Polycyanofurans

C. D. WEIS

Explosives Department, Experimental Station Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Delaware

Received April 9, 1962

Tetracyanofuran has been prepared by two independent routes. The chemistry of this novel percyano compound has been investigated in some detail. The four cyano groups are not equally reactive and reactions are described which differentiate between the 2,5 and the 3,4 substituents. The carboxyl functions of 3,4-dicyano-2,5-furandicarboxylic acid have been converted to a variety of acyl derivatives, reduced to the corresponding diol, and removed to yield 3,4-dicyanofuran. 3,4-Dicyanofuran was also synthesized from ethyl 3,4-furandicarboxylate, and the amminolysis of such furan esters has been qualitatively explored.

In the course of a study of heterocyclic polycyano compounds the preparation of the unknown members of the furan series was undertaken as a prelude to an investigation of the chemistry of these novel structures.

In an initial approach, ethyl furantetracarboxylate (I)[1] was converted into the tetracarbamylfuran (II) by treatment with ammonium hydroxide in methanol. Tetracarbamylfuran in turn was converted to the desired tetracyanofuran (furantetracarbonitrile) (III), which was obtained as a white crystalline solid in 50–65% yield. This complex multidehydration could be effected only with phosphorus oxychloride. Other dehydrating agents such as phosphorus pentachloride, phosgene, acetic anhydride, or thionyl chloride in dimethylformamide either were completely inactive or achieved only a partial dehydration and the reactions were not improved by the use of such solvents as benzene, dioxane, or pyridine. A similar apparent selectivity of reagents in the dehydration of polyamides has been observed in the preparation of 1,2,4,5-tetracyanobenzene.[2]

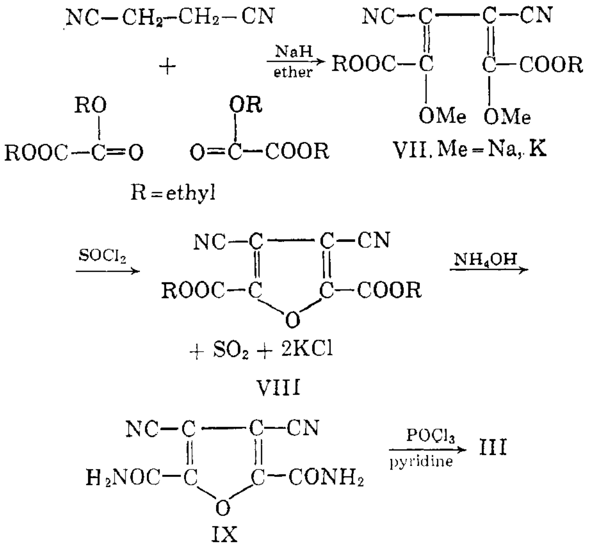
Reduction of the reaction time suppressed the formation of the percyanoheterocycle and furnished a dicyanodicarbamylfuran having the presumed structure (IV).

When ethyl furantetracarboxylate (I) was treated with ammonia in anhydrous methanol simultaneous amidation and base-catalyzed transesterification occurred and the product was methyl 2,4,5-tricarbamyl-3-furancarboxylate (V). The corresponding ethyl ester was not readily accessible since this ammonolysis proceeded extremely slow in ethanol solution.

The methyl ester was dehydrated using phosphorus oxychloride to obtain methyl 2,4,5-tricyano-3-furancarboxylate (VI), the constitution of which is established below.

A second approach to the synthesis of tetracyanofuran was *via* the disodium or dipotassium salt of ethyl 2,5-dioxo-3,4-dicyanoadipate (VII), which was first described by W. Wislicenus and H. Elvert.[3] The disodium salt could readily be prepared from diethyl oxalate and succinonitrile when sodium hydride was used as the condensing agent in ether or benzene. The yield of the salt was determined by acidification of the crude product with dilute sulfuric acid and isolation of the desired ketone and averaged about 50%. The older method of Wislicenus[3] using potassium ethylate as the condensing agent gave the pure salt in about 32% yield.

When the sodium or the potassium dienolate (VII) was treated with thionyl chloride, cyclization occurred and diethyl 3,4-dicyano-2,5-furandicarboxylate (VIII) was isolated.



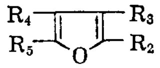
Careful treatment of this diester with ammonium hydroxide yielded 3,4-dicyano-2,5-dicarbamylfuran (IX). The amidation conditions are critical and failure to follow the prescribed procedure leads to a reaction of the carbamyl groups probably with adjacent cyano functions, with the consequent formation of dark colored products. Infrared examination of these materials failed to disclose the presence of the absorption bands characteristic of cyano groups.

---

[1] T. Reichstein, A. Grussner, K. Schindler, and E. Hardmeier, *Helv. Chim. Acta*, **16**, 276 (1933).

[2] E. A. Lawton and D. D. MacRitchie, *J. Org. Chem.*, **24**, 26 (1959).

[3] W. Wislicenus and H. Elvert, *Ber.*, **43**, 230 (1910).



No.	R_2	R_3	R_4	R_5
I	$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$
II	$CONH_2$	$CONH_2$	$CONH_2$	$CONH_2$
III	CN	CN	CN	CN
IV	CN	$CONH_2$	$CONH_2$	CN
V	$CONH_2$	$COOCH_3$	$CONH_2$	$CONH_2$
VI	CN	$COOCH_3$	CN	CN
VIII	$COOC_2H_5$	CN	CN	$COOC_2H_5$
IX	$CONH_2$	CN	CN	$CONH_2$
XI	$COOC_2H_5$	$COOCH_3$	CN	$COOC_2H_5$
XII	$CONH_2$	$COOCH_3$	CN	$CONH_2$
XIV	NHOH	CN	CN	$CONH_2$
XV	NH—NH—$CONH_2$	CN	CN	CN
XVI	COOH	CN	CN	COOH
XVII	COCl	CN	CN	COCl
XVIII	CON_3	CN	CN	CON_3
XXI	CH_2OH	CN	CN	CH_2OH
XXII	H	CN	CN	H
XXVI	H	$COOC_2H_5$	$COOC_2H_5$	H
XXVII	H	$CONH_2$	$CONH_2$	H
XXVIII	CH_3	$COOC_2H_5$	$COOC_2H_5$	CH_3
XXIX	CH_3	$COOCH_3$	$COOCH_3$	CH_3
XXX	CH_3	$CONH_2$	$CONH_2$	CH_3
XXXI	CH_3	CN	CN	CH_3
XXXII	CH_2Br	$COOC_2H_5$	$COOC_2H_5$	CH_2Br

All attempts to cyclize similarly the diketone of VII *via* its dienol diacetate or the dichloride of the dienol to the corresponding pyrrol derivative were unsuccessful.

