered triazole (2 g.) was suspended in water (100 c.c.), and sodium peroxide added in small quantities until the precipitate first formed redissolved. The mixture was then heated on a water-bath until evolution of ammonia had ceased (1 hour), acidified with hydrochloric acid, and well cooled (ice–salt). The white precipitate so obtained (2·39 g.) was crystallised from dilute hydrochloric acid and finally from hot water. 1 : 2 : 3-Triazole-4 : 5-dicarboxylic acid crystallised in colourless laminæ, m. p. 200° (decomp.), unchanged by admixture with an authentic specimen prepared by oxidation of aziminobenzene (Bladin, *loc. cit.*).

Action of Nitrous Acid on Acetamidoiminosuccinonitrile.—A solution of sodium nitrite (1 g.) in water (5 c.c.) was slowly added to a suspension of finely powdered acetamidoiminosuccinonitrile (4 g.) in water (20 c.c.) and 4*N*-hydrochloric acid (4 c.c.). The solution was kept stirred, and warmed to 40° to complete the reaction. The solution was cooled to 0°, and the white solid filtered off (filtrate A). Crystallisation from alcohol yielded 4(or 5)-*cyano*-1 : 2 : 3-*triazole*-5(or 4)-*carboxyamide* in colourless needles, m. p. 219° (decomp.) (Found : C, 34·7; H, 2·26; N, 50·8. $C_4H_3ON_5$ requires C, 35·4; H, 2·2; N, 51·0%); this is strongly acid in solution, being soluble in alkali and reprecipitated by acids; hydrolysis with sodium peroxide as above yields 1 : 2 : 3-triazole-4 : 5-dicarboxylic acid.

The filtrate A was extracted with ether, the extract dried (sodium sulphate), and the ether removed, yielding 4 : 5-dicyano-1 : 2 : 3-triazole (1·6 g.), m. p. 145°, unchanged by admixture with the compound prepared as above.

Oxidation of Benzylideneaminoiminosuccinonitrile.—Nitrous fumes were led into a solution of the nitrile (2 g.) in ether (200 c.c.) until a yellow solid separated; the filtrate from the solid on concentration gave a further yield (total 1·8 g.). The solid was crystallised from alcohol, and 4 : 5-*dicyano*-2-*phenyliminazole* separated as minute, cream-coloured needles, m. p. 261° (decomp.) (Found : C, 68·3; H, 3·0; N, 28·55. $C_{11}H_6N_4$ requires C, 68·05; H, 3·1; N, 28·3%).

Hydrolysis of 4 : 5-*Dicyano*-2-*phenyliminazole*.—The iminazole (7 g.) was added to caustic soda (7 g.) in alcohol (40 c.c.) and heated under reflux for 1 hour. After removal of the alcohol, the residue was dissolved in water, and 2-phenyliminazole-4 : 5-dicarboxylic acid (7·2 g.) precipitated with hydrochloric acid. It was purified by dissolution in alkali and reprecipitation with acid; m. p. 243—244° (Maquenne, *loc. cit.*, does not record m. p.). Dry distillation of the acid under reduced pressure yielded phenyliminazole as a colourless liquid, which solidified to white crystals, m. p. 147—148° (compare Maquenne, *loc. cit.*).

The authors' thanks are due to the Chemical Society for a grant, and to Imperial Chemical Industries, Ltd., for a grant and gifts of chemicals.

UNIVERSITY COLLEGE, SWANSEA.

[*Received, June 18th*, 1937.]