929. Some Condensation Products of Malononitrile.

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Malononitrile has been condensed with a variety of carbonyl compounds, and the infrared spectra of the products are recorded.

OSTLING[1] obtained a compound, $C_{15}H_{14}N_6$, volatile above 400°, by the interaction of acetone with a molecular amount of malononitrile in the presence of piperidine. Under the same conditions, but using a large excess of acetone, he obtained crystals, m. p. 175—180°, but analytical difficulties prevented assignment of an empirical formula. Schenck and Finken[2] by the condensation of acetone with malononitrile in the presence of potassium ethoxide obtained a compound, m. p. 171·5° (with gas evolution at a slightly higher temperature), which they regarded as isopropylidenemalononitrile (I). Cope and Hoyle[3] found, however, that isopropylidenemalononitrile is a liquid which can be readily converted into a dimer; they regarded this dimer as identical with Schenck and Finken's compound, and claim that the molecular weight determinations made by the latter authors, and which had indicated a monomer, must have been in error. Prout[4] has verified Cope and Hoyle's description of isopropylidenemalononitrile. All these experiments have now been repeated with somewhat conflicting results.

It is verified that the liquid isopropylidenemalononitrile is readily prepared by Cope and Hoyle's method but it is accompanied by a non-volatile pale yellow product, which undergoes indefinite decomposition above 300°. Schenck and Finken's method gives mainly a potassium salt which, after decomposition by acetic acid and crystallisation, yields colourless prisms or plates. These rapidly decompose at about 170° with evolution of isobutene and leave a pale yellow residue, which undergoes indefinite decomposition above 300°, and is very sparingly soluble in all common solvents. The same change can be brought about by dissolving the material in boiling acetic acid; the initially clear solution rapidly deposits the vary sparingly soluble decomposition product. Both of these compounds are readily soluble in aqueous ammonia and can be recovered by addition of acetic acid. Their relationship appears to be expressed by the equation $C_{15}H_{14}N_6 - C_4H_8 = C_{11}H_6N_6$. Since the C_{15} compound can be obtained by the condensation of mesityl oxide with malononitrile it appears probable that the readily expelled isobutene arises from the $Me_2C{:}CH$ group.

Ostling's second method gave crystals, m. p. 171—174°, which could be recrystallised from boiling acetic acid without change. This compound, which was identical with Cope and Hoyle's dimer, is sparingly soluble in aqueous ammonia in the cold but on boiling slowly dissolves with elimination of acetone. On acidification of this solution there is precipitated the compound of decomposition point >300°.

In the polymerisation of isopropylidenemalononitrile very slight changes in conditions determine whether there is produced Cope and Hoyle's dimer or Schenck and Finken's compound. If aqueous ammonia is used to bring about the condensation of malononitrile with acetone, the compound of decomposition point >300° is produced together with a trimer of malononitrile. The two are somewhat similar in properties but malononitrile trimer is sparingly soluble in aqueous ammonia, and can be sublimed without decomposition, whereas the acetone condensation product when heated slowly decomposes with only slight sublimation of product.

The infrared spectra suggest that the acetone–malononitrile reaction may follow the course:

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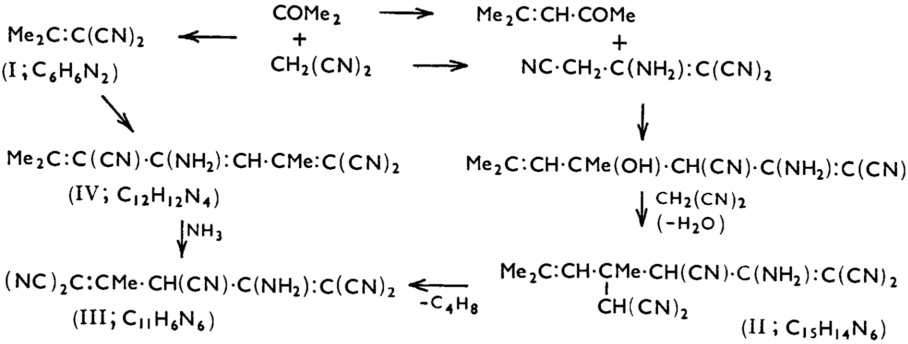
[1] Ostling, *Chem. Zentr.*, 1921, **1**, 613.

