

tion might be expected in hot aqueous acids. The initial product was allowed to stand for 12 hr. at room temp. in 60% sulfuric acid and recovered as before, and then gave a good yield of pure lactone, m.p. 153°.

Acknowledgment.—This work was supported by a grant, G-8821, from the National Science Foundation.

[CONTRIBUTION NO. 623 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Cyanocarbon Chemistry. XVIII.¹ Tricyanovinylolation of Hydrazones and Other Nucleophilic Substances

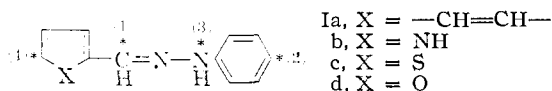
BY J. R. ROLAND AND B. C. MCKUSICK

RECEIVED NOVEMBER 4, 1960

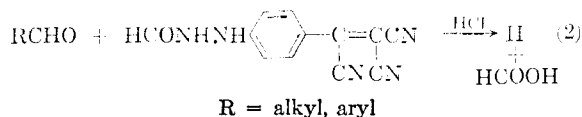
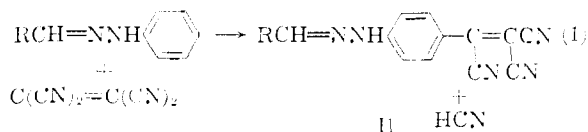
The strongly electrophilic nature of tetracyanoethylene is shown by its reaction with the wide range of nucleophilic substances represented by aromatic hydrazones, azulene, pyrrocoline and 2-methylfuran. The condensation that occurs introduces a tricyanovinyl group at one of the positions of high electron density. Tricyanovinyl chloride complements tetracyanoethylene as a tricyanovinylolation agent in showing increased reactivity and condensing with sterically hindered compounds. The tricyanovinyl aromatic compounds are new classes of dyes.

Tetracyanoethylene reacts with aromatic amines to give N-tricyanovinylamines or *p*-tricyanovinylarylamines, depending on the structure of the aromatic amine.² The present paper describes related reactions of tetracyanoethylene with other types of nucleophilic compounds.

***p*-Tricyanovinylphenylhydrazones.**—The class of compounds most investigated was the *p*-tricyanovinylphenylhydrazones. Examination of I suggests that electrophilic substitution might occur at any of the starred atoms. The general order of re-



activity toward tetracyanoethylene was found to be position 4 for the strongly nucleophilic heterocycles Ib and Id, position 2 for Ia and Ic, position 3 for compounds having positions 2 and 4 substituted, and finally position 1. The *p*-tricyanovinylphenylhydrazones were prepared by two general methods: (A) stirring a phenylhydrazone with tetracyanoethylene in a strongly polar solvent such as dimethylformamide at 20–60° (eq. 1) and (B) refluxing a carbonyl compound with 1-formyl-2-*p*-tricyanovinylphenylhydrazine in aqueous alcoholic solution containing hydrogen chloride (eq. 2).

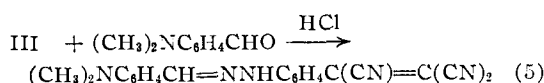
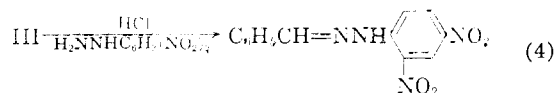
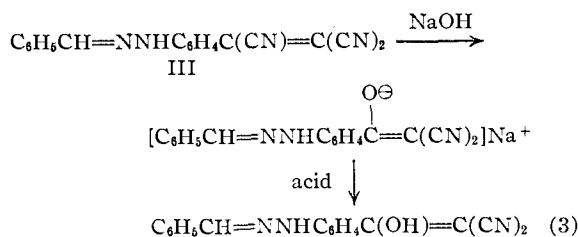


The condensation products are crystalline solids that range in color from red to green and give red to blue solutions (Table I). The presence of strong

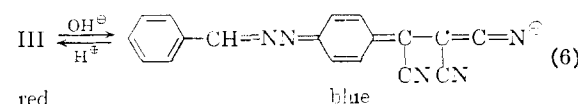
(1) Paper XVII, Tetracyanoethylene and Tricyanovinyl Chloride, C. L. Dickinson, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).

(2) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).

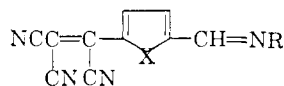
chromophores is shown by molecular extinction coefficients that range from 19,000 to 53,000, mostly above 30,000. The visible spectra strongly support the structures assigned, and infrared spectra confirm conclusions based on the visible spectra. Chemical evidence for the structures is based on the hydrolytic reaction (eq. 3), hydrazine interchanges (eq. 4, 5), the identity of products prepared by both methods A and B, and the behavior toward aqueous alkali.



The products of this group react reversibly with aqueous alkali to cause large bathochromic shifts in absorption maxima whereas N-substituted compounds (Table I, no. 12) are instantly and irreversibly bleached by alkali. This behavior is explained by the formation of a stable anion through loss of a proton (eq. 6). Compounds that have no removable proton undergo hydrolysis according to eq. 3 to yield colorless or pale yellow products.