The dicarbamyl compound (IX), unlike the tetracarbamylfuran(II), could not be dehydrated using phosphorus oxychloride alone but required the use of pyridine as a reaction medium[4] whereby III was obtained in 80% yield.

This facile formation of furan derivatives by the simple ring closure of a dienol salt with thionyl chloride permitted the preparation of a selection of tetrasubstituted furans by appropriate variation of the starting materials. Thus, methyl β-cyanopropionate[5] and diethyl oxalate, when condensed with sodium hydride in ether, gave the expected sodium dienolate of ethyl 2,5-dioxo-3-cyano-4-carboxymethyladipate (X), which was readily cyclized with thionyl chloride to 3-methyl 2,5-diethyl 4-cyanofurantricarboxylate (XI). Ammonolysis of XI using ammonia in anhydrous methanol gave 3-methyl 4-cyano-2,5-dicarbamylfuran (XII), which underwent dehydration with phosphorus oxychloride in pyridine. The product obtained gave no depression in melting point on admixture with VI, and the infrared spectra of the two components were superimposable.

The Reactivity of the Cyano Groups in Tetracyanofuran.—With the preparative routes to tetracyanofuran in hand, attention was turned to an investigation of the properties of this percyano heterocycle. Although this material is moderately stable in storage, exposure to air results in browning and the odor of hydrogen cyanide is perceptible. Hydrolysis with ethanolic hydrogen chloride gave a product identical with the above described diethyl 3,4-dicyano-2,5-furandicarboxylate (VIII). In contrast to this behavior, concentrated hydrochloric acid at 25° converted III to a dicyanodicarbamylfuran in which the carbamyl groups are assumed to be located in the 2,5 positions by analogy with the configurations established by the previous milder hydrolysis.

Therefore, the two types of cyano groups present in tetracyanofuran differ considerably in character and the α-moities are more susceptible to reaction than their β-counterparts. Roger and Nelson[6] have cited many examples to demonstrate that in *ortho* dinitriles one nitrile group is always more reactive than its neighbor.

While III is quite stable toward cold dilute acids, it proved to be extraordinarily sensitive to base. However, though the reaction of III with ammonia, hydrazine, or aniline led only to highly colored ill-defined amorphous products, the substantially diminished basicity of substituted hydrazines permitted the isolation of some well defined crystalline compounds. Thus 1,1-dimethylhydrazine in dilute acetic acid yielded 3,4-dicyano-2,5-dicarbamylfuran (IX). An entirely different and unusual behavior was observed when a solution of phenylhydrazine in 50% acetic acid was mixed with III at room temperature. An instantaneous reaction occurred, and a product considered to be an aminofuropyrrole (XIII) was isolated. A carbomethoxyaminopyrrole (XIII. R_1 = —$COOCH_3$) could be obtained when VI was substituted

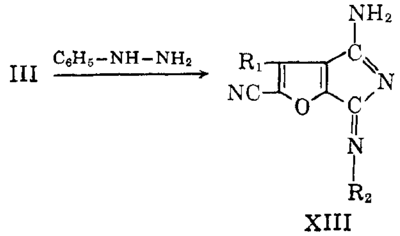
---

[4] R. Delaby, G. Tsatsas, and X. Lusinchi, *Bull. soc. chim. France*, 409 (1958).

[5] P. Kurtz, *Ann.*, **572**, 23 (1951).

[6] R. Roger and D. Nelson, *Chem. Rev.*, **61**, 179 (1961).

for III, but a slight elevation of the reaction temperature was mandatory. It is suggested that in both these related reactions the phenylhydrazine adds to an α-cyano function with the initial formation of an imino group which further reacts with the adjacent cyano function to form a pyrrole ring which stabilizes as the acylatable amine derivative. A similar but more sluggish reaction was effected using *p*-nitrophenylhydrazine but no reaction could be acheived using 2,4-dinitrophenylhydrazine. Related types of ring closures of *o*-nitriles have been reported in the literature.[7] It is of interest to note that even at elevated temperature, this cyclization occurs only on one side of the tetracyanofuran.



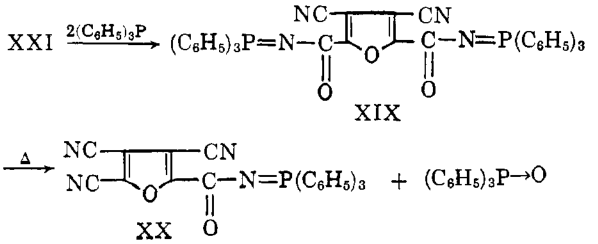
XIII

XIIIa. R_1 = —CN
b. R_1 = —$COOCH_3$
c. R_2 = —NH—C_6H_5
d. R_2 = —NH—C_6H_4—NO_2

When III reacted with hydroxylamine or semicarbazide hydrochloride in a solution buffered with sodium acetate, another type of transformation was encountered. Evolution of hydrogen cyanide occurred and compounds of the type XIV and XV were formed. The structures of the products were based on analyses and infrared spectra. Only one cyano group, presumably in α-position, can be substituted in this manner.

