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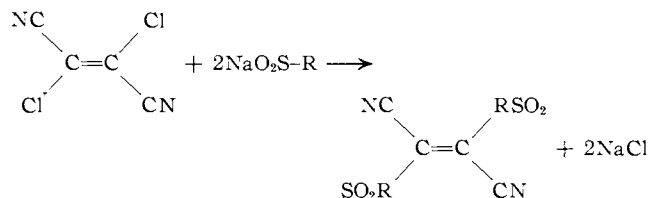
Preparation and Reactions of 1,2-Dicyano-1,2-disulfonylethylenes

BY E. L. MARTIN

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A new class of tetra-(negatively-substituted)-ethylenes, the 1,2-dicyano-1,2-disulfonylethylenes, has been synthesized. These new compounds undergo many of the reactions of tetracyanoethylene, including addition, replacement and cyclization reactions. Dyes, strong acids and heterocyclic compounds have been prepared from the 1,2-dicyano-1,2-disulfonylethylenes. Many of the same products are obtained by condensing dichlorofumarionitrile with a salt of a sulfinic acid in the presence of a third reactant.

Tetracyanoethylene is a very reactive compound that undergoes a variety of reactions, including addition, replacement and cyclization reactions.¹ Theoretical considerations suggested that 1,2-dicyano-1,2-disulfonylethylenes should likewise be highly reactive. A brief investigation of these compounds has shown that this is true and that they can be used to prepare a large number of compounds containing cyano and sulfonyl groups.

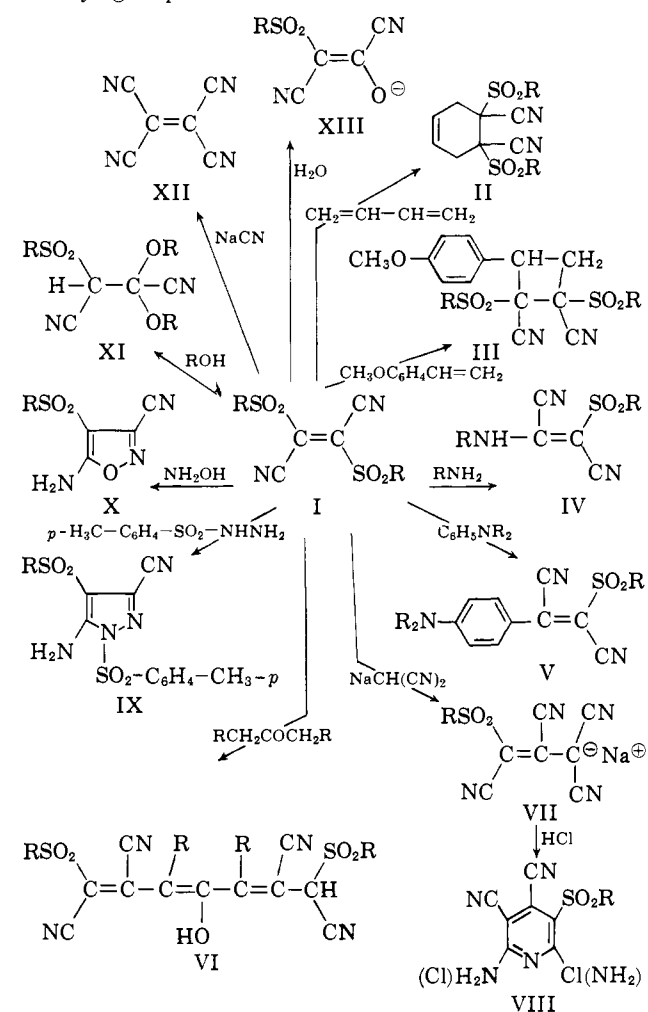


dicyanosulfonylethylenes (XV) are readily hydrolyzed to dicyanosulfonylethenolates (XIII). The use of dichloromaleonitrile or tetrachlorosuccinonitrile in the above reaction gives the same dicyanodisulfonylethylene. The symmetrical configuration has been assigned these products and is based on the above observations, the weak nitrile absorption at 4.5 μ and a study of molecular models.

The dicyanodisulfonylethylenes are colorless to faintly yellow solids that decompose on melting or at temperatures in excess of about 200°. They are sparingly soluble in most organic solvents when R is an aromatic or lower aliphatic radical. The compound in which R is *n*-butyl melts at 118–119° and is readily soluble in most organic solvents. When R is *p*-acetamidophenyl, *p*-H₃C-CONHC₆H₄-, the compound decomposes at temperatures above about 280° and is insoluble in all the usual organic solvents.

The dicyanodisulfonylethylenes undergo addition reactions at the double bond as illustrated by the Diels-Alder reaction with butadiene (II) and anthracene and formation of cyclobutanes (III) with electron-rich monoolefins such as *p*-methoxystyrene. Like the corresponding reactions of tetracyanoethylene,^{2,3} these addition reactions take place under mild reaction conditions and in high yields. Primary aromatic amines react with dicyanodisulfonylethylenes to give *N*-(1,2-dicyano-2-sulfonylvinyl)-arylamines (IV) by replacement of a sulfonyl group. Reaction of these tetra-substituted ethylenes with secondary and tertiary aromatic amines gives 4-(1,2-dicyano-2-sulfonylvinyl)-arylamines (V), a new class of brilliant yellow to blue dyes. Like tetracyanoethylene⁴ and 3-chloro-2-cyanomaleimides,⁵ they also react with phenols, pyrazolones and most active couplers that form an azo compound with benzenediazonium chloride.

The 4-(1,2-dicyano-2-sulfonylvinyl)-arylamines (V) give brilliant dyeings on fibers of materials such as cellulose acetate, polyethylene terephthalate and polyacrylonitrile. The dyeings have good washfastness and sublimation-fastness and fair lightfastness, and they can be applied from a moderately acidic bath (pH 5–6) without serious decomposition. They de-



The 1,2-dicyano-1,2-disulfonylethylenes have been synthesized by the condensation of dichlorofumarionitrile and a salt of a sulfinic acid in a suitable reaction medium such as dimethylformamide or acetonitrile. The reaction has been carried out within the temperature range of -70 to 40°. The reaction is best carried out under anhydrous reaction conditions as the dicyanodisulfonylethylenes (I) and the intermediate chloro-

(1) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(2) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

(3) J. K. Williams, D. W. Wiley and B. C. McKusick, presented before the Organic Division of the American Chemical Society, 139th National Meeting, St. Louis, Mo., March, 1961, p. 90.

(4) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

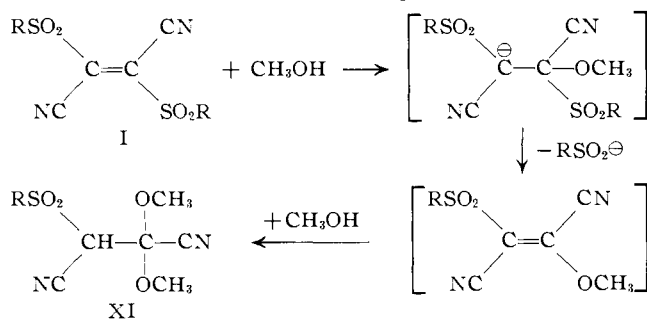
(5) E. L. Martin, C. L. Dickinson and J. R. Roland, presented before the Organic Division of the American Chemical Society, 138th National Meeting, New York, N. Y., September, 1960, p. 94P.

compose rapidly in basic dye baths but once on the fibers they have good washfastness toward alkaline soap solutions. The 4-(1,2-dicyano-2-sulfonylvinyl)-arylamines absorb visible light very strongly, with molecular extinction coefficients of 34,000–42,000 as compared to 37,000–47,000 for the 4-tricyanovinylarylamines. The 4-(1,2-dicyano-2-sulfonylvinyl)-arylamines and 4-tricyanovinylarylamines have very similar visible absorption maxima.⁴

Deep blue compounds are obtained by the reaction of two moles of these tetrasubstituted ethylenes with one mole of a ketone having methylene groups adjacent to the carbonyl group. By analogy to compounds obtained by Melby and Wiley⁶ from tetracyanoethylene and such ketones, the products are believed to be tetracyanodisulfonyl-1,3,5-heptatrienes (VI) or cyclized isomers thereof.