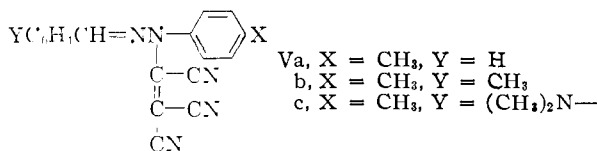
Tricyanovinylolation of Furfural and 2-Pyrrole-carboxaldehyde Hydrazones. Table IIA.—These strongly nucleophilic heterocycles yield blue products on tricyanovinylolation. The structure IV is assigned primarily on spectral evidence since



- IVa, X = >O, R = NHC₆H₅
 b, X = >O, R = N(CH₃)₂
 c, X = >NH, R = NHC₆H₅
 d, X = >NH, R = N(CH₃)₂
 e, X = >NH, R = NHCONH₂

no other location of the tricyanovinyl group would be expected to give the observed absorption. The infrared spectra support this structure in showing unsubstituted phenyl groups in IVa and IVc. In contrast, furfural *p*-tricyanovinylphenylhydrazone (Table I, no. 17) prepared by method B is magenta as is 5-methylfurfural *p*-tricyanovinylphenylhydrazone (Table I, no. 18).

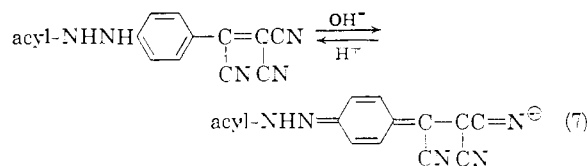
Tricyanovinyl Derivatives of *p*-Substituted Phenylhydrazones. Table IIB.—*p*-Substituted phenylhydrazones of aldehydes condense with tetracyanoethylene to give products that are yellow to orange. The strong hypsochromic shift from the *p*-tricyanovinylphenylhydrazones points to a shorter conjugated system, suggesting that the tricyanovinyl group replaces one of the hydrogens in the -CH=NNH- portion of the molecule. The infrared spectra support this evidence in showing no NH absorption. These spectral data suffice to assign the structures Va–Vc (Table IIB).



Chemical evidence in accord with the N-tricyanovinyl structure is found in the instantaneous and irreversible bleaching of this group of compounds by aqueous alkali.

1-Acyl-2-(*p*-tricyanovinylphenyl)-hydrazines.

Table IIC.—Tetracyanoethylene reacts with 1-acyl-2-phenylhydrazines to form 1-acyl-2-(*p*-tricyanovinylphenyl)-hydrazines. These all have infrared bands showing the presence of a *p*-phenylene group. The acyl *p*-tricyanovinylphenylhydrazines are bright orange compounds that react with alkali to produce a stable blue product, perhaps through proton removal as shown in eq. 7.



Tricyanovinylation with Tricyanovinyl Chloride (Method C).—Tricyanovinylation could also be effected by use of tricyanovinyl chloride¹ or an equimolar mixture of tetracyanoethylene and silver nitrate (method D).

Tricyanovinyl chloride is an interesting tricyanovinylation agent in complementing the utility of tetracyanoethylene through enhanced reactivity and condensation with different types of nucleophilic centers. For example, phenylhydrazones that give magenta or blue *p*-tricyanovinylphenyl-

hydrazones with tetracyanoethylene were found to give yellow or orange products with tricyanovinyl chloride. The products from tetracyanoethylene and the phenylhydrazones of benzaldehyde, *p*-dimethylaminobenzaldehyde and *p*-(methyl- β -cyanoethylamino)-benzaldehyde absorb at 520, 580 and 575 m μ (Table I) while the corresponding products from tricyanovinyl chloride absorb at 344, 414 and 450 m μ .³ In the light of the reaction of tricyanovinyl chloride with N-methylaniline to give N-tricyanovinyl-N-methylaniline,¹ the spectral data clearly indicate that the tricyanovinyl group is introduced on the hydrazine nitrogen. Use of tricyanovinyl chloride with a hindered compound is described in the following section.

Tricyanovinylation of Non-activated Aromatic Nuclei. Table IID.—In addition to reaction with amine-activated and hydroxyl-activated aromatic nuclei, tetracyanoethylene has been shown to tricyanovinylate the highly nucleophilic 9-position of phenanthrene,⁴ the 2-position of pyrroles⁴ and the 3-position of indoles.⁴ In the present work, extensions were made to azulenes, pyrrocoline and 2-methylfuran. The structure of azulene⁵ leads to the prediction that tricyanovinylation should occur with considerable ease. This was confirmed by experiment,⁶ and, based on extensions of the Plattner rule,⁷ the location of the principal absorption band at 490 m μ shows the product to be 1-tricyanovinylazulene (Table II, no. 12).

