

After processing,⁶ there was obtained 35.0 g. (82%) of colorless material, b.p. 96–98° (1.5 mm.), n_D^{20} 1.6165. Upon refrigeration crystals, m.p. 9°, were obtained.

Nitration of I.—A solution of 1.8 g. (0.011 mole) of I in 5 ml. of acetic anhydride was cooled to 5° and added rapidly with stirring to a nitrating solution, prepared at room temperature by adding (with cooling) 0.70 ml. (0.011 mole) of 70% nitric acid to 5 ml. of acetic anhydride and cooling to –5°. Despite ice–salt cooling, the temperature rose to 35° before slowly returning to 0°. After 20 min. the mixture was poured into ice–water. After hydrolysis, the solution was neutralized with sodium bicarbonate and extracted with ether. The 1.8 g. of yellow solid obtained on concentration of the ether layer was chromatographed on silica gel, eluting with hexane and finally ether–hexane. In this manner there was obtained, in order of elution, 0.22 g. (9.6%) of IV, m.p. 124–125°; 0.75 g. (32.6%) of III, m.p. 103–104°; 0.12 g. (6.1%) of II, m.p. 88–89°; and 0.45 g. of polymeric material. From a similar run, except that the nitration mixture was allowed to stand overnight at 0° prior to processing, the yields were much lower, larger amounts of polymeric material being formed. In this run a small amount of an additional product, m.p. 159–160°, crystallized from the hexane solution being prepared for chromatography. When the nitrating solution was added to a solution of I at 0° and the mixture was allowed to stand overnight at 0° and processed as before, the yields of IV and II were 2% and 18%, respectively; no III was isolated, the major amount of material was polymeric.

3-Methyl-2-benzo[b]thiophenecarboxaldehyde (II) was obtained as pale yellow needles, m.p. 88–89°. In addition to a strong C=O band at 6.02 μ , it had an aldehydic C–H band at 3.50 μ , and other infrared peaks at 3.25, 3.42, 6.23, 6.36, 6.52, 6.96, 7.23, 7.40, 7.55, 7.87, 8.20, 8.58, 9.25, 9.40, 10.64, 13.19, 13.72, 13.92, 14.83, and 15.15 μ . The n.m.r. spectrum in carbon tetrachloride showed a singlet at τ –0.23 for the aldehydic proton, a multiplet from τ 2.12 to 2.67 for the aromatic protons, and a singlet at τ 7.32 for the methyl group.

Anal. Calcd. for C₁₀H₈OS: C, 68.18; H, 4.58. Found: C, 68.02; H, 4.49.

The oxime, recrystallized from hexane, melted at 161–162°.

Anal. Calcd. for C₁₀H₉NOS: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.66; H, 5.01; N, 7.29.

3-Methyl-2-nitromethylbenzo[b]thiophene (III) was obtained as nearly colorless crystals, m.p. 103–104°. It dissolved slowly in warm dilute sodium hydroxide and was recovered by acidification. The infrared spectrum showed strong unconjugated nitro peaks at 6.45 and 7.30 μ , and other peaks at 3.35, 3.51, 6.99, 7.45, 7.66, 8.24, 8.52, 8.63, 8.80, 9.41, 9.82, 10.82, 12.47, 12.70, 13.19, 13.70, 14.00, and 14.89 μ . The n.m.r. spectrum showed a multiplet from τ 2.18 to 2.77 for the aromatic protons, a singlet at τ 4.48 for the methylene α to the nitro, and a singlet at τ 7.60 for the methyl group.

Anal. Calcd. for C₁₀H₉NO₂S₂: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.85; H, 4.56; N, 6.32.

