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

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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

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[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).

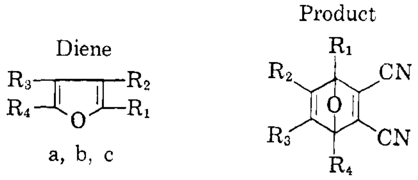
[7] K. Alder, "Die Methoden der Dien Synthese in Neuere Methoden der präparativen org. Chemie," Verlag Chemie, Berlin, 1944.

when bearing electronegative moieties in the 3- and 4-positions was left in abeyance. Previous studies[8] on the chemistry of cyano heterocycles indicated that 3,4-dicyanofuran would afford a convenient means of studying this particular question.

Although tetracyanoethylene is one of the most active alkenes it did not add to 3,4-dicyanofuran over a temperature range of 20–150°. This behavior is of course parallel to furan itself. Similarly, fumaronitrile could not be induced to react with 3,4-dicyanofuran. However, 3,4-dicyanofuran gave a normal diene addition reaction with dimethyl acetylenedicarboxylate and dicyanoacetylene. These reactions are summarized in Table I.

The additions were best carried out in the absence of solvent, in a sealed tube, for in the course of these investigations it became apparent that the retrodiene reaction is strongly enhanced in the presence of a solvent. Furthermore, the considerable volatility of dicyanoacetylene forbade conventional reaction in refluxing solvents. All the diene adducts collected in Table I are stable, colorless, crystalline compounds. The tetracyano derivatives are rather insoluble in the common organic solvents but may be conveniently recrystallized from acetonitrile or benzonitrile and may be sublimed, without decomposition, in a vacuum. The nuclear magnetic resonance (n.m.r.) spectra are consistent with their structures.

Table I



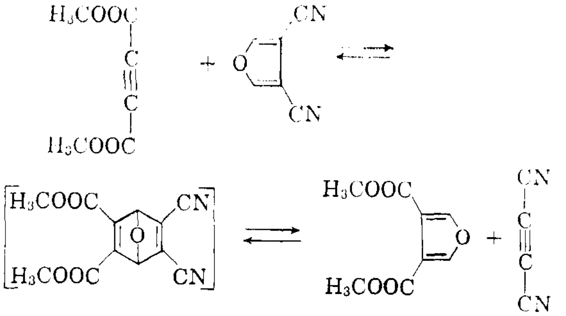
	^{a,b,c}	R_4	Yield, %
II	$R_1 = R_4 = H$ $R_2 = R_3 = COOCH_3$	$R_1 = R_4 = H$ $R_2 = R = COOCH_3$	93.5
III	$R_1 = R_4 = CH_3$ $R_2 = R_3 = COOCH_3$	$R_1 = R_4 = CH_3$ $R_2 = R_3 = COOC_2H_5$	100
IV	$R_1 = R_4 = H$ $R = R_3 = CN$	$R_1 = R_4 = H$ $R_2 = R_3 = CN$	96
V	$R_1 = R_4 = CH_3$ $R_2 = R_3 = CN$	$R_1 = R_4 = CH_3$ $R_2 = R_3 = CN$	52
VI	$R_1 = R_4 = CH_2Br$ $R_3 = R_4 = COOC_2H_5$	$R_1 = R_2 = CH_2Br$ $R_3 = R_4 = COOC_2H_5$	100

[a] Molar ratios are 1:1. [b] Reaction temp. 110°. [c] Reaction period 18 hr.

The reaction of 3,4-dicyanofuran with methyl acetylenedicarboxylate is of particular interest since the product was the diadduct dimethyl 6,7,9,10-tetracyano-1,4,5,8-diepoxy-1,4,5,8,9,10-hexahydro-2,3-naphthalenedicarboxylate (I) and not the mono adduct. The related 9,10-diester of this diepoxynaphthalene system was obtained as a by-product of the reaction of furan and acetylene dicarboxylic ester.[9] It was not possible to isolate the 1:1 adduct regardless of the ratios of the starting materials, since it immediately reacts further with a second mole of dicyanofuran. The postulated structure is based on the greater electrophilicity of the nitrile substituted double bond relative to the carboxylic substituted alkene and is fully endorsed by the n.m.r. spectrum. The infrared absorption of the ester groups appears at 5.75 μ (1740 cm.$^{-1}$).

