Whalley, *J. Chem. Soc.,* 3722 (1955)] the NMR spectra of such a mixture should be more complicated than that obtained.

(6) W. F. Beech and H. A. Piggott, *J. Chem. Soc.,* 423 (1955).

(7) Further corroboration of this assignment is the slight shift in the opposite direction observed for the nitrile carbons. Although not as well demonstrated, steric perturbations apparently shift sp carbon resonances in a direction opposite to that found for sp[3] carbons. See, e.g., G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 130.

(8) See ref 4a and references cited therein.

(9) It is appropriate to note that the diene 1 undergoes facile polymerization to give an intractable and often dark-colored product under such diverse conditions as solution in or contact with dimethylformamide, dimethyl sulfoxide, triphenylphosphine, some samples of ethanol, acetone, acetonitrile, amine vapors, aqueous alkali, and often with alkali–metal salts of weak acids.

(10) These conditions allow a "normal" addition of diphenylamine to acrylonitrile; see, e.g., R. C. Cookson and F. G. Mann, *J. Chem. Soc.,* 67 (1949), and J. T. Braunholtz and F. G. Mann, *ibid.,* 1817 (1953).

(11) By column chromatography, a small amount of an oily cyano (by IR) product was isolated which exhibited ^{1}H NMR resonances at δ 7.0–7.6 and 1.2–1.9 (a pair of doublets superimposed on a multiplet) in a proton ratio of 3–4:1. The resonances of the nonaromatic protons are too far upfield to correspond to any conceivable structure containing Ar_2NCH_2 and HCCN groups.

(12) While both *E* and *Z* isomers of **14** are possible, the single olefinic resonance suggests that only one is present. No attempt was made to determine this further.

(13) Addition of the amine at the γ position (cf. eq 2), which may also occur, would not be observed, since proton abstraction and elimination would result in formation of the starting adduct
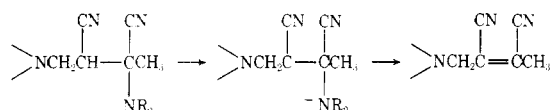

(14) Separation of these products by TLC was unsatisfactory. Analysis (by IR) of two isolated fractions showed strong cyanoenamine absorptions at ca. 2170 and 1640 cm⁻¹, but NMR studies of these same materials were equivocal. Crude product from a similar reaction of **10** and **11** with methylamine and with *tert*-butylamine also gave spectral evidence for the presence of a cyanoenamine.

(15) We are grateful to a referee for suggesting that amine participation would activate the γ nitrile to protonation and hydrolysis, yielding **16** rather than the alternative 1-(1-piperidino)-3-cyano-2-butene-2-carboxamide.

(16) Formation of a sulfonate ester by this means is unprecedented. If this structure is correct, a mechanism involving participation of the sulfonate and cyano groups may be visualized:
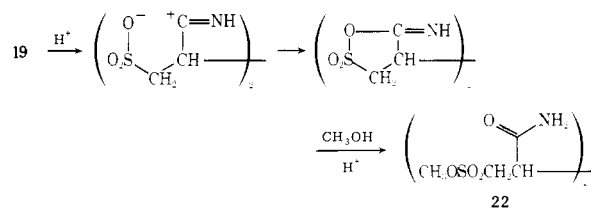
(17) Melting points (uncorrected) were recorded on a Mel-Temp apparatus; IR spectra were obtained on a Perkin-Elmer Model 137 Infracord; NMR spectra (vs. internal Me₄Si) were determined on Varian T60 and CFT20 instruments; mass spectra were recorded on a CEC 110B instrument (70 eV).

(18) There was insufficient material for a careful analysis. However, the data available give substantial confirmation of the structure.

(19) The resonances for the methyl and allylic methylene hydrogens were complicated by long-range coupling effects.

(20) (a) Although not investigated, this oil may have been largely **12**. (b) The shoulder on this resonance may be due to the presence of **12** as an impurity.

(21) The broad resonance at δ 7.5 is due to active proton exchange, while the narrow singlet at δ 7.5 represents the aldehydic and enolic protons. The two "quartets" at δ 3.7 and 4.0 are due to the methine hydrogens of respectively, and the integral ratio (1:1.4) suggests that the latter (enol form) predominates in the equilibrium.
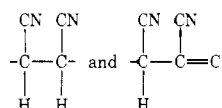
(22) Cooling the hexane extracts at −70 °C gave 0.44 g of a white crystalline solid which may have been the cyanoamide related to **24**
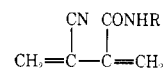
IR (KBr) 3225 (NH), 2275 (CN), 1640 and 1650 (CONH), 960, 925 (CH₂=) cm⁻¹.

Chemistry of 1,3-Butadiene-2,3-dicarbonitrile. 2. Reactions with Dienophiles

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Reaction of butadiene-2,3-dicarbonitrile (1) with diazomethane yielded the bipyrazoline 2, which lost nitrogen thermally to give the bicyclopropane 3. With ethyl diazoacetate, 1 gave the bipyrazoline 7, but the major product was an intractable solid. 1 yielded the expected (4 + 2) cycloadducts with maleic anhydride, *N*-ethylmaleimide, methyl acrylate, acrylonitrile, 1-cyanovinyl acetate, ethyl vinyl ether, divinyl ether, 1-methoxycyclohexene, dimethylisobutenylamine, and 1-methoxycyclohexene. With furan, 1 gave both 1:1 benzofuran and 2:1 dibenzofuran types of adducts; with *N*-methylpyrrole, only the corresponding 2:1 type of adduct was isolated. With dimethyl acetylenedicarboxylate, 1 gave dimethyl 4,5-dicyanophthalate.

Because of its multifunctionality, the chemistry of 1,3-butadiene-2,3-dicarbonitrile (1) is rich and varied. It undergoes reactions characteristic of a conjugated diolefin,[1,2] an activated olefin,[3,4] and a nitrile.[3] As a strongly electron-deficient diene, 1 is an example of the less-studied class of dienes which exhibit an "inverse electron demand" in Diels–Alder reactions.[5] These are considered to undergo normal (2 + 4) cycloadditions only with electron-rich dienophiles, although other types of cycloadditions, e.g., (3 + 2), are not necessarily subject to these electronic restrictions. While some Diels–Alder reactions of 1 have been reported,[4] we wish to describe here the results of our study utilizing 1 as a diene in both (3 + 2) and (4 + 2) cycloaddition processes.

(3 + 2) Cycloadditions. The diene 1 underwent facile reaction with diazomethane to give 3,3'-bi(1-pyrazolinyl)-3,3'-dicarbonitrile (2) as a mixture of (probably) two (chiral) isomers. While there were subtle differences in the ^{1}H NMR spectra of these products (only one of which was isolated in

a pure form), no attempt was made to assign specific structures. This NMR evidence also ruled out the formation of the isomeric 4,4′-bipyrazoline.


