

752. *The Ehrlich-Sachs Reaction. Part II.*¹

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Although normally one molecule of the nitroso-compound reacts with one molecule of the methylene compound it is now shown that other modes of reaction are possible.

The products of reaction of nitrosobenzene with malononitrile and with nitromethane are identified.

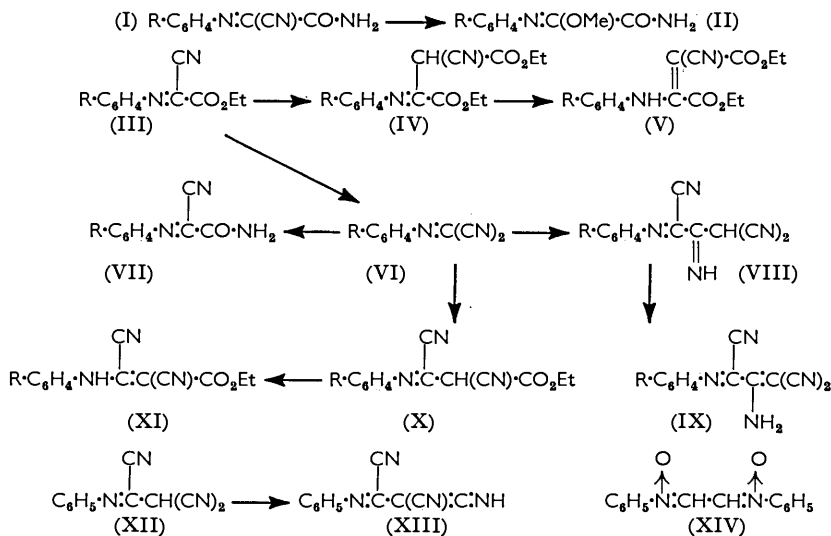
The infrared spectra of these compounds are outlined.

IN Part I it was shown that the primary product (I) of the interaction of an aromatic nitroso-compound, such as *NN*-dimethyl-*p*-nitrosoaniline, with cyanoacetamide was liable to react with the alcohol used as solvent to give, by elimination of hydrocyanic acid, an alkoxyacetamide (II). It is now found that the α -substituted cyanoacetic ester (III), produced initially from interaction of an aromatic nitroso-compound with a cyanoacetic ester, is liable to interact with another molecule of the ester to give a cyano-diester (IV) or, as indicated by the infrared spectra, more probably (V). This reaction goes so readily with *NN*-diethyl-*p*-nitrosoaniline that it has not been possible to isolate an intermediate of type (III). In other examples the intermediate (III) is the preferred product but a slow further condensation can be brought about in warm alcohol in the presence of potassium carbonate.

¹ Part I, *J.*, 1957, 516.

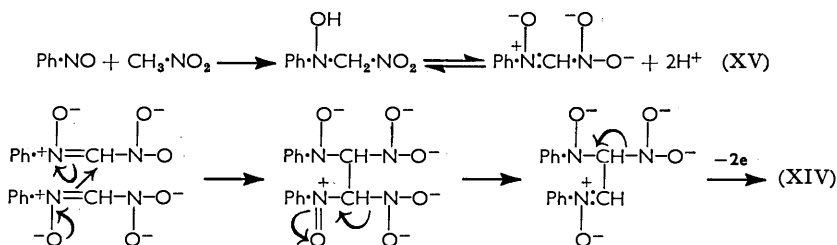
From the interaction of *NN*-dimethyl-*p*-nitrosoaniline and ethyl cyanoacetate compounds (III; R = NMe₂) and (IV or V; R = NMe₂) have been isolated and, rather unexpectedly, *N*-dicyanomethylene- (VI; R = NMe₂) and *N*-carbamoylcyanomethylene-*N'**N'*-dimethyl-*p*-phenylenediamine (VII; R = NMe₂). Similarly the dicyano-compound (VI; R = NEt₂) was isolated from interaction of *NN*-diethyl-*p*-nitrosoaniline and ethyl cyanoacetate.

