solution of 17.0 g. (0.10 mole) of silver nitrate in 30 ml. of acetonitrile. The precipitate was removed by suction filtration, washed with two 10-ml. portions of acetonitrile, and dried. The dry silver ethyl mercaptide amounted to 17.0 g. (theory 16.9 g.). Most of the acetonitrile was evaporated from the filtrate, and 50 ml. of water was added to the residue. The oil which separated was extracted into two 50-ml. portions of ether, and the solution was dried over anhydrous magnesium sulfate. Evaporation of the ether left 10.5 g. (66%) of crude ethyl isothiocyanatopropionate. Distillation under reduced pressure gave 8.4 g. (53%) of purified material, b.p. 59.5–61° (0.2 mm.), $n^{27}D$ 1.4970. Redistillation gave pure ethyl 3-isothiocyanatopropionate, b.p. 58.5–60° (0.2 mm.), $n^{27}D$ 1.4983, d^{20}_4 1.114. Because the physical properties of this material did not agree well with those reported in the literature[20] [b.p. 92–94° (0.04 mm.), $n^{25}D$ 1.4904, d^{20}_4 1.132], the compound was analyzed.

Anal. Calcd. for $C_6H_9O_2NS$: C, 45.26; H, 5.70; N, 8.80; S, 20.14. Found: C, 45.43; H, 5.63; N, 8.68; S, 20.39.

1-Cyclohexyl-3-(2-ethoxycarbonylethyl)-2-thiourea.—A solution of ethyl 3-isothiocyanatopropionate in 150 ml. of acetonitrile prepared as described above from 61.1 g. (0.324 mole) of ethyl 3-(S-ethyldithiocarbamoyl)propionate was treated with 32.2 g. (0.324 mole) of cyclohexylamine. The temperature rose from 27 to 76°. After 1 hr. the reaction mixture was poured into 500 ml. of cold water. An oil separated and coagulated to a solid when the mixture was neutralized with 15 ml. of 5 *N* hydrochloric acid. After recovery by suction filtration and drying, the crude 1-cyclohexyl-3-(2-ethoxycarbonylethyl)-2-thiourea amounted to 52.1 g. (64%). Two recrystallizations from 1:1 benzene–petroleum ether gave 19.9 g. of brownish solid, m.p. 53–58°. A portion was recrystallized twice more from 1:1 benzene–petroleum ether to give pure white 1-cyclohexyl-3-(2-ethoxycarbonylethyl)-2-thiourea, m.p. 56–60°.

Anal. Calcd. for $C_{12}H_{22}O_2N_2S$: C, 55.78; H, 8.38; N, 10.85; S, 12.41. Found: C, 55.58; H, 8.34; N, 10.69; S, 12.52.

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[20] D. L. Garmaise, P. Schwartz, and A. F. McKay, *J. Am. Chem. Soc.*, **80**, 3332 (1958).

Reactions of Dicyanoacetylene

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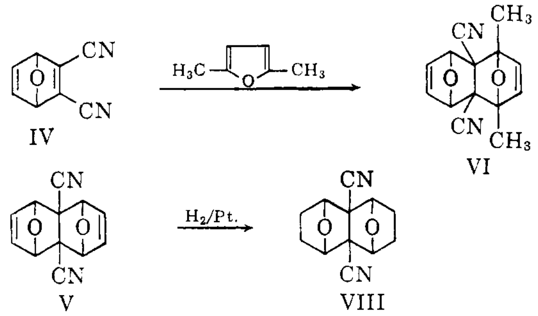
Dicyanoacetylene proved to be a highly reactive acetylenic dienophile. 1,4- Addition to durene gave the bicyclooctatriene skeleton. Other reactions with benzonitrile oxide, mercuric chloride, and diazomethane have been studied.