Derivatives of 3,4-Dicyanofuran-2,5-dicarboxylic Acid.—In continuing the study of the chemistry of polycyanofurans, the chemistry of 3,4-dicyanofuran-2,5-dicarboxylic acid (XVI) and derivatives was investigated. The free diacid was obtained by saponification of the corresponding ethyl ester (VIII) in aqueous medium at 25°. It is noteworthy that when the solution of the alkali salt was heated and subsequently acidified while still hot, the product was a cyano-free compound which presumably was formed by the interaction of a carbonyl group and a vicinal cyano function. This material has not been studied further.

Though 3,4-dicyano-2,5-furandicarbonylchloride (XVII) could not be prepared from the dicarboxylic acid using thionyl chloride, it was obtained using phosphorus pentachloride and converted, in low yield, to 3,4-dicyano-2,5-furandicarbonyl azide (XVIII) using sodium azide in acetone. This diazide is relatively stable and can be recrystallized from toluene with slight decomposition only. Prolonged heating however does cause extensive decomposition. Addition of the diazide to a solution of triphenylphosphine[8] in benzene gave an immediate yellow coloration which subsequently faded with concomitant evolution of nitrogen and decomposition of colorless crystals of 3,4-dicyano-2,5 - di(triphenylphosphazocarbonyl)furan (XIX). Vacuum heating of XIX effected scission of one of the nitrogen-phosphorus bonds with the simultaneous formation of a new cyano group and the release of triphenylphosphine oxide.



XIX

XX

However, the second nitrogen-phosphorus bond was not cleaved by further heating, and 2,3,4-tricyano - 5 - (triphenylphosphazocarbonyl)furan (XX) decomposed before the second mole of triphenylphosphine was expelled. No tetracyanofuran was therefore formed. The infrared carbonyl absorption band for XIX is located at 6.18 μ and for XX at 6.14 μ.

In a brief study of the reduction of the ester groups in VIII, the diethyl ester was treated with lithium di(*t*-butoxy)alumino hydride[9] in dimethoxyethane to yield the corresponding 3,4-dicyano-2,5-bismethylolfuran (XXI). The comparable reduction with lithium borohydride gave a boron-containing complex which was not further investigated.

The decarboxylation of XVI also was examined. The copper-catalyzed reaction proceeded smoothly to yield 3,4-dicyanofuran (3,4-furandicarbonitrile) (XXII) which could also be obtained by a purely thermal reaction although in considerably lower yield. The structure of XXII was established by a comparison with a sample prepared from ethyl 3,4-furandicarboxylate[10] (XXVI) *via* its dicarbamyl compound[11]. Ammonolysis of the diester which was saturated with ammonia was quite slow and 3,4-dicarbamylfuran (XXVII) was obtained in small yield only. At 100°, however, a 69% yield was realized. Final dehydration was effected using phosphorus oxychloride.

In previous ammonolysis studies Linstead, *et al.*,[12] reported the failure of diethyl 2,5-dimethyl-3,4-furandicarboxylate (XXVIII) to undergo this reaction. This ester is surprisingly inert, and treatment with aqueous ammonia at elevated temperatures (150°) in a sealed tube yielded only the cyclic

---

(7) (a) Brit. Pat. 698,049 (1953); (b) Ger. Pat. 955,178 (1956).

(8) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

(9) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **78**, 252 (1956).

(10) E. C. Kornfeld and R. G. Jones, *J. Org. Chem.*, **19**, 1674 (1954).

(11) G. Stork, *J. Am. Chem. Soc.*, **67**, 884 (1954).

(12) J. A. Bilton and R. P. Linstead, *J. Chem. Soc.*, 922 (1937).

imide. The dimethyl ester (XXIX) on the other hand is smoothly converted to the corresponding dicarbamyl compound (XXX) by this treatment. Similar observations have been made by Zahn and Schäfer.[13] Apparently, polymethyl esters undergo ammonolysis much more readily than their ethyl homologs.

In another segment of this study, some halogenation reactions of 2,5-dimethyl-3,4-dicyanofuran (XXXI) were investigated. XXXI was prepared from the diamide (XXX) by dehydration with phosphorus oxychloride and was not effected by N-bromosuccinimide or peroxidic sulfuryl chloride. This was in striking contrast to the behavior of the closely related XXIX which underwent normal and facile bromination using *N*-bromosuccinimide in carbon tetrachloride affording XXXII in good yield.

Experimental

Tetracarbamylfuran (II).—Crystalline ethyl furantetracarboxylate (150 g., 0.44 mole) was placed in a mixture (1:1) of methanol and ammonium hydroxide which had been previously saturated with gaseous ammonia at ice bath temperature. The slurry was stirred for 20 hr. and then filtered. The solid was washed with about 100 ml. of water. After washing with ethanol and drying at 75°, the slightly water soluble solid weighed 99.5 g. (94%), m.p. > 300°.

Anal. Calcd. for $C_8H_8N_4O_5$: C, 40.44; H, 3.33; N, 23.32. Found: C, 40.33; H, 3.73; N, 23.42.

Tetracyanofuran (III). **Dehydration of Tetracarbamylfuran.**—Tetracarbamylfuran (24 g., 0.1 mole) was placed in 80 ml. of phosphorus oxychloride and refluxed for 3 hr. There was a dark brown precipitate. The excess phosphorus oxychloride was removed *in vacuo* and the residue carefully decomposed with ice. After standing for 30 min. the solid was filtered off (9.45 g.) and the aqueous solution extracted with ether in a Soxhlet. Evaporation of the ethereal solution left a crystalline residue (4.3 g.). Both fractions were dissolved in hot benzene (100 ml.) and filtered. This procedure removed any amide present. Recrystallization from benzene gave colorless crystals, m.p. 124–125°. The crude product could also be recrystallized from aqueous methanol.

Anal. Calcd. for C_8N_4O: C, 57.15; N, 33.33. Found: C, 57.05; N, 33.42.

The product started to sublime at 120° and was soluble in most organic solvents with the exception of petroleum ether. It was slightly soluble in boiling water (about 1 g./100 ml. of boiling water). The infrared spectrum showed bands at 4.44 μ (m); 6.48 μ (m); 7.99 μ (s); 8.52 μ (s); 9.44 μ (s).