2,3-Dimethyl-6-nitrobenzo[b]thiophene (IV) was obtained as bright yellow needles, m.p. 124–125°. The infrared spectrum showed strong conjugated nitro peaks at 6.60 and 7.48 μ , and other peaks at 3.20, 3.40, 6.22, 6.42, 6.82, 7.10, 7.16, 8.46, 8.77, 8.89, 9.56, 1.12, 11.25, 11.92, 12.18, 12.59, 13.27, and 13.88 μ . The n.m.r. spectrum (τ) in carbon tetrachloride showed the aromatic protons individually as follows: a doublet at τ 1.67 ($J = 2$ c.p.s.) for the 7-*H*; a pair of doublets at 2.10 ($J_1 = 9$ c.p.s., $J_2 = 2$ c.p.s.) for the 5-*H*; and a doublet at 2.67 ($J = 9$ c.p.s.) for the 4-*H*. The methyl groups gave two singlets of equal intensity at 7.53 and 7.77.

Anal. Calcd. for C₁₀H₉NO₂S: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.39; H, 4.53; N, 6.47.

3-Methyl-2-hydroxymethylbenzo[b]thiophene (V).—A solution consisting of 10 ml. of 95% alcohol, 0.40 g. (0.0025 mole) of II, and 0.05 g. (0.0013 mole) of sodium borohydride was allowed to stand for 1 hr. A pellet of sodium hydroxide was added, and the alcohol was removed by distillation, adding water to maintain the volume. The crude alcohol, which separated on cooling, was recrystallized from ether–hexane to give 0.22 g. (54%) of material, m.p. 90–91°, lit.⁷ m.p. 90.6–91.6°. Infrared peaks were at 3.05, 3.40, 3.48, 6.82, 6.95, 7.22, 7.33, 8.47, 8.60, 8.77, 10.0 broad, 10.65, 13.20, 13.67, 14.00, and 14.55 μ . The n.m.r.

spectrum in carbon tetrachloride showed a multiplet from τ 2.38 to 2.98 for the aromatic protons, a singlet at 5.40 for the methylene group, a singlet at 6.83 for the hydroxylic proton, and a singlet at 7.83 for the methyl group.

3-Methyl-2-aminomethylbenzo[b]thiophene Hydrochloride—A solution of 0.1 g. of lithium aluminum hydride and 0.20 g. (0.0010 mole) of III in 25 ml. of ether was refluxed overnight, and water was added dropwise to decompose the excess reducing agent. Excess dilute sodium hydroxide was added to dissolve the aluminum hydroxide, and the solution was extracted with ether. The amine was extracted from the ethereal solution with dilute hydrochloric acid, the acid extract was neutralized, and the amine, 0.1 g. (56%), m.p. 59–60°, was recovered by ether extraction. On drying *in vacuo*, it was converted to a brown oil. The latter was treated with dilute hydrochloric acid to give a sparingly soluble hydrochloride, which was collected on a filter and washed with ether and with water; the solid melted at 220° with decomposition.

Anal. Calcd. for C₁₀H₁₁NS·HCl: N, 6.56. Found: N, 6.43.

An excess of cold aqueous sodium nitrite was added to a cold solution of the amine hydrochloride dissolved in dilute hydrochloric acid. After standing at room temperature for an hour, the solution was warmed briefly on the steam bath, cooled, and extracted with ether. After crystallization from pentane, V, m.p. 91–92°, was recovered from the ether solution (identity was established by its infrared spectrum and a mixture melting point determination).