When compounds (VI) are prepared from the appropriate nitroso-compound and malononitrile they are accompanied by traces of dark-blue compounds (IX), probably



produced *via* (VIII). They are readily prepared by the interaction of the dicyano-compounds (VI) and malononitrile or of the nitroso-compound and malononitrile dimer (2-amino-1,1,3-tricyanopropene)² in the presence of potassium carbonate. On the other hand, the dicyanomethylene compounds (VI) react with cyanoacetates to yield dicyanoesters (X) or (XI). These are analogous to (XII) or (XIII), a strongly acidic compound obtained by the interaction of nitrosobenzene with malononitrile.

Nitrosobenzene with nitromethane gives a bright yellow compound (XIV). The authors are indebted to one of the referees for the suggestion that it is formed from the primary product of condensation (XV) by a dimerisation somewhat akin to those described by Bamberger³ and by Hellmann and Teichmann.⁴



² Carboni, Coffman, and Howard, *J. Amer. Chem. Soc.*, 1958, **80**, 2838.

³ Bamberger, *Ber.*, 1900, **33**, 941.

⁴ Hellmann and Teichmann, *Chem. Ber.*, 1956, **89**, 1134.

The structure was confirmed by synthesis from glyoxal and phenylhydroxylamine; it is comparable with *N*-cinnamylideneaniline *N*-oxide, which was prepared by the interaction of cinnamaldehyde with phenylhydroxylamine.⁵

EXPERIMENTAL

The infrared spectra were determined in Nujol and hexachlorobutadiene mulls on a Hilger H 800 spectrophotometer fitted with sodium chloride and lithium fluoride prisms. Results are recorded in cm.⁻¹.

Ehrlich-Sachs Amides.—*N*-Carbamoylcyanomethylene-*N'**N'*-di-*n*-propyl-*p*-phenylenediamine, produced by the interaction of *p*-nitroso-*NN*-di-*n*-propylaniline with cyanoacetamide in presence of potassium carbonate, crystallised from ethanol in fine, red needles, m. p. 148—151° (Found: C, 65.8; H, 6.9. C₁₅H₂₀ON₄ requires C, 66.2; H, 7.3%).

Infrared spectra of 4,2,1-R₂N·C₆H₃R'·N:C(CN)·CO·NH₂.

R	R'	NH ₂	-C:N	CO	>C:N-	
Et	H	3430, 3180	2210	1687 (s)	1618	1505
Me	H	3440, 3200	2220	1690 (s)	1625	1550, 1520
Me	Me	3440, 3160	2200	1682 (s)	1615	1593, 1520
Et	Me	3440, 3150	2200	1681 (s)	1615	1593, 1500
Pr ⁿ	H	3360, 3190	2200	1714 (w), 1657 (s)	1615	1542, 1525

Ehrlich-Sachs Esters.—(a) *From tertiary bases*. *N*-(α -Cyano- α -ethoxycarbonylmethylene)-*N'*,*N'*,2-trimethyl-*p*-phenylenediamine, from *N,N*,3-trimethyl-4-nitrosoaniline and ethyl cyanoacetate in ethanol (K₂CO₃), formed red needles, m. p. 118° (Found: C, 64.7; H, 6.2. C₁₄H₁₇O₂N₃ requires C, 64.8; H, 6.6%).

Infrared spectra of 4,2,1-R₂N·C₆H₃R'·N:C(CN)·CO₂R''.