Under the same conditions, guaiazulene (1,4-dimethyl-7-isopropylazulene) and tetracyanoethylene merely form a π -complex⁸ that readily reverts to the components on elution from an alumina column with petroleum ether.⁶ The 4-methyl group hinders attack of tetracyanoethylene at the nucleophilic 3-position, an effect similar to that noted in work on aromatic amines² where steric hindrance makes substitution *ortho* to the amino group far more difficult than *para* to it. The high reactivity of tricyanovinyl chloride is dramatically shown by its rapid condensation with guaiazulene at room temperature to give 1,4-dimethyl-7-isopropyl-3-tricyanovinylazulene. The same product was prepared in lower yield by heating guaiazulene with tetracyanoethylene on a steam-bath for an hour.

Pyrrocoline (VII)⁹ can be considered as being electronically similar to azulene and its easy tricyanovinylation to give a similarly colored product, VIII, supports this view (Table II, no. 14).

(3) These experiments were done by Dr. C. L. Dickinson.

(4) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958).

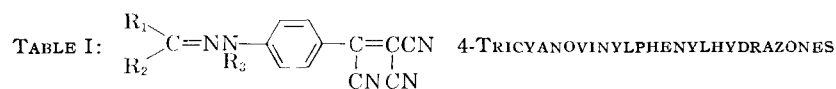
(5) R. D. Brown, *Trans. Faraday Soc.*, **44**, 984 (1948); K. Hafner, *Angew. Chem.*, **70**, 419 (1958).

(6) K. Hafner and K. L. Moritz, *ibid.*, **72**, 918 (1960), have independently prepared a number of tricyanovinylazulenes from azulenes and tetracyanoethylene. In addition, they prepared stable π -complexes from tetracyanoethylene and various azulenes.

(7) E. J. Cowles, *J. Am. Chem. Soc.*, **79**, 1093 (1957); A. G. Anderson, Jr., R. Scotoni, Jr., E. J. Cowles and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1951).

(8) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2779 (1958).

(9) The pyrrocoline used in this work was prepared according to the improved procedure of V. Boekelheide and R. J. Windgassen, *ibid.*, **81**, 1456 (1959).



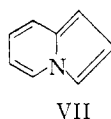
Cmpd.	R ₁	R ₂	R ₃	M.p., °C.	λ _{max} , mμ	ε	Prepn. method	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
										Calcd.	Found	Calcd.	Found	Calcd.	Found
1	C ₃ H ₇	H	H		508	42600	B	68	C ₁₅ H ₁₃ N ₅	68.42	69.10	4.97	5.07	26.60	25.67
2	CH ₃	CH ₃	H	212	513	40300	B	79	C ₁₄ H ₁₁ N ₅	67.45	67.20	4.41	4.61	28.10	27.79
3	C ₆ H ₅	H	H	288	520	46300	A, B, D	98	C ₁₈ H ₁₁ N ₅	72.71	72.70	3.73	3.99	23.56	23.13
4	C ₆ H ₅	CH ₃	H	277	526	42200	A	46	C ₁₉ H ₁₃ N ₅	73.30	72.85	4.21	4.23	22.50	22.13
5	<i>p</i> -CH ₃ C ₆ H ₄	H	H	264	529	48700	A	72	C ₁₉ H ₁₃ N ₅	73.30	72.77	4.21	4.30	22.50	22.67
6	<i>p</i> -ClC ₆ H ₄	H	H	304	520	48000	A	60	C ₁₈ H ₁₀ ClN ₅	65.16	64.91	3.04	3.33	21.11	21.35
7	<i>o</i> -HOOC ₆ H ₄	H	H	281	519	41300	A, B	26	C ₁₈ H ₁₁ N ₅ O	69.00	68.69	3.54	3.54	22.35	21.75
					348	10300									
8	2,4(OH) ₂ C ₆ H ₃	H	H	344	542	43900	A, B	19	C ₁₈ H ₁₁ N ₅ O ₂	65.65	65.58	3.37	3.34	21.27	21.19
9	3,4(CH ₃ O) ₂ C ₆ H ₃	H	H	274	542	44600	A	71	C ₂₀ H ₁₅ N ₅ O ₂	67.21	67.15	4.23	4.61	19.60	20.25
10	3,4-(CH ₂ O) ₂ C ₆ H ₃	H	H	266	540	47700	A	62	C ₁₉ H ₁₁ N ₅ O ₂	66.86	67.49	3.25	3.56	20.52	20.05
11	<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	H	H	321	582	41500	A, B	82	C ₂₀ H ₁₆ N ₆	70.57	70.25	4.74	4.75	24.69	24.60
					363	20400									
12	<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	H	CH ₃	289	588	34700	A	65	C ₂₁ H ₁₅ N ₆	71.16	70.80	5.12	5.18	23.71	23.22
					358	20900									
13	<i>p</i> -(C ₂ H ₅) ₂ NC ₆ H ₄	H	H	267	592	41200	A	24	C ₂₂ H ₂₀ N ₆	71.72	72.06	5.47	5.79	22.81	22.10
					419	7360									
					368	22000									
14	<i>p</i> -NCCH ₂ CH ₂ N(CH ₃)C ₆ H ₄	H	H	256	575	42500	A	69	C ₂₂ H ₁₇ N ₇	69.64	69.89	4.41	4.91	25.84	25.23
					359	21200									
15	C ₆ H ₅ CH=CH	H	H	252	538	53000	B	61	C ₂₀ H ₁₃ N ₆	74.29	74.45	4.05	4.14	21.67	21.33
17	2-Furyl	H	H	230 d.	530	43000	B	93	C ₁₆ H ₉ N ₅ O	66.89	67.08	3.16	3.36	24.38	24.63
18	5-Methyl-2-furyl	H	H	..	545	41600	A	57	C ₁₇ H ₁₁ N ₅ O	67.76	67.45	3.68	3.77	23.25	22.32
19	2-Thenyl	H	H	270	535	41500	A, B	68	C ₁₆ H ₉ N ₅ S	63.35	64.00	2.99	3.27	23.09	23.26
20	2-Pyrryl	H	H		578	22300	B	43	C ₁₆ H ₁₀ N ₆	This product could not be obtained analytically pure					
21	3-Pyridyl	H	H	231	512	27400	A	48	C ₁₇ H ₁₀ N ₆	68.45	68.60	3.38	3.50	28.18	27.60
22	3-Indolyl	H	H		573	43300	A, B	98	C ₂₀ H ₁₁ N ₆	71.61	71.40	3.30	3.88	25.06	24.51
23	3-Isloxazolyl	H	H	159	491	34600	A	11	C ₁₅ H ₈ N ₆ O					29.16	29.8