One of the sulfonyl groups of the dicyanodisulfonyl-ethylenes is replaced when these compounds are condensed with the sodium salt of an active methylene compound, *e.g.*, sodium malononitrile. Like analogous propenes prepared from tetracyanoethylene,⁷ the resulting pentasubstituted propenes (VII) are strong acids and are readily isolated as tetraalkylammonium salts. The tetracyanopropenes (VII) and hydrogen chloride yield 2(6)-amino-6(2)-chloro-4,5-dicyano-3-sulfonylpyridines (VIII). Treatment of pentacyanopropene with hydrochloric acid gives 2-amino-3,4,5-tricyano-6-chloropyridine.⁸ 1-Acyl-5-amino-3-cyano-4-sulfonylpyrazoles (IX) are obtained by the reaction of dicyanodisulfonyl-ethylenes with monoacyl derivatives of hydrazine. Hydroxylamine and dicyanodisulfonyl-ethylenes yield 5-amino-3-cyano-4-sulfonylisoxazoles (X). The preparation of pyrazoles and isoxazoles from tetracyanoethylene has been reported.⁹

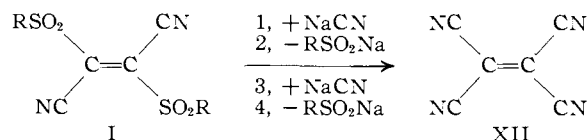
1,2-Dicyano-1,2-disulfonyl-ethylenes and alcohols in the presence of urea give α,α -dialkoxy- β -sulfonylsuccinonitriles (XI). The reaction probably proceeds as



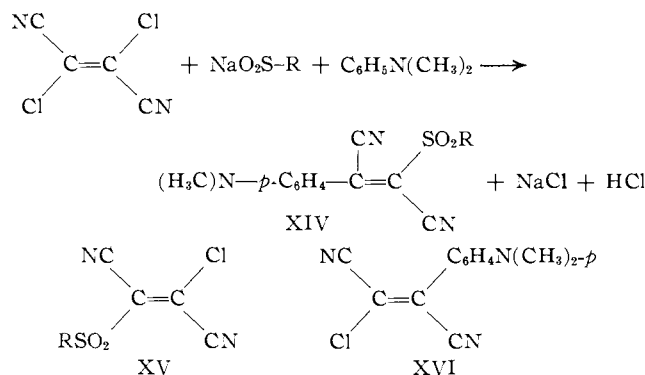
Tetracyanoethylene reacts with alcohols in the presence of urea to give dicyanoketene acetals¹⁰ or tricyanovinyl ethers.¹¹ Addition of water to a solution of the dicyanodisulfonyl-ethylenes in a water-miscible solvent results in the formation of the strongly acidic dicyanosulfonyl-ethenolates (XIII) and sulfonic acid. Boiling an aqueous suspension of tetracyanoethylene gives tricyanoethenol and hydrogen cyanide.¹²

The formation of π -complexes from 1,2-dicyano-1,2-disulfonyl-ethylenes is complicated by the low solubility of most of these tetrasubstituted ethylenes in usual

organic solvents, whereas tetracyanoethylene readily forms molecular complexes with various aromatic compounds.¹³ However, methylene chloride solutions of the readily soluble 1,2-dicyano-1,2-bis-(*n*-butylsulfonyl)-ethylene give colors on the addition of xylene (yellow), mesitylene (yellow), anisole (orange) and anthracene (purple). Tetracyanoethylene (XII) has been prepared in poor yield by the addition of sodium cyanide to a suspension of 1,2-dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene in acetonitrile. On the basis of the reaction products that can be isolated from the reaction mixture, it is believed the reaction proceeds as



In many of the above reactions, it is not necessary to prepare the dicyanodisulfonyl-ethylene. For example, the addition of a sulfinate to a solution of dichlorofumaronitrile and *N,N*-dimethylaniline in dimethylformamide gives a good yield of 4-(1,2-dicyano-2-sulfonylvinyl)-*N,N*-dimethylaniline (XIV), a compound identical with that obtained from the corresponding



1,2-dicyano-1,2-disulfonyl-ethylene and *N,N*-dimethylaniline. The probable intermediate in this reaction is the 1,2-dicyano-2-sulfonylvinyl chloride (XV), which then condenses with the tertiary aromatic amine. The intermediate is not a chlorodicyanovinyl compound XVI, for dichlorofumaronitrile and *N,N*-dimethylaniline form a stable 1:1 orange complex that can be isolated and purified. The complex is recovered unchanged after heating a dimethylformamide solution to 150°.

The reaction of dichlorofumaronitrile and sodium α -toluenesulfinate gave the expected 1,2-dicyano-1,2-bis-(benzylsulfonyl)-ethylene (XVII). The compound is only slightly soluble in methylene chloride and is obtained as faintly yellow crystals on concentration of a methylene chloride solution, provided the crude material has been washed thoroughly. If the washing is not efficient, the light yellow color of the methylene chloride solution disappears as the solution is concentrated and a colorless, crystalline material readily soluble in methylene chloride can be isolated. This colorless product does not give color reactions with tertiary aromatic amines and analysis indicates that the compound has lost sulfur dioxide to give a compound believed to be 1-benzyl-2-benzylsulfonyl-1,2-dicyanoethylene (XVIII). We believe that this novel transformation is brought about by traces of a base, probably dimethylformamide, and that it proceeds *via* a three-membered ring sulfone as shown. If so, it resembles the rearrangement of α -halosulfones,¹⁴ α -

(6) L. R. Melby and D. W. Wiley, R. I. du Pont de Nemours and Co., publication being prepared.

(7) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(8) E. L. Little, W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, *ibid.*, **80**, 2832 (1958).

(9) W. J. Middleton, V. A. Engelhardt and B. S. Fisher, *ibid.*, **80**, 2822 (1958).

(10) W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).

(11) C. L. Dickinson, D. W. Wiley and B. C. McKusick, *ibid.*, **82**, 6132 (1960).

(12) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *ibid.*, **80**, 2795 (1958).

(13) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(14) F. G. Bordwell and G. D. Cooper, *ibid.*, **78**, 5187 (1951).

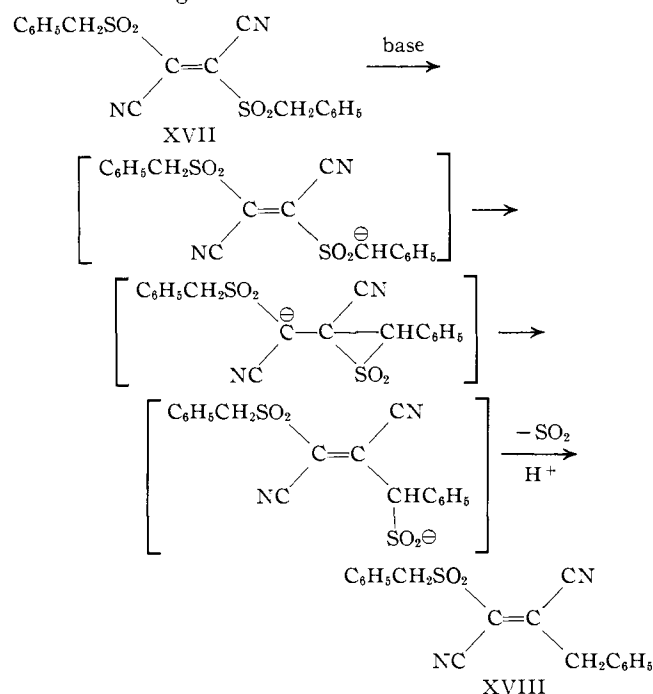
TABLE I

PROPERTIES OF 1,2-DICYANO-1,2-DISULFONYLETHYLENES,

R	Reaction temp., °C. ^a	Yield, %	M.p., °C.	Formula ^b	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₂ H ₅	-50 to -30	25	196-198	C ₈ H ₁₀ N ₂ O ₄ S ₂	36.61	36.88	3.84	3.91	10.68	10.73	24.47	24.63
CH ₂ =CHCH ₂	-70 to -60	10	136-138	C ₁₀ H ₁₀ N ₂ O ₄ S ₂	41.93	42.02	3.52	3.53	9.79	9.84	22.41	22.57
<i>n</i> -C ₄ H ₉	-30 to -15	57	118-119	C ₁₂ H ₁₈ N ₂ O ₄ S ₂	45.24	45.38	5.70	5.73	8.80	8.86	20.15	19.90
C ₆ H ₅	-40 to -20	25	264-265	C ₁₆ H ₁₀ N ₂ O ₄ S ₂	53.60	53.81	2.81	2.80	7.82	8.01	17.91	18.06
4-AcNHC ₆ H ₄	-10 to -20	60	>280	C ₂₀ H ₁₆ N ₂ O ₆ S ₂ ^c	51.70	51.66	3.87	4.04	14.43	14.57	12.02	11.91
4-MeOC ₆ H ₄	10 to 20	39	245-247	C ₁₈ H ₁₄ N ₂ O ₆ S ₂	51.64	51.81	3.37	3.23	6.70	6.31	15.34	15.53
4-ClC ₆ H ₄	-70 to -60	58	258-259	C ₁₆ H ₉ Cl ₂ N ₂ O ₄ S ₂	44.95	45.10	1.89	2.02	6.56	6.61	15.02	15.12
4-(<i>i</i> -C ₃ H ₇)	-60 to -50	40	209-211	C ₂₂ H ₂₂ N ₂ O ₄ S ₂	59.71	59.79	5.01	5.13	6.33	6.05	14.49	14.60

