in the range 190–240 °C or temperature programmed from 200 to 280 °C at 4 °C/min. Isothermal retention indices (IRI)[18,19] were determined in the temperature range 180–240 °C. Electron impact mass spectra were obtained on a Du Pont 21-492B gas chromatograph–mass spectrometer system consisting of Varian 2740 gas chromatograph interfaced to the mass spectrometer via a single stage glass jet separator. All spectral data reported here were acquired from samples of the pure compound by direct probe insertion into the ion source. When mixtures did occur, the components were separated on a 1.83 m × 2 mm i.d. glass column packed with 3% Se-30 on 100/120 mesh Gas Chrom Q and operated under the conditions described above. Mass spectra were recorded for all peaks of interest. Exact masses and most probable elemental compositions of the major ions in **4**, **1d**, and levamisole (**1c**) were obtained from high-resolution mass spectra run on a JEOL JMS-01SG-2 mass spectrometer. Compounds were tested for alkylating ability with *p*-nitrobenzylpyridine (NBP) as previously described.[2]

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Chemistry of Cyclobutene-1,2-dicarbonitrile. 2. Cycloadducts

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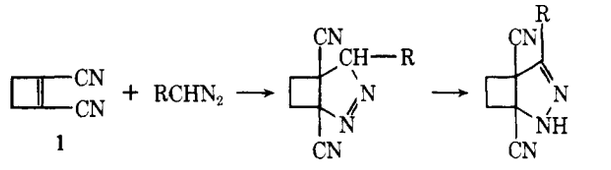
Cyclobutene-1,2-dicarbonitrile (1) undergoes [3 + 2] cycloaddition with diazomethane to give 2,3-diazabicyclo[3.2.0]hept-2-ene-1,5-dicarbonitrile (**2**) and with ethyl diazoacetate to give ethyl 3,4-diazabicyclo[3.2.0]hept-2-ene-2-carboxylate (**4**). Upon irradiation, 1 dimerizes to *anti*-tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarbonitrile (**7**). The preparation of acid, amide, and ester analogues of **7**, by dimerization and solvolytic processes, is described. In the presence of acrylonitrile, α-chloroacrylonitrile, 1-cyanovinyl acetate, dimethyl maleate, and furan, irradiation of 1 yields mixtures of **7** and bicyclo[2.2.0]hexane-1,2,4-tricarbonitrile (**15**), 2-chlorobicyclo[2.2.0]hexane-1,2,4-tricarbonitrile (**16**), 2-(1,2,4-tricyanobicyclo[2.2.0]hexyl) acetate (**17**), dimethyl 1,4-dicyanobicyclo[2.2.0]hexane-2,3-dicarboxylate (**18**), and 3-oxatricyclo[5.2.0.0^{2,6}]non-4-ene-1,7-dicarbonitrile (**19**), respectively. The adduct **18** undergoes a thermal stereospecific cycloreversion to give dimethyl 3,6-dicyano-2,6-octadiene-1,8-dioate (**21**). Spectral data suggesting similar cycloreversions for the other related adducts are noted.

The strain present in the cyclobutene ring system allows cycloaddition processes to occur with cyclobutene-1,2-dicarbonitrile[1] (**1**) at conditions under which analogous cyclohexenes and cyclooctenes react only sluggishly or not at all.[2] Since results concerning the normal Diels–Alder reaction of **1** with conjugated dienes have been reported recently,[1] this paper will describe only our observations regarding the reactions of cyclobutene **1** with diazoalkanes to give [3 + 2] cycloadducts and with activated olefins to give [2 + 2] cycloadducts, the latter being a photoinitiated process.

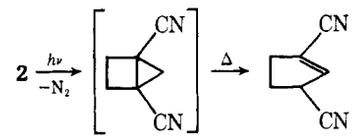
The reaction of diazomethane with **1** occurred readily at room temperature to give the known[3] adduct 2,3-diazabicyclo[3.2.0]hept-2-ene-1,5-dicarbonitrile (**2**). A similar reaction with ethyl diazoacetate gave ethyl 3,4-diaza-1,5-dicyanobicyclo[3.2.0]hept-2-ene-2-carboxylate (**4**), arising by a [1,3]



1 **2**, R = H; **3**, R = $CO_2C_2H_5$ **4**, R = $CO_2C_2H_5$

prototropic rearrangement of the initially formed adduct **3**. The evidence for the rearrangement to **4** included the presence of strong absorption bands for the NH and C=N groups, but none for the –N=N– group, in the infrared region (at ca. 3280, 1700, and 1560 cm^{-1}, respectively), and the lack of a resonance for the hydrogen α to an azo function (ca. δ 5.5) in the ^{1}H NMR spectrum. Energetically, the rearranged form **4** may be favored over **3** because of the conjugation introduced between the carbonyl and the imino groups.