1   **2**
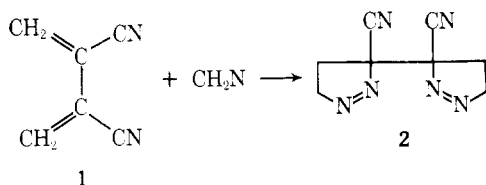
Upon heating to 100 °C, **2** underwent thermal extrusion of nitrogen to yield 1,1′-bicyclopropyl-1,1′-dicarbonitrile, **3**. Heating the crude diazomethane–diene **1** reaction product to 100 °C gave not only **3** but also 1-vinylcyclopropane-α,1-dicarbonitrile (**4**), 1-(1-propenyl)cyclopropane-α,1-dicarbonitrile (**5**), and 4-cyclopropylcyclohexene-α,1,2,4-tetracarbonitrile (**6**).[1,6] The methylated derivative **5**, the product of a

3   **4**   **5**   **6**
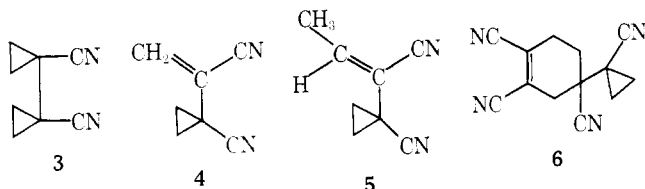
carbene insertion process, probably arose from **4** (or its pyrazoline precursor) and not by thermal rearrangement of **3** or by a secondary route during thermolysis of **2**, since decomposition of pure samples of **2** gave no spectral evidence for the presence of **5**.

Diene **1** underwent a similar reaction with ethyl diazoacetate to give a low yield of diethyl 5,5′-dicyano-5,5′-bi(2-pyrazolinyl-3-carboxylate) (**7**), the (conjugated) isomer of an


7
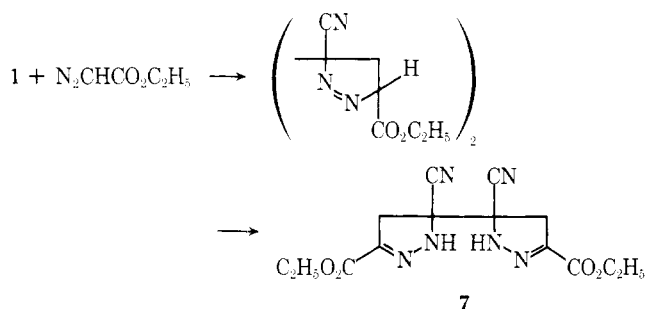
initially formed 1-pyrazoline.[7] The major product of this reaction was an almost intractable solid. Spectral data suggested the presence of NH, CN, C=N, and (ethyl) ester groups, but no reasonable single structure could be reconciled with all the data (see Experimental Section).

(4 + 2) Cycloadditions. An initial report of the failure of **1** to undergo reaction with maleic anhydride derivatives[9] was consistent with the classification of **1** as a diene with "inverse electron demand", as was a later account[4] of the types of dienophiles which do successfully add to **1** (simple olefins such as ethylene, cyclopentene, and norbornadiene; electron-rich dienophiles, such as indene, acenaphthalene, stilbene, vinylpyridine, and vinyl ethers; and *trans*-1,2-dichloroethylene). In the present work, we successfully prepared Diels–Alder adducts with these types of dienophiles and also with the electron-deficient acrylic and maleic acid derivatives. Indeed, only with strongly electronegative olefins, such as cyclobutene-1,2-dicarbonitrile (**8**), fumaronitrile, and tetracyanoethylene, and with simple olefins such as cyclohexene, vinylcyclohexene, and *cis,cis*-1,5-cyclooctadiene, were our efforts fruitless.

In some of the work with the less-reactive olefins, **8** was used as an in situ source of **1**.[10a] While little comparative study was made, with the few exceptions as noted, there was no difference in the reaction of the diene **1** itself and **8**. In the less-

reactive systems, self-dimerization[1] of **1** to 4-vinylcyclohexene-α,1,2,4-tetracarbonitrile (**9**) and *cis,cis*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile (**10**) became a major competing process.


8   **9**   **10**
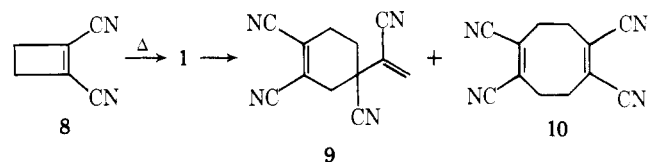
Heating a solid equimolar mixture of **1** with maleic anhydride gave a low yield of 4,5-dicyano-1,2,3,6-tetrahydrophthalic anhydride (**11**) in an exothermic process. Better yields were obtained using excess maleic anhydride, although isolation procedures resulted in hydrolysis of the initial anhydride **11** to the corresponding phthalic acid **12**. The best procedure that we found utilized the reaction of **8** with maleic anhydride in hot xylene, which gave **11** in a 50–60% yield; using no solvent gave inferior results. Interestingly, the reaction of **1** itself with maleic anhydride in hot benzene or toluene gave none of the desired Diels–Alder adduct.[10b] In a similar process, **1** with *N*-ethylmaleimide in hot THF gave a good yield of **13**, *N*-ethyl-4,5-dicyano-1,2,3,6-tetrahydrophthalimide; the product was contaminated with 15–20% of another material (not **9** or **10**) that could neither be readily removed nor (structurally) ascertained. The cyclobutene **8** with dimethyl maleate in hot xylene gave a mixture (ca. 1:1 by VPC) of (probably) dimethyl 4,5-dicyano-1,2,3,6-tetrahydrophthalate (**14**) and the dimer **9**; because separation could not be readily accomplished, confirmation of structure **14** was not attempted.

11, X = O   **12, R = H**
13, X = NC₂H₅   **14, R = CH₃**
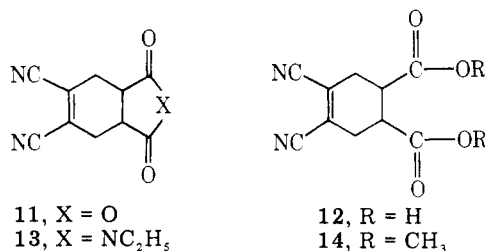
In contrast to these successful cycloaddition processes, even under prolonged reaction conditions, fumaronitrile, cyclohexene-1,2-dicarbonitrile, and tetracyanoethylene were totally inert toward diene **1**.

Condensation of methyl acrylate, acrylonitrile, and 1-cyanovinyl acetate with either diene **1** or its precursor **8** gave the expected adducts methyl 3,4-dicyano-1,2,5,6-tetrahydrobenzoate (**15**), 3,4,5,6-tetrahydrobenzene-1,2,4-tricarbonitrile (**16**), and 1,3,4-tricyanocyclohex-3-en-1-yl acetate (**17**), respectively. The yields of **15** and **16** were nearly quantitative, while the major reaction of **1** in the presence of cyanovinyl acetate was formation of the dimers **9** and **10**, resulting in an estimated 25% yield of **17**. There was no evidence for the for-

15   **16**   **17**
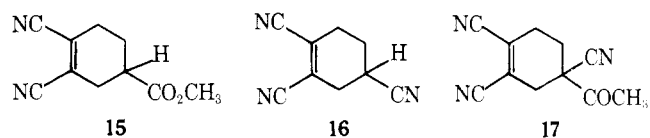
mation of cyclobutane derivatives from cyanovinyl acetate.[11] α-Chloroacrylonitrile proved to be essentially unreactive as a dienophile toward **1**, even under rigorous conditions (heating a large excess at 135 °C in cyclobutene **8**). After exhaustive work-up, the major products noted were the self-dimers **9** and **10** from diene **1**, and *cis*- and *trans*-1,2-dichlorocyclobutane-1,2-dicarbonitrile from chloroacrylonitrile;[12] there was evidence (spectral and VPC) that a small amount of the desired co-adduct may have been present in residual materials.