In contrast to this diadduct formation, the ethyl 3,4-furandicarboxylate and dicyanoacetylene yielded the mono adduct (II) exclusively. Diethyl 2,5-dimethyl-3,4-furandicarboxylate and its bisbromomethyl derivative furnished analogous derivatives (III and VI). Nuclear magnetic resonance spectra confirmed the proposed structures and excluded the possibility of 2,3-addition. Similar structures were also obtainable from dicyanoacetylene and 3,4-dicyanofuran or its 2,5-dimethyl homolog (IV and V). If, however, the two methyl groups are replaced by methylol groups or their benzoate esters then the diene reaction can no longer be effected even with dicyanoacetylene as the dienophile. Apparently the electron-withdrawing effect of the alcohol and ester groups is already powerful enough to reduce the electron density at the adjacent carbon atoms sufficiently to frustrate additions.

Retrodiene Fission of Cyano Compounds.—The course of retrodiene reactions has been the subject of several communications[10–14] and the observation that some of the polycyano adducts prepared in this work decompose on heating to the melting point prompted an investigation of the effect of such multifunctionality on this reaction. Thus dicyanoacetylene is formed on heating a solution of 3,4-dicyanofuran and dimethyl acetylenedicarboxylate in xylene or mesitylene (with considerable darkening of the solution) presumably *via* the sequence:



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(8) C. D. Weis, *J. Org. Chem.*, **27**, 3514 (1962).

(9) O. Diels and S. Olsen, *J. prakt. Chem.*, **156**, 289 (1940).

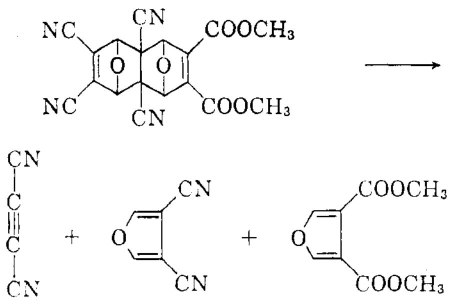
(10) K. Alder and K. H. Backendorf, *Ann.*, **535**, 101 (1938).

(11) A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart, and H. L. Trumbull, *J. Am. Chem. Soc.*, **72**, 3127 (1950).

(12) K. Alder, F. H. Flock, and H. Beumling, *Chem. Ber.*, **93**, 1896 (1960).

(13) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

Similarly, if I is heated at 218° in an inert atmosphere, it does not simply revert to the starting components but forms dicyanoacetylene, 3,4-dicyanofuran, and dimethyl 3,4-furandicarboxylate as expressed by the equation below. The isolated



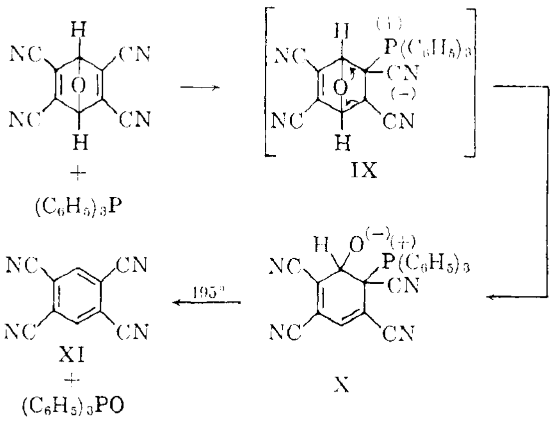
dicyanoacetylene was characterized by its refractive index and infrared spectrum. The 3,4-dicyanofuran was identified by a mixed melting point determination and a comparison of its infrared spectrum with an authentic specimen. The furan diester was characterized as the bishydrazide and it was also shown that no pyrazolone derivative conceivably originating from acetylenedicarboxylic ester and hydrazine had been formed.

The mechanism of this reaction is best explained by considering the electron-withdrawing effect of the cyano groups. This effect weakens the neighboring C—C bond apparently more than the similar effect of the ester groups and therefore the decomposition begins with the cleavage of a dicyano fragment and the consequent formation of dicyanoacetylene. If the first step of the fission involves the rupture of the carbon to carbon bond between the 1,9- and the 4,10-position, then IV would be expected to be an intermediate. This compound however required heating to 320° before decomposing irreversibly into 3,4-dicyanofuran and dicyanoacetylene.

