(70%) of VII was obtained. Redistillation at 125–128° yielded a colorless liquid, $n^{25}D$ 1.3612.

Anal. Calcd. for $C_8H_6OF_6$: C, 41.38; H, 2.59; F, 49.10. Found: C, 41.62; H, 2.40; F, 49.42.

The infrared spectrum showed a band for the double bond at 5.89 μ.

3,4-Bis(trifluoromethyl)furan (III).—VII (32 g., 0.138 mole) was passed dropwise in a slow current of nitrogen through a glass tube (450 mm. × 19 mm.) heated to 400°. The product was collected in a Dry Ice trap (22.1 g., 96.5%). Distillation at 88–89°/760 mm. gave a colorless liquid, $n^{25}D$ 1.3302.

Anal. Calcd. for $C_6H_2F_6O$: C, 35.51; H, 0.99; F, 55.86. Found: C, 35.23; H, 1.38; F, 55.60. The infrared spectrum showed the peak of the furan aromaticity at 6.32.

2,3,5,6-Tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (V).—III (4 g., 0.0196 mole) and hexafluoro-2-butyne (3.5 g., 0.0216 mole) were heated together in a sealed tube at 140° for 24 hr. Evaporation of the excess hexafluorobutyne left V (6.18 g., 86%) as a white crystalline solid. It was purified by sublimation at 40–50° (bath temperature) and obtained as long white needles. The identity with the previously obtained material was confirmed by their superimposable infrared spectrum and by the n.m.r. spectrum.

3,4,5-Tricyanopyrazole

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Received April 9, 1962

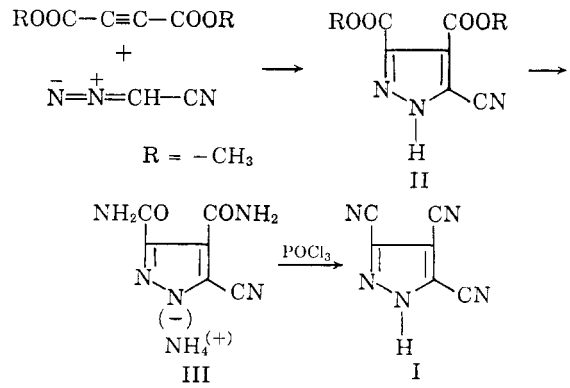
It is reported that the multiple dehydration of tri- or tetracarbamoylamides bearing the functional groups on adjacent carbon atoms proceeds well only under selected conditions[1] and is often thwarted entirely.[2]

We have encountered a similar situation in the heterocyclic series while attempting to prepare 3,4,5-tricyanopyrazole (I) by dehydration of 3,4,5-tricarbamoylpyrazole[3] with phosphorus oxychloride. Only a mixture of partially dehydrated compounds was obtained, the separation of which proved to be rather cumbersome.

Therefore, the preparation of I was attempted by way of a Büchner pyrazole synthesis that is illustrated below. By choosing a combination of suitable starting materials—*e.g.* compounds bearing nitrile groups—the multidehydration of amide groups was circumvented.

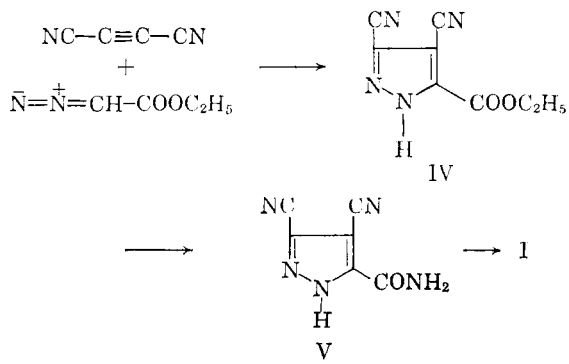
Whereas dicyanoacetylene and diazoacetonitrile gave only a tarry product in ether solution, dimethyl acetylenedicarboxylate and a freshly prepared ethereal solution of diazoacetonitrile gave dimethyl 5-cyanopyrazole-3,4-dicarboxylate (II).