R	R'	R''	-C:N	CO	>C:N-	
Pr ⁿ	H	Me	2195	1737(s)	1615	1530
Me	H	Et	2200	1740(s)	1618	1530
Me	Me	Et	2205	1705(s)	1622	1520
Me	Me	Me	2200	1705(s)	1617	1520
Me	H	Me	2220	1708(s)	1625	1540, 1515
Et	Me	Me	2200	1755(w), 1693(s)	1615	1515
Et	Me	Et	2200	1694(s)	1615	1515

(b) *From secondary bases*. *N*-(α -Cyano- α -methoxycarbonylmethylene)-*N'*-ethyl-*p*-phenylenediamine, from *N*-ethyl-*p*-nitrosoaniline and methyl cyanoacetate in methanol (K₂CO₃), formed red needles, m. p. 157°, from ethanol (Found: C, 62.3; H, 5.2. C₁₂H₁₃O₂N₃ requires C, 62.4; H, 5.6%). *N*-(α -Cyano- α -ethoxycarbonylmethylene)-*N'*-ethyl-*p*-phenylenediamine, from *N*-ethyl-*p*-nitrosoaniline and ethyl cyanoacetate in ethanol (K₂CO₃), formed orange needles, m. p. 106—107°, after elution from alumina by ethyl acetate and subsequent recrystallisation from benzene (Found: C, 63.9; H, 5.5. C₁₃H₁₅O₂N₃ requires C, 63.7; H, 6.1%). *N*-(α -Cyano- α -methoxycarbonylmethylene)-*N'*-methyl-*p*-phenylenediamine, from *N*-methyl-*p*-nitrosoaniline and methyl cyanoacetate in methanol (K₂CO₃), crystallised from benzene in orange needles, m. p. 170° (Found: C, 61.6; H, 5.1. C₁₁H₁₁O₂N₃ requires C, 60.8; H, 5.1%). The mother-liquor deposited dark blue prisms of an *isomer*, m. p. 168° (Found: C, 60.9; H, 4.9%), which was slowly transformed into the orange compound by boiling chloroform or benzene. *N*-(α -Cyano- α -ethoxycarbonylmethylene)-*N'*-methyl-*p*-phenylenediamine, from *N*-methyl-*p*-nitrosoaniline and ethyl cyanoacetate (K₂CO₃), crystallised from ethanol in purple prisms, m. p. 136°, in agreement with Sachs and Bry.⁶

Ehrlich-Sachs Dinitriles.—*N*-Dicyanomethylene-*N'**N'*-diethyl-, m. p. 114°, and *N*-dicyanomethylene-*N'**N'*-dimethyl-*p*-phenyldiamine, m. p. 167°, were prepared by Sachs's method.⁷

⁵ Bamberger and Weitnauer, *Ber.*, 1922, **55**, 3381.

⁶ Sachs and Bry, *Ber.*, 1901, **34**, 120.

⁷ Sachs, *Ber.*, 1900, **33**, 964.

Infrared spectra of $\text{RNH}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}(\text{CN})\cdot\text{CO}_2\text{R}'$.

R	R'	NH	-C \equiv N	CO	>C:N-	
Et	Et	3400	2220	1750(s)	1625	1535
Et	Me	3350	2210	1731(s)	1628	1544
Me	Et	3330	2215	1741(s)	1627	1548
Me	Me (yellow)	3410	2210	1713(s)	1630	1552, 1508
Me	Me (blue)	3410	2215	1733(m), 1706(m)	1622	1580, 1544

N-Dicyanomethylene-N'-ethyl-N'-methyl-p-phenylenediamine was obtained by boiling an ethanolic solution of *N*-ethyl-*N*-methyl-*p*-nitrosoaniline (2.4 g.) and malononitrile (1.2 g.) for $\frac{3}{4}$ hr. On cooling, the solution deposited dark-violet crystals, which contained a small amount of an intensely blue compound, sparingly soluble in ethyl acetate. This impurity was removed completely on alumina, yielding red needles, m. p. 128° (Found: C, 67.9; H, 5.6. $\text{C}_{12}\text{H}_{12}\text{N}_4$ requires C, 67.9; H, 5.7%).