TABLE II: TRICYANOVINYL COMPOUNDS

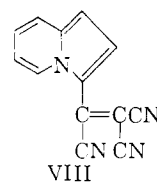
Compound	M.p., °C.	λ _{max} , mμ	ε	Prepn. method	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		
							Calcd.	Found	Calcd.	Found	Calcd.	Found	
A. Tricyanovinyl derivatives of furfural and pyrrole-2-aldehyde													
1	5-TCV-C ₄ H ₂ OCH=NNHC ₆ H ₅ ^a	249	588	32,400	A	50	C ₁₆ H ₉ N ₆ O	66.89	67.49	3.16	3.52	24.38	24.51
2	5-TCV-C ₄ H ₃ NCH=NNHC ₆ H ₅		580	8,300	A		C ₁₆ H ₁₀ N ₆						
			385	7,700									
3	5-TCV-C ₄ H ₂ OCH=NN(CH ₃) ₂	223	570	41,100	A	58	C ₁₂ H ₉ N ₆ O	60.24	60.44	3.79	4.03	29.28	28.77
4	5-TCV-C ₄ H ₃ NCH=NN(CH ₃) ₂	232	562	35,500	A	65	C ₁₂ H ₁₀ N ₆	60.49	60.79	4.23	4.49	35.28	33.19
5	5-TCV-C ₄ H ₃ NCH=NNHCONH ₂	333	498	38,500	A	70	C ₁₁ H ₇ N ₇ O	52.17	52.65	2.79	2.97	38.72	37.70

B. <i>p</i> -Substituted phenylhydrazones		C. 1-Acyl-2-(4-tricyanovinylphenyl)-hydrazines		D. Miscellaneous tricyanovinyl derivatives							
6	$C_6H_5CH=NN(TCV)C_6H_4CH_3-p$	20,400	A, C	2.2	$C_{19}H_{13}N_5$	73.30	73.23	4.21	4.41	22.50	22.28
		13,800									
		370(sh) ^f									
7	<i>p</i> - $CH_3C_6H_4CH=NN(TCV)C_6H_4CH_3-p$	6,470	A, C	4.7	$C_{20}H_{15}N_5$	73.83	73.32	4.65	5.14	21.53	21.90
		374									
8	HCONHNHC ₆ H ₄ (<i>p</i>)TCV	27,400	A	57	$C_{12}H_7N_5O$	60.76	60.73	2.97	2.89	29.53	29.51
9	CH ₃ CONHNHC ₆ H ₄ (<i>p</i>)TCV	29,900	A	54	$C_{13}H_9N_5O$	62.14	62.60	3.61	3.79	27.88	27.21
10	$C_6H_5CONHNHC_6H_4(p)TCV$	29,800	A	58	$C_{13}H_{11}N_5O$	69.00	69.02	3.54	3.51	22.36	22.43
11	<i>p</i> - $NO_2C_6H_4CONHNHC_6H_4(p)TCV$	29,600	A	81	$C_{18}H_{10}N_5O_3$	60.33	60.42	2.81	3.07	23.46	22.91
12	1-Tricyanovinylazulene	26,800	A	70	$C_{16}H_7N_3$	78.65	78.63	3.06	3.66	18.32	18.28
		6,400									
13	1,4-Dimethyl-7-isopropyl-3-tricyanovinylazulene	20,000	C	75	$C_{20}H_{17}N_3$	80.24	79.92	5.72	5.84	14.04	13.74
		6,400									
14	3-Tricyanovinylpyrrocoline	29,600	A	81	$C_{14}H_8N_4$	71.56	71.02	2.77	2.82	25.68	24.76
15	5-Methyl-2-tricyanovinylfuran	26,900	A	36	$C_{10}H_5N_3O$	65.57	65.18	2.75	2.88	22.94	23.23