Literature reports on the reactivity of dicyanoacetylene (I) and its reaction products are noteworthy for their paucity. Only the addition of hydrogen chloride, ammonia, some amines,[1] and the Diels–Alder reaction with cyclopentadiene[2] have been reported. More recently it has been shown that dicyanoacetylene exhibited an exceptional reactivity as an acetylenic dienophile toward a number of 3,4-negatively substituted furan derivatives.[3] Its nature as a strong dienophile is further attested by the fact that fumaronitrile or tetracyanoethylene failed to undergo diene reaction with these 3,4-substituted furan derivatives as well in solution as in a solvent free phase.[3] Acetylene dicarboxylic acid[4] or its methyl ester[5] on the other hand may serve as a dienophile in a number of reactions, but the yields are not so good as with dicyanoacetylene. Hexafluoro-2-butyne, whose dienophilic activity was demonstrated even in the special case of 1,4- additions to benzene derivatives,[6] also underwent a facile diene reaction with 3,4-negatively disubstituted furan derivatives.[7] However, it led to an unstable adduct which underwent a retrodiene reaction as soon as it formed. In general, Diels–Alder reactions with hexafluoro-2-butyne require a higher temperature[6] than the ones with dicyanoacetylene.

The diene reaction of dicyanoacetylene with furan was of some interest because the tetracyclic system of 1,4,5,8-diepoxy-4a,8a-dicyano-1,4,4a,5,8,8a-hexahydronaphthalene(V) is formed with unusual ease.

The two components gave in molar ratios a mixture of the 1:1 adduct 1,4-epoxy-2,3-dicyanocyclohexa-2,5-diene (IV) and the 2:1 adduct (V). A 2:1 ratio of the starting materials led quantitatively to structure V at room temperature.



IV VI V VIII

IV reacted with a second mole of furan and yielded again the tetracyclic system (V) or, with 2,5-dimethylfuran as diene, 1,4-dimethyl-4a,8a-dicyano-1,4,5,8-diepoxy-4a,5,8,8a-tetrahydronaphthalene (VI) was obtained.

The structure of all these products was supported by the n.m.r. and infrared spectra which showed them to be regular diene adducts.

1,4,5,8-Diepoxy-4a,8a-dicyano-1,4,4a,5,8,8a-hexahydronaphthalene (V) was hydrogenated and consumed two moles of hydrogen giving the tetrahydro derivative 1,4,5,8-diepoxy-4a,8a-dicyanodecalin (VIII).

Since the attack of the 1:1 adduct (IV) by a second mole of furan occurs at the more hindered side, the formation of these diene adducts seems governed by the strong electron-withdrawing effect of the nitrile substituents. It seems, therefore, not limited to compounds with an exceptionally low electron density at the double bond such as is found in 2,3-dicyanobenzoquinone.[8] While dicyanoacetylene yielded this tetra-

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[1] (a) C. Moureu and J. C. Bongrand, *Compt. rend.*, **158**, 1092 (1920); (b) *Ann.*, **14**, 5 (1920).

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

[3] C. D. Weis, *ibid.*, **27**, 3520 (1962).

[4] H. Stockmann, *ibid.*, **26**, 2025 (1961).

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

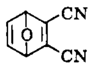
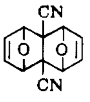
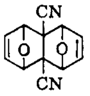
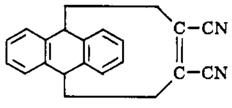
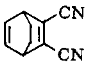
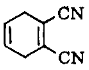
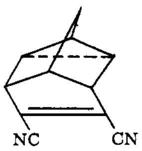
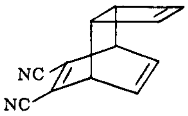
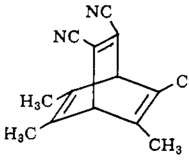
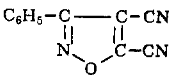
[6] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

[7] C. D. Weis, *J. Org. Chem.*, **27**, 3693 (1962).

[8] H. D. Hartzler and R. E. Benson, *ibid.*, **26**, 3507 (1961).

TABLE I

THE DIELS-ALDER ADDITION OF DICYANOACETYLENE TO DIENES

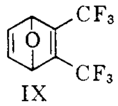
Addends	Products	Solvent	Temperature, °C.	Time	Yield, %
Furan	 IV +  V	Tetrahydrofuran	25	3 days	71 (IV) 11.5 (V)
Furan[a]	 V	Tetrahydrofuran	25	3 days	96
Anthracene	 X	None	100	1 hr.	100
1,3-Cyclohexadiene	 XI	None	0	1 hr.	93
Butadiene	 XIII	Tetrahydrofuran Benzene	100 25	5 hr. 15	94 88
Bicycloheptadiene	 XII	Tetrahydrofuran	56	6 hr.	66.5
Cycloöctatetraene	 XIV	Tetrahydrofuran	56	43 hr.	16.8
1,2,4,5-Tetramethylbenzene	 XVII	None	135	6 hr.	3.8
Benzonitrile oxide	 XVIII	Ether	33	40 hr.	81

[a] Ratio of diene to dienophile, 2:1.

cyclic structure with ease, it seems noteworthy that acetylene derivatives with substituents of less electron-withdrawing character such as acetylenedicarboxylic acid or esters yielded analogous compounds only after considerably longer reaction periods[4,5] and more drastic conditions.