^a Reactions carried out in dimethylformamide. ^b Crystallized from methylene chloride unless otherwise noted. ^c Contains 1.5 CH₃CN of crystallization.

haloacetanilides,¹⁵ α -haloketones¹⁶ and oxime *p*-toluenesulfonates,¹⁷ reactions thought to proceed *via* three-membered ring intermediates.



Experimental

Preparation of 1,2-Dicyano-1,2-disulfonylethylenes (Table I).
General Procedure.—A solution of 0.01 mole of dichlorofumaronitrile¹⁸ in 5-10 ml. of a solvent is cooled to between -20° and -60° and 0.02 mole of a salt of a sulfonic acid is added in small portions with stirring. Suitable solvents include acetonitrile, dimethylformamide, dimethyl sulfoxide, dimethoxyethane and dioxane. The reaction is mildly exothermic. The mixture is stirred for an additional period of 10-15 minutes after the exothermic reaction ceases. In many cases, the dicyanodisulfonylethylene separates in crystalline form and is isolated by the rapid addition of ice and water followed by filtration. The filter cake is washed thoroughly with ice-water and the moist filter cake is dissolved in methylene chloride. The methylene chloride solution is dried with anhydrous magnesium sulfate, which is removed by filtration, and the filtrate is concentrated to a small volume. In case the dicyanodisulfonylethylene does not separate during the concentration, anhydrous ether is added to the concentrated solution and the concentration is repeated whereupon the dicyanodisulfonylethylene separates in crystalline form. Specific examples are given below.

1,2-Dicyano-1,2-bis-(methylsulfonyl)-ethylene.—A solution of 3.0 g. (0.02 mole) of dichlorofumaronitrile in 5 ml. of dimethylformamide was cooled to -40° and 4 g. (0.04 mole) of anhydrous sodium methanesulfinate was added in small portions with stirring, the temperature being maintained at -20° to -30° by

external cooling. After being stirred for 5 minutes at -20° to -30°, the reaction mixture was diluted to 200 ml. with cold water and filtered. The filter cake was washed first with water and then with methylene chloride. The yield of essentially pure 1,2-dicyano-1,2-bis-(methylsulfonyl)-ethylene was 1.8 g. (39%). Crystallization from acetonitrile gave colorless crystals melting at 220-222° with decomposition.

Anal. Calcd. for C₈H₈N₂O₄S₂: C, 30.74; H, 2.58; N, 11.96; S, 27.39. Found: C, 31.03; H, 2.73; N, 11.64; S, 27.29.

When the above experiment was repeated using 5 g. of anhydrous potassium methanesulfinate in place of the sodium methanesulfinate, the yield of 1,2-dicyano-1,2-bis-(methylsulfonyl)-ethylene, m.p. 220-222° dec., was 2.0 g. (43%).

1,2-Dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene. A. From Dichlorofumaronitrile and Sodium *p*-Toluenesulfinate.—A solution of 14.7 g. (0.1 mole) of dichlorofumaronitrile in 50 ml. of dimethylformamide was cooled to -10° and 36 g. (0.2 mole) of sodium *p*-toluenesulfinate (dried to constant weight at 100° and 15 mm.) was added in small portions with stirring. The temperature was maintained at -20° to -10° during the addition and for an additional period of 10 minutes. The thick paste was diluted to 1 l. with ice-water and the precipitate was collected and washed successively with cold water, cold methanol, and ether. The yield of nearly colorless fine crystals, m.p. 245-247° dec., was 29.4 g. (76%). Crystallization from methylene chloride or acetonitrile gave faintly yellow crystals, m.p. 245-247° dec., $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 327 m μ (ϵ 9,340).

Anal. Calcd. for C₁₈H₁₄N₂O₄S₂: C, 55.94; H, 3.65; N, 7.26; S, 16.58. Found: C, 56.21; H, 3.67; N, 6.78; S, 16.66.

B. From Dichloromaleonitrile and Sodium *p*-Toluenesulfinate.—To a solution of 1.47 g. (0.01 mole) of dichloromaleonitrile in 5 ml. of dimethylformamide was added 3.6 g. (0.02 mole) of anhydrous sodium *p*-toluenesulfinate in small portions with stirring, the temperature being maintained at -10° to 0° by means of external cooling. After stirring at this temperature for an additional period of 5 minutes, the reaction mixture was diluted to 200 ml. with ice-water and the precipitate was isolated as described above. The yield of essentially pure 1,2-dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene, m.p. 245-247° dec. alone or in admixture with the above product, was 2.8 g. (73%).

C. From Tetrachlorosuccinonitrile and Sodium *p*-Toluenesulfinate.—A solution of 2.18 g. (0.01 mole) of tetrachlorosuccinonitrile in 15 ml. of dimethylformamide was cooled to 5° and 5.4 g. (0.05 mole) of anhydrous sodium *p*-toluenesulfinate was added in small portions with stirring. After stirring at 5-10° for 5 minutes, the reaction mixture was warmed to 20° and diluted to 200 ml. with ice-water. The nearly colorless precipitate was collected, washed with cold water and air-dried. Crystallization from methylene chloride gave 1.8 g. (47%) of faintly yellow crystals, m.p. 245-247° dec. alone or in admixture with the compound prepared as described in above section A.

To the mother liquors obtained from the crystallization of the above 1,2-dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene was added 4 g. of aniline and the methylene chloride was removed by distillation on a steam-bath. The residue was treated with cold dilute hydrochloric acid to remove excess aniline, whereupon the reaction mass solidified. The solid material was collected, washed with cold water and dissolved in dilute potassium hydroxide solution. The alkaline solution was filtered and acidified with dilute hydrochloric acid. Crystallization of the precipitate first from aqueous methanol and then from ether-petroleum ether give colorless crystals, m.p. 101-102°, alone or in admixture with an authentic sample of *p*-toluenesulfonamide.

1,2-Dicyano-1,2-bis-(cyclohexylsulfonyl)-ethylene.—A solution of 2.2 g. (0.15 mole) of dichlorofumaronitrile in a mixture of 10 ml. of dimethylformamide and 5 ml. of tetrahydrofuran

(15) S. Sarel and A. Greenberger, *J. Org. Chem.*, **23**, 330 (1958).

(16) A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(17) M. J. Hatch and D. J. Cram, *J. Am. Chem. Soc.*, **75**, 38 (1953).

(18) N. R. Eldred and P. M. Young, *ibid.*, **75**, 4338 (1953).

was cooled to -20° and 10 g. (0.03 mole) of magnesium cyclohexanesulfinate dihydrate and 10 g. of anhydrous magnesium sulfate were added. The reaction mixture was allowed to warm to 20° , whereupon an exothermic reaction took place and the temperatures rose to 35° . After stirring at $25-30^{\circ}$ for 5 minutes, the reaction mixture was diluted with ice-water, the precipitate was collected, washed thoroughly with cold water and crystallized from methylene chloride. The yield of colorless crystals melting at $215-216^{\circ}$ dec. was 3.2 g. (58%).

Anal. Calcd. for $C_{16}H_{22}N_2O_4S_2$: C, 51.84; H, 5.99; N, 7.57; S, 17.31. Found: C, 51.70; H, 6.19; N, 7.59; S, 17.54.