Styrene, with either **1** or **8**, gave a high yield of 4-phenyl-3,4,5,6-tetrahydrophthalonitrile, **18**. This existed in two crystalline modifications, a stable form, mp ca. 140 °C, and an unstable (to recrystallization) form, mp ca. 195 °C.
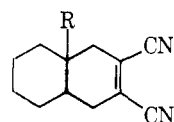
With vinyl ethers, cycloaddition occurred with **1** to give the expected adducts. Ethyl vinyl ether, divinyl ether, and 1-methoxycyclohexene gave 4-ethoxy-1-cyclohexene-1,2-dicarbonitrile (**19**), bis(3,4-dicyano-3-cyclohexen-1-yl) ether (**20**)
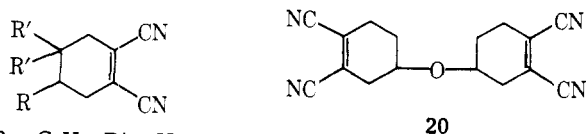
18, R = C$_6$H$_5$; R' = H
19, R = C$_2$H$_5$O; R' = H
**25**, R = (CH$_3$)$_2$N; R' = CH$_3$

20

21, R = OCH$_3$
26, R = N(CH$_3$)$_2$

(as a mixture of two isomers), and 4a-methoxy-1,4,4a,5,6,7,8,8a-octahydronaphthalene-2,3-dicarbonitrile (**21**), respectively. Interestingly, **21** was found only by utilizing **8** as an in situ source of **1** at a higher temperature than normally used (175 °C); reaction of this vinyl ether with **1** itself gave no cycloaddition, even at 135 °C.[10b] Methyl isopropenyl ether also failed to undergo reaction with **1**.

Furan, a vinyl ether as well as a diene, serves as a dienophile in its reactions with diene **1**.[4] The initial adduct, 7-oxabicyclo[4.3.0]nona-3,8-diene-3,4-dicarbonitrile (**22**), itself a vinyl ether, underwent further reaction with **1** to give 2-oxatricyclo[7.4.0.0^{3,8}]trideca-5,11-diene-5,6,11,12-tetracarbonitrile (**23**). The adduct **22** also underwent facile (2 + 2) cycloaddition with tetracyanoethylene (TCNE), giving 2-oxatricyclo[7.2.0.0^{3,8}]undec-5-ene-5,6,10,10,11,11-hexacarbonitrile (**24**). It was found also that diene **1** cycloadds to
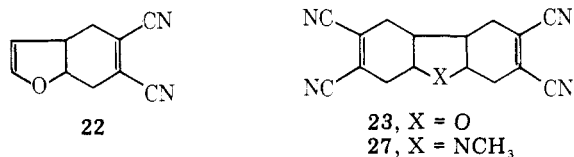
22


23, X = O
27, X = NCH$_3$
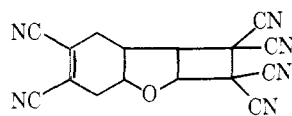
24

certain allylic ethers, e.g., those arising by reaction of furan as a diene with activated olefins.[13] On the other hand, 2,5-dimethoxy-2,5-dihydrofuran, another type of allylic ether, while apparently reacting with **1**, gave a complex mixture from which no discrete product could be isolated.

Enamines represent another class of electron-rich dienophiles that undergo cycloaddition with **1**. Dimethylisobutenylamine and 1-dimethylaminocyclohexene gave 4,4-dimethyl-5-dimethylamino-1-cyclohexene-1,2-dicarbonitrile (**25**) and 4a-dimethylamino-1,4,4a,5,6,7,8,8a-octahydronaphthalene-2,3-dicarbonitrile (**26**), respectively. Formation of **25** was very rapid, being essentially complete upon mixing at room temperature (NMR monitoring); there was also no evidence for formation of a cyclobutane that would have arisen by a (2 + 2) cycloaddition.[14] This mode of addition has been noted in reactions of enamines with electron-deficient olefins such as acrylonitrile.[15] Thus, the diene **1** underwent reaction with this enamine strictly as a diene rather than as a substi-

tuted acrylonitrile. With either of these enamines, the reaction of **1** was characterized by the development of intensely (and variously) colored mixtures. Further, the yield of **26** was temperature dependent, as were the rate of the color change and the intensity and shade of the final reaction solution; the only by-product that could be isolated was a variously colored amorphous solid. Thus, at −20 °C the gray-green reaction solution deposited 46% of the amorphous product as a dark green-black solid, and yielded 13% of **26**. At room temperature, the colors were similar, but yields of the amorphous solid and **26** were 4 and 65%, respectively. At 50 °C, the reaction mixture was dark blue; only a trace of the amorphous solid could be isolated, but the yield of **26** was high (86%). The structure of the amorphous solid was not deduced. The intense colorations of the reaction mixture suggest the formation of a charge-transfer complex of the electron-rich enamine with the electron-deficient dinitrile **1**. In the absence of further information, it is futile at this time to speculate whether this complex is actually the intermediate to either the cycloadduct or the by-product.

Pyrrole, also an enamine, is a poor diene or dienophile vis-a-vis the analogous furan. In reaction with diene **1** (from **8** in situ), it gave only intractable material. With *N*-methylpyrrole, however, slow reaction occurred to give the nitrogen analogue of **23**, 2-aza-2-methyltricyclo[7.4.0.0^{3,8}]trideca-5,11-diene-5,6,11,12-tetracarbonitrile, **27**.

Dimethyl acetylenedicarboxylate underwent slow reaction with **1** to give dimethyl 4,5-dicyanophthalate (**29**), arising by aromatization of the initially formed cycloadduct **28**, as the

28

29
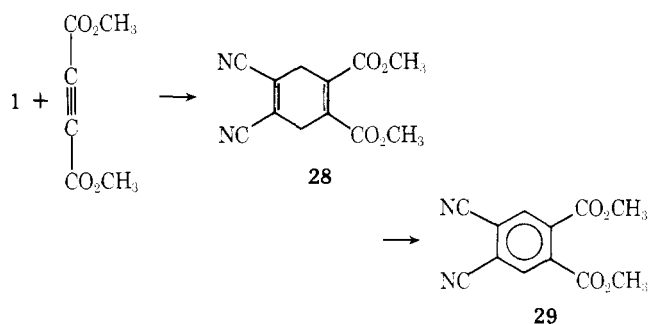
major product. A number of by-products were noted in the reaction mixture, but separation and purification problems precluded meaningful structural studies. Interestingly, diene **1** underwent cycloaddition with 1-penten-3-yne at the olefinic rather than the acetylenic bond; further details of this work will be reported separately.