A related tetracyclic system with angular cyano-substituents was formed during the reaction between dimethyl acetylenedicarboxylate and 3,4-dicyanofuran.[3] Its formation, however, required an extended reaction period at 110°.

The electron density of the substituted olefinic double bond in 2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene[7] (IX) is not sufficiently low to serve as a dienophile and lead to a tetracyclic structure.


IX

IV decomposed on heating into furan and dicyanoacetylene, but no 3,4-dicyanofuran was observed.

The thermal decomposition of V is at least partially a retrogression of its formation. Thus, dicyanoacetylene and furan were the main products together with a small amount of IV, some unidentified product and much tar. No 3,4-dicyanofuran was formed, as might be expected from an alternative path of the cleavage.

1,4,5,8-Diepoxy-4a,8a-dicyanodecaline (VIII) did not show any indication of undergoing a thermal cleavage.

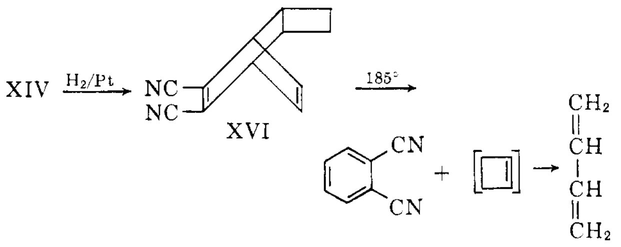
A number of Diels–Alder adducts obtained with acetylenic dienophiles are listed in Table I.

The preparation of 11,12-dicyano-9,10-dihydro-9,10-ethenoanthracene (X) has been reported earlier[9] by means of a different route. It could be heated to 400° without noticeable decomposition.

On heating, 2,3-dicyanobicyclo[2.2.2]octa-2,5-diene (XI) cleaved quantitatively into phthalonitrile and ethylene.

Bicycloheptadiene gave an adduct of the nortricyclene type, (XII) analogous to the one reported in the literature.[10,16] The retrogressive cleavage of 1,2-dicyanocyclohexadiene-1,4 (XIII) was accompanied by a considerable formation of charry products and gave phthalonitrile, traces of benzonitrile, and probably hydrogen cyanide.

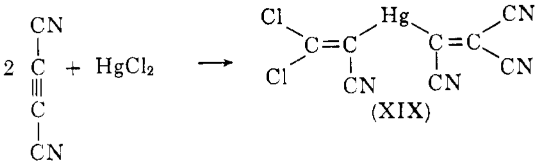
7,8-Dicyanotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (XIV) might be assumed to have the *cis–cis* form by analogy with the structures of the addition products of cycloöctatetraene and dimethyl maleate.[11] The palladium chloride–benzonitrile complex could not be purified because of its insolubility. The retrodiene fission of 7,8 - dicyanotricyclo[4.2.2.$0^{2,5}$] - 3,4 - dihydrodeca-3,9-diene (XVI) obtained by partial hydrogenation of XIV, yielded phthalonitrile and as transient intermediate cyclobutene the ring of which opened under the applied experimental conditions[12] and 1,3-butadiene was isolated.



Dicyanoacetylene added 1,4 to durene to provide another example of a Diels–Alder addition of an acetylene to a substituted benzene ring[6] giving 2,3,5,6-tetramethyl-7,8-dicyanobicyclo[2.2.2]octa-2,5,7-triene (XVII). There was only a narrow temperature range in which its formation was observed.

Proof of the symmetrical structure of XVII was obtained from the nuclear magnetic resonance spectrum which contained the expected sharp bands for allylic methyl and tertiary allylic hydrogen in a 6:1 ratio of intensities. The light yellow color of XVII might be indicative of considerable overlap of the π-systems of the cyanosubstituted double bond and the methyl substituted ones.