[2] Schenck and Finken, *Annalen*, 1928, **462**, 273.

[3] Cope and Hoyle, *J. Amer. Chem. Soc.*, 1941, **63**, 733.

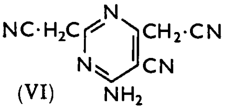
[4] Prout, *J. Org. Chem.*, 1953, **18**, 928.



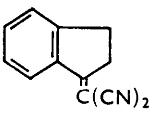
Schenck and Finken described two, possibly three, forms of malononitrile trimer. Their experiments have been repeated, and infrared examination shows only two distinct modifications, one of which is vigorously transformed into the other at 230°. The stable form has a spectrum most readily interpreted as that of an unsaturated aliphatic compound (V); the spectrum of the less stable form strongly suggests a ring structure such as (VI), although this suggestion is difficult to accept chemically.

$\mathrm{NC{\cdot}CH_2{\cdot}C(NH_2){:}C(CN){\cdot}C(NH_2){:}C(CN)_2}$

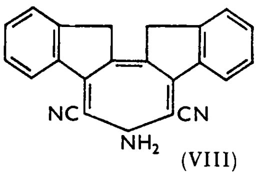
(V)



(VI)



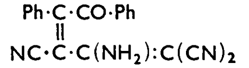
(VII)



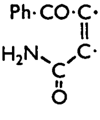
(VIII)

Benzophenone and fluorenone condense with malononitrile to yield uniform products already described,[2] analogous to (I). Mowry [5] described the preparation of $\mathrm{PhMeC{:}C(CN)_2}$ from acetophenone and malononitrile. It is now found that slightly more vigorous conditions result in the production of a yellow isomer with an as yet unexplained infrared spectrum.

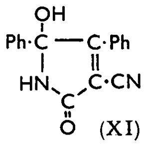
The interaction of malononitrile with indanone is complex. Compound (VII) is obtained by boiling the components in pyridine, or in ethanol containing piperidine. Use of potassium carbonate produces an orange compound, m. p. 250°, whose formation appears to be represented by the equation $2C_9H_8O + 2C_3H_2N_2 - HCN - 2H_2O = C_{23}H_{15}N_3$; structure (VIII) suggested for this does not conflict with the infrared evidence. However, attempts to prepare it from malononitrile dimer or 2-1′-indanylideneindan-1-one were unsuccessful. On the other hand indanone condenses normally with cyanoacetic esters.[6]



(IX)



(X)



(XI)

Benzoin condensed with malononitrile to give a compound of type (I), but benzil gave material to which structure (IX) is assigned. The condensation of benzil with cyanoacetamide occurred in 1 : 1 ratio but the infrared spectrum suggested that the product is (XI) rather than (X). Bacher's results [7] with ethyl cyanoacetate were verified in that

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[5] Mowry, U.S.P. 2,458,017 (1949).

[6] Ingold and Thorpe, *J.*, 1919, **115**, 150.

[7] Bacher, *J. prakt. Chem.*, 1929, [2], **120**, 323.

two compounds were obtained but the infrared spectrum of the higher-melting compound did not correspond to the structure assigned by Bacher.

Various derivatives of isatin were examined and all the products proved to be of type (I). Acenaphthenequinone and phenanthraquinone both reacted readily with malononitrile in the presence of potassium carbonate to give coloured products. Neither product was obtained sufficiently pure for an empirical formula to be suggested.

Sachs [8] described a series of condensation products of nitriles with nitrosophenols. We examined the interaction of various nitrosophenols with malononitrile but obtained only black, amorphous solids, which resisted purification. Most of the other compounds described by Sachs were similar and the only clearly defined one was *N*-α-cyanobenzylidene-*p*-hydroxyaniline, from benzyl cyanide. Too long contact of this with the sodium hydroxide used as condensing agent resulted in its complete conversion into *p*-hydroxybenzanilide.

EXPERIMENTAL

Infrared spectra were determined as Nujol and hexachlorobutadiene mulls with a Hilger H 800 spectrophotometer. Where indicated, spectra were also obtained as dilute solutions (0·01M) in methylene dichloride. Results are recorded in $cm.^{-1}$.