Methyl 2,4,5-Tricarbamyl-3-furancarboxylate (V).—Distilled ethyl furantetracarboxylate (20 g., 0.056 mole) was added to 240 ml. of anhydrous methanol, which had been previously saturated with gaseous ammonia at ice bath temperature. The mixture was stirred for 2.5 hr. Filtration gave crude methyl 2,4,5-tricarbamyl-3-furancarboxylate (15 g.) which melted at about 220°. Upon recrystallization from acetic acid the compound melted at 244–246° (decomp.) (11 g., 77%).

Anal. Calcd. for $C_9H_9N_3O_6$: C, 42.35; H, 3.56; N, 16.47. Found: C, 42.62; H, 3.30; N, 16.42.

Methyl 2,4,5-Tricyano-3-furancarboxylate (VI).—Methyl 2,4,5-tricarbamyl-3-furancarboxylate (10 g., 0.05 mole) was refluxed in 40 ml. of phosphorus oxychloride for 40 min. The excess of phosphorus oxychloride was removed *in vacuo*, and the residue decomposed with ice. The crystalline product was filtered off and dried (6.26 g., 77%). Recrystallization from methanol (charcoal) yielded white crystals, m.p. 114–115°.

Anal. Calcd. for $C_9H_3N_3O_3$: C, 53.94; H, 1.49; N, 20.89. Found: C, 54.14; H, 1.65; N, 20.90. The infrared spectrum exhibited characteristic absorption bands at 4.46 μ (CN) 5.78 μ (ester).

Disodium Ethyl 1,4-Dioxo-2,3-dicyanoadipate (VII).—Diethyl oxalate (160 g., 1.1 mole) was added to a stirred suspension of sodium hydride–50% mineral oil suspension (52 g., 1.08 mole) in 200 ml. of benzene and the mixture heated to 55°. A solution of succinonitrile (40 g., 0.5 mole) in 350 ml. of benzene was added over a 3-hr. period without heating the mixture any further. During the addition the temperature remained at 35–40°. After the addition was complete, stirring was continued for another hour. Anhydrous ether (500 ml.) was added to make the yellow precipitate more suitable for filtration. After filtration the adherent solvent was pumped off under reduced pressure to yield 180 g. of product.

Decomposition of the sodium salt with dilute sulfuric acid showed the salt contained about 50% of the desired diketone.

Ethyl 1,4-Dioxo-2,3-dicyanoadipate.—The disodium salt (32 g.) was dissolved in 60 ml. of water, filtered, and a mixture of 12 g. concentrated sulfuric acid and 30 ml. of water was added. The oily precipitate was kept at 50–60° for 5 min., cooled, and the yellow crystals filtered off, washed with water, and dried. Recrystallization from ethanol gave 14.2–15 g. (50.8–53.8%) of pure ethyl-1,4-dioxo-2,3-dicyanoadipate, m.p. 123–124°.

Diethyl 3,4-Dicyano-2,5-furandicarboxylate (VIII). **A. Cyclization of the Crude Potassium Salt VII.**—Dipotassium ethyl 1,4-dioxo-2,3-dicyanoadipate (360 g., 1 mole) was powdered and placed in 1500 ml. of anhydrous ether and 5 drops of pyridine added. The slurry was stirred and a solution of thionyl chloride (130 g., 1.1 moles) in 300 ml. of ether added over a 0.5-hr. period. After the addition was complete the solution was stirred overnight. The warm solution was filtered and the filtrate neutralized with aqueous sodium bicarbonate solution and washed with water. The solid residue on the filter was dissolved in water, extracted with ether, and treated as above. Both ether extracts were combined and dried over calcium chloride. Evaporation of the ether left a brown crystalline residue (135 g.). Recrystallization from ether yielded 85.5 g. of white crystals, m.p. 74–75.5°. Since the starting material consisted of about 33% of the potassium salt of the diketone, the yield in this reaction was 90%.

B. Cyclization of the Crude Sodium Salt.—The disodium salt (64.8 g., 0.2 mole) was dispersed in a mixture of 300 ml. of absolute ether and four drops of pyridine. A solution of thionyl chloride (24 g., 0.1 mole) in 100 ml. of ether was added over a 15-min. period and the mixture refluxed for 2 hr. The mixture was filtered while warm and the residue extracted twice with ether. The combined ethereal extracts were washed with aqueous sodium bicarbonate solution, then with water, and dried over sodium sulfate. Evaporation of the ether yielded 20 g. of crude ethyl 3,4-dicyano-2,5-furandicarboxylate. Recrystallization from ether gave almost white crystals (12.5 g.), m.p. 74–74.5° (from ether–methanol).

Anal. Calcd. for $C_{12}H_{10}N_2O_5$: C, 55.00; H, 3.85; N, 10.74. Found: C, 54.94; H, 3.77; N, 10.83.

3,4-Dicyano-2,5-dicarbamylfuran (IX).—Diethyl 3,4-dicyano-2,5-furandicarboxylate (26 g., 0.1 mole) was dispersed in 170 ml. methanol and 15 ml. aqueous ammonia added. A white precipitate started to form after about 1 min. The mixture was stirred for 15 min., filtered, and washed with ether (15 g., 73.8%), m.p. 320° (from pyridine).

Anal. Calcd. for $C_8H_4N_4O_3$: N, 27.45. Found: N, 27.25.

---

(13) H. Zahn and P. Schäfer, *Ber.*, **92**, 736 (1959).

Tetracyanofuran (III).—3,4-Dicyano-2,5-dicarbamylfuran (4.08 g., 0.02 mole) was dispersed in phosphorus oxychloride (6 g., 0.04 mole) and 10 ml. of pyridine slowly added. Dehydration occurred with considerable evolution of heat, and the solution turned dark red. Upon cooling to room temperature, the entire contents of the flask solidified and were added to about 80 ml. of ice water and allowed to stand for 2 hr. The brown crystals were filtered off, washed with water, and dried over phosphorus pentoxide, to yield 2.78 g. (82.3%) of brown crystals. Recrystallization from ethanol and water with charcoal gave white crystals, m.p. 124°. The mixed melting point with the previously prepared tetracyanofuran showed no depression. The infrared spectra were also identical.