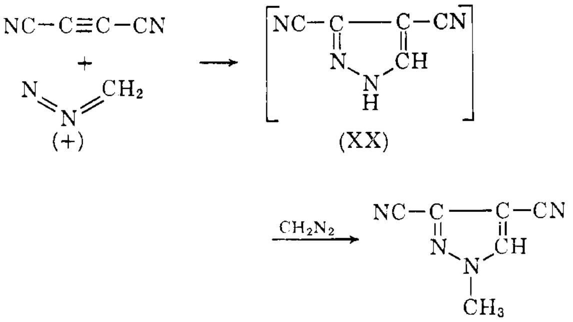
A slurry of dicyanoethylene in an aqueous mercuric chloride solution gave bis(1,2-dicyano-1-chloroethene)-mercury (XVIII). This type of reaction of acetylenes with mercuric chloride has been mentioned by Freidlina.[13]



(XIX)

The reaction of dicyanoacetylene with diazomethane followed the general pattern of the Büchner pyrazole synthesis as has already been described for its reaction with diazoacetic ester.[14]

The acidity of the N-bonded hydrogen did not permit the isolation of the intermediate 3,4-dicyanopyrazole (XIX). It reacted further to yield solely N-methyldicyanopyrazole (XX). Changing the conditions—

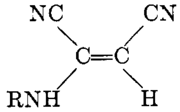


(XX)

(XXI)

e.g., an excess of dicyanoacetylene or changing the order of addition of the two reactants gave again the N-methylated product only.

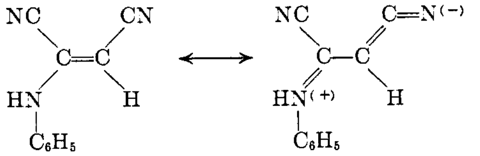
The addition of substituted amines to dicyanoacetylene has already been mentioned by Moureau and Bongrand,[1] who first isolated dicyanoacetylene. Since no characteristic data of the compounds obtained were given, some typical reactions have been included in this investigation. While aliphatic amines gave intractable tars only, aniline or benzylamine added to the acetylenic bond forming N-substituted aminomaleonitrile derivatives (XXII).



$R = C_6H_5, C_6H_5CH_2$

(XXII)

The infrared spectrum of XXII showed a doublet for the nitrile absorption at 4.46 and 4.53 μ. There are bands of strong intensity at 6.18 and 6.27 μ, which are believed to be due to the absorption of the ethylenic double bond and the phenyl ring, respectively. The presence of the phenyl group interferes with the assignment of NH deformation absorption. The very strong intensity of the aromatic absorption band may be indicative of resonance between the structures XXIIIa and XXIIIb.



XXIIIa XXIIIb

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(9) O. Diels and W. Thiele, *Ber.*, **71**, 1173 (1938).

(10) A. T. Blomquist and Y. Meinwald, *J. Am. Chem. Soc.*, **81**, 669 (1959).

(11) M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960).

(12) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

(13) R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **14**, (1942); *Chem. Abstr.*, 3050 (1943).

(14) C. D. Weis, *J. Org. Chem.*, **27**, 3695 (1962).

Experimental

Melting points are uncorrected.

Dicyanoacetylene (I) was prepared according to the method of Blomquist and Winslow.[15]

Furan and Dicyanoacetylene. (a) Molar Ratio 1:1. 1,4-Epoxy-2,3-dicyanocyclohexadiene-2,5- (IV) and 1,4,5,8-Diepoxy-4a,8a-dicyano-1,4,4a,5,8,8a-hexahydronaphthalene (V).—A cold solution of dicyanoacetylene (4 g., 0.0530 mole) in tetrahydrofuran (10 ml.) was slowly added to a solution of furan (3.5 g., 0.0510 mole) in tetrahydrofuran (10 ml.). The mixture had to be cooled in ice during the addition of the furan. Then it was allowed to stand at room temperature for 3 days. The crystals which precipitated (V) were filtered off (1.26 g.) and repeatedly recrystallized from ethanol, m.p. 240° dec.

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.21. Found: C, 67.92; H, 3.57; N, 13.54.