1,2-Bis-(benzylsulfonyl)-1,2-dicyanoethylene.—A solution of 1.5 g. (0.01 mole) of dichlorofumarionitrile in 5 ml. of dimethylformamide was cooled to -60° to -70° and 3.6 g. (0.02 mole) of anhydrous sodium α -toluenesulfinate was added in small portions with stirring. The reaction mixture was stirred an additional 5 minutes at -60° to -70° and diluted with 150 ml. of ice-water. The precipitate was collected and washed thoroughly with ice-water. The filter cake was dissolved in methylene chloride, the methylene chloride solution was dried with anhydrous magnesium sulfate and the faintly yellow solution was concentrated to a small volume. Pale yellow crystals separated during the concentration process. After cooling, the crystals were collected and washed with ether. Recrystallization from methylene chloride gave 0.4 g. (10%) of pale yellow crystals melting at $183-185^{\circ}$ dec.

Anal. Calcd. for $C_{18}H_{14}N_2O_4S_2$: C, 55.94; H, 3.65; N, 7.26; S, 16.58. Found: C, 56.09; H, 3.74; N, 7.42; S, 16.70.

1-Benzyl-2-benzylsulfonyl-1,2-dicyanoethylene.—The crude 1,2-bis-(benzylsulfonyl)-1,2-dicyanoethylene was prepared as described above except that the filter cake was washed with two small portions of cold water. The moist filter cake was dissolved in methylene chloride and the methylene chloride solution was dried with anhydrous magnesium sulfate. The pale yellow color of the resulting filtrate disappeared as the solution was concentrated, and crystals did not separate. After removal of essentially all the methylene chloride, the colorless liquid solidified. Crystallization from ether gave 0.3 g. (10%) of colorless crystals, m.p. $127-128^{\circ}$.

Anal. Calcd. for $C_{18}H_{14}N_2O_4S_2$: C, 67.04; H, 4.37; N, 8.70; S, 9.95. Found: C, 66.96; H, 4.48; N, 8.80; S, 9.97.

The infrared spectrum (KBr pellet) showed absorption at 3.26 , 3.30 μ (unsaturated CH), 3.35 , 3.44 μ (saturated CH), 4.45 , 4.52 μ (conjugated nitriles), 6.31 , 6.33 , 6.7 μ (aromatic C=C), 7.45 , 8.6 μ (sulfonyl) and 13.15 , 14.35 μ (monosubstituted benzene). The proton nuclear magnetic resonance (Varian A-60, $CDCl_3$ solution, δ in p.p.m. vs. internal tetramethylsilane) showed peaks at 3.98 ($-CH_2$), 4.67 ($-CH_2$) and 7.50 (aromatic H).

Tetracyanoethylene.—Five grams of finely powdered, anhydrous sodium cyanide was added to a mechanically stirred suspension of 3.86 g. of 1,2-dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene in 40 ml. of anhydrous acetonitrile cooled in an ice-bath. After stirring for 1 hr. under an atmosphere of dry nitrogen, an additional 2 g. of sodium cyanide was added and the stirring was continued for 1 hour. At the end of this time, a test portion did not give a magenta dye on the addition of *N,N*-dimethylaniline. The bright yellow reaction mixture contained unreacted sodium cyanide and a suspension of a finely divided solid. The acetonitrile suspension of the solid was decanted from the unreacted sodium cyanide, the decanted portion was filtered and the filter cake was washed with acetonitrile. Addition of a test portion of the filter cake to a solution of dichlorofumarionitrile and *N,N*-dimethylaniline in dimethylformamide gave a magenta dye (XIV), a very sensitive test for sulfonates. No color was obtained when the dichlorofumarionitrile was omitted. Addition of *N,N*-dimethylaniline to the acetonitrile filtrate immediately after filtration gave no color reaction. After standing for several minutes at room temperature, or by warming to $50-60^{\circ}$, a magenta color developed, indicating the presence of tetracyanoethylene. The main portion of the acetonitrile filtrate was warmed to $50-60^{\circ}$; the precipitated sodium *p*-toluenesulfinate was removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with benzene and the benzene solution was evaporated to dryness under reduced pressure. The residue was sublimed at 0.2 mm. from a bath at $130-140^{\circ}$ to give 0.05 g. (4%) of colorless tetracyanoethylene, m.p. $197-199^{\circ}$ (sealed tube) alone or in admixture with a known sample of tetracyanoethylene.

Preparation of 4-(1,2-Dicyano-2-sulfonylvinyl)-arylamines. (Table II). **A. From 1,2-Dicyano-1,2-disulfonylethylenes.**—The general procedure is to add the dicyanodisulfonylethylene to a solution of a slight excess of the amine in about 5-10 volumes of a solvent and stir the reaction mixture at $24-30^{\circ}$ for 5-30 minutes. Suitable solvents include dimethylformamide, dimethyl sulfoxide, acetonitrile and dimethoxyethane. In some cases, the dye separates in crystalline form and is recovered by filtration. Otherwise, the reaction mixture is diluted with

ice-water, the precipitate is collected by filtration, washed and crystallized. The procedure is illustrated in the following example.

4-[1,2-Dicyano-2-(4-acetamidophenylsulfonyl)-vinyl]-*N,N*-dimethylaniline.—A suspension of 1.2 g. (0.0025 mole) of 1,2-dicyano-1,2-bis-(4-acetamidophenylsulfonyl)-ethylene in a solution of 10 ml. of dimethylformamide and 0.6 g. (0.005 mole) of *N,N*-dimethylaniline was stirred at 25° for 10 minutes. After dilution to 200 ml. with ice and water, the crystalline dye was collected, washed with water and dissolved in methylene chloride. The methylene chloride solution was washed in turn with dilute hydrochloric acid, dilute sodium bicarbonate and water. After drying with anhydrous magnesium sulfate, the filtrate was concentrated to a small volume, anhydrous ether was added and the concentration was continued. During this concentration, red felt-like crystals separated. The yield of 4-[1,2-dicyano-2-(4-acetamidophenylsulfonyl)-vinyl]-*N,N*-dimethylaniline was 0.3 g. (31%), m.p. $204-206^{\circ}$, $\lambda_{max}^{CH_2Cl_2}$ 520 $m\mu$ (ϵ 38,600).

Anal. Calcd. for $C_{20}H_{18}N_4O_3S_2$: C, 60.88; H, 4.60; N, 14.22. Found: C, 60.98; H, 4.54; N, 14.21.

B. From Dichlorofumarionitrile.—The general procedure is to add slightly more than an equivalent of a salt of sulfonic acid to a solution of one equivalent of dichlorofumarionitrile and a slight excess of amine in 5-10 volumes of dimethylformamide and stir the reaction mixture at $10-40^{\circ}$ for 5-30 minutes. The dye is isolated and crystallized as described above. Specific examples are described below.

4-(1,2-Dicyano-2-phenylsulfonylvinyl)-*N,N*-dimethylaniline.—A solution of 4.5 g. (0.03 mole) of dichlorofumarionitrile and 7.3 g. (0.06 mole) of *N,N*-dimethylaniline in 25 ml. of dimethylformamide was cooled to 10° and 6.2 g. (0.03 mole) of anhydrous sodium benzenesulfinate was added in small portions with stirring. The temperature was maintained at $10-15^{\circ}$ by external cooling. Crystals of the dye began to separate when about one-half of the sulfinate had been added. After stirring for an additional period of 15 minutes, the reaction mixture was diluted with water, the crystalline dye was collected and washed with water. The moist filter cake was dissolved in methylene chloride, washed in turn with dilute hydrochloric acid, dilute sodium bicarbonate and water. After drying with anhydrous magnesium sulfate, the filtrate was concentrated to a small volume during which time short, deep red, needles separated. The yield of 4-(1,2-dicyano-2-phenylsulfonylvinyl)-*N,N*-dimethylaniline was 7.2 g. (71%), m.p. $180-181^{\circ}$, $\lambda_{max}^{CH_2Cl_2}$ 518 $m\mu$ (ϵ 37,800).

Anal. Calcd. for $C_{18}H_{16}N_4O_3S_2$: C, 64.06; H, 4.88; N, 12.46; S, 9.51. Found: C, 64.28; H, 4.70; N, 12.67; S, 9.49.