Experimental Section[16]

3,3'-Bi(1-pyrazolinyl)-3,3'-dicarbonitrile (2). A filtered solution of 2.1 g (0.02 mol) of **1** in tetrahydrofuran (THF) was treated with ethereal diazomethane at room temperature until the yellow color persisted; some nitrogen was envolved during the reaction. The solution was concentrated in a stream of nitrogen to a volume of 10 mL; chilling of the solution at −70 °C gave 0.83 g (22%) of **2** as white crystals (from ether–pentane): mp 93 °C, with gentle effervescence; IR (KBr) 2250 (CN), 1565 (N=N) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.15 (t, 4, CH$_2$N=N), 2.40 (overlapping t, 4, CH$_2$); ^{13}C NMR (acetone-d_6) δ 119.4 (CN), 91.3 (quaternary C), 81.8 (CH$_2$N=N), 26.8 (CH$_2$).[17] After removal of this solid crop, ether was added to the mother liquor. Chilling at −70 °C gave another 0.29 g (8%) of the adduct **2**, mp 94 °C dec. The mother liquor was evaporated to dryness (keeping at room temperature), and the residue was taken up in ether. Addition of a little pentane and chilling at −70 °C gave white crystals, mp 67–68 °C. Recrystallization from ether gave a mixture of the adduct **2** and an isomer: mp 76–77 °C; IR (KBr) 2260 (CN), 1570 (N=N) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.06 and 5.15 (overlapping t, 4, CH$_2$ N=N), 2.2–2.8 (m, 4, CH$_2$); mass spectrum *m/e* (rel intensity) 132 (M$^+$ − 2N$_2$, 38), 131 (100), 117 (59), 105 (51), 104 (91), 66 (27).

A solution of 6.0 g (0.058 mol) of **1** in 50 mL of ether was treated in the same manner with a slight excess of ethereal diazomethane. After

2 weeks at room temperature, a small amount of insoluble polymer was removed and the solution was stripped in vacuo. Recrystallization of the residual oil from ether containing a little THF at −20 °C gave 1.88 g (17%) of white crystalline 2, mp 98 °C dec. The filtrate was stripped in vacuo, and the residual oil was triturated three times with 150-mL portions of ether; concentration and chilling of the ether solution at −70 °C gave 0.14 g of a low-melting solid. The residue from the ether extraction was taken up in THF and added slowly to 100 mL of toluene at ca. 100 °C. Evolution of nitrogen was brisk. After an hour or so at 100 °C, the toluene was removed and the residual oil was digested twice with 150-mL portions of ether. Concentration of the ether solution gave 1.11 g (9%) of 6[1] in two crops: mp 144–146 °C (from ether and THF). Removal of the ether from the filtrate gave 1–2 g of a residual oil, which was distilled under high vacuum through a short head. Analysis by VPC indicated the oily product was composed of (in the order of elution) 19, 58, and 20% of 4, 5, and 3, respectively. These products were separated by preparative VPC. 3: IR (neat) 2230 (CN) cm⁻¹; ¹H NMR (CDCl₃) δ 1.3 (A₂B₂ pattern, CH₂);[18] mass spectrum m/e (rel intensity) 132 (21), 131 (100), 117 (55), 105 (48), 104 (99), 92 (26), 90 (28). 4 (a crystalline solid): IR (KBr) 2220 (CN), 1620 (C=C), 960 (=CH₂, with overtone at 1920) cm⁻¹; ¹H NMR (CDCl₃) δ 6.30 and 6.10 (s, 2, =CH₂), 1.4–1.75 (m, 4, CH₂); mass spectrum m/e (rel intensity) 118 (45), 117 (55), 91 (100), 78 (27). 5: IR (neat) 2240 and 2220 (CN), 1640 (C=C) cm⁻¹; ¹H NMR (CDCl₃) δ 6.80 (q, 1, HC=), 2.05 (d, 3, CH₃), 1.50 (m, 4, CH₂); mass spectrum m/e (rel intensity) 132 (41), 131 (64), 117 (35), 105 (26), 104 (51), 92 (11), 90 (15).

A small sample of 2 (mp 93 °C dec) was added to toluene at 100 °C. Evolution of nitrogen was momentarily brisk. Removal of the toluene gave a pleasant-smelling oil; spectral details (IR and ¹H NMR) were practically identical with those of 3.

Diethyl 5,5′-Dicyano-5,5′-bi(2-pyrazolinyl-3-carboxylate) (7). A solution of 5.2 g (0.05 mol) of 1 in 150 mL of THF was mixed with 11.4 g (0.10 mol) of ethyl diazoacetate in 50 mL of THF, giving an immediate white solid. After several days at room temperature, the insoluble solid (3.72 g) was removed and washed several times with acetone; this product could not be purified: IR (KBr) 3330 (NH), 2250 (CN), 1725 (C=O), 1615 (C=N, ?) cm⁻¹; ¹H NMR (acetone-d₆) δ 6.6 (broad s, 3, NH?), 4.2 (q, 2, ethyl CH₂), 2.4–3.4 (m, 24), 1.3 (t, 3, CH₃). Anal. Found: C, 65.38; H, 3.98; N, 25.77.[19] The THF mother liquor was concentrated to a volume of about 25 mL and chilled at −70 °C, giving another 1.27 g of gray product that was similar (spectrally) to the initial insoluble product. The THF mother liquor was stripped and the residue was taken up in ether, giving 1.82 g of an insoluble solid (evaporation of the ether gave ca. 4 g of unreacted ethyl diazoacetate). The solid was taken up in THF, removing 0.30 g of insoluble material. From the THF solution was isolated ca. 0.3 g of 7: mp 223–225 °C (from a mixture of THF and ether); IR (KBr) 3335 (NH), 1710 (C=O), 1590 (C=N) cm⁻¹; ¹H NMR (perfluoroacetone deuterate) δ 4.95 (broad s, NH, 2), 4.43 (q, 4, ethyl CH₂), 3.55 (d, 4, ring CH₂), 1.39 (t, 6, CH₃); mass spectrum m/e (rel intensity) 278 (M⁺ − 2HCN, 13), 277 (13), 232 (27), 231 (70), 203 (29).

Reaction of 1 with Maleic Anhydride. An intimate mixture of 0.60 g (0.006 mol) of polymer-free 1 and 0.58 (0.006 mol) g of maleic anhydride, under nitrogen, was heated gently in an open flame. When an exothermic reaction ensued, the flame was removed. The dark oily product was taken up in THF, removing 0.09 g of insoluble material. Cooling the THF gave 0.10 g (8%) of 4,5-dicyano-1,2,3,6-tetrahydrophthalic anhydride (11) as off-white crystals: mp 181–184 °C dec (gaseous) (from a mixture of THF and ether); IR (KBr) 2210 (CN), 1850 and 1755 (anhydride C=O), 1600 (C=C) cm⁻¹; ¹H NMR (acetone-d₆) δ 3.95 (m, 2, CH), 2.9–3.2 (m, 4, CH₂).

In another similar experiment, using 0.58 g (0.0056 mol) of 1 and 1.97 g (0.02 mol) of maleic anhydride, slow heating under nitrogen in an oil bath gave a moderately exothermic reaction at 80 °C as the melt became turbid; the temperature rose to about 120 °C (bath at 98 °C) over a 7-min interval and then began to drop. After another 15 min, the reaction mixture was added to 50 mL of water. The mixture was stirred vigorously at room temperature for an hour or so. Filtering gave 0.87 g (53%) of solid, mp 193 °C dec (gaseous). Recrystallization from acetone containing a little hexane gave 0.26 g of white crystalline 4,5-dicyano-1,2,3,6-tetrahydrophthalic acid (12): mp 205–207 °C dec (gaseous); IR (KBr) 3030–2630 (broad), 2250 (CN), 1725 (C=O), 1640 (C=C) cm⁻¹; ¹H NMR (acetone-d₆) δ ca. 3.3 (m, 2, CH), ca. 3.0 (m, 4, CH₂). Anal. Calcd for C₁₀H₈N₂O₄: C, 54.55; H, 3.66; N, 12.72. Found: C, 54.6; H, 4.1; N, 12.4.

