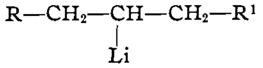
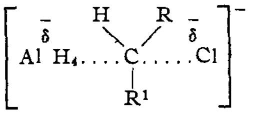
Polymer association could be a contributing cause to the high number average molecular weights. The infrared spectrum revealed absorption of low intensity at 2.94 μ due to an estimated ratio of OH/CH_2 of 0.003–0.005.

Trementozzi, *et al.*,[12] have demonstrated that the presence of relatively few hydroxyl groups in a hydrocarbon polymer can lead to polymer association in non-polar solvents. The hydroxyl groups in reduced polyvinyl chloride are probably causing association in xylene, even at 89°. It is questionable that the few remaining chlorines could be producing associated polyvinyl chloride like clusters. The observation that most of the hydroxyl groups must be along the polymer backbone has as a consequence that introduction of hydroxyl into the polymer does not necessarily correspond to chain scission.

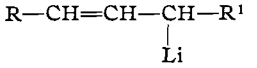
There is no clear cut explanation of the route by which oxygen is introduced in the polymer during reduction. Direct oxidation of polymer to groups which are subsequently reduced cannot be excluded. However, the ready reaction of lithium aluminum hydride in solution[13] with oxygen to yield hydrogen gas, suggests that the oxygen concentration in solutions of lithium aluminum hydride is negligible. It is a reasonable assumption that alumino hydride ion is oxidized to an oxyanion of indefinite structure, liberating hydrogen. Displacement of chloride by such an oxyanion could lead to a product which on hydrolysis would yield a secondary hydroxyl group. This mechanism of hydroxyl introduction, speculative as it is, is not unreasonable. An alternative mechanism of hydroxyl introduction into the polyhydrocarbon has been considered. Oxidation of a secondary alkyl lithium produced by reaction between lithium aluminum hydride and secondary halide


$$R—CH_2—\underset{\displaystyle Li}{\underset{|}{CH}}—CH_2—R^1$$

could be involved. This does not necessarily imply such an organolithium intermediate in the reduction process. The weight of evidence[5,6] on the mechanism of reaction between alkyl halides and lithium aluminum hydride favors nucleophilic displacement on carbon



halogen departing as halide ion as the negative aluminohydride complex approaches the carbon from the backside. The incidence of organolithium intermediates of the halides of acidic hydrocarbons such as diphenylmethane and fluorene during reduction with lithium aluminum hydride has been reported.[6] However, there has been no clear evidence of such organolithium intermediates as transient species in the reduction of simple alkyl monohalides. The detailed fine structure of polyvinyl chloride is still a matter for conjecture. Unsaturation in the polymer chain may favor the formation of α,β unsaturated organometallic compounds, *e.g.*


$$R—CH{=}CH—\underset{\displaystyle Li}{\underset{|}{CH}}—R^1$$

SPRINGFIELD, MASS.

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[12] Q. A. Trementozzi, R. F. Steiner and P. Doty, THIS JOURNAL, **72**, 2070 (1952); Q. A. Trementozzi, *J. Phys. Colloid Chem.*, **54**, 1227 (1950).

[13] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., p. 472; Hochstein, THIS JOURNAL, **71**, 305 (1949).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

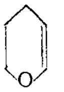
Reactions of 2,3-Dihydropyran[1]

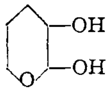
BY CHARLES D. HURD, JAMES MOFFAT AND LUIGI ROSNATI

RECEIVED JANUARY 14, 1955

In the hydroxylation of 2,3-dihydropyran (I) to 3,4-dideoxypentose (II) some closely-related, unidentified material also is formed which gives rise to formaldehyde on periodate cleavage. It is possible to purify II by careful fractional distillation of the acetyl derivative. Hydroxylation of I by means of aqueous sodium chlorate and osmium tetroxide gives II, but in poor yield. N-Bromophthalimide adds to I, yielding a phthalimidobromotetrahydropyran. Several new hydrazones and osazones of II are reported.

In previous work[2,3] it was shown that 2,3-dihydropyran (I) could be hydroxylated to yield 3,4-dideoxypentose(II). The latter should give rise to 4-hydroxybutanal and formic acid on periodate oxidation, but in the present work we observed that a large amount of formaldehyde was obtained. This unexpected result led to the examination of the reactions involved with the purpose of finding a way of of getting pure 3,4-dideoxypentose and of discovering, if possible, the source of the formaldehyde produced in the periodate cleavage. The former objective has been satisfactorily achieved, the latter only in part.


