Anal. Calcd for $C_{18}H_{16}N_2S$: C, 73.93; H, 5.52; N, 9.58; S, 10.97. Found: C, 74.18; H, 6.08; N, 9.38; S, 11.10.

Acknowledgment.—The author wishes to thank J. D. Anderson for preparing compound V, J. H. Wagenknecht for the experiment with compound III, and Hanne Albertson for polarographic data.

Cyanovinyltetrazoles

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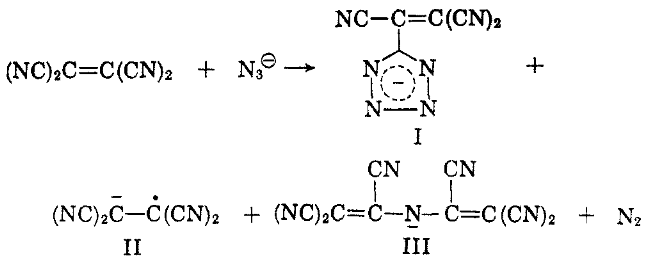
The preparation of 5-substituted tetrazoles by reaction of inorganic azides with nitriles has been found to proceed most rapidly with negatively substituted nitriles.[1,2] Norris[2] has stated that in the case of electronegatively substituted nitriles the initial step is a nucleophilic addition of azide ion to the nitrile group without aid of a catalyst. Subsequent ring closure of the iminoazide forms the tetrazole ring. With an electropositively substituted nitrile the initial addition of azide ion requires the assistance of an acid catalyst, *e.g.*, ammonium chloride, and higher temperatures. An extreme example of the former case is the reaction of sodium azide with trifluoroacetonitrile which proceeds exothermically at room temperature in acetonitrile.[2]

In an investigation of the reaction of inorganic azides with selected cyanoethylenes, particularly tetracyanoethylene (TCNE), it has been found that the reaction proceeds rapidly at temperatures as low as the freezing point of dimethylformamide (−61°) or acetonitrile (−41°). The reaction gives salts of 5-tricyanovinyltetrazole (I), tetracyanoethylene anion radical (TCNE$^{-}\cdot$)[3,4] (II), and bistricyanovinylamine[5] (III), and the yields of these products are markedly temperature and solvent dependent.



Early experiments in acetonitrile at 0° using commercial sodium azide gave erratic results with incomplete utilization of azide ion. Nitrogen was evolved, and gross mixtures of I, II, and III were formed. Subsequent experiments utilized a recrystallized, finely divided form of sodium azide (see the Experimental Section) which gave rapid reactions at the freezing point of the solvent.

Addition of TCNE to a suspension of sodium azide in acetonitrile at temperatures as low as −25° resulted in a slow evolution of nitrogen (20–25% molar equiv based on azide ion). The ultraviolet absorption spectrum of the crude product indicated the presence of III in molar amount approximately equivalent to that of the evolved nitrogen, and large amounts of an unknown material later shown to be I. The amount of TCNE$\cdot^{-}$ was so low that it could not be detected satisfactorily by ultraviolet absorption spectroscopy. However, the presence of TCNE$\cdot^{-}$ was demonstrated by electron paramagnetic resonance studies.[3] Thus, the reaction below

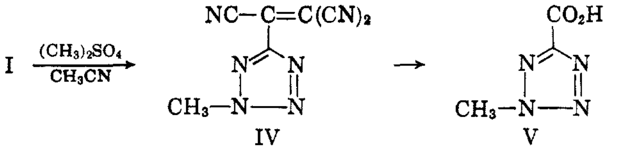
$$2(NC)_2C{=}C(CN)_2 + 2N_3^- \longrightarrow 2(NC)_2\bar{C}{-}\dot{C}(CN)_2 + 3N_2$$

is of minor importance. In other experiments TCNE$\cdot^{-}$ was found to be inert to azide ion under these conditions. The tetrazole (I) formed a tetramethylammonium salt, but initial attempts to separate it from III by crystallization or chromatography were only partly successful because of its hydrolytic and thermal instability.