Because of the favored hydrazone structure, **4** was photolytically and (relatively) thermally stable; at 175 °C for 24 h, there was no evolution of nitrogen, although only 20% of **4** was recovered. On the other hand, the adduct **2** was photolabile in the presence of a photosensitizer (acetone), undergoing a

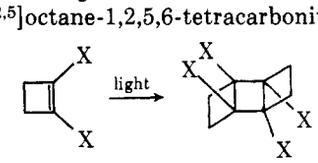


5 **6**

slow evolution of nitrogen. The major organic product isolated, by preparative VPC, was cyclopentene-1,3-dicarbonitrile (**6**), probably arising via thermolysis of initially formed bicyclo[2.1.0]pentane-1,3-dicarbonitrile (**5**). Although no comparisons were made, the dinitrile adduct **2** is apparently appreciably more stable than the related ester dimethyl 2,3-diazabicyclo[3.2.0]hept-2-ene-1,5-dicarboxylate,[3,4] since the latter ester reportedly[3] undergoes facile and rapid loss of nitrogen in the absence of a sensitizer, conditions under which the dinitrile **2** was remarkably stable (a 70% recovery after 72 h irradiation).

The cyclobutene **1** is a strong absorber of light at ca. 234 nm (ϵ_{max} 12 200 in acetonitrile).[2,5] This, coupled with the strain present in the cyclobutene ring system,[6] allows photoinitiated [2 + 2] cycloaddition of **1** with suitable olefins to occur.

Cyclobutene **1** undergoes self-dimerization[8] to yield *anti*-tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarbonitrile (**7**). We



1, X = CN; **8**, X = CO_2CH_3; **9**, X = CO_2H; **10**, X = $CONH_2$
7, X = CN; **11**, X = CO_2CH_3; **12**, X = CO_2H; **13**, X = $CONH_2$

studied this reaction, using both sunlight and a medium-pressure (unfiltered) mercury vapor lamp as light sources. In sunlight (in a quartz apparatus), the reaction was extremely slow, with a 20% conversion after several weeks; this process was not subject to photosensitization, since comparable con-

Table I. Photocatalyzed Dimerization of Cyclobutene-1,2-dicarbonitrile (1)[a]

Solvent	Sensitizer	Time, h	Mol % yield (7)
Methanol	None	120	12
Acetone	Acetone	24	75
Benzene	None	144	17
Benzene	Benzophenone[b]	48	56
Benzene	Benzophenone[b]	96	85
Methylene chloride	Benzophenone[b]	40	82
Methylene chloride	Benzophenone[b]	96	89

[a] Used an unfiltered medium-pressure mercury vapor lamp through a quartz window at ca. 15–20 °C. Concentration of 1 in solvent was varied from ca. 0.3–1.2 M with no apparent effect on yield. [b] Ca. 10–15 mol % relative to 1.

versions were obtained in either methylene chloride or in acetone as solvents. With the "artificial" light source, however, the reaction was practical only in the presence of a sensitizer (Table I). The extreme insolubility of the dimer 7 prevented acquisition of NMR data. However, a solution in trifluoromethanesulfonic acid (which remained colorless for several hours) allowed NMR spectral data of the protonated species to be obtained.[9] Thus, in this solvent, 7 exhibited a broad multiplet centered at ca. δ 2.75 (from Me_4Si). On a higher resolution instrument, this multiplet was resolved into a pair of doublets, $J \sim 8.2$ Hz (chemical shift between hydrogens is 0.53 ppm).[10] The ^{13}C NMR spectrum consisted of three resonances, at δ 26.8, 44.4, and 111.9, for methylene, quaternary, and protonated nitrile carbons, respectively.

For comparative purposes, several derivatives of the nitrile 1 were also photodimerized. Thus, the dimethyl ester 8 gave good yields (even in sunlight) of the tricyclic ester 11,[8,11] the acid 9 gave the dimer 12, and the amide 10 gave the tricyclic amide 13. The latter derivative showed remarkable thermal stability. It could be sublimed unchanged under high vacuum at about 300 °C; at the same temperature but at 20 mm pressure, sublimation was accompanied by slow cycloreversion and loss of ammonia to *cis,cis*-1,5-cyclooctadiene-1,2,5,6-tetracarboxdiimide.[2] In structural studies, these derivatives were all interrelated chemically (Scheme I). Thus treatment

Scheme I

nitrile 7 $\xrightarrow[H_2O]{H_2SO_4}$ amide 13 $\xrightarrow{HNO_2}$ acid 12 $\xrightarrow{CH_2N_2}$ ester 11

$\xrightarrow{NH_3}$ amide 13

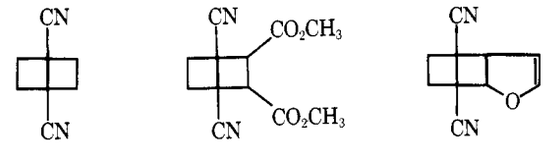
of the nitrile 7 with sulfuric acid followed by water or methanol gave the amide 13, identical with that prepared by dimerization of 10. Although this amide 13 resisted further hydrolysis under mild conditions, it could be converted to the acid 12 by treatment with nitrous acid. The latter, with diazomethane, gave the tricyclic ester 11, identical with that prepared from 8. The tricyclic ester 11 could be converted to the amide 13 by reaction with methanolic ammonia; this was a slow process, requiring several weeks at room temperature. There was no evidence of cycloreversion to cyclooctadienes[8] occurring during any of these reactions, run, to be sure, under very mild conditions.