I


II

The suspicion that the dihydropyran may have contained 2-methylenetetrahydrofuran (III) caused us to inspect critically the evidence used in proof of

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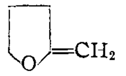
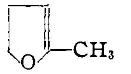
[1] This paper reports research undertaken in coöperation with the Quartermaster Food and Container Institute for the Armed Forces, and has been assigned number 526 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not be construed as necessarily reflecting the views or indorsement of the Department of Defense.

[2] C. D. Hurd and C. D. Kelso, THIS JOURNAL, **70**, 1484 (1948).

[3] C. D. Hurd and O. E. Edwards, *J. Org. Chem.*, **14**, 680 (1949).

structure. At the time[4] of the discovery of I, III was unknown. III, however, now is available[5] as a liquid of b.p. 98–99°. Since I boils at 83–84° this effectively argues against any substantial quantity of III in I. Acids do cause isomerization of III into 2-methyl-4,5-dihydrofuran[5] (IV), b.p. 81–82°, but since a diol derived from this compound could yield no formaldehyde on periodate oxidation it need not be considered as the cause of the formaldehyde which was mentioned above.


III


IV

Paul's evidence for the structure of I was convincing. He hydrogenated it (platinum catalyst) in the cold and reported a 72% yield of tetrahydropyran, b.p. 86–90° (note that 2-methyltetrahydrofuran boils at 80°), and 1-pentanol of b.p. 136–139°. He treated the reduced compound with hydrogen bromide and obtained a dibromide from which N-phenylpiperidine was formed on reaction with aniline.

The anomalous result might conceivably be caused by any of these reasons: (1) the presence of a large amount of 2-methylenetetrahydrofuran in the starting dihydropyran; (2) some sort of rearrangement during the hydroxylation; (3) formation of isobutylene glycol from the *t*-butyl alcohol used in the hydroxylation; (4) rearrangement during deacetylation of the dideoxypentose; (5) rearrangement during deacetylation of the dideoxypentose diacetate; (6) anomalous periodate oxidation.

It has been found that if the dideoxypentose was prepared in the ordinary way and acetylated, and if the acetate was carefully fractionally distilled and then deacetylated, there was formed a dideoxypentose that yielded only a small amount of formaldehyde when it was treated with sodium periodate. This clearly rules out causes 5 and 6.

A sample of dihydropyran was carefully fractionated to obtain a fraction boiling within a 0.1° range. Infrared analysis showed that this fraction contained no terminal ethylenic unsaturation. This sample was submitted to hydroxylation, acetylation, distillation (but not careful fractionation), deacetylation and periodate oxidation. The yield of formaldehyde was about 25%. These data make the first proposed cause seem untenable.

Attempts to check on the third possibility by running blanks without dihydropyran gave only insignificant amounts of material at the acetate stage, in no way sufficient to explain the previous results. The possibility that some sort of induced oxidation of the solvent goes on during reaction with dihydropyran was not excluded, however. As yet, therefore, the source of the formaldehyde is unknown.

Experiments designed to obtain II by hydroxylation of I with a mixture of sodium chlorate and osmium tetroxide in aqueous solution gave only a small amount of product. It was also shown, not unexpectedly, that II was unobtainable by stepwise hydrolysis of 2,3-dibromotetrahydropyran, since the bromine atom in the 3-position could not be displaced either by hydroxide ion or by acetate ion.

These new reactions of I were investigated. One was the reaction of dihydropyran and N-bromosuccinimide in an attempt to obtain 4-bromo-2,3-dihydropyran by allylic bromination. Tars only were formed, but when N-bromophthalimide was substituted for the bromosuccinimide an addition compound was obtained. The latter was either 2-bromo-3-phthalimidotetrahydropyran or 2-phthalimido-3-bromotetrahydropyran. The former would be expected to arise from a radical attack and the latter from an ionic, positive bromine mechanism. The compound is dissolved slowly by hot, dilute alkali with liberation of bromide ion and non-formation of ammonia. This evidence favors 2-bromo-3-phthalimidotetrahydropyran but more evidence is necessary for rigorous proof.

Several new hydrazones and osazones of 3,4-dideoxypentose were prepared which are useful in characterizations.