The infrared spectrum exhibited absorption bands at 4.42, 7.60, 9.42, 9.50, 10.48, 10.51, 10.77, 11.20, 11.83, 13.35, 13.60 μ.

The mother liquor from the above filtrate was evaporated to dryness and the residue (IV) (5.27 g., 71%) recrystallized from methanol–water, m.p. 112.5–113.5°.

Anal. Calcd. for $C_8H_4N_2O$: C, 66.65; H, 2.80; N, 19.63. Found: C, 67.09; H, 2.95; N, 20.03.

The infrared spectrum exhibited principal bands at 4.47, 7.88, 7.95, 9.58, 11.20, 11.75, 13.56, 13.68 μ.

IV (39.9 mg., 0.276 mmole) consumed 7.1 ml. of hydrogen (calcd. 6.95 ml.) on hydrogenation with platinum in 90% methanol. The hydrogenated compound did not give off dicyanoacetylene on heating while IV decomposes into furan and dicyanoacetylene.

(b) Molar Ratio 2:1. 1,4,5,8-Diepoxy-4a,8a-dicyano-1,4,-4a,5,8,8a-hexahydronaphthalene (V).—Furan (7 g., 0.1 mole) and dicyanoacetylene (3.5 g., 0.046 mole) were added to tetrahydrofuran (20 ml.) and kept at room temperature for 3 days. The content of the flask was evaporated to dryness and gave colorless crystals (9.4 g., 96%). A sample (2 g.) was recrystallized from dioxane, m.p. 240° dec.

The infrared spectrum was identical with the one of the previously isolated sample. Evaporation of the mother liquor left 0.1 g., the infrared spectrum of which showed the pattern of the diepoxynaphthalene system only.

1,4,5,8-Diepoxy-4a,8a-dicyanodecalin (VIII).—1,4,5,8-Diepoxy-4a,8a-dicyano-1,4,4a,5,8,8a-hexahydronaphthalene (V) (0.0628 g., 2.96×10^{-4} mole) was hydrogenated in methanol (90%) with palladium on charcoal and consumed 14.2 ml. of hydrogen (Calcd. 14.8 ml.). The compound was recrystallized from methanol, m.p. 205°.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 67.15; H, 5.85; N, 13.19.

No dicyanoacetylene was given off on heating the compound to its decomposition point.

The infrared spectrum exhibited nitrile absorption at 4.50 μ.

1,4-Dimethyl-4a,8a-dicyano-1,4,5,8-diepoxy-4a,5,8,8a-tetrahydronaphthalene (VI).—1,4-Epoxy-2,3-dicyanocyclohexadiene (2,5) (IV) (0.5 g., 0.0347 mole) and 2,5-dimethylfuran (0.5 g., 0.0520 mole) in a solution of tetrahydrofuran (8 ml.) were kept in slight reflux for a period of 6 hr. Evaporation of the solvent left white crystals (0.8 g., 96%), which were recrystallized from methanol, m.p. 182–183°.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 4.92; N, 11.66. Found: C, 70.10; H, 4.81; N, 11.36.

The Thermal Cleavage of V.—The procedure was essentially the same as described earlier.[3]

1,4,5,8-Diepoxy-4a,8a-dicyano-1,4,4a,5,8,8a-hexahydronaphthalene (V) (0.465 g., 0.0022 mole) was heated to 240–245° and maintained at this temperature for a period of 20 min. The dicyanoacetylene and furan formed were swept in a current of nitrogen into a small cold trap. The over-all yield was 0.33 g. A sample of the liquid phase was withdrawn and identified as furan by its infrared spectrum. The solid crystals in the top of the cold trap were mechanically removed and identified by their infrared spectrum as dicyanoacetylene. Crystals (0.069 g.) had deposited in the upper part of the decomposition tube. Recrystallization from acetonitrile gave traces of the 1:2 (V) and 0.052 g. of 1:1 (IV) adducts. Both were identified by their infrared spectrum. No 3,4-dicyanofuran could be detected. Carbonaceous residue (0.021 g.) was left.

11,12-Dicyano-9,10-dihydro-9,10-ethenoanthracene (X).—Anthracene (1.78 g., 0.010 mole) and dicyanoacetylene (0.97 g., 0.014 mole) were placed in a sealed tube and heated on a steam bath for a period of 1 hr. The crystalline reaction product was recrystallized from acetonitrile, m.p. 267–268°.