The use of dimethylformamide or dimethylacetamide as solvent at −20° resulted in the formation of the tetrazole anion in good yield with little nitrogen evolution. The tetrazole was obtained as the tetramethylammonium salt in 65% yield by rapid recrystallization from acetonitrile–ether. The infrared and ultraviolet spectra of this salt, as well as a structural degradation, are in complete accord with proposed structure I. The infrared spectrum gives no evidence for the presence of a free azide group and shows strong absorption at 4.52 (conjugated C≡N) and 6.35 μ (N=N or C=N). The ultraviolet spectrum in acetonitrile has λ_{max} 360 mμ (ϵ_{max} 10,800) and 237 mμ (ϵ_{max} 3640). A freshly prepared aqueous solution has λ_{max} 327 mμ, but the solution does not obey Beer's law because of reaction with the solvent.

The formation of tetrazole I may be accounted for by the mechanism proposed by previous authors,[1,2] and the extreme ease of reaction of azides with an electronegatively substituted nitrile is in accord with their data.

The structure of I was rigorously established by the following reaction sequence; I, as a tetramethylammonium salt, was methylated at 25° by excess methyl sulfate in acetonitrile. A single product was isolated to which was assigned structure IV; *i.e.*, methylation occurred in the 2 position. This is in accord with the observation of Henry and Finnegan[6] that alkylation of tetrazole salts having electronegative substituents at the 5 position gives predominantly the 2-substituted product while those with electropositive groups in the 5 position give predominantly the 1-substituted compound. The validity of this structural assignment was shown by degradation of IV to the known 2-methyl-



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[4] O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

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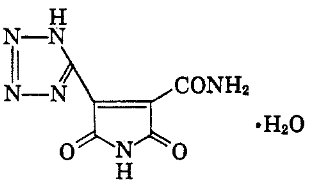
tetrazole-5-carboxylic acid[7] (V), mp 205° dec, in almost quantitative yield. The conversion of IV to V also conclusively establishes the presence of a tetrazole ring in I. The degradation of a tricyanovinyl group to a carboxylic acid is normally performed with methanolic hydrogen chloride[8] since the α-carbon atom is already in the proper oxidation state. In our hands this procedure gave only poor yields, while the use of basic permanganate to degrade the tricyanovinyl group gave the acid V in high purity and almost quantitative yield.

Treatment of the tetramethylammonium salt I with concentrated hydrochloric acid at 25° resulted in the formation of light yellow microcrystals, dec pt ~275°, having a molecular formula $C_6H_6N_6O_6$. The infrared spectrum indicates that nitrile groups are absent, but shows strong broad absorption at 3.0 (NH and or OH), 5.6 and 5.8 (cyclic imide), 5.93 (amide C=O), and 6.15 μ (NH_2 bending). The ultraviolet spectrum has $\lambda_{max}^{H_2O}$ 251 mμ (ϵ_{max} 5800), 327 mμ (ϵ_{max} 15,500). The spectra are consistent with the maleimide structure VI. Other 1,2-dicyanoethylenes have been converted to maleimides in the same way.[9]



VI

1,2-Dicyano-1,2-di-p-toluenesulfonylethylene[10] has been previously found to undergo many of the reactions of TCNE. Accordingly, it was of interest to examine the reaction of azide ion with this dicyanoethylene. Lithium azide reacted with 1,2-dicyano-1,2-di-p-toluenesulfonylethylene at low temperature to give lithium 5-(2-cyano-1,2-di-p-toluenesulfonylvinyl)tetrazole. Like the product derived from TCNE, the compound is sensitive to heat and to hydroxylic solvents.

Experimental Section

Commercial grade acetonitrile, dimethylformamide, and dimethylacetamide were distilled from phosphorus pentoxide, stored in rubber-capped brown bottles, and transferred with nitrogen-flushed syringes. Sodium azide was purified by the following procedure.

Seventy grams of commercial grade sodium azide was dissolved in the minimum quantity of distilled water at 25° (about 280 ml), and 10 ml of 99+% hydrazine hydrate was added. The mixture was stirred at room temperature for 15 min and then filtered into 3 l. of reagent-grade acetone. The fine, white precipitate was collected by filtration, pressed dry with a rubber dam, and finally dried in a vacuum desiccator over P_2O_5 at <0.1 mm. The resulting powder was stored under nitrogen in a tightly capped brown bottle. Material prepared and handled in this fashion was highly reactive and gave reproducible results.