Experimental

A few modifications of the directions of Hurd and Kelso[2] resulted in a slightly better yield of II and lesser formation of by-products, besides being somewhat faster. These modifications consisted in adding the first quarter of the hydrogen peroxide solution at 10°, the second quarter at 10–15°, and the rest at 15–20°. Also, after acetylation, the ethanol which was added to destroy the excess of acetic anhydride was added at 30° instead of at 10°, and the solution was let stand at this stage for only 6 hours instead of the previous 12. With these changes the yield of diacetate was improved to 127 g. (b.p. 115–120° (5 mm.)) from 180 g. of dihydropyran and the amount of "disaccharide" was reduced by about one-fourth.

A sample of this diacetate, with no further purification, was deacetylated, mixed with acetone, evaporated, dissolved in ether, treated with Norit and filtered. Petroleum hexane was added to cause precipitation of II. The solvent was decanted and the residue was dried at 20 mm. over sulfuric acid. Samples of this material were titrated for aldose content with iodine in weakly alkaline solution by the method of Kline and Acree.[6]

Anal. Subs. 0.1260, 0.0786 g. Found by iodimetry, 0.1087, 0.0728 g. (86.3, 92.6%). Found by acidimetry, 0.1110, 0.0721 g. (88.1, 91.8%).

The same sample of II, analyzed by sodium periodate oxidation, gave these data: subs. 2.4079 g., dissolved with 10.068 g. of sodium periodate in 250 ml. of water; periodate consumed after 30 hours, 89.7%; formic acid found (by distillation and titration of distillate to methyl red end-point), 45.8%; formaldehyde found (by neutralization with sodium bicarbonate, distillation, and precipitation from the distillate with dimedon), 20.9%.

Distillation of the Diacetate.—Two large batches of crude diacetate of II from separate runs were distilled from an ordinary Claisen flask to give material boiling from 95–115° at 1–2 mm., the weights of these fractions being 160 and 396 g., respectively. Both fractions were then carefully fractionated through a Widmer distilling column equipped with an electrically heated jacket. A low-boiling cut (fraction A) was collected at 95–105° (1–3 mm.), then the desired fraction was collected.

That from the 160-g. fraction was collected at 109–111° (1–2 mm.) and weighed 50 g. It was redistilled through the same column and the highest boiling cut (109–111° at 1–2 mm.) was analyzed. A sample which was deacetylated and let stand with excess sodium periodate for 24 hours gave in duplicate analyses 98.3, 98.4% of formic acid and only 5.3, 6.0% of formaldehyde.

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(4) R. Paul. *Bull. soc. chim.*, [4] **53**, 1489 (1933); [5] **1**, 971 (1934).

(5) R. Paul and S. Tchelitcheff, *ibid.*, [5] **17**, 520 (1950); H. P. Thomas and C. L. Wilson, THIS JOURNAL, **73**, 4803 (1951).

(6) G. M. Kline and S. F. Acree, *Bur. Standards J. Research*, **5** 1063 (1930).

That from the 396-g. fraction gave rise to 225 g. at 108–116° (1–2 mm.) which, on redistillation, yielded 125 g. at 114–115° (1–2 mm.). A sample of this last fraction was deacetylated in methanol with barium methoxide. After carbonation, evaporation of the methanol, solution in ether, filtration to remove barium salts, and concentration, the concentrated ether solution of the diol was poured into petroleum hexane, the mixed solvents decanted from the precipitated oily diol, and the diol was dried *in vacuo* over sulfuric acid for 36 hours. In this manner, 15 g. of diol was obtained from 50 g. of diacetate. Duplicate samples of this material submitted to periodate analysis gave 94.6% formic acid. Formaldehyde was determined iodimetrically in the distillate, giving 5.89%.

The low-boiling "fractions A" were combined (55 g.) and distilled at 2 mm. through a 50-cm. column filled with glass helices. All material distilling below 110° was washed thrice with water, dried 24 hours over Drierite, and redistilled. Besides a small forerun (5 g.) and about 20 g. of higher boiling (95–110°) material there was collected 30 g. at 92–95° at 3 mm., $n^{25}\text{D}$ 1.4360. This fraction was redistilled at 2 mm. from a modified Claisen flask, passing almost completely at 87–88°; $n^{25}\text{D}$ 1.4362. A determination of the acetyl revealed 22.74% acetyl. Deacetylation (sodium methoxide method) and reaction with sodium periodate showed that only about 4% of the periodate was consumed in 28 hours. The products were formic acid (about 3%) and a trace of aldehyde. These findings suggest that the fraction is composed chiefly of ethyl 3,4-dideoxy-2-*O*-acetylpentoside, for which the calculated acetyl content is 22.86%, formation of which must have involved reaction of the acylal function of the diacetate with ethanol.