The cyclobutene 1 also underwent [2 + 2] cycloaddition with other olefins. The parent derivative, bicyclo[2.2.0]hexane-1,4-dicarbonitrile (14), from the reaction with ethylene has been reported.[12] In our hands, cyclobutene-1,2-dicarbonitrile underwent benzophenone-sensitized cycloadditions with acrylonitrile, α-chloroacrylonitrile, 1-cyanovinyl acetate, dimethyl maleate, and furan to give bicyclo[2.2.0]hexane-1,2,4-tricarbonitrile (15), 2-chlorobicyclo[2.2.0]hexane-1,2,4-tricarbonitrile (16), 2-(1,2,4-tricyanobicyclo[2.2.0]hexyl) acetate (17), dimethyl 1,4-dicyanobicyclo[2.2.0]hexane-2,3-dicarboxylate (18), and 3-oxatricyclo[5.2.0.$0^{2,6}$]non-4-ene-1,7-dicarbonitrile (19), in variable yields (Table II). Self-dimerization of cyclobutene 1 to give 7 was a competing process in all of these reactions. In addition, the reaction with furan gave the normal [4 + 2] Diels–Alder adduct 20, 9-oxatricyclo[4.2.$1^{2,5}$.0]non-3-ene-1,6-dicarbonitrile,[1,2] as the major product. With 2-chloro-, 2-bromo-, and 2,3-dichloromaleic anhydrides, there was little indication that any of the desired bicyclic anhydrides were obtained. Fumaronitrile and dimethyl acetylenedicarboxylate also failed to undergo (photo) cycloaddition with the cyclobutene 1. Spectral evidence suggesting the presence of endo–exo isomers was obtained from some of the reaction products (see Experimental Section), and these isomers of the adduct 15 from acrylonitrile were actually isolated.

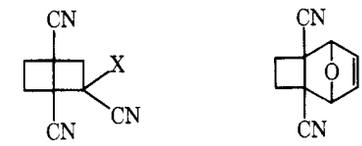
Table II. [2 + 2] Cycloadducts with Cyclobutene-1,2-dicarbonitrile[a]

Reactant	Mol % yield: Dimer 7	Mol % yield: Codimer
Ethylene		57 (14)[b]
Acrylonitrile	42	40 (15)
α-Chloroacrylonitrile	28	8 (16)
1-Cyanovinyl acetate	42	46 (17)
Dimethyl maleate	81	10 (18)
Furan	<10	<10 (19)[c]
2-Chloromaleic anhydride	19	0–1
2-Bromomaleic anhydride	16	0–1
2,3-Dichloromaleic anhydride	21	0–1
Fumaronitrile	11	0
Dimethyl acetylenedicarboxylate	39	0

[a] See Experimental Section for conditions. [b] From ref 12. [c] Adduct 20 isolated in 15–20% yield.

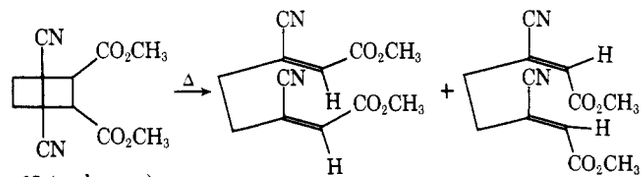


14 18 19



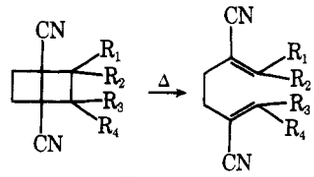
15, X = H
16, X = Cl
17, X = $OCOCH_3$

20



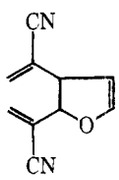
18 (endo, exo) 21a 21b

Scheme II

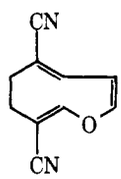


From adduct	Registry no.	R_1	R_2	R_3	R_4	Product hexadiene, absorption for group, cm^{-1} =CH	C=C	$=CH_2$	Registry no.
14[12]	52999-04-9	H	H	H	H		1632	945	52999-05-0
15	62198-07-6 (endo) 62249-47-2 (exo)	CN	H	H	H	3120	1630	960	62198-12-3
16	62198-08-7	CN	Cl	H	H		1640, 1600	960	62198-13-4
17	62198-09-8 (endo) 62249-48-3 (exo)	CN	OAc	H	H		1635	960	62198-14-5
18	62198-10-1 (endo) 62249-49-4 (exo)	CO_2CH_3	H	CO_2CH_3	H	3070	1640		62198-15-6 (*E*) 62198-16-7 (*Z*)
19	62198-11-2	(See Discussion)				3110	1630, 1615	950	62198-18-9