3-Methyl 2,5-Diethyl 4-Cyanofurantricarboxylate (XI).—Diethyl oxalate (160 g., 1.1 mole) and ethanol (8 ml.) were added to a suspension of sodium hydride (48 g., 2.0 mole) 50% in mineral oil suspension in 400 ml. of absolute ether and the mixture stirred for 20 min. A solution of methyl β-cyanopropionate (57 g., 0.5 mole) in a mixture of 100 ml. of absolute ether and 100 ml. of benzene was added over a 2.5-hr. period. A thick precipitate formed soon. After the addition was complete the mixture was refluxed for 1 hr. and then stirred overnight. The product was then completely solid. It was filtered and washed with ether, to give 181 g. of a yellow powder (X), which was carefully protected from moisture. The crude disodium salt (X) (181 g.) was suspended in 600 ml. of ether and 5 drops of pyridine was added. Thionyl chloride (55 g., 0.46 mole) was added over a period of 20 min. The mixture was stirred and refluxed overnight, filtered, and the residue extracted with boiling ether. The combined ethereal solutions were neutralized with aqueous sodium bicarbonate solution, dried, and, after removal of the ether, subjected to distillation.

The fraction which boiled at 210–215° (1 mm.) was collected and redistilled (37 g.).

The oily product crystallized after standing for several weeks. A sample was freed from adherent oil and recrystallized from benzene–petroleum ether (1:20). The white needles melted at 48°.

Anal. Calcd. for $C_{13}H_{13}NO_7$: C, 54.11; H, 4.54; N, 4.85. Found: C, 54.55; H, 4.59; N, 4.76. The infrared spectrum showed characteristic bands at: 4.46 μ; 5.75 μ; 6.26 μ; 9.58 μ.

Methyl 4-Cyano-2,5-dicarbamyl-3-furancarboxylate (XII).—3-Methyl 2,5-diethyl 4-cyanofurantricarboxylate (13 g., 0.44 mole) was added to 100 ml. of methanol which had previously been saturated with gaseous ammonia. A reaction temperature of 5° was maintained. The mixture was stirred for 10 min. and the white precipitate (9.5 g., 76%) filtered off. A sample was recrystallized from a large volume of hot water, yielding long white needles, m.p. 247–249° (dec.).

Anal. Calcd. for $C_9H_7N_3O_5$: C, 45.58; H, 2.98; N, 17.72. Found: C, 45.75; H, 3.15; N, 17.70.

Methyl 2,4,5-Tricyano-3-furancarboxylate (VI).—Recrystallized methyl 4-cyano-2,5-dicarbamyl-3-furancarboxylate (2 g., 0.084 mole) was suspended in 10 ml. of pyridine and 3 ml. of phosphorus oxychloride was slowly added. The temperature rose from 5 to 30°. After the addition had been completed, it was stirred for 20 min. and the mixture poured into 50 ml. of water and acidified with hydrochloric acid. The crystalline material (1.04 g., 61%) was filtered off after standing for 1 hr. After several recrystallizations from a chloroform–petroleum ether mixture, the sample melted at 115°. The mixed melting point and the infrared spectrum of the product were identical with those of the sample obtained earlier. The final product was extremely difficult to purify if the starting material had not been carefully recrystallized.

Tetracyanofuran and Phenylhydrazine (XIIIc).—To a solution of tetracyanofuran (3.36 g., 0.02 mole) in 20 ml. acetic acid was added a solution of phenylhydrazine (4 g., 0.043 mole) in 10 ml. of 50% acetic acid. The solution turned red and a precipitate soon appeared. After 2 hr., it was filtered off and washed with a few milliliters of cold ethanol, 4.58 g., 83%, m.p. 285–280° dec. Recrystallization from pyridine afforded bright orange crystals. They were slightly soluble in acetic acid or methyl ethyl ketone.

Anal. Calcd. for $C_{14}H_8N_6O$: C, 60.86; H, 2.92; N, 30.41. Found: C, 60.82; H, 3.07; N, 30.52. Mol. wt. (Rast): Calcd.: 276. Found: 250.

Extinction coefficient in ethanol: ϵ 13.82 × 10^3 at λ 253 mμ. The infrared spectrum exhibited characteristic absorption bands at 2.98 μ, 4.48 μ, 6.00 μ, 6.27 μ, 6.46 μ, 6.53 μ, 6.69 μ, 7.61 μ, 7.72 μ, 7.95 μ, 9.30 μ. The acetate was prepared using acetyl chloride in pyridine. Recrystallization from pyridine furnished yellow crystals, m.p. 190–195° dec.

Anal. Calcd. for $C_{16}H_{10}N_6O_2$: C, 60.38; H, 3.61; N, 26.40. Found: C, 60.44; H, 3.67; N, 26.22.

Tetracyanofuran and *p*-Nitrophenylhydrazine (XIIId).—A filtered solution of p-nitrophenylhydrazine (4 g., 0.0262 mole) was added to a solution of tetracyanofuran (3.36 g., 0.02 mole) in 20 ml. of acetic acid. After 3 hr. the red precipitate was filtered and washed with a few milliliters of alcohol, 3.16 g., 49%, m.p. 310–320° dec. Recrystallization from pyridine yielded deep orange crystals which melted at 310–320° dec.

Anal. Calcd. for $C_{14}H_7N_7O_3$: C, 52.34; H, 2.19; N, 30.52. Found: C, 52.33; H, 2.26; N, 30.28.

Methyl 2,4,5-Tricyanofuran-3-carboxylate and Phenylhydrazine (XIIIb. R_2 = —NH—C_6H_5).—A solution of phenylhydrazine (3 g. 0.0278 mole) in 6 ml. of 50% acetic acid was added to a hot solution of methyl 2,4,5-tricyano-3-furancarboxylate (1.68 g., 0.0083 mole) in 5 ml. of acetic acid. The solution was held close to boiling point for 2 min. A voluminous precipitate was formed. After 1 hr. it was filtered off and washed with water to give 1.55 g. (60%), m.p. 265–266° (decomp.). Recrystallization from methanol or acetonitrile gave yellow crystals.