Preparation of Salts of 5-Tricyanovinyltetrazole (I). A. From Sodium Azide in Dimethylformamide.—A mixture of 7.5 g of sodium azide and 50 ml of dimethylformamide was cooled to 0° under nitrogen, and a chilled solution of 12.8 g (0.1 mole) of TCNE in 50 ml of dimethylformamide was added dropwise over 1 hr.[11] The reaction was mildly exothermic, and essentially no nitrogen evolution was observed at this stage. The mixture was stirred for an additional 2 hr at 0 to −10° and then rapidly filtered under nitrogen. The filtrate at this point showed an epr spectrum indicating the presence of $TCNE\cdot^-$,[3] but the visible spectrum gave no evidence for its formation. This filtrate was flash distilled at the lowest pressure obtainable with a vacuum pump and <25°, leaving a red-brown syrup which partially solidified. The syrup was taken up in the minimum amount of ice–water and added to a cold, saturated solution of tetramethylammonium chloride.[12] The crude, brownish orange salt was collected on a filter, pressed dry with a rubber dam, and dried in a vacuum desiccator over P_2O_5 at <0.1 mm. The product weighed 17.5 g (72%), mp 149–150.5° dec (with gas evolution). An analytical sample was prepared by dissolving the crude product in acetonitrile with gentle warming.[13] Ether was added to the cloud point, and slow cooling to −40° afforded tetramethylammonium 5-tricyanovinyltetrazole as coarse, yellow-orange needles, mp 150–150.5° dec.

Anal. Calcd for $C_{10}H_{12}N_8$: C, 49.18; H, 4.96; N, 45.86. Found: C, 49.09; H, 4.99; N, 45.82.

B. From Lithium Azide in Dimethylformamide.—Nine grams of lithium azide[14] was dissolved in 60 ml of dry dimethylformamide (mildly exothermic) under nitrogen. The solution was cooled to −20°, and a chilled solution of 16.5 g of TCNE in 100 ml of dry dimethylformamide[13] was added dropwise over 2 hr at −10 to −20°. After stirring for an additional 2 hr at −20°, the product was isolated as a tetramethylammonium salt, 14 g (45%), which assayed 94% pure by spectral analysis. This material was found to be of sufficient purity for subsequent reactions without further purification.

C. From Sodium Azide in Acetonitrile at 25°.—To a suspension of 3.35 g (0.05 mole) of sodium azide in 100 ml of dry acetonitrile at room temperature was added dropwise with stirring 6.4 g (0.05 mole) of TCNE in 50 ml of acetonitrile over a 1-hr period. The mildly exothermic reaction was moderated by use of a cold-water bath. Stirring was continued for an additional 2 hr at the end of which time the total nitrogen evolved amounted to ~20% of theoretical for the reaction $N_3^- \rightarrow N_2\uparrow$. The solvent was evaporated at room temperature and the residue treated with tetramethylammonium chloride. The product, 9.5 g of a red-brown solid, assayed as 78% tricyanovinyltetrazole salt and 22% bis(tricyanovinyl)amine salt by spectral analyses.

2-Methyl-5-tricyanovinyltetrazole.—A mixture of 5.71 g (23.4 mmoles) of tetramethylammonium 5-tricyanovinyltetrazole, 50 ml of dry acetonitrile, and 3.15 g (25 mmoles) of methyl sulfate was stirred at room temperature for 48 hr. The dark mixture was added to 100 ml of ice–water and extracted with three 25-ml portions of ether. The combined extracts were dried and concentrated *in vacuo*. The residual oil was taken up in benzene and chromatographed on neutral alumina (Woelm). Elution with 10–25% ether in benzene afforded 1.78 g (41%) of 2-methyl-5-tricyanovinyltetrazole as coarse, colorless needles, mp 97–97.5° after sublimation; $\lambda_{max}^{CH_3CN}$ 297 mμ (ϵ 16,380), 233 mμ (ϵ 6000).

Anal. Calcd for $C_7H_3N_7$: C, 45.40; H, 1.63; N, 52.97. Found: C, 45.40; H, 1.80; N, 52.83.