4-[1,2-Dicyano-2-(4-tolylsulfonyl)-vinyl]-*N*-methylaniline.—A solution of 5.9 g. (0.04 mole) of dichlorofumarionitrile in 15 ml. of dimethylformamide was cooled to -20° and 7.2 g. (0.04 mole) of anhydrous sodium *p*-toluenesulfinate and 8.6 g. (0.08 mole) of *N*-methylaniline were added simultaneously at approximately equivalent rates with stirring. The temperature was maintained at -20° to -15° during the addition and then allowed to increase to 25° . After stirring for 50 minutes at 25° , the reaction mixture was diluted with a large volume of cold water. Two crystallizations from methylene chloride-ether as described above gave 10.6 g. (78%) of bright red crystals, m.p. $156-157^{\circ}$, $\lambda_{max}^{CH_2Cl_2}$ 490 $m\mu$ (ϵ 11,000).

Anal. Calcd. for $C_{18}H_{16}N_3O_3S_2$: C, 64.06; H, 4.48; S, 9.51. Found: C, 64.08; H, 4.63; S, 9.31.

A suspension of 0.398 g. of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene in 2 ml. of dimethylformamide and 0.3 g. of *N*-methylaniline was warmed to 60° , whereupon a homogeneous solution was obtained. The reaction mixture was diluted with water; the precipitate was collected and crystallized as above to give 0.25 g. (75%) of bright red crystals, m.p. $156-157^{\circ}$, alone or in admixture with the above-prepared 4-[1,2-dicyano-2-(4-tolylsulfonyl)-vinyl]-*N*-methylaniline.

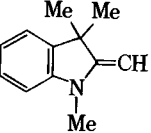
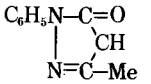
***N*-(1,2-Dicyano-2-sulfonylvinyl)-arylamines.**—The *N*-(1,2-dicyano-2-sulfonylvinyl)-arylamines are prepared by (1) interaction of 1,2-dicyano-1,2-disulfonylethylene and the primary amine and (2) interaction of dichlorofumarionitrile, the primary amine and a salt of the sulfonic acid. Typical experiments are given below.

***N*-(1,2-Dicyano-2-(4-tolylsulfonyl)-vinyl)-4-chloroaniline.**—A solution of 7.3 g. (0.05 mole) of dichlorofumarionitrile in 25 ml. of dimethylformamide was cooled to 20° , 12.7 g. (0.1 mole) of 4-chloroaniline was added, followed by the addition of 9 g. (0.05 mole) of sodium *p*-toluenesulfinate in small portions with stirring. The temperature of the reaction mixture was increased slowly to 50° during which time crystals of the reaction product separated. After dilution with a large volume of water, the crystals were collected and crystallized from methylene chloride-ether or aqueous acetone. The yield of the pale yellow crystals, m.p. $193-194^{\circ}$, was 17.2 g. (96%), $\lambda_{max}^{CH_2Cl_2}$ 377 $m\mu$ (ϵ 17,800).

Anal. Calcd. for $C_{17}H_{12}ClN_3O_3S_2$: C, 57.04; H, 3.38; Cl, 9.91. Found: C, 56.98; H, 3.33; Cl, 9.90.

TABLE II

PROPERTIES OF 4-(1,2-DICYANO-2-SULFONYLVINYL)-ARYLAMINES AND RELATED COMPOUNDS OF FORMULA $\text{RC}=\text{C}(\text{CN})_2\text{SO}_2\text{R}'$

Compound ^a		Yield, %	M. p., °C.	Crystn. solvent	$\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$, m μ	ϵ_{max} $\times 10^{-2}$	Formula	Carbon, %		Hydrogen, %		Additional analysis, %		
R	R'							Calcd.	Found	Calcd.	Found	Element	Calcd.	Found
4-Me ₂ NC ₆ H ₄	CH ₃	50	189-191	CH ₂ Cl ₂ -ether	514	398	C ₁₃ H ₁₃ N ₃ O ₂ S ^b	57.24	57.40	5.23	5.02	N	14.32	14.34
4-Me ₂ NC ₆ H ₄	C ₂ H ₅	68	185-186	CH ₂ Cl ₂ -ether	513	365	C ₁₄ H ₁₅ N ₃ O ₂ S	58.09	58.37	5.23	5.40	S	11.09	11.12
4-Me ₂ NC ₆ H ₄	CH ₂ CH=CH ₂	20	172-173	CH ₂ Cl ₂ -ether	515	367	C ₁₅ H ₁₅ N ₃ O ₂ S	59.76	59.69	5.02	4.81	N	13.96	13.86
4-Me ₂ NC ₆ H ₄	<i>n</i> -C ₄ H ₉	52	151-153	CH ₂ Cl ₂ -ether	513	336	C ₁₆ H ₁₉ N ₃ O ₂ S	60.52	60.43	6.04	5.94	S	10.10	10.23
4-Me ₂ NC ₆ H ₄	C ₆ H ₁₁ (cyclo)	30	212-213	CH ₂ Cl ₂ -ether	510	368	C ₁₈ H ₂₁ N ₃ O ₂ S	62.95	62.54	6.16	6.28	N	12.24	12.63
4-Me ₂ NC ₆ H ₄	C ₆ H ₅ CH ₂	25	186-188	CH ₂ Cl ₂ -CH ₃ OH	518	380	C ₁₉ H ₁₇ N ₃ O ₂ S	64.92	64.49	4.88	5.37	S	9.13	9.17
4-Me ₂ NC ₆ H ₄	C ₆ H ₄ CH ₃ -4	55	193-195	CH ₂ Cl ₂ -ether	517	386	C ₁₉ H ₁₇ N ₃ O ₂ S	64.92	65.17	4.88	5.00	N	11.97	11.99
4-Me ₂ NC ₆ H ₄	C ₆ H ₄ OCH ₃ -4	50	173-175	CH ₂ Cl ₂ -ether	516	379	C ₁₉ H ₁₇ N ₃ O ₃ S	62.08	62.02	4.67	4.82	N	11.44	11.47
4-Me ₂ NC ₆ H ₄	C ₆ H ₄ Cl-4	46	185-186	CH ₂ Cl ₂ -ether	524	405	C ₁₈ H ₁₄ ClN ₃ O ₂ S	58.11	58.34	3.80	3.94	N	11.31	11.38
4-Me ₂ NC ₆ H ₄	C ₆ H ₄ CN-2	49	222-224	CH ₂ Cl ₂ -ether	532	420	C ₁₉ H ₁₄ N ₄ O ₂ S	62.94	62.49	3.89	4.01	N	15.47	15.42
4-Me ₂ NC ₆ H ₄	C ₆ H ₄ NO ₂ -4	63	209-210	CH ₂ Cl ₂ -ether	537	406	C ₁₈ H ₁₄ N ₄ O ₄ S ^c	52.27	52.29	3.56	3.58	N	13.20	12.69
4-Me ₂ NC ₆ H ₄	CH ₂ -CH ₂ ^d	10	240-242	CH ₂ Cl ₂ -CH ₃ OH	518	338	C ₂₆ H ₂₄ N ₆ O ₄ S ₂	56.89	56.94	4.41	4.43	S	11.70	11.52
4-Me ₂ NC ₆ H ₄	C ₆ H ₄ -(<i>i</i> -C ₃ H ₇)-4	79	153-155	Ether	517	382	C ₂₁ H ₂₁ N ₃ O ₂ S	66.49	66.56	5.58	5.70	S	8.45	8.34
4-Et ₂ NC ₆ H ₄	CH ₃	84	145-146	CH ₂ Cl ₂ -ether	522	410	C ₁₅ H ₁₇ N ₃ O ₂ S	59.38	59.73	5.65	5.84	S	10.57	10.60
4-Et ₂ NC ₆ H ₄	C ₆ H ₄ CH ₃ -4	61	171-173	CH ₂ Cl ₂ -ether	525	425	C ₂₁ H ₂₁ N ₃ O ₂ S	66.46	66.74	5.58	5.67	S	8.42	8.29
4-NCCH ₂ CH ₂ N(Me) ₂ C ₆ H ₄	C ₆ H ₄ CH ₃ -4	30	173-175	CH ₂ Cl ₂ -CH ₃ OH	492	350	C ₂₁ H ₁₈ N ₄ O ₂ S	64.57	64.64	4.65	4.73	S	8.22	8.31
(4-Me ₂ NC ₆ H ₄) ₂ C=CH	CH ₃	68	191-193	CH ₂ Cl ₂ -ether	590	580	C ₂₃ H ₂₄ N ₄ O ₂ S	65.67	65.50	5.75	5.84	N	13.33	13.40
(4-Me ₂ NC ₆ H ₄) ₂ C=CH	C ₂ H ₅	76	198-199	CH ₂ Cl ₂ -ether	588	573	C ₂₄ H ₂₆ N ₄ O ₂ S	66.31	66.73	6.03	6.02	S	7.38	7.24
4-(Me ₂ NC ₆ H ₄) ₂ C=CH	CH ₂ CH=CH ₂	87	172-173	CH ₂ Cl ₂ -ether	592	580	C ₂₅ H ₂₆ N ₄ O ₂ S	67.24	67.58	5.87	5.99	S	7.18	7.35
(4-Me ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₁₁ (cyclo)	63	185-186	CH ₂ Cl ₂ -ether	587	576	C ₂₈ H ₃₂ N ₄ O ₂ S	68.32	68.63	6.60	6.75	N	11.47	11.44
4-(Me ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₅	79	189-191	CH ₂ Cl ₂ -CH ₃ OH	602	583	C ₂₈ H ₂₆ N ₄ O ₂ S	69.68	69.41	5.43	5.45	S	6.64	6.77
4-(Me ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₄ CH ₃ -4	87	187-188	CH ₂ Cl ₂ -CH ₃ OH	597	540	C ₂₉ H ₂₈ N ₄ O ₂ S	70.13	70.58	5.68	5.74	N	11.28	11.47
4-(Me ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₄ -(<i>i</i> -C ₃ H ₇)-4	67	140-145	Ether	597	534	C ₃₁ H ₃₂ N ₄ O ₂ S	70.96	71.13	6.15	6.62	N	10.68	10.28
(4-Me ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₅ CH ₂	50	188-189	CH ₂ Cl ₂ -CH ₃ OH	595	615	C ₂₉ H ₂₈ N ₄ O ₂ S	70.13	69.91	5.68	5.85	N	11.28	11.14
(4-Me ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₄ NO ₂ -4	54	204-205	CH ₂ Cl ₂ -CH ₃ OH	626	697	C ₂₈ H ₂₅ N ₄ O ₄ S	63.74	63.55	4.77	5.08	N	13.29	12.96
4-(Me ₂ NC ₆ H ₄) ₂ C=CH	CH ₂ OSO ₂ C ₆ H ₄ CH ₃ -4	26	170-172	CH ₂ Cl ₂ -ether	532	417	C ₂₀ H ₁₉ N ₃ O ₅ S ^e	50.43	50.80	4.13	4.62	S	13.15	13.15
4-(Et ₂ NC ₆ H ₄) ₂ C=CH	CH ₃	84	178-179	CH ₂ Cl ₂ -ether	598	720	C ₂₇ H ₃₂ N ₄ O ₂ S	68.03	68.11	6.77	6.81	S	6.73	6.68
4-(Et ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₅	95	171-172	CH ₂ Cl ₂ -ether	598	704	C ₂₈ H ₃₄ N ₄ O ₂ S	68.54	68.24	6.98	6.79	S	6.53	6.66
4-(Et ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₅	75	171-172	CH ₂ Cl ₂ -CH ₃ OH	610	715	C ₃₂ H ₃₄ N ₄ O ₂ S	71.34	71.26	6.36	6.42	S	5.95	5.90
4-(Et ₂ NC ₆ H ₄) ₂ C=CH	C ₆ H ₄ CH ₃ -4	55	120-121	Ether	605	670	C ₃₃ H ₃₆ N ₄ O ₂ S	71.71	72.09	6.57	6.63	S	5.80	5.73
	C ₆ H ₄ CH ₃ -4	89	222-223	CH ₂ Cl ₂ -ether	502	485	C ₂₃ H ₂₁ N ₃ O ₂ S	68.46	68.50	5.25	5.62	S	7.95	7.99
	C ₆ H ₄ CH ₃ -4	66	171-173	Acetone-H ₂ O	405	87	C ₂₁ H ₁₆ N ₄ O ₃ S ^f	61.00	61.18	4.15	4.15	S	7.76	7.80