Ammonolysis of the cyanopyrazole ester (II) in aqueous ammonia at room temperature furnished



a monocarbamoyl derivative which reacted further at room temperature over a period of four to five days to yield the ammonium salt of 3,4-dicarbamoyl-5-cyanopyrazole (III). The reaction could be conveniently accelerated by carrying it out in a sealed tube at elevated temperature. The neighboring cyano group causes the N-bonded hydrogen to exhibit acidic properties sufficient to form a stable ammonium salt. Subsequent dehydration in refluxing phosphorus oxychloride occurred smoothly with the formation of 3,4,5-tricyanopyrazole (I).

An alternative route is based on the treatment of dicyanoacetylene with ethyl diazoacetate which yielded ethyl 3,4-dicyanopyrazole-5-carboxylate (IV) together with an oily by-product. The ammonolysis of IV occurred smoothly at room temperature yielding 3,4-dicyano-5-carbamoylpyrazole (V). In this case no ammonium salt of V was formed. It was subsequently dehydrated with phosphorus oxychloride to I, which was found to be identical with a previously prepared sample.



I is a colorless crystalline compound which dissolves slightly in water to give a strongly acid solution. Salts are easily formed by neutralization of the aqueous solution and I is recovered upon acidification with mineral acids. With diazomethane, N-methyl-3,4,5-tricyanopyrazole (VI) is obtained. The silver salt of I was found to be light stable upon exposure to daylight over a period of several months; it is similar in this respect to the silver salt of cyanoform.

(1) E. A. Lawton and D. D. MacRitchie, *J. Org. Chem.*, **24**, 26 (1959).
(2) C. D. Weis, to be published.
(3) Th. Curtius, *J. prakt. Chem.*, [2] **91**, 68 (1915).

Experimental

Dimethyl 5-Cyano-3,4-pyrazoledicarboxylate (II).—Dimethyl acetylenedicarboxylate (40 g., 0.282 mole) was added to a solution of diazoacetonitrile[4] (approximately 20–25 g., 0.3–0.37 mole) in 3.5 l. of ether and the mixture allowed to stand overnight. Evaporation of the solvent left a crystalline residue which was pressed dry on a porous clay plate (45 g., 76.3%). In several runs the yield varied slightly (72–90%) because of the somewhat erratic results in the preparation of the diazoacetonitrile solution. Diazoacetonitrile was always allowed to react in dry ethereal solution because it was inconvenient to isolate large quantities of the rather explosive compound. Recrystallization from an ether–petroleum ether mixture yielded white crystals, m.p. 102–103.5°.

Anal. Calcd. for $C_8H_7N_3O_4$: C, 45.94; H, 3.38; N, 20.09. Found: C, 45.87; H, 3.30; N, 20.34.

Ammonium Salt of 3,4-Dicarbamoyl-5-cyanopyrazole (III).—A mixture of dimethyl 5-cyanopyrazole-3,4-dicarboxylate (2 g., 0.096 mole) and concentrated aqueous ammonia was heated in a sealed tube in a steam bath for 2 hr. The light yellow mass (1.3 g., 70%) which precipitated on cooling was filtered and recrystallized from hot water, m.p. 275–280° (dec. with gas evolution).

Anal. Calcd. for $C_6H_8N_6O_2$: N, 42.84. Found: N, 43.02.

The same compound was obtained after having allowed the diester to stand with aqueous ammonia for 4 days.

3,4,5-Tricyanopyrazole (I).—The ammonium salt of 3,4-dicarbamoyl-5-cyanopyrazole (5 g., 0.026 mole) was suspended in 25 ml. of phosphorus oxychloride and the mixture refluxed for 1 hr. Then it was decomposed with ice not allowing the temperature to rise above 10–15° and extracted with ether in a Soxhlet apparatus for 0.5 hr. Evaporation of the ether gave a crude product (3.14 g., 86%), m.p. 170–183°. Recrystallization from water (charcoal) yielded white needles, m.p. 193–194°. The compound is very soluble in hot water, but only slightly in cold water.

Anal. Calcd. for C_6HN_5: C, 51.53; H, 0.71; N, 48.92. Found: C, 51.50; H, 0.85; N, 48.43.

The infrared spectrum exhibited characteristic absorptions at 3.10 μ, 4.42 μ, 6.42 μ, 6.80 μ, 7.78 μ, 8.68 μ, 9.74 μ, 13.22 μ.

The silver salt of I was prepared by adding an equimolar amount of silver nitrate solution to an aqueous solution of tricyanopyrazole which had been previously neutralized with sodium bicarbonate.