Acetone and Malononitrile.—(*a*) Isopropylidenemalononitrile (I), b. p. 98°/10 mm., was prepared by the method of Cope and Hoyle.[3] The residue from the distillation formed, after removal of more soluble material by ethanol, a pale yellow powder, decomp. >300°, sparingly soluble in the usual organic solvents. It was easily soluble in aqueous ammonia from which it could be reprecipitated by addition of acetic acid (Found: C, 59·3; H, 3·2%), and was identical with the compound described under (*b*).

(*b*) Interaction of acetone with malononitrile under the conditions given by Schenck and Finken yielded a pale yellow potassium salt. Decomposition of this by acetic acid gave a product fairly soluble in acetone. Dilution of the hot acetone solution led to the formation of plates [Found: C, 64·6, 64·6; H, 5·2, 5·0; N, 29·7, 29·1. $C_{15}H_{14}N_6$ (II) requires C, 64·7; H, 5·0; N, 30·2%], which underwent vigorous disintegration at *ca.* 170° with evolution of isobutene (loss in weight; 19·7, 20·0. $C_{15}H_{14}N_6 \longrightarrow C_{11}H_6N_6$ requires loss, 20·1%; isobutene identified by infrared spectrum) to yield a pale yellow powder of indefinite decomp. >300° (Found: C, 59·3, 60·3; H, 3·3, 3·1; N, 36·5. $C_{11}H_6N_6$ requires C, 59·4; H, 2·7; N, 37·8%). The primary product is soluble in aqueous ammonia and can be recovered by addition of acetic acid; it is fairly soluble in acetic acid but if the solution is boiled the isobutene-free compound separates.

(*c*) Diethylamine (0·2 c.c.) in acetone (2 c.c.) was added to a cold solution of malononitrile (5 g.) in acetone (25 c.c.). The mixture immediately became very hot. Next day the crystals, m. p. 170—174°, were removed (2·4 g.) and recrystallised from ethanol, giving isopropylidenemalononitrile dimer (IV)[3] as prisms, m. p. 171—174° (Found: C, 67·8; H, 5·9. Calc. for $C_{12}H_{12}N_4$: C, 67·9; H, 5·7%). This compound can be recrystallised from boiling acetic acid without change. It is slowly soluble in cold aqueous ammonia but on boiling passes into solution from which acetic acid precipitates the compound of high decomp. point described under (*b*); the solution contains acetone, which was identified as the 2,4-dinitrophenylhydrazone.

If in this experiment the concentration of the malononitrile is raised (*e.g.*, 5 g. in 10 c.c. of acetone) the principal product is no longer the dimer but the compound, decomp. 170°, described under (*b*).

(*d*) Diethylamine (0·2 c.c.) in ethanol (2 c.c.) was added to a mixture of mesityl oxide (3 c.c.) and malononitrile (1·7 g.) in ethanol (5 c.c.), and the whole was kept at about 70° for 2 hr. Almost colourless prisms were deposited (1·1 g.), identical with the compound, decomp. 170°, described under (*b*). Further crops were less pure. If in this experiment the ethanol is omitted there is obtained the compound, decomp. >300°.

(*e*) Isopropylidenemalononitrile was treated (i) with piperidine or (ii) in benzene solution with piperidine, or (iii) in acetone solution with diethylamine. In each case the product disintegrated at *ca.* 170° [*i.e.*, it was identical with the compound described under (*b*) and not with the dimer described under (*c*); cf. ref. 3].

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[8] Sachs, D.R.-P., 121, 974.

(*f*) Mesityl oxide did not react with malononitrile under the conditions used to prepare isopropylidenemalononitrile. No condensation product was isolated from a mixture of phorone and malononitrile containing diethylamine.

(*g*) No reaction occurred between malononitrile dimer and acetone in the presence of diethylamine. Attempted condensation in ethanol by potassium ethoxide also failed.

(*h*) When aqueous ammonia was added to a solution of malononitrile (3 g.) in acetone (5 c.c.) the whole became very hot and in a few minutes had set to a yellow crystalline mass. After acidification with hydrochloric acid the precipitate proved to be essentially compound (III). A further deposit consisted of malononitrile trimer, which could be purified by sublimation.