2,3-Dimethyl-6-nitrobenzo[b]thiophene 1,1-Dioxide.—Oxidation of 1.0 g. of I with 2.5 ml. of 40% peracetic acid in 10 ml. of acetic acid gave 0.95 g. (79%) of the 1,1-dioxide, m.p. 150–151°, lit.⁶ m.p. 149–150°. The n.m.r. spectrum in 1,1,2,2-tetrachloroethane showed a multiplet at τ 2.38 to 2.60 and a singlet at 7.87 for the two methyl groups. A 0.85-g. sample of the dioxide was dissolved in 5 ml. of concentrated sulfuric acid, the solution was cooled to 0°, and a solution of 0.27 ml. of concentrated nitric acid in 1 ml. of concentrated sulfuric acid was added dropwise. Processing in the usual manner gave a product, m.p. 199–200° after two crystallizations from 95% alcohol. This material had an infrared spectrum identical with that of a sample of 2,3-dimethyl-6-nitrobenzo[b]thiophene 1,1-dioxide, m.p. 201–202°, obtained in 71% yield by oxidation of IV with 40% peracetic acid, and a mixture melting point determination showed no depression. The n.m.r. spectrum in 1,1,2,2-tetrachloroethane showed a singlet (1.5) at τ 1.48 and a doublet (0.5) at τ 1.64 ($J = 2$ c.p.s.), which probably resulted from superimposition of a doublet at τ 1.48 ($J = 2$ c.p.s.) for the 7-*H* aromatic proton with a pair of doublets centered at 1.57 ($J_1 = 9$ c.p.s., $J_2 = 2$ c.p.s.) for the 5-*H* aromatic proton. There was a doublet (1) at τ 2.47 ($J = 9$ c.p.s.) for the 4-*H* aromatic proton and a singlet (6) at 7.80 for the two methyl groups.

Anal. Calcd. for C₁₀H₉NO₄S: C, 50.21; H, 3.79; N, 5.86. Found: C, 50.64; H, 3.72; N, 5.94.

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Preparation of 5-Dinitromethyltetrazole from Salts of Dinitroacetone

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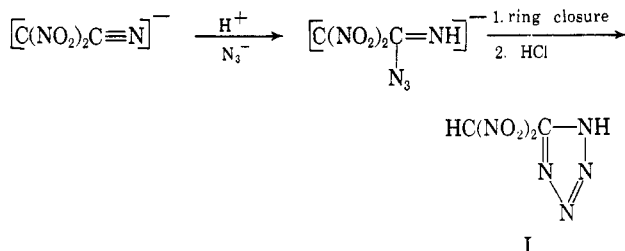
A general method for preparing tetrazoles by the reaction of nitriles with sodium azide in the presence or absence of ammonium ion in dimethylformamide has recently been described.^{1,2} We attempted to extend

(7) R. Gaertner, *J. Am. Chem. Soc.*, **74**, 2185 (1952). The isomer, 2-methyl-3-hydroxymethylbenzo[b]thiophene, is reported to melt at 145.8–147.4° [**74**, 766 (1952)].

(1) W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).

(2) W. P. Norris, *J. Org. Chem.*, **27**, 3248 (1962).

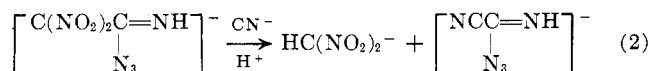
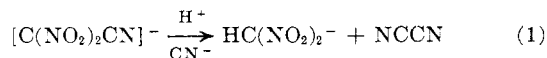
this to the preparation of the previously unknown dinitromethyltetrazole by the reaction of dinitroacetonitrile and sodium azide in water but with negative results, probably due to generation of the sodium salt of dinitroacetonitrile and the highly associated hydrazoic acid. It has now been found that the product can be obtained using salts of dinitroacetonitrile (sodium or ammonium, but not potassium) in refluxing water but not in dimethylformamide. This appears to be the first example of the use of an organonitrile salt³ to form a tetrazole and the product is the first example of a 5-nitroalkyltetrazole. The reaction may be represented as shown.



It would appear that the strong electron-withdrawing effect of the *gem*-dinitro group would greatly enhance nucleophilic attack by the azide ion on the carbon of the nitrile group.⁴ The product, however, was obtained in only 8–12% yields after purification. This may have been partly due to hindrance of the reaction by repulsion of the negative azide ion by the dinitroacetonitrile anion, or sterically by the bulky dinitromethyl group.

Over 70% of the dinitroacetonitrile salt was recovered after 24 hrs. of refluxing, starting with either the sodium or ammonium salt. In the reaction of sodium dinitroacetonitrile, however, most of the nitrile was recovered as the ammonium salt and the yield of product was somewhat reduced apparently because of depletion of available ammonium ion. A much lower yield of 5-dinitromethyltetrazole was obtained using one-tenth the original amount of ammonium chloride catalyst in the reaction of azide ion with ammonium dinitroacetonitrile. Available ammonium ion may also be depleted by formation of ammonium salts of the products.