^a TCV is the tricyanovinyl group $-C(CN)=C(CN)_2$, C_4H_5O is 2,5-furylene, C_4H_3N is 2,5-pyrroline. ^b Could not obtain this product analytically pure; the best sample had C, 64.27; H, 3.86; N, 27.06. Calcd.: C, 67.12; H, 3.52; N, 29.36. ^c Shoulders on side of main band. ^d In acetonitrile.



VII



VIII

2-Methylfuran condenses with tetracyanoethylene in dimethylformamide at room temperature to give 2-methyl-5-tricyanovinylfuran in good yield. In contrast, no reaction of furan with tetracyanoethylene was detected under the same conditions. It is remarkable that a methyl group should have sufficient electron-releasing capacity to cause a qualitative difference between furan and 2-methylfuran.

Dyeing Properties.—Like the *p*-tricyanovinylarylamines,¹ the tricyanovinyl derivatives described herein give brilliant dyeings. Cellulose acetate, silk and nylon usually show the greatest affinity for the dyes, but hydrophobic fibers such as polyethylene terephthalate and polyacrylonitrile are also dyed medium to deep shades. The dyed fabrics range in color from yellow to deep blue. The *p*-tricyanovinylphenylhydrazones show improvement over the *p*-tricyanovinylarylamines in resistance to degradation by alkali.

Acknowledgments.—We are indebted to Drs. Rolf Dessauer, Alex Kotch¹⁰ and D. G. Coe of the Organic Chemicals Department, E. I. du Pont de Nemours and Co., for advice, supplying intermediates and conducting dye evaluations. Particularly valuable contributions were made by Dr. T. L. Cairns of this Laboratory in discussions throughout the work.

Experimental

Melting points were taken on a preheated copper block and the temperatures given are the lowest at which the powdered crystals melted instantaneously on contact with the block. The melting points agreed with capillary melting points for the compounds for which the latter method was feasible.

Visible spectra were determined in acetone solutions, unless otherwise designated, in a Cary model 14 recording spectrophotometer by Mr. C. B. Matthews and Miss Ellen Wallace.

Infrared spectra were determined on a Perkin and Elmer model 21 double beam spectrometer by Miss Naomi Schlichter who rendered valuable interpretative assistance.

4-Tricyanovinylphenylhydrazones. Benzaldehyde tricyanovinylphenylhydrazone (III). **Method A.**—A solution of 39.2 g. (0.2 mole) of benzaldehyde phenylhydrazone in 50 ml. of dimethylformamide was warmed to 50°, stirred, and heated or cooled as needed while adding 25.6 g. (0.2 mole) of tetracyanoethylene in small portions over a period of 10–20 minutes. The temperature was maintained at 50 ± 2° throughout this period and for an additional 10 minutes. The reaction mixture was cooled overnight in ice. Filtration yielded 6.2 g. of benzaldehyde *p*-tricyanovinylphenylhydrazone, m.p. 288° after recrystallization from *n*-butyl alcohol. The filtrate was poured into a well-stirred mixture of ice and water to give a tarry precipitate. The water was decanted and the tar was solidified by trituration with a small amount of glacial acetic acid. The crude product was recrystallized from *n*-butyl alcohol to yield 33.0 g. of the same product, m.p. 287–288°. A small residue of 5.8 g., not soluble in the volume of *n*-butyl alcohol used, did not differ in properties from the foregoing fractions. The yield totaled 45.0 g. (98%).

Method B.—A mixture of 0.23 g. (1 mmole) of 1-formyl-2-*p*-tricyanovinylphenylhydrazine and 0.10 g. (1 mmole) of

(10) National Science Foundation, Washington, D. C.

benzaldehyde was refluxed for 20 minutes in a mixture of 20 ml. of alcohol, 5 ml. of water and 0.5 ml. of concentrated hydrochloric acid. The reaction mixture was poured onto ice and the solid product collected by filtration. The crude product was recrystallized from *n*-butyl alcohol to yield 0.2 g. (67%) of glistening purple needles. The infrared and visible spectra of this product are identical with those of the product prepared by procedure A. The infrared spectrum shows NH stretching at 3280 cm^{-1} , =CH at 3075 cm^{-1} , conjugated CN at 2222 cm^{-1} , and unsaturation bands at 1613, 1538 and 1480 cm^{-1} . The longer wave length region was at first confusing in the multiplicity of bands but the alternative synthesis (method B) permitted assignment of the 758, 693 cm^{-1} bands to the unsubstituted phenyl and a 838 cm^{-1} to the *p*-phenylene group. Other products of the series have spectral variations consistent with known differences in structure of reactants.