If the alternative primary cleavage of I yielding dicyanofuran and dimethyl 5,6-dicyano-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (VII) occurred, then more than one molar equivalent of the dicyanofuran would be isolable since subsequent cleavage of VII would furnish more dicyanofuran and acetylenedicarboxylate. A study of the cleavage of the related II showed this mechanism to be unacceptable. Thus, thermal cleavage of II at 170–180° gave random bond fission with the formation of 3,4-dicyanofuran, diethyl 3,4-furandicarboxylate, dicyanoacetylene, and ethyl acetylenedicarboxylate which was not isolated *per se* but is a necessary and concomitant adjunct of the dicyanofuran. In a similar fashion dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (VIII), on standing, cleaved slowly into its initial components. However, if the preparation of the corresponding diamide was attempted using aqueous ammonia, a retrodiene fission ensued and 3,4-dicarbamylfuran was obtained. The dicarbamyl compound was characterized by comparison with a previously prepared sample and by its dehydration to 3,4-dicyanofuran.[8]

Elimination of the Ether Bridges in Polycyano Compounds.—A means of eliminating the ether bridges in such compounds as IV or V would afford a route to polycyano aromatics.

Attempts to cleave the ether bridge in IV with boron trifluoride etherate in dimethylformamide (DMF)[15] or with triphenylmethyl bromide[16] were without success. Refluxing with methanolic hydrochloric acid gave only 3,4-dicyanofuran. However, when triphenylphosphine was added to a suspension of IV in hot acetonitrile, deep blue crystals could be obtained on cooling. The reaction also occurred at room temperature and the air stable product could be readily isolated in analytical purity by filtration and subsequent washing with acetonitrile. Recrystallization of this material was frustrated by its extremely low solubility. Thermal cleavage at 195° yielded 1,2,4,5-tetracyanobenzene[17] (XI) and triphenylphosphine oxide which were characterized by appropriate comparisons with authentic samples. The analytical results and the infrared spectrum are consistent with the following reaction path:



Triphenylphosphine adds with its electron pair to a double bond and the transient intermediate (IX) stabilizes itself by transfer of the electrons to the oxygen atom with synchronous opening of the oxide bridge to give X. This structure corresponds formally to the ylide intermediate in the triphenylphosphine cleavage of epoxides.[18] Though n.m.r. examination of the blue crystals was hampered by low solubility, infrared studies provided

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[14] K. Alder, K. Kaiser, and M. Schuhmacher, *Ann.*, **602**, 80 (1957).

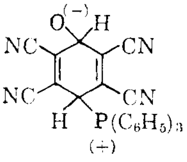
[15] A. Bowers, E. Denot, R. Urquiza, and L. M. Sanchez-Hidalgo, *Tetrahedron*, **8**, 116 (1960).

[16] F. R. Jansen and R. L. Bedard, *Angew. Chem.*, **72**, 144 (1960).

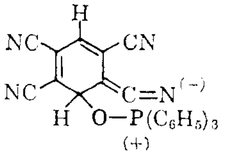
[17] E. A. Lawton and D. D. MacRitchie, *J. Org. Chem.*, **24**, 26 (1959).

[18] (a) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955); (b) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

further support for the above formulation. Thus, while the CN and C—O—C absorption in IV was found at 4.48 μ and 9.58 μ, respectively, X shows two cyano bands at 4.52 μ and 4.60 μ (ratio of intensities about 1:2). The band ascribed to the C—O—C absorption has disappeared and no band attributable to the P—O frequency can be found. The facts are in accord with the findings of F. Ramirez and S. Dershowitz[19] who showed, using a series of zwitterionic phosphonium compounds of a similar type that the absorption of the P—O frequency generally remains constant. The above representation is therefore preferred to structures XII and XIII. Although treatment of IV with tributylphosphine gave a blue solution in an analogous fashion, a crystalline product could not be isolated and facile decomposition occurred in solvents suitable for the determination of nuclear magnetic resonance spectra.



XII



XIII

When V was treated with triphenylphosphine in acetonitrile a deep red solution was obtained, from which crystals of 1,4-dimethyltetracyanobenzene (XIV) deposited. The intermediate phosphonium zwitterion may be obtained as a blue-green solid which is only stable in air for a few minutes.

This ether cleavage with triphenylphosphine is not generally known to proceed under such mild conditions and temperatures of 100° are usually required. The reactions described above seem to be peculiar to IV and V, for the other adducts do not react with triphenylphosphine even under reflux conditions.