A mixture of 5.2 g (0.05 mol) of 8 and 4.9 g (0.05 mol) of maleic anhydride in 30 mL of xylene was heated under reflux for 3–4 h. As a crystalline solid gradually precipitated the mixture became quite dark. After cooling, the crude product (6.1 g, 60%) was recovered. This was

recrystallized from a mixture of THF and ether to give 3.5 g of 11, mp 200–202 °C.

N-Ethyl-4,5-dicyano-1,2,3,6-tetrahydrophthalimide (13). A solution of 0.45 g (0.004 mol) of 1 and 0.50 g (0.004 mol) of N-ethylmaleimide in 20 mL of THF was heated under reflux overnight; VPC showed almost complete reaction. The solvent was removed and the residue was recrystallized from a mixture of THF and ether to give 0.48 g (50%) of 13 as fibrous, pearlescent crystals (VPC indicated about 80% purity): mp 95–96 °C; IR (KBr) 2220 (CN), 1785 and 1695 (imide C=O), 1615 (C=C) cm⁻¹; ¹H NMR (acetone-d₆) δ 3.50 (q superimposed on m, 5, CHCO and CH₂N), 2.95 (m, 4, ring CH₂), 1.80 (m, 1, ?), 1.08 (t, 3, CH₃); mass spectrum m/e (rel intensity) 229 (63), 214 (100), 202 (14), 200 (26), 187 (14), 185 (55), 130 (85), 103 (44). Anal.[20] Found: C, 64.8; H, 5.5; N, 16.3.

Methyl 3,4-Dicyano-1,2,5,6-tetrahydrobenzoate (15). A solution of 5.0 g (0.048 mol) of 1 and 0.25 g of hydroquinone in 25 mL of methyl acrylate was heated with (magnetic) stirring in a sealed glass bottle at ca. 100 °C for 4 days. After cooling and removing volatile material in vacuo, the residual solid (9.8 g) was recrystallized several times from mixtures of ether with THF or toluene to give 15 as small white crystals: mp 55–57 °C; IR (KBr) 2220 (CN), 1725 (C=O), 1615 (C=C) cm⁻¹; ¹H NMR (CDCl₃) δ 3.77 (s, 3, CH₃), 2.4–2.8 (m, 5, allylic CH₂, CH), 2.1 (m, 2, CH₂); mass spectrum m/e (rel intensity) 190 (16), 163 (15), 159 (13), 131 (70), 104 (100). Anal. Calcd for C₁₀H₁₀N₂O₂: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.22; H, 5.26; N, 14.77.

A mixture of 20 g (0.19 mol) of 8 and 0.25 g of hydroquinone in 100 mL of methyl acrylate was agitated in an autoclave at 130 °C for 24 h. The resulting solution was stripped in vacuo; the residue was recrystallized at −70 °C from 150 mL of ether containing a little hexane to give 32.3 g (91%) of 15: mp 55–57 °C (another recrystallization from carbon tetrachloride gave off-white crystals, mp 57–58 °C).

3,4,5,6-Tetrahydrobenzene-1,2,4-tricarbonitrile (16). A solution of 5.0 g (0.048 mol) of 1 and 0.25 g of hydroquinone was treated with 50 mL of acrylonitrile in the manner described for the preparation of 15. After removal of the excess acrylonitrile, the residual material was triturated eight times with 250-mL portions of ether. Concentration of the ether gave several crops of 16 as crystalline solid.

A solution of 20 g (0.19 mol) of 8 and 0.25 g of hydroquinone in 100 mL of acrylonitrile was heated as described for the preparation of 15. After removal of excess acrylonitrile, the residual oil (29 g) was recrystallized at −70 °C from a mixture of ether and THF to give 24.4 g (82%) of 16 as cream-colored crystals: mp 62–64 °C (from toluene and ether); IR (KBr) 2250 and 2220 (CN), 1615 (C=C) cm⁻¹; ¹H NMR (CDCl₃) δ 2.7–3.2 (m, 1, HCCN), 2.4–2.8 (m, 4, allylic CH₂), 1.9–2.2 (m, 2, CH₂); mass spectrum m/e (rel intensity) 157 (43), 156 (31), 131 (26), 130 (89), 129 (35), 104 (100). Anal. Calcd for C₉H₇N₃: C, 68.77; H, 4.49; N, 26.74. Found: C, 69.06; H, 4.54; N, 27.00.

1,3,4-Tricyanocyclohex-3-en-1-yl Acetate (17). A solution of 5.2 g (0.05 mol) of 1, 6.0 g (0.054 mol) of 1-cyanovinyl acetate, and 0.25 g of hydroquinone in 100 mL of toluene was stirred under reflux for 40 h. Filtering the hot mixture gave 0.92 g (18%) of the dimer 10,[1] mp 255–260 °C. Cooling the filtrate to −70 °C gave another 0.11 g (2%) of 10. The mother liquor was stripped, and the residual, pale-yellow oil (9 g) was shaken with ether, causing precipitation of 2.89 g (56%) of the dimer 9,[1] mp 123–125 °C. Concentration of the ether solution to a volume of 10 mL and chilling at −70 °C gave 0.10 g (4%) of unreacted 1, mp 119–121 °C (by comparison spectrally with authentic 1). The ether was removed from the filtrate, and the residue was heated at 100 °C under high vacuum. The residual oil (1.6 g) was recrystallized twice from ether to give a solid, mp 100–101 °C, that proved (by mass and NMR spectral data) to be a mixture of 9 and 17.

A solution of 25 g (0.24 mol) of 8, 25 g (0.23 mol) of 1-cyanovinyl acetate, and 0.5 g of hydroquinone in 100 mL of xylene was heated under reflux for 42 h. A dark-colored, intractable solid, 2.38 g, was removed, and the xylene solution was cooled in an ice bath to give 2.32 g (9%) of 10, mp ca. 230 °C. Xylene was removed from the filtrate, and the residue was triturated four times with 200-mL portions of ether. The ether solution, upon concentration to a volume of 250 mL and cooling at 5 °C, gave 7.37 g of a mixture (by NMR) of 9 and 17. Recrystallization three times from benzene gave 17 (another 1.5 g was recovered from the ether-insoluble material by recrystallization from THF): mp 123–125 °C; IR (KBr) 2250 (CN), 1770 (C=O), 1640 (C=C) cm⁻¹; ¹H NMR (acetone-d₆) δ 3.33 (m, 2, allylic CH₂ β to nitrile), 2.3–2.9 (m, 4, other CH₂'s), 2.16 (s, 3, CH₃); mass spectrum m/e (rel intensity) 157 (M⁺ − C₂H₂O₂, 12), 153 (100), 128 (58), 104 (46), 60 (54).