Anal. Calcd. for $C_{18}H_{10}N_2$: C, 85.03; H, 3.96; N, 11.02. Found: C, 84.77; H, 4.00; N, 10.92.

2,3-Dicyanobicyclo[2.2.2]octa-2,5-diene (XI).—Cyclohexadiene(1,3) (2 g., 0.025 mole) and dicyanoacetylene (2 g., 0.026 mole) were added to tetrahydrofuran (20 ml.). The mixture was kept in ice while the reaction took place. The solvent was evaporated after standing overnight. The solid (3.8 g., 93%) was recrystallized from methanol (charcoal) and yielded white crystals, m.p. 105°.

Anal. Calcd. for $C_{10}H_8N_2$: C, 76.97; H, 5.16; N, 17.94. Found: C, 77.07; H, 5.22; N, 17.92.

There was no indication of any 2:1 adduct formed. The nitrile absorption appeared at 4.50 μ.

The Thermal Cleavage of 2,3-Dicyanobicyclo[2.2.2]octa-2,5-diene (XI).—(160.7 mg., 0.0010 mole) was placed in a sealed tube and kept for 15 min. at 180°. Ethylene (1.002 mmoles, calcd. 1.025 mmoles) was characterized by the infrared spectrum. Neither acetylene nor dicyanoacetylene could be detected.

The solid material (126 mg., 98%) was identified as phthalonitrile, m.p. 141°, by the mixture m.p. with an authentic sample.

2,3-Dicyanocyclohexa-2,5-diene (XIII).—Buta-1,3-diene (approximately 0.9 g., 0.0167 mole) was added to tetrahydrofuran (15 ml.) followed by dicyanoacetylene (1 g., 0.0130 mole). The mixture was placed in a sealed tube and kept in a steam bath for 5 hr. Evaporation of the solvent and subsequent sublimation at 90°, 1 mm., gave white crystals (1.61 g., 94%), m.p. 109–110°.

Anal. Calcd. for $C_8H_6N_2$: C, 73.82; H, 4.65; N, 21.53. Found: C, 73.81; H, 4.71; N, 21.26.

The nitrile absorption appeared at 4.48 μ.

A similar run in benzene as solvent was allowed to stand at room temperature for 15 hr. Crystalline material (1.5 g., 88%) was obtained, m.p. 110°. The infrared spectrum was identical with the one above.

The Thermal Cleavage of 2,3-Dicyanocyclohexa-2,5-diene (XIII).—A small sample (0.64 g.) was heated to its decomposition point and the gaseous products pumped into a cold trap. Benzonitrile could be identified by its infrared spectrum. Phthalonitrile (0.15 g.), m.p. 140–141° (mixed m.p.), was collected in the decomposition tube.

6,7-Dicyanotetracyclo[3.2.1.1^{3,8}.O^{2,4}]non-6-ene (XII).—Bicycloheptadiene (2 g., 0.0217 mole) and dicyanoacetylene (1.8 g., 0.0237 mole) were refluxed in a solution of tetrahydrofuran (15 ml.) for a period of 6 hr. The dark brown solution was evaporated to dryness. The solid residue was taken up in chloroform and filtered through aluminum oxide. Evaporation of the solvent gave a colorless crystalline material (2.43 g., 66.5%) which was recrystallized from methanol, m.p. 89°.

Anal. Calcd. for $C_{11}H_8N_2$: C, 78.55; H, 4.80; N, 16.66. Found: C, 78.62; H, 4.88; N, 16.27.

The infrared spectrum showed principal absorption bands at 4.51, 6.34, 7.91, 10.52, 10.72, 11.12, 12.05, 12.30, and 12.49 μ (nortricyclene bands),[16] 13.13 μ.