It is further interesting to note that although the analogs of triphenylphosphine, triphenylarsine, and triphenylstibine may serve as deoxygenation reagents,[20] IV and V, are unaffected by either of these.

Experimental

Dimethyl 6,7,9,10-Tetracyano-1,4,5,8-diepoxy-1,4,5,8,9,-10-hexahydro-2,3-naphthalenedicarboxylate (I).—3,4-Dicyanofuran (1.18 g., 0.01 mole) and dimethylacetylenedicarboxylate (0.85 g., 0.0118 mole) were placed in a sealed tube and heated to 110° (refluxing toluene) for 18 hr. The cold solid residue was treated with 20 ml. of boiling methanol and filtered. The residue weighed 1.26 g. (66.5%). Recrystallization from acetonitrile yielded white crystals, m.p. 216–218° (slight dec.).

Anal. Calcd. for $C_{18}H_{10}N_4O_6$: C, 57.16; H, 2.66; N, 14.81. Found: C, 56.91; H, 2.65; N, 14.57.

The infrared spectrum exhibits characteristic bands at 4.48, 5.78, 6.93, 7.75, 9.41 μ. The compound is soluble in boiling acetonitrile, benzonitrile, and slightly soluble in boiling acetic acid.

Dicyanoacetylene was prepared by dehydration of dicarbamoylacetylene with phosphorus pentoxide in 25–35% yield.[21]

Diethyl 2,3-Dicyano-7-oxabicyclo[2.2.1]hepta-2,5-diene-5,6-dicarboxylate (II).—Diethyl 3,4-furandicarboxylate (1.94 g., 0.01 mole) and dicyanoacetylene (1.05 g., 0.014 mole) were heated together in a sealed tube for 12 hr. at 110°.. The solid reaction product was mechanically removed from the tube and after the excess of dicyanoacetylene had evaporated, it was washed with ether and weighed 2.51 g., 93.5%. Recrystallization from methanol yielded colorless crystals, m.p. 156.5–157°.

Anal. Calcd. for $C_{14}H_{12}N_2O_5$: C, 58.34; H, 4.20; N, 9.72. Found: C, 58.23; H, 4.16; N, 9.23.

Diethyl 1,4-Dimethyl-2,3-dicyano-7-oxabicyclo[2.2.1]-hepta-2,5-diene-5,6-dicarboxylate (III).—Diethyl 2,5-dimethyl-3,4-furandicarboxylate (1.2 g., 0.005 mole) and dicyanoacetylene (0.5 g., 0.0066 mole) were heated together in a sealed tube for 15 hr. at 110°. The solid reaction product was mechanically removed from the tube (1.59 g., 100%). Recrystallization from ethanol gave white crystals, m.p. 63–64°. The same result was obtained by heating the components at 56° (refluxing acetone) for 16 hr.

Anal. Calcd. for $C_{16}H_{16}N_2O_5$: C, 60.76; H, 5.10; N, 8.86. Found: C, 61.01; H, 5.19; N, 8.85.

2,3,5,6-Tetracyano-7-oxabicyclo[2.2.1]hepta-2,5-diene (IV).—3,4-Dicyanofuran (2.36 g., 0.02 mole) and dicyanoacetylene (2 g., 0.026 mole) were heated together in a sealed tube at 156° (refluxing bromobenzene) for 18 hr. After cooling the tube the gray crystalline product was mechanically removed from the tube and extracted with 20 ml. of boiling methanol. Filtration yielded 3.72 g., (96%). Sublimation through a thin layer of glass wool at 180° gave white crystals, m.p. 325–330° dec. The material can also be purified by careful recrystallization from benzonitrile and is obtained in small needles. It is cumbersome, however, to free the crystals completely from the adherent solvent.

Anal. Calcd. for $C_{10}H_2N_4O$: C, 61.81; H, 1.04; N, 28.86. Found: C, 61.75; H, 1.09; N, 28.72.

IV (140 mg., 0.0072 mole) was suspended in 10 ml. of absolute ethanol, 5 drops of concentrated hydrochloric acid was added, and the mixture refluxed for 14 hr. The starting material had completely dissolved. The solvent was evaporated in a current of dry nitrogen and 98 mg. of light yellow crystals were left. Sublimation at 1 mm. gave 3,4-dicyanofuran, m.p. 159–160° (mixed melting point with an authentic sample).