Purification of Dihydropyran.—A sample of dihydropyran that had been drying for a long time over excess Drierite was fractionated twice through a Widmer column. The material obtained from the second distillation, after a small forerun, was collected at 83.8–83.9° (740 mm.).

An infrared spectrum of this material showed no methyl band at or near 7.25 μ, and no terminal double bond band in the 5.55–5.72 region. The infrared data thus clearly indicate the absence of such compounds as III and IV in the dihydropyran. The spectrum was run by William Fately of this Laboratory. The most prominent absorption bands, apart from the various CH bands between 3.2 and 3.5 μ were a very strong band at 6.07 μ which is assigned to the double bond, a very strong band at 8.06 μ assigned to the ether link, and a very strong band at 9.32 μ unassigned. All of the major peaks were "knife-edge" peaks. Comparison with the spectrum of tetrahydropyran, through the courtesy of Dr. Scott Searles, was helpful in making some assignments.

Preparation of II from Pure I.—From 143 g. (1.74 moles) of pure dihydropyran and 651.7 g. of 8.57% hydrogen peroxide in *t*-butyl alcohol (1.64 moles) and a total of 12 ml. of 0.5% osmium tetroxide solution was prepared a sample of 3,4-dideoxypentose which was isolated by evaporation, acetylation and distillation. There was obtained 84.5 g. (25%) of twice-distilled acetate, b.p. 109–114° (2–3 mm.).

Deacetylation and Periodate Oxidation.—A sample of the diacetate prepared above was deacetylated in methanol with a catalytic amount of barium methoxide, and the diol thus obtained was submitted to periodate oxidation. An aliquot taken after 7.5 hr. showed 95.4% periodate consumption. After 18.5 hours the periodate consumption was 96.8%.

The remaining nine-tenths of the reaction mixture was neutralized with an excess of sodium bicarbonate and distilled into dimedon solution. The crude formaldehyde derivative melting from 173–182° was obtained in about 25% yield. The distillate smelled very strongly of formaldehyde.

Repetition of this experiment with the modification that the iodate and excess periodate were precipitated with barium carbonate before distilling off the formaldehyde revealed essentially the same amount of formaldehyde.

Hydroxylation of Dihydropyran by Osmium Tetroxide and Sodium Chlorate.—To a stirred suspension of 100 g. (1.18 moles) of dihydropyran in 600 ml. of water at 50° was added 25 ml. of 1% osmium tetroxide solution followed by 1500 ml. of a 20% sodium chlorate solution (2.8 moles) added at such a rate as to keep the temperature between 50 and 55°. This required about six hours. Twenty-five ml. more of the osmium tetroxide solution was then added, and the solution was stirred overnight at room temperature. The solution was heated for one hour to 80–85° at which time it was water-white and free from undissolved dihydropyran. The solution was concentrated to 200–250 ml. at 30 mm. pressure and a bath temperature of about 80°. The residue was cooled and the salts were separated. The salt cake was washed with 300 ml. of ether. The ether was combined with the aqueous filtrate and treated with anhydrous sodium sulfate until the disappearance of the aqueous layer. The ether layer was decanted, dried with fresh sodium sulfate, evaporated, and the residue acetylated by the previously described method. Distillation of the acetate at 1–2 mm. gave 1 g. of material boiling at 80–105°, 13 g. of diol diacetate boiling at 105–120°, and 1.5 g. of residue. The 13 g. portion represents a 5.4% yield.

Reaction of Dihydropyran with N-Bromophthalimide.—To 20 g. of dihydropyran (0.24 mole) dissolved in 50 ml. of carbon tetrachloride was added 24 g. (0.1 mole) of N-bromophthalimide in about 15 minutes. Much heat was evolved. The solution was set aside for one hour, and was then refluxed for three hours. On cooling the solution to 0° 11 g. of white crystalline solid precipitated. The crystals were separated and from the solvent another 14.9 g. was obtained by evaporation. This is an 83.5% yield, based on N-bromophthalimide. The material was recrystallized from ethanol and then from acetone; m.p. 144°. It is fairly soluble in ethanol and in acetone, not so soluble in benzene and ether. It is insoluble in water, and does not dissolve in boiling hydrochloric acid or hot 85% phosphoric acid. It dissolves slowly in hot dilute alkali with liberation of bromide ion, but no ammonia. Shaking the compound with excess of silver acetate in acetic acid for one week caused no replacement of bromide. The compound was recovered unchanged. Oxidation with alkaline permanganate gave phthalic acid as the only isolable product.