products synthesized in this work. However, the adduct **18** from dimethyl maleate, as an endo–exo mixture, was smoothly converted upon heating to dimethyl (*E,E*)- and (*Z,Z*)-3,6-dicyano-2,6-octadiene-1,8-dioate (**21a** and **21b**). Significantly, there was no evidence for the presence of the *E,Z* isomer of **21**. This cycloreversion was demonstrated qualitatively on a micro scale with several of the other adducts. Thus after holding the samples at their melting points (120–130 °C) for several minutes, infrared spectral examination clearly revealed the presence of strong absorptions for conjugated olefinic and vinylidenic unsaturation, suggesting that the cleavage occurred in the direction shown in Scheme II. The strong vinylidenic absorption (at 950 cm^{-1}) for the cycloreversion product from the furan adduct **19** suggests that the cleavage, not unexpectedly, occurred in the other direction, to give **22a** rather than the alternative **22b**.



22a



22b

Experimental Section[13]

2,3-Diazabicyclo[3.2.0]hept-2-ene-1,5-dicarbonitrile (2). A solution of 3.5 g of cyclobutene **1** in ether was treated with an excess of ethereal diazomethane at room temperature; there was no immediate discharge of color upon addition, but after a short induction period a rapid reaction occurred with the simultaneous precipitation of a white solid. After several hours standing, the latter was collected to give **2** (3.92 g) as fine, white crystals: mp 134–136 °C (from tetrahydrofuran at −70 °C) (lit.[3] mp 139–140 °C); IR (KBr) 2270 (CN), 1565 cm^{-1} (N=N); ^1H NMR[14] (acetone-d_6) δ 5.37 (s, CH_2N=N, 2) 2.2–3.2 (m, CH_2, 4); mass spectrum *m/e* (rel intensity) 146 (1.2, M^+), 118 (50, M − N_2), 91 (100, 118 − HCN). Anal. Calcd for $C_7H_6N_4$: C, 57.52; H, 4.14; N, 38.34. Found: C, 57.52; H, 4.07; N, 37.55.

Ethyl 3,4-Diaza-1,5-dicyanobicyclo[3.2.0]hept-2-ene-2-carboxylate (4). To a solution of 5.2 g of **1** in 100 mL of tetrahydrofuran was added 6.7 g of ethyl diazoacetate. After the solution was allowed to stand at room temperature for several weeks, concentration to a volume of about 25 mL gave 4.0 g of **4** as white crystals: mp 146–148 °C, melt dec at 180 °C (from tetrahydrofuran); IR (KBr) 3280 (NH), 2220 (CN), 1760 (C=O), 1640 cm^{-1} (C=N); ^1H NMR (acetone-d_6) δ 10.07 (broad s, NH, <1 H), 4.41 (quartet, ester CH_2, 2), 3.0 (s, ring CH_2, 4), 1.36 (t, CH_3, 3); mass spectrum *m/e* (rel intensity) 218 (59, M^+), 190 (29, M − N_2), 172 (32), 145 (30), 118 (22).

Photolytic Decomposition of Adduct 2. A solution of 1.0 g of **2** in ca. 150 mL of acetone, in a quartz apparatus, was irradiated with a medium-pressure (unfiltered) mercury vapor lamp for several days at room temperature. Nitrogen was evolved at the rate of ca. 2mL/h (has buret; similar treatment of a solution of **2** in methylene chloride gave no nitrogen) for 50 h or so, then no more during another 115 h. The amber-colored solution was stripped under reduced pressure. Recrystallization of the residual solid at −70 °C gave a total of 0.44 g of recovered unreacted **2**; nothing more could be crystallized. Removal of the solvent and taking up the residual oil in ether allowed removal of a small amount of an insoluble material. After evaporation of the ether, preparative VPC allowed isolation of cyclopentene-1,3-dicarbonitrile (**6**): IR (neat) 3080 (CH=), 2230 and 2240 (CN), 1620 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 6.5 (m, CH=, 1), 3.6–4.0 (m, CH, 1), 2.0–3.0 (m, CH_2, 4); mass spectrum *m/e* (rel intensity) 118 (20, M^+), 91 (100, M − HCN), 64 (12, M − 2HCN).

General Procedure for Photocatalyzed Reactions of 1 and Analogues. The reactor was similar to those available commercially (e.g., from Ace Glass Co., No. 6522); it consisted essentially of a jacketed (for coolant circulation) tube provided with adaptors for a condensor and a concentric (inner) quartz thimble (for the lamp) and with a glass frit at the bottom for introduction of nitrogen. Irradiation was by a 100-W medium-pressure Hanovia mercury vapor immersion lamp. The liquid capacity of the assembled reactor was about 160 mL. The reactions were carried out at room temperature by using tap water in the cooling jacket and with a slow nitrogen sweep for agitation.

Tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarbonitrile (7) (See Table I). Irradiation of a solution of 20 g of **1** and 5 g of benzophenone in 150 mL of methylene chloride for 4 days gave 17.8 g of **7** as an insoluble, crystalline mass: mp 183–184 °C (with subsequent resolidification of the melt at 190 °C or so; the resulting solid, mp 255–257 °C) (lit.[8] mp 182 °C; IR (KBr) 2260 (CN), 805 cm^{-1} (very strong); ^1H and ^{13}C NMR, see Discussion; mass spectrum *m/e* (rel intensity) 208 (9, M^+), 181 (5, M − HCN), 104 (100, $C_6H_4N_2$), 77 (87, 104 − HCN). Alternatively, allowing a solution of 25 g of freshly distilled **1** in 500 mL of methylene chloride to stand in the sunlight in a stoppered quartz flask for 4 weeks afforded 3.78 g of **7** as well-formed, insoluble crystals.

Tetramethyl Tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarboxylate (11). A. Irradiation of 8. A solution of 5.10 g of the ester **8** in 150 mL of acetone, upon irradiation for 24 h, gave 2.40 g (two crops) of the dimer **11**, mp 134–136 °C (from ether at −70 °C) (lit.[11b] mp 135–136 °C).

B. Esterification of 12. A solution of the dimer acid **17** (prepared from the amide **13**, see below) in a mixture of ether and tetrahydrofuran was treated with an excess of ethereal diazomethane. After the solution was allowed to stand for 1 h at room temperature, the solvents were removed in vacuo; the residual oil was recrystallized from ether at −70 °C to give **11**, mp 132–133 °C, identical with the material prepared by dimerization of **8**.

Tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarboxylic Acid (12). A. Irradiation of 9. A suspension of 2.0 g of the acid **9** and 0.5 g of benzophenone in methylene chloride, with agitation by a slow nitrogen purge, was irradiated in the photochemical reactor for 4 days. The mixture remained heterogeneous, although solution–precipitation appeared to be occurring. The solid (0.41 g), mp 247–250 °C, was removed and another 0.37 g was recovered from the methylene chloride solution. Both crops were combined and recrystallized (with difficulty) from a mixture of acetone and ether at −70 °C: mp 259–261 °C

(giving a red melt with gaseous decomposition); IR (KBr) broad absorptions at ca. 3000, 2650, 1800, 1425, and 1200–1300 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.4–2.9 (A_2B_2 m, CH_2); ^{13}C NMR (acetone-d_6) δ 177.12 (CO_2H), 53.89 (quaternary C), 26.18 (CH_2). Anal. Calcd for $C_{12}H_{12}O_8$: C, 50.71; H, 4.26. Found: C, 50.44; H, 3.93.

B. Hydrolysis of 13. The amide **13** (see below) (0.5 g) was added to 17 mL of 75% sulfuric acid in a 100-mL beaker at 35 °C. After the mixture was stirred at room temperature for 10–15 min (solution was incomplete), 4.0 g of sodium nitrite was added, a few crystals at a time, over a 2-h period, keeping the beaker covered with a watch glass. After about 3 g of the salt had been added, each addition caused the appearance of a transient green color. The mixture was stirred at room temperature overnight and was then poured over 50 mL of crushed ice. A white solid appeared, but redissolved as the ice melted. The solution was concentrated to a volume of 15–20 mL under high vacuum and at room temperature. Cooling the residual viscous solution to −20 °C gave 4.5 g of insoluble sodium sulfate. The filtered solution was taken up in a mixture of isopropyl alcohol and tetrahydrofuran. This solution was washed once with aqueous saturated salt solution, once with saturated calcium chloride solution, and again with the salt solution. The organic phase was stripped in vacuo, and the residue was stripped several times from toluene at 35–40 °C to dry. Recrystallization of the residue from a mixture of ether, tetrahydrofuran, and pentane gave the dimer acid **12** as white crystals, mp 265–268 °C, identical with the product obtained by dimerization of **9**.

Tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarboxamide (13). A. Irradiation of 10. A suspension of 2.0 g of **10**[1,3] (prepared by the cautious addition of a solution of **1** in concentrated sulfuric acid to ice[2]) in benzene was irradiated under nitrogen agitation for 4 days. The resulting solid product (1.90 g), after washing with benzene and water, was treated with 700 mL of boiling water in several portions to give 1.28 g of the insoluble amide **13**, mp 358–360 °C.

B. Hydrolysis of 7. The nitrile **7** (0.5 g) was added to 10 mL of concentrated sulfuric acid; solution was complete in 30 min. After 2 days at room temperature, the colorless solution was added slowly to 150 mL of methanol, giving the insoluble amide **13** immediately. This product, 0.66 g, totally insoluble in hot water, methanol, acetic acid, and dimethylformamide, was "purified" by dissolving in 5 mL of sulfuric acid, filtering, and reprecipitating with 150 mL of methanol to give snow-white crystals of **13**: mp 355 °C dec with loss of ammonia; IR (KBr) 3230 and 3130 (NH_2), 1665 and 1610 cm^{-1} ($CONH_2$). Anal. Calcd for $C_{12}H_{16}N_4O_4$: C, 51.43; H, 5.75; N, 19.99. Found: C, 51,43; H, 5.82; N, 19.97.