1,4-Dimethyl-2,3,5,6-tetracyano-7-oxabicyclo[2.2.1]-hepta-2,5-diene (V).—2,5-Dimethyl-3,4-dicyanofuran (4.38 g., 0.03 mole) and dicyanoacetylene (2.8 g., 0.037 mole) were heated together in a sealed tube at 110° for 69 hr. The crystalline reaction product was mechanically removed and weighed (5.81 g.). Fractional sublimation at 1 mm. through a thin layer of glass wool gave at 130° some starting material (1.74 g.) and at 180–190° the product V (3.45 g., 52%). (Unchanged starting material may also be extracted with boiling carbon tetrachloride.)

An analytical sample was resublimed at 160° (1 mm.) and recrystallized from acetonitrile, m.p. 208°.

Anal. Calcd. for $C_{12}H_6N_4O$: C, 64.87; H, 2.72; N, 25.22. Found: C, 65.08; H, 3.09; N, 24.97.

A decrease of the reaction time to 18 hr. gave a 25% yield, and an increase to 41 hr. gave a 46% yield.

Diethyl 2,5-Bis(bromomethyl)3,4-furandicarboxylate.—

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[19] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956).

[20] L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

[21] A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

The compound was prepared according to the procedure reported earlier.[22]

Diethyl 1,4-Bis(bromomethyl)-2,3-dicyano-7-oxabicyclo-[2.2.1]hepta-2,5-diene-5,6-dicarboxylate (VI).—Diethyl 2,5-bis(bromomethyl)-3,4-furandicarboxylate (4 g., 0.01 mole) and dicyanoacetylene (1 g., 0.0128 mole) were heated in a sealed tube at 110° for 6 hr. The brown oily product was removed from the tube and crystallized (5.0 g. 100%) after a few hours. Recrystallization from ethanol (charcoal) gave white needles, m.p. 109°.

Anal. Calcd. for $C_{16}H_{14}N_2O_5Br_2$: C, 40.53; H, 2.98; N, 5.91; Br, 33.71. Found: C, 40.41; H, 2.92; N, 5.97; Br, 34.02.

The Thermal Cleavage of the Diels–Alder Adducts. The Cleavage of I.—The cleavage of the Diels–Alder adducts was carried out in a nitrogen atmosphere at a given decomposition temperature. Dicyanoacetylene was swept with nitrogen into a small trap cooled with Dry Ice. Most of the dicyanofuran sublimed to the cold part of the decomposition tube. A typical run was carried out as follows:

I (0.5 g., 0.00132 mole) was placed in a tube and a slow stream of nitrogen passed through. It was slowly heated in an oil bath to 215–220°. The solid melted and a gas evolution occurred. After it had ceased (about 15 min.) the dicyanoacetylene formed was swept into a cold trap. The yield was 0.091 g. (91%), $n^{25}\text{D}$ 1.4647. It was further characterized by its infrared spectrum.

Eight milliliters of carbon tetrachloride was added to the residue cooled in ice and the 3,4-dicyanofuran (0.14 g., 89%) filtered off. It was characterized by its mixed melting point (m.p. 159–160°) and by comparison of its infrared spectrum with an authentic sample.

The carbon tetrachloride was evaporated from the filtrate and 10 ml. of ethanol and 10 drops of hydrazine were added to the residue. It was refluxed for 1 min. and set aside for 24 hr. The crystalline dihydrazide (0.175 g., 72%) was filtered off and recrystallized from water, m.p. 225–230° dec. Comparison of the infrared spectrum and of the melting point with those of an authentic sample which was prepared from diethyl 3,4-furandicarboxylate and hydrazine hydrate confirmed its structure.

Anal. Calcd. for $C_6H_8N_4O_3$: C, 39.13; H, 4.38; N, 30.42. Found: C, 39.16; H, 4.48; N, 30.25.

The Cleavage of II.—II (0.5 g., 0.00176 mole) was decomposed as described before at 175–180°. The yield of dicyanoacetylene was 0.07 g. ($n^{25}\text{D}$ 1.4647). The semisolid residue which was mechanically removed from the decomposition tube weighed 0.08 g. after having been pressed dry on a clay plate. The mixed melting point with 3,4-dicyanofuran was 159–160°.

In a second example 0.5 g. was subjected to a distillation at 20 mm. The distillate which was collected at 160–170° was dissolved in 10 ml. of ethanol and a few drops of hydrazine hydrate added. The solution was refluxed for a few minutes and allowed to stand overnight. The precipitated colorless crystals were filtered off and recrystallized from water, m.p. 230°. The infrared spectrum was identical with that of the dihydrazide of furan-3,4-dicarboxylic acid.