N-Dicyanomethylene-N'-N'-diethyl-2-methyl-p-phenylenediamine. An ethanolic solution of *NN*-diethyl-3-methyl-4-nitrosoaniline and malononitrile was boiled for $\frac{3}{4}$ hr. and filtered from a small deposit of dark-blue needles, m. p. ca. 200° (decomp.). The filtrate deposited material, an ethyl acetate solution of which was passed through alumina. The *dicyanide* recovered from the first fraction formed prisms, m. p. 130°, from ethanol (Found: C, 70.0; H, 6.5. $\text{C}_{14}\text{H}_{16}\text{N}_4$ requires C, 70.0; H, 6.7%).

N-Dicyanomethylene-N',N',2-trimethyl-p-phenylenediamine. *N,N,3*-Trimethyl-4-nitrosoaniline was heated with malononitrile in ethanol; after $\frac{3}{4}$ hr. the crystals were filtered off and recrystallised from ethyl acetate, yielding purple needles, m. p. 208° (Found: C, 68.2; H, 5.5. $\text{C}_{12}\text{H}_{12}\text{N}_4$ requires C, 67.9; H, 5.7%). More of this *dicyanide*, in a slightly less pure condition, was obtained from the ethanolic filtrate.

Infrared spectra of $4,2,1\text{-RR}'\text{N}\cdot\text{C}_6\text{H}_3\text{R}''\cdot\text{N}:\text{C}(\text{CN})_2$.

R	R'	R''	-C \equiv N	>C:N-	
Me	Me	H	2226, 2212	1625	1540
Me	Et	H	2206, shoulder 2203	1615	1530
Et	Et	Me	2212, 2208	1616	1522
Me	Me	Me	2205, 2202	1620	1520
Et	Et	H	2204 (1 peak only)	1615	1530

Condensations involving 2 Mols. of Ester.—*N*-(2-Cyano-1,2-dimethoxycarbonylvinyl)-*N'N'*-diethyl-*p*-phenylenediamine. Freshly heated potassium carbonate (3 g.) was added to a mixture of *NN*-diethyl-*p*-nitrosoaniline (2.5 g.) and methyl cyanoacetate (2 c.c.) in methanol (15 c.c.). After 1 hr. water was stirred in and the black oil separated by decantation. The oil was dissolved in warm ethanol and the crystals which separated on cooling were purified by repeated crystallisation from ethanol or ethyl acetate, yielding the *ciano-ester* as yellow prisms, m. p. 152° (Found: C, 61.7; H, 6.3; N, 12.6; O, 19.3. $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}_3$ requires C, 61.7; H, 6.3; N, 12.7; O, 19.3%). It was readily soluble in warm, dilute sodium hydroxide from which it was reprecipitated by acetic acid; it could be recovered after solution in boiling acetic anhydride or cold concentrated hydrochloric acid.

By the same method the following *p*-phenylenediamines were obtained in small yield: *N*-(2-Cyano-1,2-diethoxycarbonylvinyl)-*N'N'*-diethyl-, as yellow prisms, m. p. 126° (Found: C, 64.0; H, 7.2; N, 11.7; O, 17.4. $\text{C}_{16}\text{H}_{25}\text{O}_4\text{N}_3$ requires C, 63.5; H, 7.0; N, 11.7; O, 17.8%), from *NN*-diethyl-*p*-nitrosoaniline and ethyl cyanoacetate. *N*-(2-Cyano-1,2-dimethoxycarbonylvinyl)-*N'N'*-dimethyl-, as yellow prisms, m. p. 122° (Found: C, 59.5; H, 5.6; N, 13.8. $\text{C}_{15}\text{H}_{17}\text{O}_4\text{N}_3$ requires C, 59.4; H, 5.6; N, 13.8%), from *NN*-dimethyl-*p*-nitrosoaniline and methyl cyanoacetate. Chromatography of the crude product in ethyl acetate on alumina led to the isolation of *N*-dicyanomethylene-*N'N'*-dimethyl-*p*-phenylenediamine and *N*-carbamoylcyanomethylene-*N'N'*-dimethyl-*p*-phenylenediamine in addition to the previously described *pp'*-dimethylaminoazoxybenzene and *N*-(α -cyano- α -ethoxycarbonylmethylene)-*N'N'*-dimethyl-*p*-phenylenediamine. This *dicyanide* was obtained when a mixture of *N*-(α -cyano- α -methoxycarbonylmethylene)-*N'N'*-dimethyl-*p*-phenylenediamine (1.5 g.), methyl cyanoacetate (1.5 c.c.),