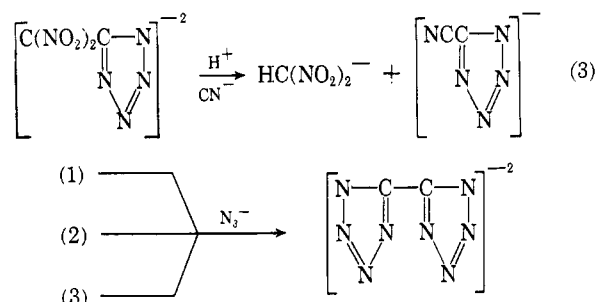
The yield of dinitromethyltetrazole obtained after 48 hr. of refluxing was nearly the same as that obtained after 24 hr., while that of diammonium bitetrazole (II), a by-product of the reaction, increased threefold. Decomposition products also increased considerably. Cyanide ion formed as a breakdown product was shown to be present in the reaction mixture after 24 hr. of refluxing (see Experimental). However, it is not clear how the cyanide ion arises. Cyanide ion, in turn, may react to produce bitetrazole in any one of these ways.



(3) Trimethylammonium cyanide has been used to prepare tetrazole.¹

(4) Electronegative groups attached to the nitrile facilitate tetrazole formation.¹

(5) C. O. Parker, W. D. Emmons, A. S. Pagano, H. A. Rolewicz, and K. S. McCallum, *Tetrahedron*, **17**, 89 (1962).



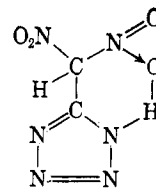
Nucleophilic displacement by cyanide ion appears to be related to a previously reported⁵ example of displacement by hydroxyl ion on the nitrile carbon of methyl 4,4-dinitro-4-cyanobutylate.

The reaction of sodium dinitroacetonitrile with sodium azide and ammonium chloride in dimethylformamide appeared to produce only decomposition products. No product was obtained with potassium dinitroacetonitrile in refluxing water or in dimethylformamide at 110–120° during 48 hr. It has been observed that potassium dinitroacetonitrile is unchanged in alkylation, addition, and other reactions contrary to the more normal behavior of the sodium and other salts of dinitroacetonitrile.⁶

Mono- and disodium, monoammonium, and mono-guanidine salts of 5-dinitromethyltetrazole also were prepared from the free dibasic acid. The disodium salt was found to be much more thermally stable than the monosodium salt. This may be attributed to a pronounced resonance stabilization of the tetrazole ring in the dianion by release of an electron pair to the ring.

Infrared bands of dinitromethyltetrazole and its salts attributed to NH stretching, the tetrazole ring, and the nitro groups are summarized in Table I.

The shift in frequency for the nitro groups from 1590 cm^{-1} for dinitromethyltetrazole, to 1570 cm^{-1} for the monosodium salt, and to 1530 cm^{-1} for the disodium and monoammonium salts, may be due to a change in character from nitro to nitronate.⁷ The absence of the NH band in the disodium salt, and its presence in the monosodium salt of dinitromethyltetrazole shows that the stronger of the two acidic hydrogens of dinitromethyltetrazole is in the dinitromethyl group. The occurrence of N–H stretching below 3300 cm^{-1} is indicative of hydrogen bonding and is probably due to intramolecular hydrogen bonding. For the free acid this may be illustrated as shown.



Intramolecular hydrogen bonding also has been observed for 2,2-dinitroethylamine.⁹

(6) C. O. Parker, W. D. Emmons, H. A. Rolewicz, and K. S. McCallum, *ibid.*, **17**, 79 (1962).

(7) A similar shift is shown by α, α -dinitronitriles compared with salts of 1,1-dinitroparaffins.³

(8) L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **25**, 1471 (1960).

(9) M. J. Kamlet and J. C. Dacons, *ibid.*, **26**, 3005 (1961).