Anal. Calcd. for $C_{15}H_{11}N_5O_3$: C, 58.25; H, 3.58; N, 22.64. Found: C, 58.22; H, 3.67; N, 22.81. Extinction coefficient in ethanol: ϵ 15.4 × 10^3 at λ 253 mμ.

Partial Hydrolysis of Tetracyanofuran. A. In Concentrated Hydrochloric Acid.—Tetracyanofuran (0.5 g., 0.003 mole) was suspended in 10 ml. of concentrated hydrochloric acid and stirred at 25°. After about 20 min. a white suspension formed. After 16 hr. the slurry was diluted with 10 ml. of water, filtered, and washed with water, and ethanol to yield 0.51 g. (85%) of product, m.p. 300° dec. The infrared spectrum showed the characteristic amide absorption at 2.92 μ, 3.05 μ, and the nitrile absorption at 4.42 μ. The infrared spectrum was identical with the spectrum of the 3,4-dicyano-2,5-dicarbamylfuran obtained previously.

B. In Ethanol.—Tetracyanofuran (3.3 g., 0.02 mole) was dissolved in a mixture of 30 ml. of absolute ethanol and 100 ml. of absolute ether and saturated with anhydrous hydrogen chloride at 5–10°. The precipitate was filtered off and 200 ml. of absolute ether was added to the filtrate and the newly formed precipitate filtered. The combined crystalline fractions were dissolved in hot 90% ethanol and part of the ethanol evaporated. The filtered and dried residue weighed 2.87 g. (55%). It was dissolved in ether, extracted with sodium bicarbonate solution, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the ether yielded 2.39 g. crystals, m.p. 86.5–87.5° (from ethanol–water with charcoal). By mixed melting point with an authentic sample and infrared spectra the product was shown to be ethyl 3,4-dicyanofuran-2,5-dicarboxylate (VIII).

Tetracyanofuran and 1,1-Dimethylhydrazine.—A solution of tetracyanofuran (1.68 g., 0.01 mole) in 10 ml. of acetic acid was added to a solution of 1,1-dimethylhydrazine (3 g., 0.05 mole) in 8 ml. of 50% acetic acid and refluxed for 5 min. The dark yellow precipitate was filtered off after 2 hr. On diluting the mother liquor, a second crop of crystals was obtained, 1.64 g. (80%). Recrystallization from pyridine gave white needles, m.p. 275° dec.

Anal. Calcd. for $C_8H_4N_4O_3$: C, 47.07; H, 1.97; N, 27.45. Found: C, 47.20; H, 2.21; N, 27.37.

The same product was also obtained using either diethylamine or aminobenzothiazole in dilute acetic acid, as shown by infrared analysis.

Tetracyanofuran and Hydroxylamine (XIV).—A hot solution of tetracyanofuran (1.68 g., 0.01 mole) in 15 ml. of ethanol was added to a hot solution of hydroxylamine hydrochloride (2 g., 0.029 mole) and sodium acetate (1 g., 0.012 mole) in 20 ml. of water. There was a light yellow precipitate. It was filtered after 3 hr. (1.51 g.), dissolved in hot pyridine and precipitated with benzene, m.p. 250° (slow decomp.).

Anal. Calcd. for $C_7H_4N_4O_3$: C, 43.76; H, 2.10; N, 20.17. Found: C, 43.53; H, 2.47; N, 20.73. The infrared spectra exhibited major bands at 2.98 μ; 5.95 μ; 6.0 μ.

Tetracyanofuran and Semicarbazide Hydrochloride (XV).—To a solution of tetracyanofuran (3 g., 0.0178 mole) in 20 ml. of ethanol was added an aqueous solution of semicarbazide hydrochloride (5 g., 0.045 mole), and the mixture refluxed for 20 min. A yellow precipitate appeared which was filtered after 4 hr. and washed with water and methanol, m.p. 260–270° (decomp.).

Anal. Calcd. for $C_8H_4N_6O_2$: C, 44.44; H, 1.85; N, 38.88. Found: C, 44.41; H, 2.16; N, 39.22. The infrared spectrum exhibited major bands at 2.91 μ; 3.0 μ; 4.47 μ; 5.89 μ; 6.34 μ; 7.08 μ.

3,4-Dicyano-2,5-furandicarboxylic Acid (XVI).—Ethyl 3,4-dicyano-2,5-furandicarboxylate (26.2 g., 0.1 mole) was dispersed in a solution of sodium hydroxide (9 g., 0.22 mole) in 200 ml. of water and 10 ml. of ethanol. The mixture was stirred for 3 hr. at room temperature, filtered, and acidified with 26 ml. of concentrated hydrochloric acid. The solution was heated to 50° for 1 min. and cooled in ice. Then the acid was extracted with ether. Evaporation of the ether yielded 15.5 g. (75%) of nearly pure 3,4-dicyano-2,5-furandicarboxylic acid. An analytical sample was recrystallized from ethanol and melted at 240–245° dec. The product also could be recrystallized from acetonitrile.

Anal. Calcd. for $C_8H_2N_2O_5$: C, 46.61; H, 0.98; N, 13.59. Found: C, 46.55; H, 1.05; N, 13.70. Monosodium salt: *Anal.* Calcd. for $C_8H_5N_2O_7Na \cdot 2H_2O$: C, 36.37; H, 1.89; N, 10.61. Found: C, 36.00; H, 1.85; N, 10.70.

3,4-Dicyano-2,5-furandicarbonyl Chloride (XVII).—Finely powdered 3,4-dicyano-2,5-furandicarboxylic acid (10 g., 0.049 mole) and phosphorus pentachloride (22 g., 0.106 mole) were mixed together and heated until a reaction occurred (*ca.* 40°). The mixture slowly solidified. The temperature was kept at 70–85° until all the acid had dissolved. It was filtered, and the filtrate was added to a large excess of petroleum ether. The precipitated oil crystallized and was filtered and washed with petroleum ether. The excess of phosphorus pentachloride was removed in a vacuum at 30–40°. The yield was 9.6 g. (82%). Recrystallization from chloroform gave almost white crystals, m.p. 124–125°.