potassium carbonate (3 g.), and methanol (15 c.c.) was gently warmed for $\frac{1}{2}$ hr. and poured into water. The sticky black product was repeatedly recrystallised from ethanol. *N*-(2-Cyano-1,2-diethoxycarbonylvinyl)-*N,N'*-dimethyl-, as yellow needles, m. p. 118° (Found: C, 62.0; H, 6.1. $C_{17}H_{21}O_4N_3$ requires C, 61.6; H, 6.3%), from *NN*-dimethyl-*p*-nitrosoaniline and ethyl cyanoacetate. *N*-(2-Cyano-1,2-dimethoxycarbonylvinyl)-*N'*-ethyl-*N'*-methyl-, as yellow prisms, m. p. 103—105° (Found: C, 61.1; H, 5.9. $C_{16}H_{19}O_4N_3$ requires C, 60.6; H, 6.0%), from *N*-ethyl-*N*-methyl-*p*-nitrosoaniline and methyl cyanoacetate. *N*-(2-Cyano-1,2-diethoxycarbonylvinyl)-*N'*-ethyl-*N'*-methyl-, as yellow plates, m. p. 116—118° (Found: C, 62.7; H, 7.0. $C_{18}H_{23}O_4N_3$ requires C, 62.6; H, 6.7%), from *N*-ethyl-*N*-methyl-*p*-nitrosoaniline and ethyl cyanoacetate. *N*-(2-Cyano-1,2-diethoxycarbonylvinyl)-*N',N',2*-trimethyl-, as needles, m. p. 138° (Found: C, 62.7; H, 6.7. $C_{18}H_{23}O_4N_3$ requires C, 62.6; H, 6.7%), by the interaction of ethyl cyanoacetate with *N*-(α -cyano- α -ethoxycarbonylmethylene)-*N',N',2*-trimethyl-*p*-phenylenediamine in ethanol (K_2CO_3). It was purified by elution from alumina by ethyl acetate, solution in dilute sodium hydroxide, reprecipitation by acetic acid, and subsequent crystallisation from ethanol.

Infrared spectra of 4,2,1-RR'N·C₆H₃R''·NH·C(CO₂R'''):C(CN)·CO₂R'''.

R	R'	R''	R'''	NH	-C ₂ N	CO	C:C
Me	Me	H	Me	3290	2220	1765(s), 1680(s), 1720(w)	1620 1600, 1575, 1530
Me	Me	H	Et	3260	2220	1760(s), 1672(s)	1617 1587, 1568, 1527
Me	Et	H	Et	3255	2220	1755(s), 1670(s)	1612 1580, 1560, 1510
Me	Et	H	Me	3265	2220	1755(s), 1675(s)	1615 1590, 1567, 1520
Et	Et	H	Me	3280	2230	1760(s), 1680(s)	1620 1600, 1575, 1530
Et	Et	H	Et	3250	2235	1762(s), 1680(s)	1620 1590, 1570, 1530
Me	Me	Me	Et	3270	2230	1760(s), 1675(s)	1622 1590, 1525