^a Prepared by reaction of dichlorofuramionitrile, arylamine and sodium sulfinate. ^b Contains $\frac{1}{2}$ H₅C₂OC₂H₅ of crystallization. ^c Contains $\frac{1}{2}$ CH₂Cl₂ of crystallization. ^d Prepared from disodium ethanedisulfinate. ^e Contains $\frac{1}{2}$ CH₂Cl₂ of crystallization. ^f Contains $\frac{1}{2}$ H₂O of crystallization.

The same compound, m.p. 193–194° alone or in admixture with the above preparation, was obtained by the addition of 0.4 g. (0.001 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene to a solution of 0.3 g. (0.0024 mole) of 4-chloroaniline in 2 ml. of dimethylformamide and warming to 60°.

N-[1,2-Dicyano-2-(4-tolylsulfonyl)-vinyl]-4-aminobenzene-sulfonamide, m.p. 220–222° dec., was prepared in 95% yield from 10.3 g. (0.06 mole) of sulfanilamide, 4.4 g. (0.03 mole) of dichlorofumaronitrile and 5.5 g. (0.03 mole) of sodium *p*-toluenesulfinate; $\lambda_{\text{max}}^{\text{acetone}}$ 348 m μ (ϵ 18,900).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2$: C, 50.71; H, 3.51; S, 15.94. Found: C, 50.74; H, 3.63; S, 15.89.

N-[1,2-Dicyano-2-(4-tolylsulfonyl)-vinyl]-aniline.—One gram (0.011 mole) of aniline and 3.86 g. (0.01 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene gave 2.3 g. (68%) of the above compound after crystallization from methylene chloride; m.p. 156–157°, $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 343 m μ (ϵ 16,800).

Anal. Calcd. for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_3\text{S}$: C, 63.12; H, 4.05; N, 13.00. Found: C, 63.34; H, 4.01; N, 12.99.

N-(1,2-Dicyano-2-methylsulfonylvinyl)-4-chloroaniline, m.p. 197–199°, was obtained in 94% yield from 7.3 g. (0.05 mole) of dichlorofumaronitrile, 12.7 g. (0.1 mole) of 4-chloroaniline and 6.3 g. (0.05 mole) of sodium methanesulfinate after crystallization from methylene chloride.

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{ClN}_2\text{O}_3\text{S}$: C, 46.87; H, 2.86; Cl, 12.57. Found: C, 47.07; H, 2.86; Cl, 12.51.

1,2-Dicyano-1,2-bis-(4-tolylsulfonyl)-4-cyclohexene.—A suspension of 3.86 g. (0.01 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene in 50 ml. of tetrahydrofuran and 15 g. of butadiene was stirred by means of a magnetic stirrer in a flask fitted with a reflux condenser cooled by means of solid carbon dioxide and acetone. After stirring for 6 hours at 30–45°, the 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene was converted to the Diels-Alder addition product as indicated by the fact that a small test portion no longer gave a magenta dye upon the addition of a drop of *N,N*-dimethylaniline. The solid was filtered, washed with tetrahydrofuran and dried. The yield of colorless, crystalline adduct was 3.8 g. (86%), m.p. 248–250° dec. Crystallization from acetonitrile did not change the melting point.

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2$: C, 59.97; H, 4.58; S, 14.57. Found: C, 60.01; H, 4.57; S, 14.62.

11,12-Dicyano-11,12-bis-(4-tolylsulfonyl)-9,10-dihydro-9,10-ethanoanthracene.—A mixture of 1.93 g. (0.005 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene, 0.9 g. of anthracene (0.005 mole) and 100 ml. of methylene chloride was refluxed for 2 hours, during which time a homogeneous solution was obtained and a test portion did not give a magenta dye upon the addition of a drop of *N,N*-dimethylaniline. The solution was treated with decolorizing charcoal and the colorless filtrate was concentrated to a small volume. The colorless crystals were collected, dissolved in methylene chloride and the solution concentrated to a small volume. The yield of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene-anthracene adduct was 2.3 g. (82%), m.p. 218–219° dec.

Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$: C, 68.06; H, 4.28; N, 4.96; S, 11.36. Found: C, 67.87; H, 4.48; N, 4.98; S, 11.23.