Anal. Calcd. for $C_8N_2O_3Cl_2$: Cl, 29.18. Found: Cl, 28.87.

A sample was added to absolute ethanol and gave ethyl 3,4-dicyano-2,5-furandicarboxylate, as shown by its mixed melting point with an authentic sample, m.p. 75–76°, and by its infrared spectrum.

The methyl ester was likewise prepared. Recrystallization from methanol gave colorless crystals, m.p. 146.5–147°.

Anal. Calcd. for $C_{10}H_6N_2O_5$: C, 51.17; H, 2.58; N, 11.96. Found: C, 51.08; H, 2.61; N, 11.63.

3,4-Dicyano-2,5-furandicarbonyl Azide (XVIII).—A solution of 3,4-dicyano-2,5-furan dicarbonyl chloride (4.8 g., 0.0198 mole) in 20 ml. of acetone was cooled to 0° and slowly added to 15 ml. of a cold aqueous saturated solution of sodium azide. The mixture was kept at 0° and stirred for 15 min. It was filtered and the crystals washed with water and dried. Recrystallization from toluene gave buff-colored crystals which melted at 141° dec.

Anal. Calcd. for $C_8N_8O_3$: C, 37.51; N, 43.74. Found: C, 37.66; N, 43.51. The infrared spectrum exhibited characteristic bands at 4.48 μ (m); 4.59 μ (s); 5.91 μ (s); 6.24 μ (m); 6.40 μ (m); 9.59 μ (w).

If the reaction is carried out with a dilute solution of sodium azide the yield will decrease to 15.4%.

3,4-Dicyano-2,5-di(triphenylphosphazocarbonyl)furan (XIX).—3,4-Dicyano-2,5-furandicarbonyl azide (0.95 g., 0.003 mole) was added to a solution of triphenylphosphine (2.2 g., 0.0084 mole) in 20 ml. of benzene. The mixture turned red and there was a violent evolution of nitrogen. After the gas evolution had ceased, the mixture was heated to 40° for 5 min. The white crystalline precipitate was filtered, washed with benzene, and weighed. After drying, 2.33 g. (90%) of the product was obtained. It was recrystallized from acetic acid and melted at 283–285° dec.

Anal. Calcd. for $C_{44}H_{30}N_4O_3P_2$: C, 72.91; H, 4.17; N, 7.73; P, 8.54. Found: C, 72.42; H, 4.32; N, 7.78; P, 8.34. The infrared spectrum showed characteristic bands at: 4.48 μ; 6.03 μ; 6.22 μ; 6.38 μ; 6.52 μ.

2,3,4-Tricyano-5-triphenylphosphazocarbonylfuran (XX).—3,4 - Dicyano - 2,5 - di(triphenylphosphazocarbonyl)furan (0.3 g., 0.00414 mole) was heated to its decomposition point in an evacuated sublimation apparatus. A slight yellow glassy material (0.23 g.) deposited on the cold receiver. It was purified by recrystallization from chloroform–petroleum ether, m.p. 215–217°. The infrared spectrum of the crude mixture showed that no tetracyanofuran had been formed.

Anal. Calcd. for $C_{26}H_{15}N_4O_2P$: C, 69.97; H, 3.39; N, 12.55; P, 6.94. Found: C, 69.80; H, 3.70; N, 12.54; P, 6.94.

In general the infrared spectrum was similar to the spectrum of the starting material, but showed distinct differences in the fingerprint region.

3,4-Dicyano-2,5-bis(methylol)furan (XXI).—An ice-cold solution of 3,4-dicyanofuran-2,5-dicarbonyl chloride (11 g., 0.047 mole) in 50 ml. of ethylene glycol dimethyl ether was added within 20 min. to an ice-cold solution of lithium aluminum hydride-*t*-butoxide (60 g., 0.188 mole) in 100 ml. of the same solvent. The temperature was kept at 0° during the reaction, and stirring was continued for 4 hr. after the addition had been completed. The excess of reducing reagent was decomposed with ice water. It was filtered and the filter cake of aluminum hydroxide was extracted several times with ether. The combined liquid extracts were concentrated on a steam bath. The oily residue was dissolved in a small amount of water and extracted with ether. Evaporation of the ether left 2.6 g. (33%) of light yellow crystals. Recrystallization from ethyl acetate gave colorless crystals, m.p. 99–100.5°.

Anal. Calcd. for $C_8H_6N_2O_3$: C, 53.93; H, 3.39; N, 15.72. Found: C, 53.75; H, 3.36; N, 15.77.

The infrared spectrum exhibited bands at 3.09 μ; 4.49 μ; 6.29 μ; 9.40 μ; 9.80 μ. The dibenzoate was prepared with benzoyl chloride in pyridine and recrystallized from ethanol, m.p. 142–143°.

Anal. Calcd. for $C_{22}H_{14}N_2O_5$: N, 7.25. Found: N, 7.20.

3,4-Dicyanofuran (XXII). Method I.—3,4-Dicyano-2,5-furandicarboxylic acid (1 g., 0.00486 mole) was mixed with 0.2 g. of copper powder and heated to 160°. A smooth evolution of carbon dioxide took place and dicyanofuran (0.35–0.36 g., 61–63%) sublimed to the cold part of the tube. It was mechanically removed and recrystallized from methanol, m.p. 160°.

Anal. Calcd. for $C_6H_2N_2O$: C, 61.05; H, 1.71; N, 23.70. Found: C, 60.80; H, 1.81; N, 23.50.

It was soluble in methanol, boiling xylene, and acetic acid. Small samples were recrystallized from water. It did not react with phenylhydrazine in dilute boiling acetic acid. The infrared spectrum exhibited absorption bands at 3.18 μ; 4.45 μ; 6.49 μ; 8.62 μ; 9.42 μ. The absorption at 6.49 μ is due to the furan aromaticity, the one at 9.42 μ was characteristic to the C—O—C frequency.