Alkaline Hydrolysis of Benzaldehyde *p*-Tricyanovinylphenylhydrazine.—Hydrolysis of the tricyanovinyl dye was carried out by adding 4.0 g. of the dye to a boiling 10% solution of sodium hydroxide. The mixture was refluxed for 20 minutes, cooled in ice, and filtered to separate a solid that was washed with cold 10% sodium hydroxide solution. The filtrate was placed in a flask set for distillation and fitted with a dropping funnel. An excess of sulfuric acid was added from the funnel and the mixture distilled into a receiver containing 50 ml. of 10% sodium hydroxide, and having a delivery tube extending below the surface of the alkaline solution. The latter alkaline solution was washed into a 250-ml. volumetric flask and diluted to volume. A small amount of this solution was boiled with a few drops of ferrous ammonium sulfate and acidified. The precipitation of prussian blue indicated the presence of cyanide ion. Analysis of the remaining solution showed that it had cyanide predicted by eq. 3.

The solid product was dissolved in water and treated with sulfuric acid to precipitate the hydroxy compound. Crystallization was not satisfactory so the solid product was purified by precipitation from alcohol and water to give 2.8 g. (72%) of a hydroxydicyanovinyl compound melting at 234–235°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}$: C, 70.80; H, 4.17; N, 19.42. Found: C, 70.24; H, 4.54; N, 20.42.

This degradation product has an absorption maximum at 380 $\text{m}\mu$ and an extinction coefficient of 38,600. This hydrolysis corresponds to the first stage hydrolysis of *p*-tricyanovinylarylamines dyes.¹

Cleavage of Benzaldehyde *p*-Tricyanovinylphenylhydrazine.—A mixture of 0.5 g. of benzaldehyde *p*-tricyanovinylphenylhydrazine and 0.5 g. of 2,4-dinitrophenylhydrazine was refluxed in a mixture of 200 ml. of absolute alcohol and 2 ml. of concentrated hydrochloric acid for 12 hours. The reaction mixture was cooled in ice and filtered. The solid was washed with alcohol and air-dried to give 0.258 g. (40%) of brownish-red needles, m.p. 238°. A mixed melting point with authentic benzaldehyde 2,4-dinitrophenylhydrazine was 238–239°. Recrystallization from alcohol gave no change in color or melting point.

The filtrate was diluted to 250 ml. and analyzed spectrally for unchanged magenta dye. The absorbance of 140 at 510 $\text{m}\mu$ showed the presence of 0.224 g. or 45% of the original dye used. Only a small error is introduced through the use of the ϵ of 46,300 observed in acetone solution rather than determining a new value in alcohol (ref. 1, p. 280).

A 100-ml. aliquot of the diluted filtrate was refluxed for 1 hour with 0.1 g. of *p*-dimethylaminobenzaldehyde. The cooled mixture was filtered and the crude dye, brilliant dark blue needles, was recrystallized from *n*-butyl alcohol. This gave two fractions totaling 47.8 mg. that were 53% (ϵ_{580} 21,900) and 46% (ϵ_{580} 19,150) pure *p*-dimethylaminobenzaldehyde *p*-tricyanovinylphenylhydrazine (ϵ_{580} 41,500). The contaminant was the 2,4-dinitrophenylhydrazine.

Pure *p*-dimethylaminobenzaldehyde *p*-tricyanovinylphenylhydrazine was obtained by refluxing benzaldehyde *p*-tricyanovinylphenylhydrazine (0.2 g.) and *p*-dimethylaminobenzaldehyde (1.0 g.) in a mixture of 75 ml. of absolute alcohol and 1 ml. of concentrated hydrochloric acid for 3 hours. The reaction mixture was cooled and filtered to collect the product which amounted to 190 mg. (83%) of dark blue needles. The product was a mixture of 46% *p*-dimethylaminobenzaldehyde *p*-tricyanovinylphenylhydrazine (ϵ_{580} 19,180), and 54% of the original benzaldehyde *p*-tricyanovinylphenylhydrazine. One recrystallization from

n-butyl alcohol raised the purity of the *p*-dimethylaminobenzaldehyde *p*-tricyanovinylphenylhydrazine to 96%, ϵ_{580} 39,800.

Tricyanovinylation of Furfural and 2-Pyrrolicarboxaldehyde¹¹ Phenylhydrazones.—Furfural *p*-tricyanovinylphenylhydrazine (Table I, no. 17) has an infrared spectrum showing NH stretching at 3280 cm^{-1} , =CH at 3125 cm^{-1} , conjugated CN at 2220 cm^{-1} and unsaturation bands at 1610, 1505 and 1480 cm^{-1} . A band at 833 cm^{-1} shows a *p*-phenylene group and a 751 cm^{-1} band is characteristic of the α -substituted furan ring.