TABLE 1.

Infrared spectra of products from acetone and malononitrile.

Compound	NH_2 stretch	CN	NH_2 bend	C:C	CMe_2
(I)	—	2260w 2230s	—	1610s	1390s 1373s
(II)	3480m 3330m	2260vw 2230s 2220s	1660s	1612s 1585s	1395m 1372s
(III)	3340m 3230w	2220s 2210s	1660s	1620m 1595s	—
(IV)	3390m 3290m 3190m	2235w 2208s	1646s	1570s	1385s 1370s

Polymers of Malononitrile.—(*a*) Schenck and Finken's [2] "malononitrile trimer-(II)" prepared by the action of dry ammonia on a benzene suspension of malononitrile, was crystallised from a little ethanol, and the product boiled with ethyl acetate to remove coloured impurities. The residue had m. p. 220—224° (Found: C, 54·6; H, 3·5; N, 42·2. Calc. for $C_9H_6N_6$: C, 54·3; H, 3·0; N, 42·4%). Its infrared absorptions (see Table 2) indicate a structure such as (VI).

(*b*) When malononitrile trimer was heated in a bath to about 230° violent change occurred. The residual dark mass was extracted with boiling pyridine and the extract diluted with ethanol. The product, which darkened slightly above 300° but was unmelted at 360°, could be obtained as pale yellow crystals from boiling formic acid. This corresponds to Schenck and Finken's trimer-III (Found: C, 54·9; H, 3·3%).

(*c*) Malononitrile (1 g.) was added to diethylamine (~1 c.c.). The solution became very hot. After a short time excess of dilute hydrochloric acid was added and the precipitated thick oil solidified on boiling with ethanol. The product, on crystallisation from water, gave malononitrile dimer as needles, m. p. 168—170°.

(*d*) Submission of malononitrile to Schenck and Fincken's process for the preparation of trimer-I gave only the dimer, m. p. 170°. The dimer when heated above 200° underwent a complex decomposition and no definite compound could be isolated from the product.

TABLE 2.

Infrared spectra of malononitrile trimers.

Schenck and Finken designation	NH stretch.	CN	C:C	Other bonds
Trimer-II	3220m, broad bonded NH	2260w 2210s	—	1535s, 1510s 1432s, 1415s (Pyrimidine ring?)
Trimer-III	3410m, 3340m 3250m, 3175m	2275w 2230s	1595s 1550s	—

Acetophenone and Malononitrile.—A mixture of acetophenone (4 c.c.) and malononitrile (2 g.) containing a few drops of diethylamine was kept warm for a few hr. and allowed to cool. The semisolid product was treated with ethanol to remove more soluble material and the residue, m. p. 120—130°, fractionally crystallised from acetic acid to yield colourless needles of 1,1-dicyano-2-methyl-2-phenylethylene, m. p. 94° (also obtained in good yield by Mowry's method [5]), and canary-yellow needles of an *isomer*, m. p. 205—207° (Found: C, 78·5; H, 4·8. $C_{11}H_8N_2$ requires C, 78·6; H, 4·8%). The compound of low m. p. could be partially converted into the yellow compound by heating it at about 70° for 3 hr. in the presence of a small amount of diethylamine. The infrared spectrum of the yellow compound did not agree with the

TABLE 3.

Infrared spectra of products from acetophenone and malononitrile.

Compound	NH	CN	Ph	C=C	CMe	Ph
M. p. 94°	—	2235m	1598w 1587m 1492m	1568m	1439m 1374m	772s 760s
M. p. 205—207°	3240m	2220m 2205m	1578m 1490w 1457w	1603vs	—	763s, 741s 699s, 694s

expected 4-amino-1,1,5-tricyano-2,6-diphenylhepta-1,3,5-triene. The NH absorption was checked in solution (methylene dichloride).