TABLE I
 INFRARED BANDS OF 5-DINITROMETHYLTETRAZOLE AND ITS SALTS^a

Compound	Infrared, cm. ⁻¹			
	NH ^b	Tetrazole ring ^c	<i>gem</i> -Dinitro group ^d	Others ^e
5-Dinitromethyltetrazole	3130	1070, 1048, 1016, 997	1590, 1330	1518, 1407, 1350
Monosodium-5-dinitromethyltetrazole	3170	1070 .. 1018, 1005	1570, 1350	1485, 1412 ..
Disodium-5-dinitromethyltetrazole 1032, 1015 ..	1530, 1365
Monoammonium-5-dinitromethyltetrazole	3230	.. 1045, 1022 ..	1530, 1360	.. 1400 ..

^a All spectra were obtained on Nujol mulls (Perkin-Elmer spectrophotometer Model 321). ^b Bands corresponding to hydrogen bonded NH (3230–3030 cm.⁻¹) [R. A. Braun and W. A. Mosher, *J. Am. Chem. Soc.*, **80**, 4919 (1958)]. ^c In general, the tetrazole ring absorbs between 1100–1000 cm.⁻¹ [E. Lieber, D. R. Levering, and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951)]. ^d In general, *gem*-dinitro absorbs near 1580 and 1330 cm.⁻¹ [J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955)]. ^e Possibly due to nitro.

Experimental¹⁰

Potassium dinitroacetonitrile¹¹ was treated with decolorizing charcoal and recrystallized from water. Sodium and ammonium dinitroacetonitrile were prepared from the potassium salt according to a previously described method.⁶ The salts were dried at 100° for 2 hr., and kept in a desiccator over Drierite.¹² Sodium dinitroacetonitrile had m.p. 224–226° (lit.⁸ m.p. 224–226°) and ammonium dinitroacetonitrile had m.p. 175–176° dec. (lit.⁶ m.p. 182° dec.). Sodium azide was treated with decolorizing carbon and crystallized from water. Ammonium chloride and guanidine carbonate were reagent grade and were used without further treatment.

Reaction of Sodium Dinitroacetonitrile, Sodium Azide, and Ammonium Chloride.—A solution of sodium dinitroacetonitrile (15.30 g., 0.100 mole), sodium azide (6.65 g., 0.102 mole), and ammonium chloride (5.50 g., 0.102 mole) in 50 ml. of water in a round-bottomed flask fitted with a condenser and magnetic stirrer was stirred and refluxed for 24 hr.¹³

Isolation of Diammonium Bitetrazole and Its Conversion to Bitetrazole.—The solution was cooled and kept at 5° for several hours; the yellowish solid was collected on a filter, washed with cold water, and dried at 110°. The yield of the salt was 0.59 g. (7.0%). In another run using half the quantities, the yield after 48 hr. of refluxing was 0.90 g. (21.2%). Crystallization from water gave white needles which did not melt up to 300°.

Anal. Calcd. for C₂H₈N₁₀: C, 13.95; H, 4.65; N, 81.40. Found: C, 13.78, 13.98; H, 4.88, 5.02; N, 81.50, 82.03.

The diammonium bitetrazole was dissolved in an excess of hot 10% hydrochloric acid (1 g. of salt in 10 ml. of acid). The solution was filtered hot and the filtrate cooled to 5° causing bitetrazole to precipitate as a white, crystalline solid. The product was highly acidic in aqueous solution. For analysis, a sample was recrystallized twice from water and dried at 110°, m.p. 255.0–255.5° dec. (lit.¹⁴ m.p. 254–255° dec.).

Anal. Calcd. for C₂H₂N₈: C, 17.38; H, 1.45; N, 81.16; neut. equiv., 69.0. Found: C, 17.33, 17.36; H, 1.46, 1.51; N, 82.40, 82.43; neut. equiv., 69.1.