The Cleavage of IV.—IV (0.5 g., 0.00258 mole) was decomposed at 315–320° as described before. Dicyanoacetylene [0.173 g. (88%), $n^{25}\text{D}$ 1.4647] was obtained and 3,4-dicyanofuran [0.258 g. (85%)] sublimed to the upper parts of the apparatus and was mechanically removed. It was identified by its mixed melting point with an authentic sample, m.p. 159–160°.

The Cleavage of VIII.—Freshly distilled VIII[23] (10 g., 0.0048 mole) was added to 40 ml. of aqueous ammonia. The suspension became homogeneous within a few minutes. It was allowed to stand for 40 hr., then the precipitate was filtered off (4.1 g., 56%) and recrystallized from water (charcoal) yielding white crystals, m.p. 275° dec. The infrared spectrum was superimposable to the known 3,4-dicarbamylfuran.

The dehydration with phosphorus oxychloride was carried out as described in the previous paper.[14] The obtained product, m.p. 159–169° (mixed melting point) proved to be identical with the known 3,4-dicyanofuran.

The Reaction of IV with Triphenylphosphine, Betain X.—a. IV (0.48 g., 0.00248 mole) and triphenylphosphine (0.70 g., 0.00266 mole) in 10 ml. of acetonitrile were brought to reflux for 2 min. The solution was allowed to cool slowly. The dark blue precipitate (0.91 g., 100%) was filtered off from the ice-cold solution and washed with cold ether. The crystals were subjected to analysis without further purification, m.p. 193–195°.

Anal. Calcd. for $C_{28}H_{17}N_4OP$: C, 73.67; H, 3.75; N, 12.28; P, 6.79. Found: C, 73.49; H, 3.85; N, 12.65; P, 6.79.

The compound is only slightly soluble in cold, somewhat better in hot acetonitrile. Heating it in other high-boiling solvents causes decomposition. The compound in the dry state is blue; the acetonitrile solution, however, is deep red.

b. A solution of IV (0.242 g., 0.00125 mole) and triphenylphosphine (0.35 g., 0.00134 mole) in 6 ml. of acetonitrile was stirred for 21 hr. The blue precipitate (X) was filtered off and weighed (0.508 g., 86%). The product consists of very small crystals while the one described above, prepared in boiling acetonitrile, consists of larger crystals.

The infrared spectrum exhibited bands at: 4.52, and 4.60 μ (about 1:2); 6.09, 6.62, 6.98, 7.75, 8.22, 8.45, 8.92, 9.08, 13.12, 13.36, 13.89 μ.

1,2,4,5-Tetracyanobenzene.—The betain (X) (0.16 g., 0.00035 mole) was heated to its decomposition point at 195°. The blue color disappeared and on cooling, the mixture solidified. It was extracted with 4 ml. of boiling ethanol. The ice-cold solution was filtered and gave tetracyanobenzene (48 mg., 76.8%). It was characterized by its mixed melting point with an authentic sample,[17] m.p. 270–272° and by comparison of their infrared spectra. The alcoholic solution yielded triphenylphosphine oxide [42 mg. (43%)] m.p. 151–153° (mixed melting point).

1,4-Dimethyltetracyanobenzene.—V (2.83 g., 0.0127 mole) was dissolved in 30 ml. of acetonitrile and triphenylphosphine (3.38 g., 0.0129 mole) added. The solution became deep blue and had to be cooled occasionally, otherwise the temperature rose to about 50°. The blue color slowly started to fade out after about 15–20 min. and crystals of dimethyltetracyanobenzene deposited. The cold mixture was filtered after 4 hr. and the crystals were washed with a few milliliters of cold acetonitrile. The dimethyltetracyanobenzene [1.47 g. (52%)] was obtained in pale brown crystals crystals which became colorless after sublimation at 200° (1 mm.).

Recrystallization from acetonitrile yielded long colorless needles, m.p. 337–339° dec. in a sealed capillary.

Anal. Calcd. for $C_{12}H_6N_4$: C, 69.89; H, 2.93; N, 27.17. Found: C, 69.95; H, 3.01; N, 27.10.

The infrared spectrum showed absorption at 4.49, 7.01, 7.25, 7.93, 9.95 μ (very weak).

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