Ethyl α-cyano-1-indanylideneacetate, prepared by Ingold and Thorpe's method,[6] formed needles, m. p. 100—102°; ν 2234w (CN), 1718s (ester C=O), and 1570s (C=C). The *methyl* ester, prepared similarly, crystallised from methanol as needles, m. p. 142—144° (Found: C, 73·5; H, 4·9. $C_{13}H_{11}O_2N$ requires C, 73·3; H, 5·2%); ν 2235vw (CN), 1728s (ester C=O), 1575s (C:C).

1-*Indanone and Malononitrile*.—(*a*) 1-*Dicyanomethyleneindane*, prepared by boiling indanone and malononitrile either in pyridine or in ethanol containing one drop of piperidine, crystallised from ethanol in needles, m. p. 152° (Found: C, 80·1; H, 4·5. $C_{12}H_8N_2$ requires C, 80·0; H, 4·5%); ν 2236w (CN), 1575m (C:C). 2-1′-Indanylideneindan-1-one was unchanged after boiling with malononitrile, malononitrile dimer, or ethyl cyanoacetate in ethanol even in the presence of piperidine or potassium carbonate; it shows the following infrared bands: 1655s (αβ-unsaturated ketone), 1615w (C:C).

(*b*) Potassium carbonate (3 g.) was added to a mixture of 1-indanone (2 g.) and malononitrile (1·5 g.) in ethanol and the whole warmed on a steam bath for 10 min. and cooled. Water was added and the precipitate filtered off; from this the more soluble material was removed by boiling ethanol. The residue yielded from pyridine–ethanol a *compound* as yellow prisms, m. p. *ca*. 250° (Found: C, 82·2; H, 4·6; N, 12·6. $C_{23}H_{15}N_3$ requires C, 82·9; H, 4·5; N, 12·6%); ν 3390, 3330, 3240, 2228 (all m), 2190s, 1655s, 1617m, 1595m, 1537m. The analyses and spectrum suggest a structure such as (VIII).

(*c*) Potassium carbonate (2·5 g.) was added to a boiling solution of indanone (1·3 g.) and 1-dicyanomethyleneindane (1·8 g.) in ethanol (40 c.c.) and the boiling continued for ½ hr. Water was then added and a small amount of precipitated 1-dicyanomethyleneindane filtered off. The filtrate was acidified with acetic acid and the precipitated plastic mass recrystallised from acetic acid. A *compound* was obtained as almost colourless needles, m. p. 250—255° to a deep-green melt (Found: C, 80·6; H, 5·1; N, 8·8. $C_{21}H_{16}N_2O$ requires C, 80·7; H, 5·1; N, 9·0%); ν 3420m, 3350m, 3200w, 2200s, 1715s, 1655m, 1635m, 1590m, 1575m.

Fluorenone and Malononitrile.—Fluorenylidenemalononitrile crystallised from acetic acid in red needles, m. p. 234—235° (lit., m. p. 213°,[2] 234° [11]); ν 2225, 1615, 1575, 1562 (all m).

Benzophenone and Malononitrile.—1,1-Dicyano-2,2-diphenylethylene crystallised from ethanol in needles, m. p. 138° (lit.[2] m. p. 136°); ν 2225m (CN), 1530m (C:C).

Benzoin and Malononitrile.—A few drops of diethylamine were added to a hot solution of benzoin (2·1 g.) and malononitrile (1·4 g.) in ethanol (20 c.c.), and the mixture kept warm for 2 hr. On cooling, benzil (0·7 g.) separated. The filtrate was re-heated and diluted. The resultant crop was recrystallised from ethanol to yield almost colourless needles, m. p. 204—206° (Found: C, 78·1; H, 4·5; N, 10·9. $C_{17}H_{12}N_2O$ requires C, 78·5; H, 4·6; N, 10·8%); ν 3450, 3315, 3260, 3200 (all m) (OH), 2235s, (CN), and 1658s (C=C).