Anal. Calcd. for $C_{13}H_{12}BrNO_3$: Br, 25.77; N, 4.52; mol. wt., 310. Found: Br, 25.97; N, 3.96; mol. wt. (Rast), 316.

An attempt to form this compound by the reaction of 2,3-dibromotetrahydropyran with potassium phthalimide resulted in the abstraction of HBr from the dibromo compound and gave 3-bromo-5,6-dihydropyran.

The following experiments dealing with hydrazone and osazone derivatives of II were performed by Patricia Craig.

3,4-Dideoxypentose *p*-Nitrophenylhydrazone.—Half-gram quantities of the dideoxypentose (II) and *p*-nitrophenylhydrazine were dissolved in 15 ml. of ethanol. A few drops of acetic acid were added and the mixture was heated to boiling for ten minutes. After concentrating the mixture and cooling it to 0°, 0.6 g. of yellow crystals separated which, after two recrystallizations from methanol, melted at 128.5–129.5°.

Anal. Calcd. for $C_{11}H_{15}N_3O_4$: C, 52.16; H, 5.97. Found: C, 52.29; H, 5.90.

3,4-Dideoxypentose *p*-Nitrophenylosazone.—A mixture of 0.5 g. of the dideoxypentose, 1.5 g. of *p*-nitrophenylhydrazine, 75 ml. of ethanol and 3 ml. of concd. hydrochloric acid was refluxed for 15 minutes. The dark red crystals (1.5 g.) which separated on cooling were recrystallized from a 3:1 mixture of Cellosolve and water: m.p. 246–257° dec.

Anal. Calcd. for $C_{17}H_{18}N_6O_6$: C, 52.85; H, 4.70. Found: C, 52.84; H, 4.76.

Diacetate of 3,4-Dideoxypentose 2,4-Dinitrophenylhydrazone.—A mixture of 1.4 g. of 3,4-dideoxypentose 2,4-dinitrophenylhydrazone,[3] 2 ml. of acetic anhydride, 8 ml. of pyridine was shaken for ten minutes and then let stand for several hours. The mixture was added to 150 g. of ice and water and the product was extracted with chloroform. The chloroform extract was washed with solutions of sodium bicarbonate and copper sulfate, then with water, and finally was dried over sodium sulfate. Solvent was removed, and the brown oil was dissolved in hot methanol. The first crystals were again crystallized from methanol (Norit) to yield a pure product in yellow crystals of m.p. 97.0–97.5°.

Anal. Calcd. for $C_{15}H_{18}N_4O_8$: C, 47.56; H, 4.79. Found: C, 47.46; H, 4.94.

Monoacetate of 3,4-Dideoxypentose 2,4-Dinitrophenylosazone.—A mixture of 1.3 g. of dideoxypentose 2,4-dinitrophenylosazone,[2] 2 ml. of acetic anhydride, and 8 ml. of pyridine was shaken for ten minutes, then was left over night. The mixture was poured into ice-water and the

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°, $\mu = 7.98\ D$); *trans*-α,β-dicyanostyrene (m.p. 42–43°, $\mu = 2.71\ D$).

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

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

where

ϵ_0 = extrapolated dielectric constant of solvent
d_0 = extrapolated density of solvent
$_{\infty}p_{\mathrm{T}}$ = 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, $_{\infty}P_{\mathrm{T}}$, 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

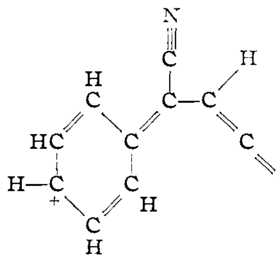
Compd.	α	β	$_{\infty}p_{\mathrm{T}}$	Mol. wt.	$_{\infty}P_{\mathrm{T}}$	P_{D}	P_{O}	$\mu \times 10^{18}$
I	24.90	0.2077	8.524	154.2	1314	39.2	1275	7.98
II	2.622	.1917	1.208	154.2	186.3	39.2	147.1	2.71

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, $\mu = 7.98\ D$ and II, $\mu = 2.71\ D$ 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: $\mu_{\mathrm{C{\equiv}N}} = 2.93\ D$ and $\mu_{\mathrm{H-C}} = 0.4\ D$. 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).