Condensations between Dinitriles and Esters.—A mixture of *N*-dicyanomethylene-*N'*-ethyl-*N'*-methyl-*p*-phenylenediamine (0.5 g.), methyl cyanoacetate (0.5 c.c.), potassium carbonate, and methanol (15 c.c.) was warmed for $\frac{1}{4}$ hr., then diluted with water, and left overnight. The aqueous layer was decanted and the residue purified by repeated recrystallisation from ethanol, giving *N*-(1,2-dicyano-2-methoxycarbonylvinyl)-*N'*-ethyl-*N'*-methyl-*p*-phenylenediamine in golden-red needles, m. p. 120—122° (Found: C, 63.2; H, 5.5. $C_{15}H_{16}O_2N_4$ requires C, 63.4; H, 5.6%). The *ethyl ester* was similarly obtained from ethyl cyanoacetate and formed orange-red plates, m. p. 130—133° (Found: C, 64.4; H, 5.8. $C_{16}H_{18}O_2N_4$ requires C, 64.4; H, 6.2%). These compounds yielded almost colourless sparingly soluble hydrochlorides, from which they could be regenerated.

In the same way the following *p*-phenylenediamines were obtained: *N*-(1,2-dicyano-2-ethoxycarbonylvinyl)-*N,N'*-diethyl-, dark red-brown prisms, m. p. 133—136°, from ethanol (Found: C, 65.5; H, 6.2. $C_{17}H_{20}O_2N_4$ requires C, 65.4; H, 6.4%); *N*-(1,2-dicyano-2-methoxycarbonylvinyl)-*N,N'*-dimethyl-, red prisms, m. p. 158—160°, from ethyl acetate (Found: C, 62.7; H, 5.4; $C_{14}H_{14}O_2N_4$ requires C, 62.2; H, 5.2%); *N*-(1,2-dicyano-2-ethoxycarbonylvinyl)-*N,N'*-dimethyl-, orange-red prisms, m. p. 170—174°, from ethyl acetate (Found: C, 63.3; H, 5.6. $C_{15}H_{16}O_2N_4$ requires C, 63.4; H, 5.6%); *N*-(1,2-dicyano-2-methoxycarbonylvinyl)-*N,N'*-diethyl-, canary-yellow plates, m. p. 122—124°, from ethanol (Found: C, 64.6; H, 6.4; N, 18.7. $C_{16}H_{18}O_2N_4$ requires C, 64.4; H, 6.0; N, 18.8%). This compound is a striking example of dimorphism. If the

Infrared spectra of RR'N·C₆H₄·NH·C(CN):C(CN)·CO₂R''.

R	R'	R''	NH	-C ₂ N	CO	C:C
Et	Et	Et	3240	2220	1682	1612 1588, 1522
Me	Me	Et	3220	2215	1685	1610 1582, 1525
Me	Me	Me	3200, 3165	2210	1688	1610 1562, 1522
Me	Et	Me	3270	2235	1692	1612 1590, 1520

yellow plates are subjected to pressure they become red; if the yellow form is recrystallised from carbon tetrachloride the compound separates in red prisms.

Condensation Products corresponding to Malononitrile Dimer.—(a) Anhydrous potassium carbonate (5 g.) was added to a mixture of malononitrile (1 g.) and *NN*-diethyl-*p*-nitrosoaniline (2.7 g.) in methanol (15 c.c.). After the brisk reaction water was added; the sticky precipitate

was heated with ethanol to remove impurities. The residue was extracted (Soxhlet) with ethyl acetate to yield *N*-(2-amino-1,3,3-tricyanoallylidene)-*N'**N'*-diethyl-*p*-phenylenediamine as dark-blue crystals, m. p. 232° (decomp.) (Found: C, 65.9; H, 5.6; N, 28.3. $C_{18}H_{16}N_6$ requires C, 65.7; H, 5.5; N, 28.8%). (b) *N*-Ethyl-*p*-nitrosoaniline was used as in (a); the resultant *N*-(2-amino-1,3,3-tricyanoallylidene)-*N'*-ethyl-*p*-phenylenediamine crystallised from aqueous pyridine or "Cellosolve" in dark-violet plates, m. p. 230° (decomp.) (Found: C, 63.4; H, 4.6; N, 31.5. $C_{14}H_{12}N_6$ requires C, 63.7; H, 4.5; N, 31.8%). (c) *NN*-Dimethyl-*p*-nitrosoaniline was used as in (a); the resultant *N*-(2-amino-1,3,3-tricyanoallylidene)-*N'**N'*-dimethyl-*p*-phenylenediamine crystallised from a large bulk of acetone as a dark-violet powder, m. p. 256° (decomp.) (Found: C, 63.7; H, 4.3; N, 31.7. $C_{14}H_{12}N_6$ requires C, 63.7; H, 4.5; N, 31.8%).