The infrared spectrum of 5-tricyanovinylfurfural phenylhydrazine (Table II, no. 1) is similar except for strong bands at 753, 691 cm^{-1} characteristic of an unsubstituted phenyl group.

2-Pyrrolicarboxaldehyde *p*-tricyanovinylphenylhydrazine (Table I, no. 20) shows 2 NH stretching bands at 3390, 3280 cm^{-1} conjugated CN at 2222 cm^{-1} , unsaturation bands at 1615, 1480 cm^{-1} and *p*-phenylene group at 833 cm^{-1} .

The infrared spectrum of the isomeric 5-tricyanovinyl-2-pyrrolicarboxaldehyde phenylhydrazine (Table II, no. 2) shows NH stretching at 3280 cm^{-1} , =CH at 3125 cm^{-1} , conjugated CN at 2198 cm^{-1} , and unsaturation bands at 1640, 1600, 1575, 1538 and 1493 cm^{-1} . Bands at 754 and 690 cm^{-1} show an unsubstituted phenyl group.

Tricyanovinylation of *p*-Substituted Phenylhydrazones.—Benzaldehyde *N*-tricyanovinyl-*p*-tolylhydrazine (Table II, no. 6) shows no NH by infrared. The expected bands were present for the rest of the known part of the structure. The band at 820 cm^{-1} shows a *p*-phenylene group and those at 750, 690 cm^{-1} show unsubstituted phenyl. The *p*-tolualdehyde analog has a similar spectrum but shows only the 820 cm^{-1} band for the *p*-phenylene group.

The 1-Acyl-2-(*p*-tricyanovinylphenyl)-hydrazines.—The compounds of this class were prepared by method A, but a side reaction resulting in evolution of a gas other than hydrogen cyanide occurred. The side reaction was minimized by carrying out the tricyanovinylation at lower temperatures than normally used.

1-Formyl-2-*p*-tricyanovinylphenylhydrazine.—A solution of 27.2 g. (0.02 mole) of 1-formyl-2-phenylhydrazine in dimethyl sulfoxide was cooled in an ice-bath. The solution was swirled manually while 25.5 g. (0.2 mole) of tetracyanoethylene was added in small portions. The addition required about 15 minutes, during which time the temperature remained at 5–15°. The reaction mixture was allowed to stand in an ice-bath overnight. The reaction mixture was poured into a well-stirred ice-water mixture. The precipitate comprised a mixture of fine needles and an orange tar. The tar was triturated with glacial formic acid to induce solidification. The product then was recrystallized from methanol to give 25.6 g. (35%) of nearly black needles melting with decomposition at 215–216°. Infrared spectra of this and other 1-acyl-2-(*p*-tricyanovinylphenyl)-hydrazines have bands near 832 cm^{-1} showing the presence of *p*-phenylene groups.

Tricyanovinylation Using Tricyanovinyl Chloride. Method C.—A solution of 0.241 g. of guaiazulene in 15 ml. of ethyl acetate was stirred while adding a solution of 0.167 g. of tricyanovinyl chloride in 3–4 ml. of ethyl acetate. Reaction occurred instantly and the mixture set to a magma too viscous to stir. The solid was collected on a filter and recrystallized from alcohol; yield 0.27 g. (75%).

Tricyanovinylation Using Tetracyanoethylene with Metal Salts. Method D.—Acetonitrile solutions of 1.96 g. of benzaldehyde phenylhydrazine and of 1.28 g. of tetracyanoethylene were mixed to form a blue π -complex. A solution of 1.7 g. of silver nitrate in acetonitrile then was added slowly with manual agitation. Reaction was rapid and appeared complete in a few seconds. Filtration yielded a colored solid that did not melt on ignition; the colored portion sublimed leaving a white residue that appeared to be silver cyanide. Silver cyanide was conclusively identified by reactions and analysis in related syntheses. The filtrate was precipitated by pouring into an ice-water mixture. The crude product was collected on a filter and crystallized from *n*-butyl alcohol. This gave 2.5 g. (84%) of impure product melting at 264° with prior decomposition from 208° and having ϵ_{522} 15,450. On the basis of the

(11) R. M. Silverstein, *et al.*, *J. Org. Chem.*, **20**, 668 (1955).

spectral data the dye was about 33% pure. Ignition gave a residue of silver and analysis showed the presence of 6.05% of silver which corresponds to 7.5% of silver cyanide.

Tricyanovinylations with tricyanovinyl chloride and tetracyanoethylene-silver nitrate offer advantages when working with materials that may be adversely affected by dimethylformamide or for preparation of tricyanovinyl compounds that are decomposed because of the basicity of normally useful solvents. A case in point is the preparation of 4-tricyanovinyl-1-*p*-tolylamino-7-*p*-tolylimino-1,3,5-cycloheptatriene.¹²

Other salts that promoted tetracyanoethylene condensations included ferric nitrate, zinc nitrate, zinc acetate, cobalt acetate, nickel acetate, nickel nitrate, cobalt nitrate and chromium acetate. These were less effective than silver nitrate and required heating. Blank experiments showed that no condensation occurred between benzaldehyde phenylhydrazone and tetracyanoethylene in acetonitrile even when boiled to dryness.

