1.5 g. of brown solid which separated was crystallized several times from acetic acid. The bright red crystals melted at 210°.

Anal. Calcd. for $C_{19}H_{18}N_8O_{10}$: C, 44.02; H, 3.50. Found: C, 43.52, 43.65; H, 3.52, 3.61.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID COMPANY]

Phenylfumaronitrile and Phenylmaleonitrile: Assignment of Configurations

BY WILLIAM C. SCHNEIDER

RECEIVED NOVEMBER 5, 1954

The electric moments of two isomeric α,β-dicyanostyrenes have been evaluated in benzene solution at 35°. The results indicate the following assignments of configurations: *cis*-α,β-dicyanostyrene (m.p. 86–87°, μ = 7.98 *D*); *trans*-α,β-dicyanostyrene (m.p. 42–43°, μ = 2.71 *D*).

In the synthesis of α,β-dicyanostyrene[1] two definite compounds were obtained, characterized by a sharp melting point and a correct analysis for the desired substance. Compound I melted at 86–87°, and compound II melted at 42–43°. Infrared, ultraviolet and chemical evidence[2] led to the tentative assignments of configurations: I, *trans* and II, *cis*. However, the evidence was not conclusive, and it was felt to be desirable to determine the dipole moments of these compounds to obtain an unequivocal assignment of configuration.

Experimental

The apparatus and measuring technique have been described previously.[3] Reagent-grade, thiophene-free benzene was used as solvent. It was dried over calcium hydride for 24 hours, followed by distillation. Table I lists the experimental values of: ϵ, dielectric constant, d, density and ω, weight fraction for benzene solutions at 35°. Dipole moments were calculated by a modified Hedestrand method similar to that introduced by Halverstadt and Kumler,[4] differing in that densities were used rather than specific volumes. The empirical equation used may be written as

$$_\infty p_T = \frac{\epsilon_0 - 1}{\epsilon_0 + 1} \times \frac{1}{d_0}\,[1 - \beta/d_0] + \frac{3\alpha}{(\epsilon_0 + 2)^2 d_0} \quad (1)$$

where

ϵ_0 = extrapolated dielectric constant of solvent
d_0 = extrapolated density of solvent
$_\infty p_T$ = specific polarization at infinite dilution
α = slope of dielectric constant *vs.* weight fraction curve
β = slope of density *vs.* weight fraction curve

The total molar polarization, $_\infty P_T$, is obtained from the specific polarization by multiplying by the molecular weight.

TABLE I

Compound I			Compound II		
ω	ϵ	d	ω	ϵ	d
0.0	2.2529	0.86251	0.0	2.2545	0.86251
.001288	2.2854	.86278	.001383	2.2578	.86278
.002528	2.3156	.86307	.002222	2.2604	.86292
.003743	2.3464	.86328	.003386	2.2634	.86316
.004964	2.3765	.86354	.004841	2.2672	.86348

TABLE II

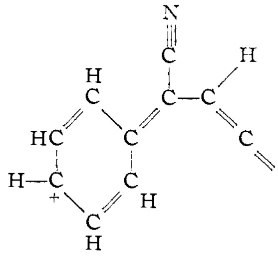
Compd.	α	β	$_\infty p_T$	Mol. wt.	$_\infty P_T$	P_D	P_O	$\mu \times 10^{18}$
I	24.90	0.2077	8.524	154.2	1314	39.2	1275	7.98
II	2.622	.1917	1.208	154.2	186.3	39.2	147.1	2.71

Atomic polarization was neglected, and molecular refractions were calculated from the atomic refractions listed in the "Landolt-Börnstein Tabellen." The values obtained from these calculations are listed in Table II, where P_D and P_O refer to the distortion and orientation polarizations, respectively.

Discussion

The observed moments I, μ = 7.98 *D* and II, μ = 2.71 *D* lead to the following assignments of configurations: I, *cis*-α,β-dicyanostyrene; II, *trans*-α,β-dicyanostyrene. It is felt that these assignments are unequivocal because Fischer–Hirschfelder models indicate these compounds to be planar (except for possible free rotation of the benzene ring about the bond connecting it to the side chain), and this condition in turn requires that the compound with the lower moment have a *trans* configuration.

There might be some reasonable doubt about the high moment (2.71 *D*) of the *trans* compound, since normally the benzene ring has zero electric moment, and assuming this condition, the *trans* compound should also have zero electric moment. Two alternatives suggest themselves as possible explanations. Firstly, the *trans* compound might be contaminated with *cis* and, secondly, structures of the type



may be contributing abnormally. A rough calculation indicates that to achieve the first possibility the *trans* compound would have to contain roughly 10% of the *cis* compound; the sharp melting point of the former precludes this.

Assuming the second possibility to be correct, one can calculate its contribution to the observed moment using the bond moments: $\mu_{C\equiv N}$ = 2.93 *D* and μ_{H-C} = 0.4 *D*. The result is shown schematically in Fig. 1.

It is possible to obtain a check on the magnitude and direction of this moment by using these quantities to calculate the moment of the *cis* compound, followed by comparison of this calculated moment

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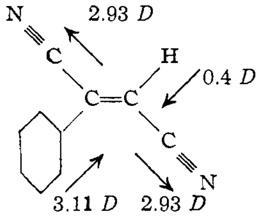
(1) D. W. Hein, THIS JOURNAL, **77**, 2797 (1955).

(2) Personal communication from Dr. D. W. Hein. Bound Brook Laboratories, American Cyanamid Company.

(3) W. C. Schneider and I. F. Halverstadt, THIS JOURNAL, **70**, 2626 (1948).

(4) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).



$\mu_{obs} = \mu_{C_6H_5} - \mu_{H-C}$
$\mu_{C_6H_5} = 3.11\ D$

Fig. 1.