The same products were obtained when malononitrile dimer (2-amino-1,1,3-tricyanopropene) was used in place of malononitrile.

Infrared spectra of $RR'N \cdot C_6H_4 \cdot N : C(CN) \cdot C(NH_2) : C(CN)_2$.

R	R'	NH ₂	-C:N	>C:N
Et	Et	3390, 3280, 3190	2212, 2204	1608
Me	Et	3390, 3200, 3195	2226, 2212	1610
Me	Me	3380, 3265, 3180	2206, 2190	1615 shoulder, 1600
H	Et	3380, 3290, 3200	2218, 2200	1615

Condensation of Nitrosobenzene with Malononitrile.—Potassium carbonate (4 g.) was added to a mixture of nitrosobenzene (2 g.), malononitrile (1.4 g.), and methanol (15 c.c.). After the brisk reaction the mixture was decomposed by water and submitted to one of the following treatments: (a) The mixture was left in the refrigerator overnight, and the deposited potassium salt then filtered off, dried on paper, and then boiled with chloroform. The residual salt was dissolved in water and decomposed by hydrochloric acid, and the precipitate recrystallised from acetic acid or chloroform. (b) The mixture was shaken with ether and then the aqueous solution was acidified with hydrochloric acid. 1,1,2-Tricyano-2-phenyliminoethane (XII) was obtained in large, pale-yellow prisms, which decomposed indefinitely at ca. 170° (Found: C, 68.5; H, 3.0; N, 28.8. $C_{11}H_8N_4$ requires C, 68.0; H, 3.1; N, 28.9%). The compound has a dissociation constant approximately three times that of acetic acid, and shows the following bands in the infrared spectrum: 3290(w), 3220(m), 3120(s), 2218(s), 2212(s), 2207(s), 1613(vs), 1582(vs). The potassium salt has bands at 2212(s), 2198(s), 1550(sh), 1538(vs).

The Interaction of Nitrosobenzene with Nitromethane.—Potassium carbonate (3 g.) was added to a mixture of nitromethane (1 g.) and nitrosobenzene (2 g.) in methanol. The dark oil that separated on addition of water was washed with ethanol to yield a small amount of solid, which after repeated recrystallisation from ethyl acetate gave glyoxal di(phenyliso-oxime) (XIV) as yellow needles, m. p. 184—186° (Found: C, 70.1, 70.3; H, 5.1, 4.9; N, 11.8, 11.6; O, 13.2. $C_{14}H_{12}O_2N_2$ requires C, 70.0; H, 5.0; N, 11.7; O, 13.3%). It could be recovered from boiling acetic anhydride, was insoluble in hot dilute sodium hydroxide or hot dilute hydrochloric acid, and gave an orange-yellow solution in concentrated sulphuric acid. It was also prepared as follows. An aqueous solution of glyoxal bisulphite was added to an ethanolic solution of phenylhydroxylamine and the mixture warmed on a steam bath for a few minutes. On cooling there was deposited a brown mass which was separated by decantation and dissolved in hot ethanol. The crop was recrystallised from ethyl acetate, giving material of the same m. p. and infrared spectrum as (XIV). The principal bands in the infrared spectrum were: 1505(m), 1330(s), 1295(m), 1185(m), 1170(m), 1157(m), 1087(m), 1072(m), 815(m), 775(s). This may be compared with the spectrum of cinnamylideneaniline oxide, with bands at 1515(m), 1335(m), 1300(m), 1180(m), 1170(sh), 1155(m), 1050(s), 968(s), 910(m), 755(s), 730(s).

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