4-Phenyl-3,4,5,6-tetrahydrophthalonitrile (18). A solution of 5.2 g (0.05 mol) of 1, 10.4 g (0.10 mol) of styrene, 0.5 g of hydroquinone, and 25 mL of toluene was heated under reflux for 48 h. After removal

of 0.5 g of insoluble polymer, the toluene was removed from the solution, leaving 10 g of a residual solid. This was recrystallized from 200 mL of boiling methanol (removing 0.04 g of insoluble polystyrene) to give a total of 8.61 g (82%) of **18**, mp 193–195 °C; recrystallization twice from methanol (Norit) gave white crystalline **18**: mp 136–138 °C (see Discussion); IR (KBr) 2220 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.1–7.4 (m, 5, aromatic CH), 2.4–2.9 (m, 5, CH and allylic CH$_2$), 1.8–2.1 (m, 2, CH$_2$); mass spectrum *m/e* (rel intensity) 208 (3.6), 104 (100). Anal. Calcd for C$_{14}$H$_{12}$N$_2$: C, 80.74; H, 5.81; N, 13.46. Found: C, 80.44; H, 5.69; N, 13.09.

A solution of 10.4 g (0.10 mol) of **8**, 40 g of styrene, 0.5 g of hydroquinone, and 35 mL of xylene was heated under reflux for 48 h. After cooling, 100 mL of ether was added. Chilling (−20 °C) gave a total of 15.6 g (75%) of **18**, mp 186–187 °C, which when recrystallized from methanol gave crystalline **18**, mp 136–137 °C (see Discussion).

4-Ethoxy-1-cyclohexene-1,2-dicarbonitrile (19). A solution of 0.76 g (0.007 mol) of **1**, 0.04 g of hydroquinone, 7.3 g of ethyl vinyl ether (freshly distilled), and 15 mL of THF was heated in a sealed tube at 80 °C for a few hours. After removal of a small amount of insoluble polymer, the solution was concentrated in a stream of nitrogen. Addition of hexane and cooling at −20 °C gave 1.20 g (93%) of **19**: mp 53–54 °C (from a mixture of ether and hexane); IR (KBr) 2175 (CN), 1615 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.60 (m, 1, HCO), 3.50 (q, 2, CH$_2$O), 2.45 (m, 4, allylic CH$_2$), 1.87 (m, 2, CH$_2$), 1.17 (t, 3, CH$_3$); mass spectrum *m/e* (rel intensity) 176 (17), 131 (14), 105 (33), 104 (15), 72 (100). Anal. Calcd for C$_{10}$H$_{12}$N$_2$O: C, 68.16; H, 6.87; N, 15.90. Found: C, 68.1; H, 6.4; N, 16.1.

Bis(3,4-dicyano-3-cyclohexen-1-yl) Ether (20). A solution of 5.2 g (0.05 mol) of **1**, 2.0 g (0.028 mol) of divinyl ether, 0.25 g of hydroquinone, and 100 mL of benzene was heated at 100 °C with agitation in an autoclave for 44 h. After removal of insoluble polymer (0.10 g) the volatiles were removed in vacuo. The residual solid (7.5 g) was taken up in toluene containing a little ether. Cooling at −20 °C gave 3.08 g (22%) of **20**, mp 175–178 °C; recrystallization once from toluene containing a little acetone and once from THF (difficultly soluble) gave **20**: mp 187–190 °C; IR (KBr) 2220 (CN), 1615 (C=C) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 4.15 (t, 2, HCO), 2.3–2.8 (m, 8, allylic CH$_2$), 1.8–2.1 (m, 4, CH$_2$); ^{13}C NMR (DMSO-d_6) δ 125.9 and 123.7 (C=C), 115.9 (CN), 66.5 (C–O), 33.2, 24.7, and 24.5 (CH$_2$, CH); mass spectrum (no volatility). Anal. Calcd for C$_{16}$H$_{14}$N$_4$O: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.91; H, 4.80; N, 21.34. After removal of this product (3.08 g, above), a total of ca. 1.0 g of crystalline product was obtained from the toluene mother liquor in several crops. Multiple recrystallization from THF and mixtures of THF and ether gave another, much-more soluble isomer of **20**: mp 159–161 °C; IR, virtually identical to the other isomer; ^{1}H NMR (acetone-d_6) δ 4.15 (quintet, 2, HCO), 2.3–2.8 (m, 8, allylic CH$_2$), 1.7–2.0 (m, 4, CH$_2$).

4a-Methoxy-1,4,4a,5,6,7,8,8a-octahydronaphthalene-2,3-dicarbonitrile (21). A solution of 5.2 g (0.05 mol) of **8** and 5.6 g (0.05 mol) of 1-methoxycyclohexene, in a pressure bottle, was heated at 170–175 °C for 12 h. After cooling, the reaction mixture was taken up in THF. After removal of a small amount of insoluble polymer, the solution was evaporated and the residue was taken up in 15 mL of ether. Cooling the solution at −70 °C gave 4.2 g (39%) of **21**, recrystallized twice from ether (Norit): mp 106–107 °C; IR (KBr) 2200 (CN), 1615 (C=C) 1075 (ether) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.24 (s, 3, CH$_3$), 1.0–2.6 (m, 13, CH$_2$, CH); mass spectrum *m/e* 216 (M$^+$), 184, 173, 142, 112 (base peak), 104, 97. Anal. Calcd for C$_{13}$H$_{16}$N$_2$O: C, 72.15; H, 7.45; N, 13.01. Found: C, 72.30; H, 7.92; N, 12.79.

Reaction of Diene 1 with Furan. A solution of 10.0 g (0.096 mol) of **1** and 0.5 g of hydroquinone in 150 mL of furan was agitated in an autoclave at 95 °C for 48 h. The resulting clear yellow solution, after removal of a little insoluble polymer, was stripped in vacuo. The residual solid (16.5 g), from ether, gave 14.8 g (90%) of **7-oxabicyclo[4.3.0]nona-3,8-diene-3,4-dicarbonitrile (22):** mp 76–77 °C (from ether, Norit) (lit.[4] mp 74.5–75 °C); ^{13}C NMR (DMSO-d_6) δ 147 (=CH-O), 128.1 and 125.4 (=CCN), 115.9 (CN), 103.4 (=CH=), 77.9 (CHO), 39.7 (CHC), 32.1 and 31.1 (CH$_2$). Anal. Calcd for C$_{10}$H$_8$N$_2$O: C, 69.75; H, 4.68; N, 16.37. Found: C, 69.31; H, 4.75; N, 16.19.

A solution of 5.2 g (0.05 mol) of **1**, 8.6 g (0.05 mol) of **22**, and 0.25 g of hydroquinone in 30 mL of xylene was stirred in a pressure bottle at 135 °C for 2 days. After removal of insoluble polymer (0.56 g, 11%), the volatiles were removed in vacuo. The residual solid (14.7 g) was taken up in THF, removing 0.20 g (4%) of insoluble **10**, mp 235–238 °C dec. The THF solution (ca. 75 mL) was treated with ether to the cloud point. Chilling at −70 °C gave a total of 5.13 g (37%) of **2-oxatricyclo[7.4.0.0^{3,8}]trideca-5,11-diene-5,6,11,12-tetracarbonitrile (23)** in 2 crops, mp ca. 175 °C. Multiple recrystallization from mixtures of THF with ether or acetone and finally from toluene (difficulty

soluble) gave **23** as off-white leaves: mp 190–192 °C; IR (KBr) 2220 (CN), 1615 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 4.4 (m, 2, HCO), 2.6 (m, 8, allylic CH$_2$), 2.3 (m, 2, CH); ^{13}C NMR (DMSO-d_6) δ 124.5 and 126.2 (C=C), 115.9 (CN), 72.0 (CHO), 29.0 and 30.9 (CH$_2$) (CH resonance obscured by the solvent); ^{13}C NMR (hexafluoroacetone deuterate) δ 75.0 (CHO), 43.5 (CH), 31.1 and 32.3 (CH$_2$) (other resonances weak or obscured by the solvent).