Isolation of 5-Dinitromethyltetrazole.—The pH of the ammonium bitetrazole filtrate was adjusted to less than 1 (measured with a pH meter) with concentrated hydrochloric acid. Hydrozoic acid and water were removed under water aspiration on the steam bath. The remaining solids were extracted with boiling acetone and the insoluble salts were removed by filtration and discarded. The acetone was evaporated under reduced pressure, the remaining dry solid was extracted several times with ethyl ether totaling several hundred milliliters, and insoluble solids were reserved for recovery of dinitroacetonitrile salt. Removal of the ether gave 2.26 g. of crude product. Crystallization from methyl alcohol gave 1.39 g. (8.0%) of white, crystalline product which produced intensely yellow, highly acidic aqueous solutions. The yield after 48 hr. of refluxing using half the quantities was 0.77 g. (8.8%). For analysis a sample was recrystallized from methyl alcohol.

Anal. Calcd. for C₂H₂N₆O₄: C, 13.80; H, 1.16; N, 48.28; neut. equiv., 87.0. Found: C, 14.01, 14.04; H, 1.50, 1.24;

N, 48.10, 48.20; neut. equiv., 87.7; pK₁, 1.65, and pK₂, 3.60 (water, 25°).¹⁵

The free acid, on heating fairly rapidly in a capillary tube produced nitrogen dioxide fumes at about 100°, gradually darkened above 150°, and went abruptly from dark brown to black, without melting, at about 180°.

Recovery of Ammonium Dinitroacetonitrile.¹⁶—The ether-insoluble solids were extracted several times with small quantities of hot ethyl acetate leaving 5.3 g. of ammonium dinitroacetonitrile which was collected on a filter. The filtrate was evaporated to a small volume (approximately 25 ml.) and cooled to 5°; an additional 3.9 g. of ammonium dinitroacetonitrile was collected. Evaporation of the final filtrate left 2.1 g. of ammonium dinitroacetonitrile containing a small amount of the sodium salt. The total recovered salt was 11.3 g. (76.4%). Total recovered salt from the reaction mixture refluxed 48 hr. using half quantities was 5.2 g. (70.7%). The ammonium salt was recrystallized twice from alcohol giving white crystals whose infrared spectrum was identical with that of a known sample prepared as described.

Preparation of Monoammonium 5-Dinitromethyltetrazole.—5-Dinitromethyltetrazole was dissolved in sufficient 10% aqueous ammonia to give a solution having a pH greater than 9. The water and excess ammonia were evaporated and the product was crystallized from ethyl alcohol. The monoammonium salt darkened above 195°, and abruptly decomposed without melting at 214°. Several attempts to prepare the diammonium salt gave monoammonium salt.

Anal. Calcd. for C₂H₅N₇O₄: C, 12.56; H, 2.62; N, 51.36. Found: C, 12.69; H, 2.70; N, 51.55.

Preparation of Monosodium and Disodium 5-Dinitromethyltetrazole.—5-Dinitromethyltetrazole was titrated electrometrically to either the first or second end points with 0.1 N sodium hydroxide. The water was removed and the dry salts were washed with alcohol, with acetone, and then dried. The disodium salt appeared to be unchanged up to 310°, and the monosodium salt exploded violently at approximately 160°.

Anal. Calcd. for C₂H₃N₆O₄Na: C, 12.21; H, 0.76; N, 42.73; Na, 11.76. Found: C, 12.24; H, 0.51; N, 42.86; Na, 11.73.

Anal. Calcd. for C₂N₆O₄Na₂: C, 11.13; N, 38.39; Na, 21.30. Found: C, 11.01; H, 0.00; N, 38.53; Na, 21.10.

Preparation of the Monoguanidine Salt of 5-Dinitromethyltetrazole.—5-Dinitromethyltetrazole (0.075 g.) and guanidine carbonate (0.098 g.) were dissolved in 2 ml. of water. The pH of the solution was adjusted to about 3 with concentrated hydrochloric acid. The light yellow, crystalline precipitate was filtered, after cooling to 5°, and recrystallized twice from water. It decomposed without melting at 164.0–164.5°.