Benzil and Malononitrile.—Diethylaniline (0·2 c.c.) was added to a warm solution of benzil (2·1 g.) and malononitrile (1·4 g.) in ethanol (25 c.c.), and the mixture kept at 70° for 2 hr. On slight dilution needles separated, m. p. *ca*. 120° with evolution of ethanol (Found: C, 71·6; H, 5·1; loss at 130°, 12·6%. $C_{20}H_{12}N_4O,C_2H_5OH$ requires C, 71·4; H, 4·9; loss, 12·4%). The residue of 2-*amino*-4-*benzoyl*-1,1,3-*tricyano*-4-*phenylbutadiene* had m. p. *ca*. 195° (decomp.) (Found: C, 73·8; H, 4·1; N, 17·3. $C_{20}H_{12}N_4O$ requires C, 74·1; H, 3·7; N, 17·3%); ν 3390m, 3310m (NH_2), 2240w (CN), 1740sh, 1722s (C=O). The ethanolate gave the same spectrum

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[9] Walter, *Ber.*, 1902, **35**, 1321.

[10] Corson and Stoughton, *J. Amer. Chem. Soc.*, 1928, **50**, 2825.

[11] Ferrier and Campbell, *J.*, 1960, 3514.

with additional bands at 3520m and 1042m due to ethanol. Similar addition compounds were obtained with other alcohols.

Benzil and Ethyl Cyanoacetate.—Condensation by Bacher's method[7] led to the two compounds described by him. One, prisms, m. p. 139—141° (Found: C, 74·7; H, 5·1. Calc. for $C_{19}H_{15}NO_3$: C, 74·7; H, 4·9%), gave the infrared spectrum expected for ethyl α-cyano-β-benzoylcinnamate: 2240w (CN), 1727s (ester C:O), and 1669s (keto-C:O). The other, prisms, m. p. 169—171° (Found: C, 69·0; H, 5·1. Calc. for $C_{24}H_{22}N_2O_5$: C, 68·9; H, 5·3%) did not give the spectrum expected for ethyl αγ-dicyano-β-phenyl-β-benzoylglutarate but gave evidence of the presence of an NH group. The main bands shown were 3180m broad (NH), 2250vw (CN), 1743s (ester C:O), and 1691s (keto-C:O).

Benzil and Cyanoacetamide.—A few drops of diethylamine were added to a hot solution of benzil (2·1 g.) and cyanoacetamide (1·7 g.) in ethanol (40 c.c.). Next day water was added and the precipitate crystallised from aqueous ethanol, giving prismatic needles, m. p. 167—170° (Found: C, 71·3; H, 4·5; N, 9·5. $C_{17}H_{12}N_2O_2,\frac{1}{2}H_2O$ requires C, 71·5; H, 4·6; N, 9·8%), or from xylene as needles, m. p. 180—182° (Found: C, 74·3; H, 4·3. $C_{17}H_{12}N_2O_2$ requires C, 73·9; H, 4·3%); ν 3300s, 1348s, 1176s (bonded –OH), 3250m (NH), 2230m (CN), 1715s (C:O), in better agreement with formula (VIII) than with (VII).

Derivatives of Oxindole.—(*a*) 3-Dicyanomethyleneoxindole was prepared by Walter's method. When boiled for 1 hr. with acetic anhydride it gave the N-*acetyl derivative* as dichromate-coloured needles, m. p. 170° (Found: C, 65·9; H, 2·9. $C_{13}H_7N_3O_2$ requires C, 65·8; H, 2·9%).

(*b*) *Methyl α-cyano-3-oxindolylideneacetate*, prepared by the addition of anhydrous potassium carbonate (2 g.) to a boiling suspension of isatin (1 g.) in methanol (10 c.c.) containing methyl cyanoacetate (1 c.c.), crystallised from acetic acid in needles, m. p. 240—242° (decomp.) (Found: C, 63·4; H, 3·6. $C_{12}H_8N_2O_3$ requires C, 63·2; H, 3·5%). When boiled with acetic anhydride it gave the N-*acetyl derivative* as bright yellow crystals, m. p. 147—149° (Found: C, 62·0; H, 3·9. $C_{14}H_{10}N_2O_4$ requires C, 62·2; H, 3·7%).

(*c*) 5-*Methyl-3-dicyanomethyleneoxindole* was formed immediately on addition of malononitrile to a boiling ethanolic solution of 5-methylisatin. It crystallised from acetic acid as brownish violet needles, m. p. 260° (Found: C, 68·7; H, 2·9. $C_{12}H_7N_3O$ requires C, 68·9; H, 3·3%), and by solution in boiling acetic anhydride gave the *acetyl derivative*, which crystallised from acetic acid as red needles, m. p. 198—200° (Found: C, 67·1; H, 3·6; N, 16·4. $C_{14}H_9N_3O_2$ requires C, 66·9; H, 3·6; N, 16·7%).