Solutions of 0.86 g (0.005 mol) of **22** and 0.64 g (0.005 mol) of TCNE, each in 20 mL of THF, were mixed; the yellow TCNE color disappeared rapidly, as the resulting solution became a dull orange-brown. The solution was allowed to stand at room temperature for 2 weeks, as the color again became yellow. Upon partial evaporation of the solvent, white crystals appeared. Two crops (0.37 and 0.36 g, respectively, 50% yield) of adduct were collected and recrystallized from THF to give white, crystalline **2-oxatricyclo[7.2.0.0^{3,8}]undeca-5-ene-5,6,10,10,11,11-hexacarbonitrile (24):** mp 213–215 °C dec; IR (KBr) 2260 and 2235 (CN), 1630 (C=C), 1080 (ether) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 5.35 (d, 1, *J* ~ 6 Hz, HCO adjacent to C$_4$ ring), 4.8–5.0 (m, 1, HCO adjacent to C$_6$ ring), 4.10 (d, 1, *J* ~ 6 Hz, HC adjacent to C$_4$ ring), ca. 3.5 (m, 1, HC adjacent to C$_6$ ring), ca. 3.0 and 2.5 (2m, 4, CH$_2$); mass spectrum (dec, giving a spectrum indicative of a mixture of furan, TCNE, and **1**).

4,4-Dimethyl-5-dimethylamino-1-cyclohexene-1,2-dicarbonitrile (25). A solution of 1.00 g (0.0096 mol) of **1** in 30 mL of THF, filtered to remove a trace of polymer, was mixed with 1.06 g (0.011 mol) of redistilled dimethylisobutenylamine. The resulting light yellow solution, stirred in a water bath under nitrogen at 50 °C, rapidly changed color to successively darker shades of green. After 90 min, the solution was concentrated. Addition of hexane and cooling at −20 °C gave 1.41 g (72%) of **25** in two crystalline crops; the product was purified by several recrystallizations from hexane (Norit): mp 101.5–102 °C; IR (KBr) 2250 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.3–2.6 (m, 5, CH, CH$_2$), 2.30 (s, 6, CH$_3$N), 1.03 (s, 6, CH$_3$C); ^{13}C NMR (CDCl$_3$) δ 125.2 and 125.0 (C=C), ca. 112 (CN), 64.1 (CHN), 43.5 and 43.0 (CH$_3$N), 34.6 (quaternary C), 23.0 and 27.7 (CH$_3$C), 24.9 (CH$_2$); mass spectrum *m/e* (rel intensity) 203 (23), 188 (27), 160 (100). Anal. Calcd for C$_{12}$H$_{17}$N$_3$: C, 70.94; H, 8.37; N, 20.69. Found: C, 71.0; H, 8.4; N, 20.6.

4a-Dimethylamino-1,4,4a,5,6,7,8,8a-octahydronaphthalene-2,3-dicarbonitrile (26). A filtered solution of 0.57 g (0.0055 mol) of **1** in 50 mL of THF, in a bath at −50 °C, was stirred while a solution of 1.51 g (0.012 mol) of 1-dimethylaminocyclohexene in 10 mL of THF was added over a 5-min period. The intensely yellow solution, upon being allowed to warm slowly, became dark yellow at −30 °C, orange at −20 °C, amber at −10 °C, and then deep red. After 3 days at −20 °C, the dark gray-green solution was evaporated, and the residue was gently boiled in ether. An amorphous solid (0.84 g), which could not be purified, was removed; IR (KBr) 2170 and 2270 (broad, CN) cm^{-1}. The filtrate was mixed with hexane and chilled at −20 °C to give 0.24 g (13%) of a solid. Recrystallization from ether (Norit) gave white, crystalline **26**: mp 106.5–107.8 °C (the melt liberated dimethylamine above ca. 115 °C); IR (KBr) 2220 (CN), 1640 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.2–2.6 (m, 4, allylic CH$_2$), 2.20 (s, 6, CH$_3$N), 1.2–2.0 (m, 9, CH$_2$, CH); ^{13}C NMR (CDCl$_3$) δ 125.2 and 123.0 (C=C), 116.0 (CN), 56.0 (CN), 34.6 (CH$_3$N), 34.3 and 32.5 (allylic CH$_2$), 29.9, 24.8, 24.4, and 22.3 (CH$_2$), 29.0 (CH); mass spectrum *m/e* 299 (M$^+$).

2-Aza-2-methyltricyclo[7.4.0.0^{3,8}]trideca-5,11-diene-5,6,11,12-tetracarbonitrile (27). A solution of 10.4 g (0.10 mol) of **8** and 7.2 g (0.089 mol) of *N*-methylpyrrole in 50 mL of benzene was stirred under reflux for 19 days. After removal of a small amount of insoluble material from the hot mixture, the solution was stripped finally under high vacuum to remove unreacted **8**. The residual oil was taken up in ether to give 1.70 g (total yield from several crops, 2.25 g) of **27** as off-white crystals: mp 194–195 °C dec (from acetonitrile); IR (KBr) 2220 (CN), 1630 and 1600 (C=C); ^{1}H NMR (acetonitrile-d_3) δ 3.0–3.2 (m, 2, HCN), 2.50 (m, 8, allylic CH$_2$), 2.33 (s, 3, CH$_3$), ca. 2.1 (m, 2, HCC); mass spectrum *m/e* (rel intensity) 289 (0.4), 27 (100).

Dimethyl 4,5-Dicyanophthalate (29). A filtered solution of 1.35 g (0.013 mol) of **1**, 5 mL of dimethyl acetylenedicarboxylate, and 0.05 g of hydroquinone in 50 mL of benzene was stirred under reflux for 3 weeks. Insoluble polymer (0.23 g, 17%) and benzene were removed from the mixture, leaving 7.3 g of an oil. This was taken up in ether and several crops of crystalline solid were obtained. Recrystallization from acetone at −70 °C gave white crystals of unknown structure (homogeneous by TLC): mp 203–204 °C; IR (KBr) 2220 (CN, w), 1760 and 1740 (CO, w and s), 1640 (C=C) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.7–3.9 (two pairs of doublets, *J* ~ 5 Hz, 5) 3.65 (s, 1), 3.47 (s, 1), 3.2–3.5 (m, 1), 2.78 (s, 1, reinforcing water impurity resonance, and thus may be exchangeable hydrogen impurity); mass spectrum *m/e* (rel intensity) 272 (0.9), 241 (1.8), 213 (11), 142 (6), 127 (5), 111 (15), 59 (83),

31 (100). After removal of this product, the ether mother liquor was chilled at −70 °C, giving 1.2 g of a yellow solid. This was dissolved in carbon tetrachloride, to remove a small amount of the insoluble dimer **9**. The solvent was removed, and the solid was purified further by HPLC (eluting with a mixture of 20% cyclohexane in chloroform), giving white, crystalline **29**: mp 135–137 °C (from ether and a little methylene chloride at −70 °C); IR (KBr) 2250 (CN), 1725 (C=O) cm⁻¹; ¹H NMR (CDCl₃) δ 8.18 (s, 2, aromatic H), 4.00 (s, 6, CH₃); mass spectrum m/e (rel intensity) 244 (3.5), 213 (100).