2-Methyltetrazole-5-carboxylic Acid.—To a solution of 2.45 g of 2-methyl-5-tricyanovinyltetrazole in 50 ml of water containing 3 g of potassium carbonate was added with stirring a solution of 3.5 g of potassium permanganate in 100 ml of water over a 30-min period. The temperature rose slowly to 40° during the addition, and stirring was continued for 2 hr while the temperature fell to 25°. The mixture was decolorized with sulfur dioxide, made strongly acidic with concentrated hydrochloric acid, and continuously extracted with ether. Evaporation of the ether yielded 1.63 g (~100%) of 2-methyltetrazole-5-carboxylic acid, mp 192–196°. Two recrystallizations from ethyl acetate gave white needles, mp 204–205°, undepressed on admixture with an authentic sample prepared by the method of Oliveri-Mandala.[7]

Anal. Calcd for $C_3H_4N_4O_2$: C, 28.13; H, 3.15; N, 43.74. Found: C, 28.46; H, 3.30; N, 43.65.

The ultraviolet spectrum showed λ_{max}^{EtOH} 295 mμ (ϵ_{max} 32). The infrared spectrum had strong absorption at 3.83 and 5.88 μ.

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[7] E. Oliveri-Mandala and T. Passalacqua, *Gazz. Chim. Ital.*, [II] **43**, 465 (1913).

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

[9] G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *ibid.*, **80**, 2815 (1958).

[10] E. L. Martin, *ibid.*, **85**, 2449 (1963).

[11] TCNE undergoes a slow decomposition in dimethylformamide; therefore the solution should be prepared and used as rapidly as possible.

[12] Since the tetrazole is unstable to hydroxylic solvents, this stage of the reaction must be carried out rapidly for maximum yield.

[13] Since the tetrazole is unstable to heat, care should be taken to keep from heating the solution above 50°.

[14] R. Huisgen and I. Ugi, *Chem. Ber.*, **90**, 2914 (1957).

1-Carbamoyl-2-(5-tetrazolyl)maleimide Monohydrate.—A mixture of 4.0 g of tetramethylammonium 5-tricyanovinyltetrazole and 25 ml of concentrated hydrochloric acid was stirred at 25° for 72 hr. The mixture was poured into 100 g of ice–water. The gray solid (1.6 g, dec pt >275°) was collected on a filter and washed with ice–water. Recrystallization from water (Darco) gave 1.25 g of light yellow microcrystals, dec pt >275°.

Anal. Calcd for $C_6H_6N_6O_4$: C, 31.86; H, 2.68; N, 37.17; mol wt, 226. Found: C, 31.27; H, 2.79; N, 36.79; mol wt (boiling acetone), 217, 213.

Preparation of Salts of 5-(2-Cyano-1,2-di-*p*-toluenesulfonylvinyl)tetrazole.—To a slurry of 1.35 g of lithium azide in 75 ml of dry dimethylformamide cooled to −10° under nitrogen was added in one portion 9.65 g (0.025 mole) of 1,2-di-*p*-toluenesulfonyl-1,2-dicyanoethylene.[10] The mixture became reddish orange, and the azide dissolved rapidly. The mixture was stirred for 1 hr at −10° and filtered cold under nitrogen, and the filtrate was evaporated at 1 mm. The glassy residue was taken up in acetone and added to ice-cold 20% aqueous tetramethylammonium chloride. The resulting oil crystallized on cooling to give 6.9 g of a yellow-orange tetramethylammonium salt (55%), mp 88–92° dec. The salt was sensitive to warm hydroxylic solvents. It was recrystallized from acetone–ether, mp 94–95°, $\lambda_{max}^{CH_2Cl_2}$ 393 mμ (ϵ_{max} 11,300).

Anal. Calcd for $C_{22}H_{26}N_6O_4S_2$: C, 52.57; H, 5.22; N, 16.72. Found: C, 52.67; H, 5.16; N, 17.07.

A reaction carried out on a similar scale and added to cold, 5% aqueous silver nitrate gave the yellow, microcrystalline silver salt in quantitative yield, dec pt >275°.

Anal. Calcd for $C_{19}H_{14}AgN_5O_4S_2$: C, 41.61; H, 2.57; N, 12.78. Found: C, 41.58; H, 2.57; N, 13.34.