Anal. Calcd. for C₃H₅N₉O₄: C, 15.52; H, 2.61; N, 54.30. Found: C, 15.56, 15.26; H, 3.57, 3.37; N, 54.41, 54.20.

Reaction of Ammonium Dinitroacetonitrile with Sodium Azide and Ammonium Chloride.—Ammonium dinitroacetonitrile (7.40 g., 0.050 mole), sodium azide (3.33 g., 0.051 mole), and ammonium chloride (2.75 g., 0.051 mole) in 25 ml. of water were refluxed for 24 and 48 hr. Both reaction mixtures then were treated as described for the reactions with sodium dinitroacetonitrile except that the ether-insoluble solids were not extracted with ethyl acetate. Yields are summarized in Table II.

(10) All melting points are uncorrected.

(11) Obtained from the Rohm and Haas Co., Redstone Arsenal Research Division.

(12) Sodium dinitroacetonitrile absorbs moisture from the atmosphere and forms a stable monohydrate.⁶

(13) Highly alkaline fumes escaped from the condenser after approximately 0.5 hr. of refluxing. The absorbed fumes in dilute hydrochloric acid gave a negative test for ammonium ion with Nessler's reagent.

(14) F. R. Benson, *Chem. Rev.*, **41**, 1 (1947).

(15) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Part II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1946, pp. 1747, 1748.

(16) Salts of dinitroacetonitrile are recovered unchanged from concentrated hydrochloric acid and, therefore, were recovered from the reaction mixture after adjusting the pH to less than 1.

TABLE II

Reflux time, hr.	Bitetrazole, g. (%)	5-Dinitromethyltetrazole, g. (%)	Recovered ammonium dinitroacetoneitrile, g. (%)
24	0.68 (8.0)	1.07 (12.3) from 2.1 g. of crude	5.37 (71.8)
48	1.80 (21.9)	0.80 (9.2) from 2.7 g. of crude	2.64 (35.2)

A reaction using 0.05 mole of ammonium dinitroacetoneitrile, 0.051 mole of sodium azide, and 0.0051 mole of ammonium chloride (10 mole % of the sodium azide) in 25 ml. of water refluxed for 24 hr. gave 0.34 g. (4.0%) of bitetrazole and 0.2 g. (2.3%) of crude 5-dinitromethyltetrazole.

After 24 hr. of refluxing, the reaction mixture gave a positive test for the presence in large concentration of cyanide ion with benzidine-copper acetate reagent.¹⁷

Elementary analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Acknowledgment.—The author gratefully acknowledges the many helpful suggestions made by Dr. G. P. Sollott of this laboratory in reviewing this paper and the helpful discussions with Drs. R. A. Henry and W. G. Finnegan of the Naval Ordnance Test Station.

(17) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, pp. 174, 175.

The Synthesis of 1-Aryl 3-Cyano-5-pyrazolones

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Kendall and Fry¹ reported a method for the preparation of certain 1-aryl 3-substituted pyrazolones by the reaction of diazotized aromatic amines with the appropriately substituted diethyl succinates in an alkaline medium. While this suggested a convenient procedure for 3-cyanopyrazolones, in the single example describing the use of diethyl cyanosuccinate,² only the 3-carboxy compound was isolated, presumably because the alkaline conditions used for the ring closure also led to hydrolysis of the cyano group.³

As suggested by Kendall and Fry, the reaction may be considered to be a three-step process. The initially formed azo compound 1 loses the carboxyl group to give an intermediate which tautomerizes to the phenylhydrazone 2. This then cyclizes to the pyrazolone 3 (see col. 2).