3,4-Dicarbamylfuran (XXVII).—The starting material, ethyl 3,4-furandicarboxylate, (XXVI) was prepared as previously reported.[10]

Ethyl 3,4-furandicarboxylate (20 g., 0.094 mole) was heated with 50 ml. of aqueous ammonia and 10 ml. of methanol in a sealed tube on a steam bath for 4 hr. On cooling, the dicarbamyl compound crystallized. It was filtered, washed with ice water, and dried. Partial evaporation of the mother liquor gave another small crop. The over-all yield was 10 g. (69%). Recrystallization from boiling water with charcoal yielded white crystals, m.p. 270–275°.

Anal. Calcd. for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18. Found: C, 47.01; H, 4.01; N, 18.26.

3,4-Dicyanofuran (XXII). Method II.—3,4-Dicarbamylfuran (30 g., 0.195 mole) was suspended in 150 ml. of phosphorus oxychloride and refluxed for 60 min. The clear solution was decomposed with excess ice. The solid material was filtered off (18 g.) and the mother liquor extracted with ether which yielded another 4 g. The over-all yield was 22 g., 95%. A sample was recrystallized from boiling water. The mixed melting point with the sample previously obtained was 160–161°; the infrared spectra were also identical.

2,5-Dimethyl-3,4-dicarbamylfuran (XXX).—Dimethyl 2,5-dimethyl-3,4-furandicarboxylate (42 g., 0.198 mole) and a mixture of 56 ml. of aqueous ammonia and 20 ml. of methanol, which had been previously saturated with gaseous ammonia, were placed in a sealed tube and heated on a steam bath for 16 hr. The content was discharged, evaporated to dryness, and washed with hot ether to remove unreacted starting material. The yield of 2,5-dimethyl-3,4-dicarbamylfuran was 25 g. (69.5%). A sample was recrystallized from water, m.p. 254–256°.

Anal. Calcd. for $C_8H_{10}N_2O_3$: C, 52.76; H, 5.54; N, 15.38. Found: C, 52.49; H, 5.62; N, 15.07.

2,5-Dimethyl-3,4-dicyanofuran (XXXI).—2,5-Dimethyl-3,4-dicarbamylfuran (10 g., 0.05 mole) was suspended in 50 ml. of phosphorus oxychloride and refluxed for 8 min. The cold mixture was decomposed with excess ice. The crystalline precipitate was filtered and the aqueous solution extracted with ether. Both fractions gave a total yield of 6.18 g. (77%) of crystalline material.

Recrystallization from carbon tetrachloride gave colorless crystals, m.p. 92–93.5°.

Anal. Calcd. for $C_8H_6N_2O$: C, 65.78; H, 4.11; N, 19.18. Found: C, 65.68; H, 4.15; N, 18.98.

Diethyl 2,5-Bromomethyl-3,4-furandicarboxylate (XXXII).—A mixture of ethyl 2,5-dimethyl-3,4-furandicarboxylate (24 g., 0.1 mole), N-bromosuccinimide (36 g., 0.2 mole), and benzoyl peroxide (0.2 g.) was refluxed in 160 ml. of carbon tetrachloride for 60 min. The solid product was removed by filtration and the solvent distilled. Distillation of the residue gave 37 g., (93%) of a light yellow oil, b.p. 175–180°, 1 mm.

Anal. Calcd. for $C_{12}H_{14}O_5Br_2$: C, 36.20; H, 3.54; Br, 40.14. Found: C, 36.17; H, 3.45; Br, 40.01.

The oil crystallized after standing for 3 weeks and gave colorless crystals, m.p. 50° (from carbon tetrachloride).

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

Diene and Retrodiene Reactions of Electronegatively 3,4-Disubstituted Furans

C. D. WEIS

E. I. du Pont de Nemours & Company, Explosives Department,
Experimental Station Laboratory, Wilmington, Delaware

Received April 9, 1962

3,4-Furandinitriles or dicarboxylic esters underwent the diene reaction with dicyanoacetylene or dimethyl acetylenedicarboxylate yielding oxabicyclo derivatives. These cleaved to dicyanoacetylene and 3,4-dicyanofuran under retrogressive thermal reaction conditions. Chemical deoxygenation of some polycyano diene adducts could be effected with triphenylphosphine *via* an isolable intermediate which decomposed into the corresponding aromatic polycyano compounds.

Literature reports on diene reactions involving a diene component bearing electron-withdrawing substituents are noteworthy for their paucity and uncertainty. Thus although the reaction between ethyl butadiene-1,4-dicarboxylate and maleic anhydride has been described,[1] other investigators[2] have been unable to duplicate this work. Other publications in this area deal with the behavior of sorbic acid and derivatives.[3-5] Kataev[6] has investigated the dienophile properties of 1-nitrobutadiene towards activated olefins and methyl acetylenedicarboxylate and found that, of these, only maleic anhydride could be added and then only in 4% yield. Other research in this field which has been cataloged by Alder[7] includes a number of unsuccessful reactions using derivatives of the furan series. However, since most of the cases investigated involved furans substituted in the 2- or 2,5-positions, the question of the behavior and characteristics of this heterocycle

---

(1) E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 897 (1929).

(2) L. I. Smith and E. J. Carlson, *J. Am. Chem. Soc.*, **61**, 288 (1939).

(3) T. Wagner-Jauregg and E. Helmert, *Ber.*, **71**, 2535 (1938).

(4) N. C. Deno and H. Chafetz, *J. Org. Chem.*, **25**, 449 (1960).

(5) (a) German Patent 527,771 (1931); French Patent 37498 (1929); (b) K. Alder, M. Schuhmacher, and O. Wolff, *Ann.*, **570**, 230 (1950).

(6) E. G. Kataev, *Soobshch. Nauchn-Issled Rabot. Chlenov Primorsk. Otd. Vses. Khim. Obshchestva*, **2**, 49 (1955).

(7) K. Alder, "Die Methoden der Dien Synthese in Neuere Methoden der präparativen org. Chemie," Verlag Chemie, Berlin, 1944.