A Novel Synthesis of 1,5-Diphenylpyrazolone-3[1]

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Received May 25, 1966

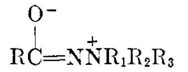
1,5-Diphenylpyrazolone-3 was first synthesized by Knorr,[3] who obtained it in vanishingly small yield by pyrolyzing cinnamoyl phenylhydrazide. Improved yields result from the reaction of monoacetyl phenylhydrazine with benzoylacetic ester in the presence of phosphorus trichloride.[4] We now report a new route to this compound which gives somewhat higher yields than Willert's method. The starting material for this synthesis is N-dimethylanilinophenylpropiolimide (II), a hitherto unreported compound which was prepared by treating N,N-dimethyl-N-phenylamine imine (I) with ethyl phenylpropiolate in an inert, anhydrous solvent such as tetrahydrofuran. The required amine imine (I) was obtained by deprotonation of dimethylphenylhydrazonium chloride with a strong base such as sodium ethylate. The over-all reaction sequence is summarized in the following equations. It was not necessary to isolate the free amine imine (I) before proceeding with the second step. The over-all yield of N-dimethylanilinophenylpropiolimide (II) was about 86%.

$$(PhN(CH_3)_2NH_2)^+Cl^- + NaOEt \longrightarrow \underset{I}{PhN^+(CH_3)_2N^-H} + NaCl + EtOH \quad (1)$$

$$I + PhC{\equiv}CCOOEt \longrightarrow \underset{II}{PhC{\equiv}CCON^-N^+(CH_3)_2Ph} + EtOH \quad (2)$$

It has been previously demonstrated[5,6] that trisubstituted hydrazonium salts deprotonate in the presence of a strong base according to eq 1 to give free amine imines. Analogous reactions have been described for the formation of phosphine imines[7,8] and arsine imines.[9]

Amine imides of type II have been reported in which the acyl moiety is benzoyl[10] and acetyl.[11] These were obtained by synthetic methods entirely independent of the procedure described here. The structure of N-dimethylanilinophenylpropiolimide (II) was established by chemical analysis, molecular weight, and infrared and nmr proton spectroscopy. An infrared peak at 4.55 μ is due to the acetylenic bond. A very strong peak at 6.35 μ is assignable, according to Wawzonek,[11] to the stretching frequency of the C=N bond as it occurs in the resonance form (III) of amine imides.

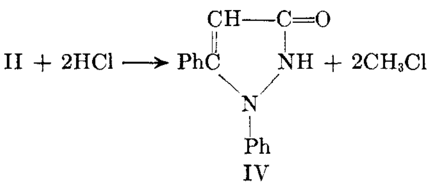


$$\overset{O^-}{\overset{|}{RC}}{=}N\overset{+}{N}R_1R_2R_3$$

III

This mesomeric form (III) is favored by the polar character of the N–N bond in the amine imide and must make a major contribution to the actual structure, since the normal carbonyl vibration is almost completely suppressed. A single peak in the nmr spectrum for methyl protons indicates that there had been no wandering of methyl groups during the reaction. The position of the methyl groups was further verified by the formation of dimethylaniline in the reductive cleavage of II.

To form 1,5-diphenylpyrazolone-3 (IV) from N-dimethylanilinophenylpropiolimide, the latter was heated at reflux with 6 *N* hydrochloric acid for several hours in an inert atmosphere. During this time, diphenylpyrazolone separated as a crystalline precipitate. Simultaneously, a gas was evolved and the reaction mixture turned green, owing to the formation of an unidentified by-product. The gas was identified by mass spectrometry as methyl chloride. The reaction, therefore, proceeded primarily according to eq 3. The yield of 1,5-diphenylpyrazolone-3 was about 80%.



(3)

IV

It was of interest to elucidate the mechanism of this rather surprising cyclization, involving as it does the loss of two methyl groups and the addition of two protons in the 2 and 4 positions of the pyrazolone ring.

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(1) This work is part of a thesis submitted by H. W. Schiessl in partial fulfillment of the requirements for the degree of Doctor of Sciences.

(2) Author to whom correspondence should be addressed at the Olin Research Center, New Haven, Conn.

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(11) S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).