(*d*) On boiling 5-methylisatin (1 g.) and malononitrile dimer (1 g.) in ethanol (20 c.c.) condensation occurred slowly to give red-violet crystals of 3-(2-*amino*-1,3,5-*tricyanoallylidene*)-5-*methyloxindole*, m. p. 333° (decomp.) (Found: C, 65·4; H, 3·5. $C_{15}H_9N_5O$ requires C, 65·4; H, 3·3%).

TABLE 4.

Infrared spectra of oxindoles.

						C=O			
R^1	R^3	R^3	R^5	NH	CN	keto	ester	acyl	C=C
H	CN	CN	H	3290m 3160m	2245w	1740s 1722s	—	—	1627m
				*3415m	2245w	1747s			1625m
Ac	CN	CN	H	—	2240w	1720s	—	—	1600m
H	CN	CO_2Me	H	3360m	2225w	1720s	1755sh 1730s	—	1620m
				*3400m	2230w	1745s, (1 peak only)	—	—	1623m
Ac	CN	CO_2Me	H	—	2220w	1720s	1740s	1762s	1610m
H	CN	CN	Me	3280m	2240w	1737s 1722s	—	—	1625m
				*3410m	2242w	1745s	—	—	1625m
Ac	CN	CN	Me	—	2235w	1725s	—	1755s	1603m

* In dichloromethane solution. Numerals attached to the R's refer to positions in the oxindole nucleus.

Acenaphthenequinone and Malononitrile.—Anhydrous potassium carbonate (3 g.) was added to a boiling mixture of acenaphthenequinone (2 g.) and malononitrile (2 g.) in ethanol (100 c.c.).

After ½ hr. the deep blue solution was diluted with hot water (100 c.c.) and allowed to cool. The product was filtered off, dried, and extracted (Soxhlet) with acetone. The blue-black product had a decomposition point >300° and contained potassium. The infrared spectrum showed extensive broad bands at 1520—1580, and 2200 (CN), but no carbonyl. Acenaphthenequinone did not condense with cyanoacetamide or ethyl cyanoacetate under the same conditions.

Phenanthraquinone and Malononitrile.—A few drops of diethylamine were added to a boiling solution of phenanthraquinone (1 g.) and malononitrile (1 g.) in ethanol (200 c.c.). The mixture immediately became deep-purple and deposited a dark-violet precipitate. This was filtered off, dried, and extracted (Soxhlet) with acetone. The almost black product decomposed at 300°, and showed infrared bands at 3270s, 2240s, 1650, 1612, 1592, 1550, and 1515 (all m).

p-*Nitrosophenol Series.*—*N*-α-Cyanobenzylidene-*p*-hydroxyaniline was prepared by Sachs's method.[8] Too long contact with the ethanolic solution of sodium hydroxide resulted in its conversion into *p*-hydroxybenzanilide, m. p. 214° (Found: C, 73·1; H, 5·0; N, 6·9. Calc. for $C_{13}H_{11}NO_2$: C, 73·3; H, 5·2; N, 6·6%).

By the same method 3-methyl-4-nitrosophenol gave *N*-α-cyanobenzylidene-4-hydroxy-2-methylaniline, which crystallised from ethanol as yellow needles, m. p. 198—200° (Found: C, 76·5; H, 5·0. $C_{15}H_{12}N_2O$ requires C, 76·3; H, 5·1%), and 2-methyl-4-nitrosophenol gave N-α-*cyanobenzylidene*-4-*hydroxy*-3-*methylaniline*, m. p. 142—144°, from ethanol (Found: C, 76·2; H, 4·6%).

TABLE 5.

Infrared spectra of 4-nitrosophenols, 4-HO·C_6H_3R·N:C(CN)Ph.

R	OH	CN	N:C
H	3323m	2220vw	1620m
2-Me	3320m	2220w	1620m
3-Me	3280m	2220vw	1622m

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