C. Ammonolysis of 11. A solution of the ester **11** (0.50 g) in 250 mL of methanol was saturated with ammonia at 25–30 °C. Prolonged standing at room temperature in a stoppered flask caused the slow appearance of a crystalline solid. After 9 weeks, the solid was collected to give 0.08 g of **13**, mp 351–353 °C dec, identical with the samples prepared by the other methods.

Bicyclo[2.2.0]hexane-1,2,4-tricarbonitrile (15) was prepared by irradiation of a solution of 5 g of **1**, 10 mL of freshly distilled acrylonitrile, and 2 g of benzophenone in methylene chloride for 44 h. After removal of 2.06 g of insoluble **7**, the solvent and other volatiles were removed under reduced pressure at room temperature. The residual semisolid was taken up in ether to give 3.06 g of a tan-colored solid, mp 103–105 °C. This was taken up in 100 mL of acetone, removing another 0.05 g of insoluble **7**. The acetone solution was concentrated to about one-third volume and chilled at −70 °C to give off-white solid, mp 107–109 °C. Fractional crystallization from mixtures of tetrahydrofuran and ether gave *endo*- and *exo*-**15** as the less and more soluble components, respectively. *endo*-**15**: mp 119–121 °C; IR (KBr) 2260 (CN), 1450, 1235 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.48 (dd, $J \sim 8$, 11 Hz, CH, 1), 2.5–3.7 (m, CH_2, 6); mass spectrum *m/e* (rel intensity) 157 (19, M^+), 130 (9.1, M − HCN), 103 (12, M − 2HCN), 66 (100, C_4H_4N). *exo*-**15**: mp 127–128 °C; IR (KBr) 2260 (CN), 1450, 1180 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.17 (dd, $J \sim 8$, 8 Hz, CH, 1), 2.6–3.3 (m, CH_2, 6); mass spectrum *m/e* (rel intensity) 157 (19, M^+), 130 (12, M − HCN), 103 (16, M − 2HCN), 66 (100, C_4H_4N).

2-Chlorobicyclo[2.2.0]hexane-1,2,4-tricarbonitrile (16) was prepared by irradiation of a solution of 5 g of **1**, 15 g of freshly distilled α-chloroacrylonitrile, and 2 g of benzophenone in methylene chloride for 45 h. After removal of 1.01 g of insoluble **7**, the solution was worked up as described under the preparation of **15** to give another 0.31 g of **7** and 0.74 g of **16** (from ether at −70 °C). Recrystallization once from a mixture of acetone and ether and then from tetrahydrofuran and ether gave **16** as off-white crystals: mp 129–131 °C dec; IR (KBr) 2260 (CN), 756 cm^{-1} (C–Cl); ^1H NMR (acetone-d_6) δ 3.4–4.2 (AB quartet, CH_2CCl, 2), 2.6–3.4 (m, CH_2, 4); mass spectrum *m/e* (rel intensity) 191, 192, 193 (8.1, 1.1, 3.0, M^+), 153 (17, M − HCl, 2 H), 129 (10, M − HCl, CN), 128 (13), 66 (100, C_4H_4N).

2-(1,2,4-Tricyanobicyclo[2.2.0]hexyl) acetate (17) was prepared by irradiation of a solution of 5 g of **1**, 21 g of α-acetoxyacrylonitrile, and 2 g of benzophenone in methylene chloride for 2 days. Removal of 1.75 g of insoluble **7** and treatment as described for the preparation of **15** gave another 0.35 g of **7** and (from ether at −70 °C) 1.08 g of **17**, mp 105–108 °C. Evaporation of the ether mother liquor and recrystallization of the residue from carbon tetrachloride at −20 °C gave another 3.75 g of **17**, mp 105–108 °C. Recrystallization of the combined crops three times from acetone and ether gave **17** as off-white crystals: mp 118–120 °C; IR (KBr) 2270 (CN), 1760 and 1220 cm^{-1} (ester); ^1H NMR ($CDCl_3$ + acetone-d_6) δ 2.3–3.8 (m, 6), 2.25 (2 s, CH_3, 3);[15] mass spectrum *m/e* (rel intensity), 215 (small, M^+), 146 (2.4), 118 (9.4), 80 (67), 52 (41), 43 (100).