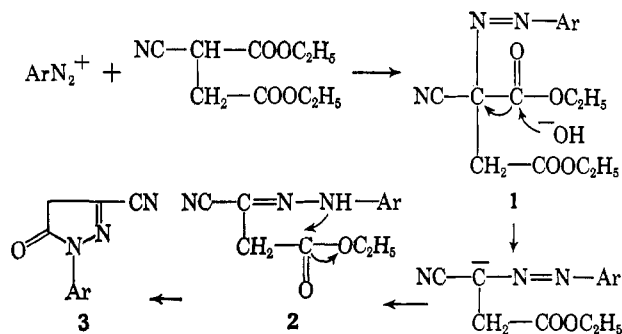
Recently Yao and Resnick⁴ have reported the isolation and spectral properties of intermediates analogous to 1 and 2. Thus, ethyl α -phenylazo- α -methylacetate (4) had a λ_{\max} of 272 m μ and ethylpyruvate phenylhydrazone (5) had absorption maxima at 290 and 312 m μ . These findings suggested that the reaction of diazonium salts with diethyl cyanosuccinate

(1) (a) J. D. Kendall and D. J. Fry, British Patent 585,780 (1947); *Chem. Abstr.*, **42**, 224b (1948). (b) See also U. S. Patent 2,459,226 (1949); *Chem. Abstr.*, **43**, 3042h (1949).

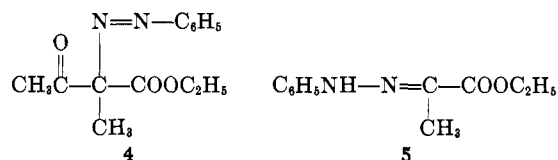
(2) Ref. 1a, example 8 in patent.

(3) This may also have resulted via displacement of the cyano group rather than the carboxyl group from the intermediate azo compound.

(4) H. C. Yao and P. Resnick, *J. Am. Chem. Soc.*, **84**, 3514 (1962).



could be followed by ultraviolet spectroscopy, and that, thereby, sufficiently mild conditions for the ring closure might be found which would permit the isolation of the desired 3-cyanopyrazolones.



When diazotized *p*-toluidine was added to diethyl cyanosuccinate in pyridine, an immediate yellow color appeared. Examination of the ultraviolet spectrum in ethanol of samples obtained by precipitating aliquots of the solution into aqueous hydrochloric acid showed the presence of strong absorption at 296 m μ , presumably due to 1. Even on several hours standing, the reaction mixture showed no further changes. Addition of triethylamine caused the very slow, but never complete, diminution in the intensity of the 296 m μ peak, and the slow increase of broad absorption at 300–350 m μ (?). However, addition of a mixture of triethylamine and 2% sodium hydroxide solution caused a rapid drop in the 296-m μ peak, transient broad absorption at 300–350 m μ , and the appearance of a new strong band centered at 254 m μ due to 3. After 1 hr., no further significant changes were observed.

The procedure as described below appears to be a general one for the preparation of 1-aryl 3-cyanopyrazolones in reasonable yields from the corresponding aryl amines. The crude products made by this procedure were usually contaminated with traces of a yellow impurity. This is believed to be due to the presence of small amounts of aryl azopyrazolone formed by the reaction of 3 with traces of unconsumed diazonium salt. The use of an excess of diethyl cyanosuccinate suppresses the formation of this impurity which is easily removed during the work-up.

Experimental⁵

1-*p*-Tolyl-3-cyano-5-pyrazolone.—To a solution of 0.0375 mole of diethyl cyanosuccinate⁶ in 175 ml. of pyridine was added a solution of the diazonium salt prepared by diazotizing, at 0–5°, 0.025 mole of *p*-toluidine in 50 ml. of water and 6 ml. of concentrated hydrochloric acid with 1.75 g. of sodium nitrite dissolved in 10 ml. of water. After the mixture had been stirred at 20° for 20 min., 50 ml. of triethylamine and 100 ml. of 2% aqueous

(5) Melting points are uncorrected and were obtained on a Mel-Temp capillary melting point apparatus. Elemental analyses were by Dr. S. M. Nagy of the Microchemical Laboratory, Massachusetts Institute of Technology. Ultraviolet spectra were determined using a Cary Model 11 spectrophotometer. Infrared spectra were determined on potassium bromide disks using a Perkin-Elmer Model 421 spectrophotometer.

(6) A. Haller and L. Barthe, *Compt. rend.*, **106**, 1413 (1888).