(12) Contribution No. 591, "N,N-Disubstituted 1-Amino-7-imino-1,3,5-cycloheptatrienes," by W. R. Brasen, H. E. Holmquist and R. E. Benson, in publication.

[CONTRIBUTION NO. 636 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

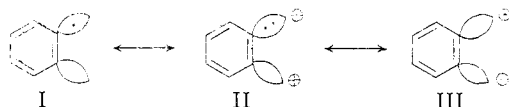
A Cycloaddition Reaction of Benzyne

By HOWARD E. SIMMONS

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The strained bicyclic hydrocarbons bicyclo[2.2.1]heptadiene and bicyclo[2.2.1]heptene reacted cleanly with benzyne to give cyclobutane derivatives, *exo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nona-3,7-diene and *exo*-3,4-benzotricyclo[4.2.1.0^{2,5}]non-3-ene, respectively. Benzyne reacted with simple olefins to give complex mixtures of products that result from hydrogen abstraction. Some implications of these results are discussed.

Introduction.—The electrically neutral intermediate benzyne (C₆H₄)¹ is highly reactive when prepared under a variety of conditions.² The kinds of reactions undergone by benzyne that have been distinguished thus far include facile attack by nucleophiles,¹⁻⁴ dimerization and trimerization,⁵ and Diels-Alder addition.^{5,6} The observed products and the conditions under which many of these reactions occur indicate that benzyne is one of the most highly reactive hydrocarbon species known. Because of this high chemical reactivity, benzyne has never been isolated and little is known of its electronic structure. Most workers have interpreted the reactions undergone by benzyne in terms of the polar structures II and III, although it is generally recognized that benzyne is probably best represented as a resonance hybrid of structures I-III.



Cycloaddition Reactions.—When benzyne was generated by the reaction of *o*-fluorobromobenzene with magnesium in tetrahydrofuran^{6a} in the presence of bicyclo[2.2.1]heptadiene, there was obtained in 15–21% yields a liquid hydrocarbon adduct IV. Vapor phase chromatography (v.p.c.) of the reaction mixture showed the presence of another product that was formed in such low yield

(1) J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

(2) For an excellent review of benzyne chemistry, see R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(3) J. D. Roberts, D. A. Semenow, H. E. Simmons and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956), and earlier references cited therein.

(4) H. E. Simmons, *J. Org. Chem.*, **25**, 691 (1960).

(5) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

(6) (a) G. Wittig and R. Ludwig, *Angew. Chem.*, **68**, 40 (1956);

(b) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958); (c) G. Wittig and W. Behnisch, *ibid.*, **91**, 2358 (1958); (d) G. Wittig and Niethammer, *ibid.*, **93**, 944 (1960); (e) other examples have been cited by Professor Wittig in a private communication.

that isolation and characterization were not feasible. The n.m.r. spectrum of the minor product showed the absence of ethylenic protons. The major product was isolated in a pure state by preparative v.p.c. and analysis showed it to be a 1:1 adduct, C₁₃H₁₂. The adduct was unsaturated as determined by the rapid decolorization of bromine and potassium permanganate solutions.

The infrared spectrum of the adduct confirmed the presence of the aromatic ring, and olefinic unsaturation of the bicyclo[2.2.1]heptene type was indicated by a band at 6.39 μ . The spectrum was in agreement with the suggestion that the adduct resulted from a cycloaddition reaction and was a benzocyclobutene derivative. Proton nuclear magnetic resonance studies showed this indeed to be the case and further proved that no skeletal rearrangement had occurred. The spectral studies are discussed in detail below.

Bicyclo[2.2.1]heptadiene has frequently been reported to give 1:1 adducts with dienophiles by addition across the 2,6-positions.⁷ In the reaction of benzyne with bicyclo[2.2.1]heptadiene it was anticipated that an analogous 2,6-adduct might be a reaction product.⁸ Since epoxidation⁹ of and addition of iodomethylzinc iodide¹⁰ to the bicycloheptene type of double bond occur with

(7) Such additions to give nortricyclic derivatives have been reported with maleic anhydride (E. F. Ullman, *Chemistry & Industry*, 1173 (1958)) and with tetracyanoethylene (A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959)). Tetrafluoroethylene gave a single adduct with this diene (W. R. Brasen, U. S. Patent 2,928,865 (1960)), and unpublished work in this Laboratory has shown conclusively that the adduct is the cyclobutane derivative i of *exo* configuration (R. E. Putnam).

(8) No saturated hydrocarbon products were detected in the crude reaction mixture with certainty, although a minor product that appeared saturated in the n.m.r. was isolated and partially purified by v.p.c. (see Experimental). This product may be the anticipated 2,6-adduct.

(9) H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

(10) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).