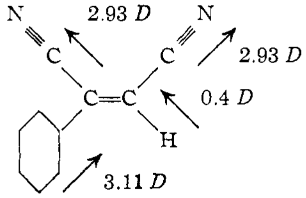


Fig. 2

with the experimental value. Figure 2 indicates the configuration of the moment vectors.

Assuming valence angles of 120°, $\mu_{calc.} = 8.3\ D$. This agreement is adequate since inductive effects should lower the calculated value in the actual molecule. Obviously, this calculation does not confirm the assumption about abnormal contributions from an ionic form, but it does demonstrate its consistency.

Acknowledgment.—The author wishes to express his indebtedness to Dr. D. W. Hein of the Bound Brook Laboratories of the American Cyanamid Company for proposing this problem and supplying the compounds.

STAMFORD, CONN.

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID COMPANY]

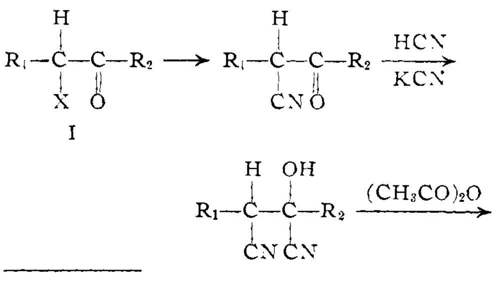
Phenylmaleonitrile and Phenylfumaronitrile. A New Reaction Observed on Activated Alumina

BY D. W. HEIN

RECEIVED NOVEMBER 6, 1954

A mixture of phenylmaleonitrile and phenylfumaronitrile was obtained in 75–85% over-all yields from α-cyanophenylacetaldehyde by conversion to the cyanohydrin, acetylation of the cyanohydrin and then splitting acetic acid from the acety derivative on an activated alumina column. The isomers were readily separated by recrystallization, chromatography on alumina or vacuum distillation. Their configurations were established.

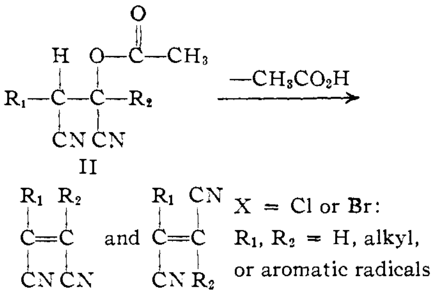
The preparation of pure phenylmaleonitrile and phenylfumaronitrile has not been reported previously. Mowry[1] has reported the preparation of "1,2-dicyano-1-phenylethylene" by the chlorination of phenylsuccinonitrile which was prepared by the method of Gitsels and Wibaut.[2] His purification techniques (vacuum distillation and dilute alcohol recrystallization) should have resulted in a separation of the isomers, but no further details are given in the patent. The preparation of phenylsuccinonitrile by the method of Gitsels and Wibaut[2] is extremely laborious. In our work we sought an easier route to substituted 1,2-dicyanoethylenes which are useful in the preparation of tetrazaporphin pigments and in the preparation of other derivatives. The splitting of acetic acid from the cyanohydrin acetates of α-cyanoaldehydes or ketones (II) as outlined below, appeared to be a particularly attractive route, as the latter



$$R_1-\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}-\underset{\underset{O}{\|}}{C}-R_2 \longrightarrow R_1-\overset{\overset{H}{|}}{\underset{\underset{CN}{|}}{C}}-\underset{\underset{O}{\|}}{C}-R_2 \xrightarrow[KCN]{HCN}$$

I

$$R_1-\overset{\overset{H}{|}}{\underset{\underset{CN}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{CN}{|}}{C}}-R_2 \xrightarrow{(CH_3CO)_2O}$$



$$R_1-\overset{\overset{H}{|}}{\underset{\underset{CN}{|}}{C}}-\overset{\overset{O-\overset{\overset{O}{\|}}{C}-CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-R_2 \xrightarrow{-CH_3CO_2H}$$

II

$$\overset{\overset{R_1}{|}}{\underset{\underset{CN}{|}}{C}}=\overset{\overset{R_2}{|}}{\underset{\underset{CN}{|}}{C}} \quad \text{and} \quad \overset{\overset{R_1}{|}}{\underset{\underset{CN}{|}}{C}}=\overset{\overset{CN}{|}}{\underset{\underset{R_2}{|}}{C}}$$

X = Cl or Br:
R_1, R_2 = H, alkyl,
or aromatic radicals

are readily prepared from α-haloketones or aldehydes (I). Since the completion of our work, France and Jones[3] have reported in patents that 3,4,5,6-tetrahydrophthalonitrile can be prepared by the dehydration of the cyanohydrin of α-cyanocyclohexanone, and that dimethylmaleonitrile can be made by the dehydration of the cyanohydrin of α-methylacetoacetonitrile, but no further details are given. However, Ficken and Linstead[4] did not use this method for the preparation of 3,4,5,6-tetrahydrophthalonitrile, when they elucidated the chemistry of hexadecahydrophthalocyanine.

We chose to test the above route by the preparation of phenylmaleonitrile, since the successful preparation of tetraphenyltetrazaporphin from it has not previously been reported. By the following sequence of reactions we were able to prepare a mixture of phenylmaleonitrile and phenylfumaronitrile

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(1) D. T. Mowry, U. S. Patent 2,447,813 (1948).

(2) H. L. P. Gitsels and J. P. Wibaut, *Rec. trav. chim.*, **59**, 1093 (1940).

(3) H. France, Brit. Patent 686,395 (1953); H. France and W. O. Jones, Brit. Patents 688,768 (1953), 689,387 (1953), and 689,389 (1953).

(4) G. E. Ficken and R. P. Linstead, *J. Chem. Soc.*, 4846 (1952).