Dimethyl 1,4-dicyanobicyclo[2.2.0]hexane-2,3-dicarboxylate (18) was prepared by irradiation of a solution of 25 g of **1**, 75 mL of dimethyl maleate, and 5 g of benzophenone in methylene chloride for 5 days. After removal of 7.58 g of insoluble **7**, the reaction solution was stripped at room temperature. Chilling of an ethereal (100 mL) solution of the residual oil at −70 °C gave 5.06 g of dimethyl fumarate. After removal of this, the ether solution was stripped again at room temperature and the residual oil was extracted twice with a 1:1 mixture of cyclohexane and ether. The residual insoluble oil was taken up in carbon tetrachloride and stored in the refrigerator. Long standing (2 weeks) caused slow crystallization of **18**: 0.75 g, mp 116–117 °C (from acetone); IR (KBr) 2270 (CN), 1755, 1740, and 1240 cm^{-1} (ester);[16] ^1H NMR ($CDCl_3$) δ 3.89 and 3.82 (2 singlets, CH_3, 6)[15] (overlapping with) 3.8–4.4 (3–4 single peaks, CH, 2), 2.4–3.2 (m, CH_2, 4); mass spectrum *m/e* (rel intensity) 248 (18, M^+), 233 (9, M − CH_3), 217 (9, M − OCH_3), 189 (30, M − CH_3CO), 157 (25, 189 − CH_3O, H), 145 (34), 131 (35), 104 (22), 59 (100, CH_3CO_2).

After removal of the solid **18**, the carbon tetrachloride solution was stripped, and the residual oil was distilled through a short-path column under high vacuum at 100 °C (steam bath) to remove dimethyl maleate. The residual semisolid was taken up in ether, and an insoluble material was removed. The latter was recrystallized several times from a mixture of tetrahydrofuran and ether and then from acetone at −70 °C to give dimethyl 3,6-dicyano-2,6-octadiene-1,8-dioate, probably the *Z,Z* isomer, **21a**,[17] as white crystals: mp 109–111 °C; IR (KBr) 3070 (HC=), 2220 (CN), 1720 and 1205 (ester), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 6.50 (s, HC=, 2), 3.86 (s, CH_3, 6), 2.76 (s, CH_2, 4); mass spectrum *m/e* (rel intensity) 248 (7, M^+), 233 (8, M − CH_3), 217 (8, M − CH_3O), 189 (27, M − CO_2CH_3), 59 (100, CH_3CO_2). The ether-soluble portion of the residue from the original distillation, after removal of the ether, was extracted several times with hot cyclohexane. The insoluble residue was recrystallized from ether containing a little tetrahydrofuran to give impure **21**, mp 90–95 °C. The cyclohexane solution was evaporated and the residual material was recrystallized once from a mixture of ether and pentane and once from ether and tetrahydrofuran, both at −70 °C, to give dimethyl 3,6-dicyano-2,6-octadiene-1,8-dioate, probably the *E,E* isomer, **21b**,[17] as white crystals: mp 124–126 °C; IR (KBr) identical with that for **21a**; ^1H NMR ($CDCl_3$) δ 6.55 (s, HC=, 2), 3.89 (s, CH_3, 6), 3.12 (s, CH_2, 4); mass spectrum essentially identical with that for **21a**.

3-Oxatricyclo[5.2.0.0^{2,6}]non-4-ene-1,7-dicarbonitrile (19). A solution of 5 g of **1**, 25 mL of furan, and 2 g of benzophenone in methylene chloride was irradiated for 2 days. The solvent was removed, and the residual amber-colored oil was mixed with 35 mL of ether. After removal of insoluble **7** (0.20 g), the ether solution was chilled at −70 °C to give 1.53 g of a white, crystalline solid. This was recrystallized from tetrahydrofuran containing a little ether at −70 °C to give **3-oxatricyclo[4.2.1^{2,5}.0]non-3-ene-1,6-dicarbonitrile**[1,2] (**20**) as the first crop, mp ca. 145 °C. A second crop of crystals, collected after adding more ether to the mother liquor, was recrystallized twice from a mixture of ether and tetrahydrofuran at −70 °C to give **19** as soft, white plates: mp 119–120 °C; IR (KBr) 3120 (HC=), 2250 (CN), 1620 (C=C), 1140, 1040 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.75 (m, OCH=, 1), 5.34 (s, HCO?, 1), 5.27 (d, HC=?, 1), 4.08 (m, HCC=, 1), 2.5–3.0 (A_2B_2 pattern, CH_2, 4); mass spectrum *m/e* (rel intensity) 172 (37, M^+), 145 (17, M − HCN), 144 (28), 143 (41, M − CHO), 120 (86, M − 2CN), 117 (35), 116 (53), 104 (22, $C_6H_4N_2$), 68 (29, furan).

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Registry No.—**1**, 3716-97-0; **2**, 62198-17-8; **4**, 62198-19-0; **6**, 62198-20-3; **7**, 53399-93-2; **8**, 1128-10-5; **9**, 16508-05-7; **10**, 23335-15-1; **11**, 62198-21-4; **12**, 62198-22-5; **13**, 62198-23-6; **20**, 62249-50-7; diazomethane, 334-88-3; ethyl diazoacetate, 623-73-4; acrylonitrile,

107-13-1; α-chloroacrylonitrile, 920-37-6; α-acetoxyacrylonitrile, 3061-65-2; dimethyl maleate, 624-48-6; furan, 110-00-9.