1,2-Dicyano-1,2-bis-(4-tolylsulfonyl)-3-(4-methoxyphenyl)-cyclobutane.—A suspension of 3.86 g. (0.01 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene in 35 ml. of tetrahydrofuran and 3.0 g. (0.022 mole) of *p*-methoxystyrene was stirred at 40–45° until a homogeneous solution was obtained (15 minutes). The resulting yellow solution was cooled and petroleum ether was added, whereupon an oil separated that soon solidified. The solid material was collected and washed with petroleum ether. Two crystallizations from methylene chloride-ether gave 4.4 g. (84%) of colorless crystals, m.p. 193–195°. The infrared spectrum shows absorption at 3 μ (saturated CH and =CH), 4.45 μ (weak CN band), 6.2, 6.25 and 6.6 μ (aromatic C=C), 7.45, 8.65 μ (sulfone) and 12.25 μ (1,4-disubstituted benzene).

Anal. Calcd. for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2$: C, 62.27; H, 4.65; N, 5.39; S, 12.33. Found: C, 62.15; H, 4.60; N, 5.27; S, 12.28.

5-Amino-3-cyano-1,4-bis-(4-tolylsulfonyl)-pyrazole.¹⁹—A solution of 4.9 g. (0.0125 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene and 2.3 g. (0.0125 mole) of 4-tolylsulfonylhydrazide in 25 ml. of dimethylformamide was heated at 90–95° for 7 hours. The resulting solution was cooled and diluted with 25 ml. of water. The colorless solid was collected by filtration and air-dried. The yield was 1.2 g. (24%). Crystallization from ethanol gave colorless crystals, m.p. 207–209°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_4\text{S}_2$: C, 51.91; H, 3.87; N, 13.45. S, 15.40. Found: C, 51.96; H, 3.96; N, 13.24; S, 15.44.

Heating a mixture of 1.86 g. (0.01 mole) of 4-tolylsulfonylhydrazide, 1.47 g. (0.01 mole) of dichlorofumaronitrile and 1.78 g. (0.01 mole) of sodium *p*-toluenesulfinate in 15 ml. of acetic acid on a steam-bath for 5 minutes gave the above compound, m.p. 207–209°, in 77% yield after crystallization from ethanol.

5-Amino-3-cyano-4-(4-tolylsulfonyl)-isoxazole.—A mixture of 2.1 g. (0.03 mole) of hydroxylamine hydrochloride, 3.0 g. (0.03 mole) of potassium acetate and 15 ml. of acetic acid was stirred at 50–60° for 5 minutes. The mixture was cooled slightly and 4.4 g. (0.03 mole) of dichlorofumaronitrile and 5.4 g. (0.03 mole) of sodium *p*-toluenesulfinate were added. After heating to 80°, the reaction mixture was diluted with water, whereupon an oil separated that soon solidified. Four crystallizations from aqueous methanol gave 3.5 g. (33%) of colorless crystals, m.p. 162–163°.

Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{N}_2\text{O}_3\text{S}$: C, 50.18; H, 3.45; N, 15.96; S, 12.18. Found: C, 50.28; H, 3.61; N, 15.95; S, 12.09.

The same compound (1.6 g., 61%) was obtained when 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene (3.86 g.), hydroxylamine hydrochloride (0.7 g.) and potassium acetate (1.0 g.) were heated in acetic acid (5 ml.) on a steam-bath for 5 minutes.

Tetramethylammonium 1,1,2,3-Tetracyano-3-(4-tolylsulfonyl)-propene.—A mechanically stirred suspension of 1.44 g. (0.06 mole) of sodium hydride in 150 ml. of anhydrous tetrahydrofuran was cooled to –10° under an atmosphere of nitrogen. A solution of 4.0 g. (0.06 mole) of malononitrile in 20 ml. of anhydrous tetrahydrofuran was added dropwise at –10° to 0°. The resulting suspension of sodiomalononitrile was cooled to –20° and a suspension of 11.6 g. (0.03 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene in 50 ml. of anhydrous tetrahydrofuran was added in small portions. The resulting deep yellow reaction mixture was warmed to 40° and the tetrahydrofuran was removed by distillation under reduced pressure from a bath at 30°. The resulting solid was dissolved in 25 ml. of water, the solution was filtered and 10 g. of solid tetramethylammonium chloride was added to the yellow filtrate, whereupon yellow crystals separated. After cooling to 5°, the crystals were collected, washed first with dilute tetramethylammonium chloride solution and finally with a small volume of cold water. Crystallization from aqueous methanol gave 6.8 g. (61%) of bright yellow crystals, m.p. 178–180°. The molecular extinction coefficients in methanol are 23,000 and 23,300 at 416 and 398 m μ , respectively.

Anal. Calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_6\text{O}_2\text{S}$: C, 58.49; H, 5.19; S, 8.67. Found: C, 58.53; H, 5.26; S, 8.27.

Tetramethylammonium 1,2,3-Tricyano-1,3-bis-(4-tolylsulfonyl)-propene.—To a mechanically stirred suspension of 1.44 g. (0.06 mole) of sodium hydride in 150 ml. of anhydrous tetrahydrofuran was added 12 g. (0.06 mole) of 4-tolylsulfonylacetonitrile at 15–20° under an atmosphere of nitrogen. To the resulting homogeneous solution was added 11.6 g. (0.03 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene in small portions at 25°. After warming the reaction mixture to 50°, the tetrahydrofuran was distilled under reduced pressure from a bath at 30°. The residue was treated with 35 ml. of water and the unchanged 4-tolylsulfonylacetonitrile was removed by filtration. Solid tetramethylammonium chloride (10 g.) was added to the filtrate, whereupon yellow crystals soon separated. After cooling to 5°, the crystals were collected, washed first with 5% tetramethylammonium chloride and finally with a small volume of cold water. The crystals were dissolved in a small volume of methanol, filtered and the filtrate was cooled to –60° by means of a solid carbon dioxide-acetone bath. The yield of bright yellow crystals, m.p. 170–171°, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 415 m μ (ϵ 23,600), was 9 g. (60%).

Anal. Calcd. for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_2$: C, 57.78; H, 5.26; N, 11.24; S, 12.87. Found: C, 57.62; H, 5.21; N, 11.35; S, 12.93.

2(6)-Amino-6(2)-chloro-4,5-dicyano-3-(4-tolylsulfonyl)-pyridine.—A solution of 0.5 g. of tetramethylammonium 1,1,2,3-tetracyano-3-(4-tolylsulfonyl)-propene in 10 ml. of acetone and 10 ml. of 36% hydrochloric acid was heated on a steam-bath for 10 minutes during which time crystals of the substituted pyridine separated. The reaction mixture was diluted with ice-water, the precipitate was collected and crystallized twice from ethanol to give 0.3 g. (67%) of faintly yellow, felt-like needles, m.p. 246–248°.

Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{ClN}_4\text{O}_2\text{S}$: C, 50.52; H, 2.73; Cl, 10.66. Found: C, 50.33; H, 2.92; Cl, 10.53.

α,α -Dimethoxy- β -(4-tolylsulfonyl)-succinonitrile.—A suspension of 7.7 g. (0.02 mole) of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene, 3 g. of urea and 25 ml. of methanol was heated on a steam-bath until a homogeneous solution was obtained (about 5 minutes). The resulting solution was filtered and the filtrate was diluted to a volume of about 400 ml. with ice-water. The gummy precipitate solidified within a few minutes. The solid was collected, air-dried and crystallized three times from ether to give 3.0 g. (57%) of colorless crystals, m.p. 108–109°. The addition of *N,N*-dimethylaniline or 1,1-bis-(4-dimethylamino-

(19) C. L. Dickinson and B. C. McKusick, U. S. Patent 2,998,426 (1961). We wish to thank Dr. C. L. Dickinson, who carried out this experiment.

phenyl)-ethylene to a dimethylformamide solution of the compound at 25° did not give any color reaction. However, on warming to about 75°, magenta and blue dyes, respectively, were obtained. The infrared spectrum shows absorption at 3.35, 3.4 and 3.5 μ (saturated CH), 6.25, 6.45 and 6.7 μ (aromatic $\text{C}=\text{C}$), 7.45 and 8.65 μ (sulfone) and 12.2 μ (1,4-disubstituted benzene).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$: C, 53.05; H, 4.79; N, 9.52; S, 10.90. Found: C, 53.24; H, 4.92; N, 9.65; S, 11.00.