Anal. Calcd. for C_6N_5Ag: Ag, 42.1. Found: Ag, 42.8.

N-Methyl-3,4,5-tricyanopyrazole (VI).—An ethereal solution of diazomethane was added to a solution of tricyanopyrazole (0.7 g., 0.0045 mole) in ether (20 ml.) until the yellow color persisted. There was a crystalline precipitate. Evaporation of the solvent and recrystallization of the crystalline residue (0.7 g., 91%) from ethanol furnished colorless crystals, m.p. 102–103°.

Anal. Calcd. for $C_7H_3N_5$: C, 53.51; H, 1.93; N, 44.58. Found: C, 53.70; H, 1.62; N, 44.07. The infrared spectrum did not exhibit any NH absorption.

Dicyanoacetylene was prepared by dehydration of dicarbamoylacetylene with phosphorus pentoxide[5] in 25–35% yield.

Ethyl 3,4-Dicyano-5-pyrazolecarboxylate (IV).—A solution of dicyanoacetylene (8 g., 0.105 mole) in 35 ml. of ether was added dropwise to a solution of ethyl diazoacetate (11.5 g., 0.1 mole) in 50 ml. of ether over a period of 10 min. The reaction flask was surrounded by an ice bath. After the addition had been completed, the mixture was kept at 0° for 2 hr. and then allowed to stand at room temperature overnight. Evaporation of the ether left an oil which crystallized after having been allowed to stand for 1 day. The crystalline mass was freed of oil by pressing it on a clay plate. The light yellow crystals (8.14 g., 40%) were recrystallized from water and gave colorless needles, m.p. 101°.

Anal. Calcd. for $C_6H_6N_4O_2 \cdot H_2O$: C, 46.14; H, 3.87; N, 26.91. Found: C, 45.86; H, 4.28; N, 26.76.

If the crystals were kept in a desiccator they liquified. Exposure to air, however, or recrystallization from water again gave the original compound.

The infrared spectrum exhibited characteristic bands at 2.89 μ, 4.52 μ, 5.82 μ.

The compound was soluble in benzene, ether, alcohol, and acetonitrile.

3,4-Dicyano-5-carbamoylpyrazole (V).—Ethyl 3,4-dicyano-5-pyrazolecarboxylate (2.2 g., 0.0107 mole) was dissolved in a mixture of 10 ml. of concentrated aqueous ammonia and 1 ml. of methanol and allowed to stand for 12 hr. Evaporation of the mixture to dryness gave a solid residue (1.67 g., 96%) which was dissolved in hot ethanol and reprecipitated with ether. The compound became yellow at 200° but did not melt.

Anal. Calcd. for $C_6H_3N_5O$: N, 43.47. Found: N, 43.58. The infrared spectrum exhibited characteristic bands at 2.96 μ, 3.22 μ, 4.55 μ, 6.05 μ.

Tricyanopyrazole.—3,4-Dicyano-5-carbamoylpyrazole (1 g., 0.0062 mole) was suspended in 8 ml. of phosphorus oxychloride and the mixture refluxed for 15 min. Then it was decomposed with ice and extracted with ether in a Soxhlet apparatus. Evaporation of the solvent gave tricyanopyrazole (0.73 g., 83%), m.p. 193° (from water).

Mixed melting point with the sample obtained earlier was 193°. The infrared spectra of both samples were identical.

Acknowledgment.—The author wishes to thank Dr. G. R. Coraor for many helpful suggestions.

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The Chemistry of Neuraminic Acids. I. The Ehrlich Reaction[1]

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Received April 9, 1962

In the process of studying the chemistry of neuraminic acid (I, R = R′ = H), it was necessary to reinvestigate the Ehrlich reaction between I (R = R′ = H) and *p*-dimethylaminobenzaldehyde (PDAB). Previously, I (R′ = H, R = Ac) has been demonstrated to undergo degradation in acid or base leading to pyrrole-2-carboxylic acid, which upon reacting with PDAB produces the violet color usually associated with the Ehrlich reaction.[2] The present note reports the formation of III from the reaction between pyrrole-2-carboxylic acid and *p*-dimethylaminobenzaldehyde and evidence for the proposed structure. The reaction between pyrrole-2-carboxylic acid (2 moles) and PDAB (1 mole) in ethanolic perchloric acid

(1) These studies were supported by funds from the National Heart Institute, Public Health Service (H-2942).

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