Registry No.—1, 19652-57-4; **2** isomer 1, 64784-29-8; **2** isomer 2, 64784-30-1; **3**, 64760-88-9; **4**, 64760-90-3; **5**, 64760-91-4; **6**, 64760-89-0; **7**, 64760-92-5; **8**, 3716-97-0; **9**, 41793-19-5; **10**, 53399-95-4; **11**, 64760-93-6; **12**, 64760-95-8; **13**, 64760-94-7; **15**, 64760-97-0; **16**, 64760-98-1; **17**, 64760-99-2; **18**, 64761-00-8; **19**, 64760-80-1; **20** isomer 1, 64760-81-2; **20** isomer 2, 64760-96-9; **21**, 64760-82-3; **22**, 64760-83-4; **23**, 64760-84-5; **24**, 64760-86-7; **25**, 64760-85-6; **26**, 64760-87-8; **27**, 64760-79-8; **19**, 64754-35-4; diazomethane, 334-88-3; ethyl diazoacetate, 623-73-4; maleic anhydride, 108-31-6; N-ethylmaleimide, 128-53-0; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; 1-cyanovinyl acetate, 3061-65-2; styrene, 100-42-5; ethyl vinyl ether, 109-92-2; divinyl ether, 109-93-3; 1-methoxycyclohexene, 931-57-7; furan, 110-00-9; TCNE, 670-54-2; dimethylisobutenylamine, 6906-32-7; 1-dimethylaminocyclohexene, 13815-46-8; N-methylpyrrole, 96-54-8; dimethyl acetylenedicarboxylate, 762-42-5.

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(6) The origin of **6** is obscure. It could have arisen from reaction of the dimer of **1** with diazomethane,¹ but this dimer was not normally present in the samples of **1** utilized in this study. Alternatively, reaction of **1** with **4** or its

pyrazoline precursor is also a plausible route to **6**. No further study of these possibilities was made.
(7) Isomerization of initially-formed 1-pyrazolines was noted also with similar products from cyclobutene-1,2-dicarbonitrile⁸ and cis,trans-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile.¹
(8) R. L. Cobb and J. E. Mahan, J. Org. Chem., **42**, 2597 (1977).
(9) D. Belluš and C. D. Weis, Tetrahedron Lett., 999 (1973).
(10) (a) Diene **1**, the valence tautomer of **8**, is prepared conveniently by thermolysis of **8**⁴ (see ref 1 for further comments on the conversion of **8** to **1** in hot solvents). (b) A study that would clarify the observed differences in the reactivity of **1** and **8** was not made. However, as a referee also noted, the rate of diene formation from **8** in hot xylene may be slow enough so that the amount of **1** produced at any one time is small relative to the concentration of the dienophile. Cycloaddition rather than polymerization is thus favored. No attempt to effect reactions of **1** itself with dienophiles above ca. 140 °C was made, since self-dimerization to **9** and **10** is a major process under these conditions. Optimum reaction conditions were not determined, and, except for the example noted (preparation of **21**), the reactions of **8** were also carried out at or below ca. 140 °C.
(11) Cyanovinyl acetate has been used as a probe in determining the dual reactivity occasionally observed in diene cycloadditions, i.e., (2 + 2) processes to cyclobutanes or (2 + 4) processes to cyclohexenes; see, e.g., J. C. Little, J. Am. Chem. Soc., **87**, 4020 (1965), and P. D. Bartlett and K. E. Schueller, ibid., **90**, 6077 (1968).
(12) The thermal dimerization of α-chloroacrylonitrile to 1,2-dichlorocyclobutane-1,2-dicarbonitrile has apparently not been previously observed.
(13) For example, the furan adduct of cis,trans-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile underwent reaction with TCNE.¹
(14) A (2 + 2) cycloaddition from equimolar amounts of **1** and the enamine would give a product with NMR resonances at δ ca. 6–7. The resonance at δ ca. 6.4 for **1** completely disappeared, and this region became and remained essentially clear of even trace (at 70X amplification) resonances.
(15) (a) I. Fleming and J. Harley-Mason, J. Chem. Soc., 2165 (1964); (b) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, J. Org. Chem., **29**, 801 (1964).
(16) Melting points, uncorrected, were obtained in a Mel-Temp apparatus; IR spectra were recorded on a Perkin-Elmer Model 137 Infracord; NMR spectra (vs. internal Me₄Si) were obtained on Varian T60, XL100, and CFT20 instruments; mass spectra were determined on a CEC 110B spectrometer (70 eV).
(17) Meaningful elemental analyses could not be obtained because of the slight instability of the product. However, spectral data adequately confirmed the structure.
(18) The complexity of the NMR spectrum suggests that this might be the meso product. Intuitively, a less complicated spectrum would be expected for the d,l isomer pair.
(19) Calcd. for C₁₈H₁₃N₆O: C, 65.64; H, 3.98; N, 25.52.
(20) Calcd. for C₁₂H₁₁N₃O₂: C, 62.87; H, 4.84; N, 18.33. The impurity in this product was not either of the dimers **9** or **10** (by IR and VPC) and remains unknown.

Quinazolines and 1,4-Benzodiazepines. 84.¹ Synthesis and Reactions of Imidazo[1,5-a][1,4]benzodiazepines

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Condensation of 1,4-benzodiazepines having a N-nitrosomethylamino group in the 2 position with a primary nitroalkane led to the nitroalkylidene derivatives 3 and 4. These nitro compounds were converted to imidazo[1,5-a]-[1,4]benzodiazepines by a sequence of steps involving catalytic reduction, condensation with triethyl orthoacetate, and oxidation with activated manganese dioxide. A variety of chemical transformations of the imidazobenzodiazepine 9 and the nitromethylene derivative 3 are described.

The synthesis of the pharmacologically active triazolo[4,3-a][1,4]benzodiazepines² revived interest in benzodiazepines with a heterocyclic ring fused to the 1,2 position and a review of such compounds has recently been published.³ We report the synthesis and reactions of imidazo[1,5-a]-[1,4]benzodiazepines, compounds which differ in their ring fusion from their more easily accessible isomers described in the literature.⁴

The synthesis of the title compounds was facilitated by the discovery of the carbon–carbon bond forming reaction of the nitrosoamidines **2** with carbanions.⁵ Thus, the condensation of the nitrosoamidine **2** (Scheme I), obtained by nitrosation

of the corresponding amidines **1**, with the anion of a nitroalkane led to the 2-nitroalkylidene benzodiazepines **3a–c** and **4**. Other methods of preparing compounds **3** have subsequently been developed in our laboratories and were published recently.⁶,⁷

The stereochemistry assigned to the nitroalkylidenes is based on NMR data and in particular on the large chemical shift (δ 11–12 ppm) of the proton in the 1 position which may be due to intramolecular hydrogen bonding.

Catalytic hydrogenation of the nitro compounds **3b** or **3d** over Raney nickel afforded the 2-aminomethylbenzodiazepine **5**, characterized as a dimaleate salt. Heating the amine **5** with