N,N-Dimethylaniline-Dichlorofumaronitrile Complex.—To a solution of 1.47 g. (0.01 mole) of dichlorofumaronitrile in 10 ml. of petroleum ether was added 2.40 g. (0.02 mole) of N,N-dimethylaniline. The resulting deep orange solution was cooled thoroughly in an ice-salt mixture. Strong, orange needles, 2.2 g. (8.5%), m.p. 44–46°, separated. A very dilute solution of the complex in ether, petroleum ether, methylene chloride, etc., is colorless but on concentration or addition of either dichlorofumaronitrile or N,N-dimethylaniline, the characteristic orange color of a solution of the complex develops.

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{Cl}_2\text{N}_3$: C, 53.73; H, 4.14; N, 26.45. Found: C, 54.10; H, 4.30; N, 26.15.

1,2,6,7-Tetracyano-4-hydroxy-1,7-bis-(4-tolylsulfonyl)-1,3,5-heptatriene.—A suspension of 2 g. of 1,2-dicyano-1,2-bis-(4-tolylsulfonyl)-ethylene in 25 ml. of acetone was refluxed for 30 minutes during which time the starting material disappeared and a deep blue crystalline product separated. The reaction mixture was concentrated to a volume of about 10 ml., the reaction product was collected by filtration and washed with methanol until the washings were essentially colorless and finally washed with ether. The yield of deep blue crystals was 1 g. (30%), m.p. 210–212° dec. The molecular extinction coefficients in acetone are 33,800, 30,600 and 11,000 at 632, 585 and 348 μ , respectively.

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_5\text{S}_2$: C, 57.88; H, 3.50; N, 10.84; S, 12.37. Found: C, 57.84; H, 3.60; N, 11.25; S, 12.37.

Tetramethylammonium 1,2-Dicyano-2-*p*-tolylsulfonylethenolate. **A.** From 1,2-Dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene.—To a suspension of 3.86 g. (0.01 mole) of 1,2-dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene in 25 ml. of tetrahydrofuran was added 2 ml. of water, and the suspension was warmed to 50°. A homogeneous solution was obtained within a period of about 1 minute. The tetrahydrofuran was distilled under reduced pressure, and the residue was neutralized with 10% tetramethylammonium hydroxide. A small amount of solid tetramethylammonium chloride was added, whereupon crystals separated. After cooling in ice, the crystals were collected and washed with a small volume of ice-water. The yield of air-dried salt was 3.0 g. (94%). Crystallization from water gave 2.4 g. of colorless crystals, m.p. 135–136°, alone or in admixture with the sample of salt prepared from dichlorofumaronitrile, sodium *p*-toluenesulfinate and sodium bicarbonate as described below.

To the aqueous filtrate (30 ml.) containing the tetramethylammonium *p*-toluenesulfinate was added 50 ml. of dimethylformamide, 4 ml. of N,N-dimethylaniline and 2 g. of dichlorofumaronitrile. After stirring for 30 minutes, the reaction mixture was diluted to 400 ml. with water, and the precipitate was collected. Crystallization from methylene chloride-ether gave 2.5 g. (71%) of 4-[1,2-dicyano-2-(*p*-tolylsulfonyl)-vinyl]-N,N-dimethylaniline, m.p. 194–195°, alone or in admixture with a known sample.

B. From Dichlorofumaronitrile and Sodium *p*-Toluenesulfinate.—To a stirred solution of 9 g. (0.05 mole) of sodium *p*-toluenesulfinate in 80 ml. of water was added dropwise a solution of 7.5 g. (0.05 mole) of dichlorofumaronitrile in 15 ml. of tetrahydrofuran, the pH of the solution being maintained at 6–7 by the addition of sodium bicarbonate. After stirring for 30 minutes, the 1,2-dicyano-1,2-bis-(*p*-tolylsulfonyl)-ethylene was filtered, and about 5 g. of solid tetramethylammonium chloride was added to the filtrate. The resulting solution was freed of tetrahydrofuran by distillation under reduced pressure. On

cooling and stirring, the oil solidified and was collected and washed with dilute tetramethylammonium chloride. Three crystallizations from water (Darco G-60) gave 2.6 g. (16%) of short, colorless crystals, m.p. 135–136°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$: C, 56.05; H, 5.96; N, 13.07; S, 9.98. Found: C, 56.46; H, 5.89; N, 13.01; S, 10.02.

Tetramethylammonium 1,2-Dicyano-2-*p*-isopropylphenylsulfonylethenolate. **A.** From 1,2-Dicyano-1,2-bis-(*p*-isopropylphenylsulfonyl)-ethylene.—To a solution of 1.8 g. (0.004 mole) of 1,2-dicyano-1,2-bis-(*p*-isopropylphenylsulfonyl)-ethylene in 15 ml. of tetrahydrofuran was added dropwise 60 ml. of water. The resulting strongly acidic solution was neutralized with 10% aqueous tetramethylammonium hydroxide and concentrated to a volume of ca. 20 ml. under reduced pressure in a bath at 30–40°. A solid separated during the concentration and, after cooling in ice, was collected and washed with a small volume of ice-water. The yield of nearly colorless crystals was 1.1 g. (80%), m.p. 114–116°. Two crystallizations from water gave colorless crystals, m.p. 114–116° alone or in admixture with the salt prepared from dichlorofumaronitrile and sodium *p*-isopropylbenzenesulfinate as described below.

To the aqueous filtrate was added ca. 40 ml. of dimethylformamide, 2 ml. of N,N-dimethylaniline and 0.5 g. of dichlorofumaronitrile. After stirring for 30 minutes, the reaction mixture was diluted with water, and the solid was collected and crystallized from methylene chloride-ether. The yield of dark green crystals of 4-1,2-dicyano-2-(*p*-isopropylphenylsulfonyl)-N,N-dimethylaniline, m.p. 153–155°, alone or in admixture with a known sample of the dye, was 0.7 g. (50%).

B. From Dichlorofumaronitrile and Sodium *p*-Isopropylbenzenesulfinate.—To a stirred solution of 10.3 g. (0.05 mole) of sodium *p*-isopropylbenzenesulfinate in 50 ml. of water was added dropwise a solution of 7.5 g. (0.05 mole) of dichlorofumaronitrile in 15 ml. of tetrahydrofuran, the pH of the reaction mixture being maintained at 6–7 by the addition of solid sodium bicarbonate. After stirring for 15 minutes, the solid 1,2-dicyano-1,2-bis-(*p*-isopropylphenylsulfonyl)-ethylene was removed by filtration and 5 g. of solid tetramethylammonium chloride was added. An oil separated that solidified on stirring and cooling in ice. The solid was collected and crystallized four times from water. The yield of colorless short crystals was 6.0 g. (35%), m.p. 117–118°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_3\text{S}$: C, 58.43; H, 6.63; N, 12.03; S, 9.18. Found: C, 58.16; H, 6.76; N, 12.00; S, 9.26.

Potassium 1,2-Dicyano-2-(*p*-isopropylphenylsulfonyl)-ethenolate.—The aqueous filtrate from the preparation of 1,2-dicyano-1,2-bis-(*p*-isopropylphenylsulfonyl)-ethylene gave a strong test for sulfinate. To the filtrate was added a solution of about 3 g. of dichlorofumaronitrile in 10 ml. of tetrahydrofuran. A colorless solid separated within a few minutes. After cooling in ice, the solid was collected, washed with a small volume of ice-water and crystallized three times from aqueous methanol. The colorless crystals melted at 273–274°.

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_3\text{SK}$: C, 49.66; H, 3.53; N, 8.91; S, 10.20. Found: C, 49.79; H, 3.68; N, 8.87; S, 10.49.

Tetramethylammonium 1,2-dicyano-2-*p*-chlorophenylsulfonylethenolate was prepared from dichlorofumaronitrile (7.5 g., 0.05 mole) and sodium *p*-chlorobenzenesulfinate (10 g., 0.05 mole) essentially as described above. After three crystallizations from water, the yield of colorless crystals, m.p. 138–139°, was 5.6 g. (33%).

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3\text{SCL}$: C, 49.19; H, 4.72; N, 12.29. Found: C, 49.27; H, 4.80; N, 12.67.

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