References and Notes

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(9) Although this solvent certainly affected the cyano groups in **7**, the integrity of the carbon skeleton remained basically unchanged for at least several hours.
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(13) Melting points, determined in a Mel-Temp apparatus, are uncorrected; IR spectra were determined on a Perkin-Elmer Model 137 Infracord; NMR spectra were determined (vs. internal Me_4Si) on Varian T60 and XL100 instruments; mass spectra were obtained on a CEC 110B instrument (70 eV), and data include some pertinent fragments produced.
(14) The ^{13}C NMR spectrum ($CDCl_3$) was not entirely satisfactory because of low solubility and some decomposition during the time required for data acquisition. However, two and possibly three methylene resonances (the latter quite far upfield and probably representing the $CH_2N{=}N$ carbon), and one due to a quaternary carbon were found (at ca. δ 29.0, 30.2, 51.5, and 50.5, respectively).
(15) The double resonance for the methyl hydrogens suggests the presence of endo, exo isomers.
(16) The double carbonyl absorption at 1755 and 1740 cm^{-1} suggests the presence of endo, exo isomers.
(17) The structures are assigned tentatively on the basis of the methylene hydrogen resonances at δ 2.76 and 3.12, deshielded by a *trans*- and *cis*-methoxycarbonyl group, respectively.

Dimers of Cyclobutene-1,2-dicarbonitrile and 1,3-Butadiene-2,3-dicarbonitrile. Preparation and Chemistry

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Thermal dimerization of 1,3-butadiene-2,3-dicarbonitrile (**2**) produces mixtures of 4-vinyl-1-cyclohexene-α,1,2,4-tetracarbonitrile (**3**) and *cis,cis*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile (**4**). The **3**:**4** product ratio is temperature independent, but both the rate of dimerization and the product ratio are affected by solvent polarity. The photodimer of cyclobutene-1,2-dicarbonitrile, *anti*-tricyclo[4.2.0.$0^{2,5}$]octane-1,2,5,6-tetracarbonitrile (**5**), undergoes stereospecific thermal cycloreversion to *cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile (**6**), which is itself thermally labile, yielding **4** at higher temperatures. Both **4** and **6** isomerize at 280 °C to **7a**, bicyclo[3.3.0]oct-2-ene-1,2,5,6-tetracarbonitrile. Upon irradiation, **4** and **6** yield **3** and the isomeric, highly stable tricyclo[3.3.0.$0^{2,6}$]-octane-1,2,5,6-tetracarbonitrile (**8**). By virtue of the strain present in the molecule, **6** undergoes reactions preferentially at the trans double bond. It acts as a dienophile toward butadiene, furan, and diene **2**, undergoes [2 + 3] cycloaddition with diazomethane and ethyl diazoacetate, gives double-bond addition products with (basic) ethanol, piperidine, and hydrogen (catalyst), isomerizes to **4** in the presence of bromine or iodine, and forms complexes with certain transition metal reagents. The dimer **3** adds bromine and undergoes cycloaddition with **2** and diazomethane at the exocyclic double bond. Diazomethane also slowly adds to **4**. The furan adduct of **6** is converted photolytically to **8** and thermally to **6**, and also exhibits dienophilic reactivity.

Cyclobutene-1,2-dicarbonitrile (**1**) and its valence tautomer, 1,3-butadiene-2,3-dicarbonitrile (**2**), exhibit a rich and varied chemistry. As a part of our investigation of these reactive, strongly electron-deficient systems, a number of dimers of the general formula $[C_4H_4(CN)_2]_2$ were prepared. We found some of these dimers themselves to have diverse and interesting chemical and physical properties. Particularly studied were thermal and photochemical behavior, cycloaddition, addition, and hydration processes, and reactions with transition metals. While preliminary accounts from another laboratory of related work have appeared,[1] we wish to report additional observations in this area.

Electron-deficient dienes related to **2** are known to be labile toward dimerization. For example, both methyl 1,3-butadiene-2-carboxylate[2] and 1,3-butadiene-2-carbonitrile[3,4] are greatly prone, even at room temperature, to undergo a Diels–Alder dimerization to yield substituted vinylcyclohexenes. The diene **2**, in our experience, was much more stable than this. It did undergo dimerization to 4-vinyl-1-cyclohexene-α,1,2,4-tetracarbonitrile[1b] (the VCH dimer **3**), upon prolonged heating in various solvents in the presence of a polymerization inhibitor (e.g., hydroquinone). The rate of dimerization was, of course, a function of temperature and, if the temperature was high enough to permit the cycloreversion of **1** to occur (100 °C or so), the process was essentially the same using either diene **2** or the cyclobutene **1** as an in situ source of **2**. Thus in aromatic hydrocarbon solvents, the time required for complete dimerization varied from 2 weeks or so at 80 °C (several months at room temperature) to 24 h at 140 °C (5 h at 165 °C[1a]). Yields of **3** were consistently 75–80%, regardless of the temperature; the only significant by-product was the isomeric *cis,cis*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile[1] (the COD dimer **4**), formed in 15–20% yields. The latter dimer has been prepared by another method[1c,d] (see