No hydrogen was taken up with platinum in 90% methanol and no bromine could be added to the double bond. XII did not indicate any retrodiene reaction on heating to 250°. The structure was further confirmed by the n.m.r. spectrum. There is no absorption at a field lower than 182 c.p.s. (60 Mc./sec.). Therefore there can be no olefinic hydrogen. A poorly resolved multiple peak of intensity (2) is observed at 182 c.p.s. (60 Mc./sec.) and is assigned to the *tert*-allylic hydrogen. There are two *tert*-hydrogens part of a cyclopropane ring and two secondary hydrogens on the bridge. Since the two *tert*-hydrogens are part of a cyclopropane ring, it is consistent that they are coincidentally at the same field (104 c.p.s., 60 Mc./sec.) as the bridgehead hydrogen. The remaining two peaks are assigned to the two non-equivalent bridgehead hydrogens. The one at lower field a broad ringlet at 147 c.p.s. (60 Mc./sec.) is assigned to the hydrogen adjacent to the dicyanoacetylene function and the other, a poorly resolved doublet centered at 124 c.p.s. (60 Mc./sec.) with a peak separation of 6 c.p.s. (60 Mc./sec.) is assigned to the bridgehead hydrogen which is part of the cyclopropane ring.

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

[16] J. D. Roberts, E. R. Trumbull, W. Bonnett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

7,8-Dicyanotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (XIV).—Cyclooctatetraene (10 g., 0.096 mole) and dicyanoacetylene (7.6 g., 0.1 mole) were refluxed in tetrahydrofuran (60 ml.) for a period of 43 hr. Removal of the solvent left a semisolid residue which was taken up in chloroform; after filtration through aluminum oxide, the filtrate was evaporated to dryness. Recrystallization of the slightly oily crystals (2.9 g., 16.8%) from 90% methanol (charcoal) gave almost white crystals which after sublimation at 130–140°, 1 mm., melted at 148–149°.

Anal. Calcd. for $C_{12}H_8N_2$: C, 79.97; H, 4.48; N, 15.48. Found: C, 79.85; H, 4.53; N, 15.55.

7,8-Dicyanotricyclo[4.2.2.0^{2,5}]-3,4-dihydrodeca-3,9-diene (XVI).—XIV (0.125 g., 0.0007 mole) was hydrogenated in methanol with platinum. The hydrogen uptake (17.3 ml., calcd., 17.4 ml.) was a very rapid one, but became rather slow after one mole had been consumed. Evaporation of the solvent and sublimation at 130°, 1 mm. with subsequent recrystallization from methanol afforded white crystals, m.p. 134.5–135.5°.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.10; H, 5.54; N, 15.38. Found: C, 78.96; H, 5.66; N, 15.27.

The Retrodiene Cleavage of 7,8-Dicyanotricyclo[4.2.2.0^{2,5}]-3,4-Dihydrodeca-3,9-diene (XVI).—XVI (0.397 g., 0.00218 mole) was placed in a sealed tube and kept at 185° for a period of 40 min. The butadiene formed (46 ml., at S.T.P., 93%) showed the following characteristic data: pressure, 10 mm. at −78° (by standard high vacuum technique); lit.[17]: 10 mm. at −79.7° for 1,3-butadiene and 10 mm. at 75° for cyclobutene. Mol. wt., 53.6; calcd. 54.

The infrared spectrum was superimposable over the one of a known sample of 1,3-butadiene. No absorption belonging to cyclobutene could be detected. The solid residue (0.2742 g., 97.3%) was identified by m.p. and by infrared spectrum as phthalonitrile.

2,3,5,6-Tetramethyl-7,8-dicyanobicyclo[2.2.2]octa-2,5,7-triene (XVII).—Durene (2 g., 0.015 mole) and dicyanoacetylene (2.6 g., (0.034 mole) were placed in a sealed tube and heated to 132° (1-nitropropane as a heat exchange medium) for a period of 6 hr. The excess of dicyanoacetylene was evaporated and the semisolid residue added to methanol (10 ml.). The tarry material was well dispersed, the solution cooled in ice, and the solid (0.57 g.) filtered off. Then it was added to ether (5 ml.) and the insoluble part (0.19 g.) filtered off. Sublimation at 120–150°/1 mm. through a thin layer of glass wool gave traces of durene and 120 mg. of XVII as a light yellow sublimate, m.p. 231–232.5°.

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.95; H, 6.71; N, 13.33. Found: C, 80.06; H, 6.66; N, 13.03.

The infrared spectrum showed CN absorption at 4.49 μ and a band for C=C at 6.25 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\max}^{\text{ethanol}}$ 241 mμ (ε 5120) shoulder at 250 mμ (ε 4440), 358 mμ (ε 299).

The n.m.r. spectrum contained peaks at 107 c.p.s. (60 Mc/sec.) characteristic for allylic methyl of intensity (6), and at 256 c.p.s. (60 Mc./sec.) characteristic for tertiary allylic hydrogen of intensity (1).

4-Benzo-2,3-dicyanoisoxazole (XVIII).—Dicyanoacetylene (1.4 g., 0.018 mole) was added to an ethereal solution of benzonitrile oxide[18] (approximately 2.3 g., 0.019 mole) and refluxed for a period of 40 min. Evaporation of the solvent and recrystallization of the residue (2.92 g., 81%) from carbon tetrachloride yielded slightly yellow crystals, m.p. 84–86°.

Anal. Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.58; N, 21.53. Found: C, 67.64; H, 2.57; N, 21.50.

Bis(1,2-dicyano-1-chloroethene)mercury (XIX).—Dicyanoacetylene (5 g., 0.0658 mole) was added to a solution of mercuric chloride (18 g., 0.066 mole) in water (50 ml.) saturated with sodium chloride. The suspension was shaken for 20 min. with occasional cooling. The yellow precipitate (8.5 g., 61%) was filtered off, washed with water, and dried.

It was dissolved in acetone, chloroform added, and precipitation of yellow crystals, m.p. 185–190° dec., brought about by cooling the mixture in ice–water.

Anal. Calcd. for $C_8Cl_4N_4Hg$: C, 22.68; Cl, 16.73; N, 13.22; Hg, 47.35. Found: C, 22.79; Cl, 16.54; N, 13.19; Hg, 47.27.

***N*-Methyl-3,4-dicyanopyrazole (XXI).**—An ethereal solution of diazomethane was slowly added to a solution of dicyanoacetylene (3.8 g., 0.05 mole) in ether until a yellow color persisted. The temperature during the reaction was kept at about 5°. (The reaction becomes a very violent one without external cooling.) Evaporation of the solvent left a crystalline residue (6.9 g., 99%). Sublimation at 200°, 20 mm. gave white crystals, m.p. 195–196.5°. The compound is slightly soluble in boiling water.

Anal. Calcd. for $C_6H_9N_4$: C, 54.55; H, 3.05; N, 42.41. Found: C, 54.51; H, 2.88; N, 42.08.

1,2-Dicyano-1-phenylaminoethene (XXIIa).—A solution of dicyanoacetylene (1.52 g., 0.02 mole) in ether (10 ml.) was added with external cooling to a solution of aniline (1.86 g., 0.02 mole) in ether (20 ml.). It was allowed to remain at room temperature for 30 min. Evaporation of the solvent gave a tan residue (3 g., 88%). Recrystallization from chloroform yielded light yellow needles, m.p. 126.5–127.5°.

Anal. Calcd. for $C_{10}H_7N_3$: C, 70.93; H, 4.17; N, 24.83. Found: C, 71.01; H, 4.59; N, 24.52.

1,2-Dicyano-1-benzylaminoethene (XXIIb).—A solution of dicyanoacetylene (1.52 g., 0.02 mole) in ether (10 ml.) was added with external cooling to a solution of benzylamine (2.1 g., 0.02 mole) in ether (20 ml.). The solution remained at room temperature for 30 min. and was then evaporated to dryness. The residue (3.3 g., 92%) was dissolved in chloroform and filtered through aluminum oxide and finally recrystallized from the same solvent. The colorless crystals melted at 119–120°.

Anal. Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 71.79; H, 4.91; N, 22.64.

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Aromatic Cyclodehydration. L. Some Bisacridizinium Systems[1]

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Starting from 2,2′- (V), 3,3′- (VI), and 4,4′-bisbromomethylbiphenyls (VII) and using the cyclization methods previously developed, the first bisacridizinium systems have been synthesized. In addition, a bis(9-acridizinium)methane (XVI) and a bis(9-acridizinium)ethane have been prepared. In contrast to the presumably planar 9,9′-bisacridizinium system, the sterically hindered 7,7′-system has an ultraviolet absorption spectrum closely resembling that of the acridizinium ion.

The current interest in the pharmacology of bisquaternary nitrogen systems, especially with regard to their application as hypotensive, ganglionic, and neuromuscular-blocking agents,[3] made it desirable to study the possibility of synthesizing some bisacridizinium

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