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

(1) D. Belluš, K. von Bredow, H. Sauter, and C. D. Weis, *Helv. Chim. Acta*, **56**, 3004 (1973).
(2) R. L. Cobb and J. E. Mahan, unpublished.
(3) H. Prinzbach and H.-D. Martin, *Chimia*, **23**, 37 (1969).
(4) R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **37**, 2418 (1972).
(5) D. Belluš and C. D. Weis, *Tetrahedron Lett.*, 999 (1973).
(6) Underscoring the importance of the ring strain factor in this system, cyclohexene-1,2-dicarbonitrile[2] and dimethyl cyclohexene-1,2-dicarboxylate[7] undergo no similar photoreactions, in contrast to the slightly strained (and reactive) analogue cyclohexene-1,2-dicarboxylic anhydride.[7]
(7) D. C. Owsley and J. J. Bloomfield, *J. Org. Chem.*, **36**, 3768 (1971).
(8) D. Belluš, H.-C. Mez, G. Rihs, and H. Sauter, *J. Am. Chem. Soc.*, **96**, 5007 (1974).
(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.
(10) We are indebted to Professor L. M. Stock for these measurements (on a 270-MHz instrument).
(11) (a) E. Vogel, O. Roos, and K. H. Disch, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962); (b) D. Seebach, *Chem. Ber.*, **97**, 2953 (1964); (c) I. Lantos and D. Ginsburg, *Tetrahedron*, **28**, 2507 (1972).
(12) D. Belluš and G. Rist, *Helv. Chim. Acta*, **57**, 194 (1974).
(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

R. Lynn Cobb,* John E. Mahan, and Darryl R. Fahey

Phillips Petroleum Company, Bartlesville, Oklahoma 74004

Received December 21, 1976

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

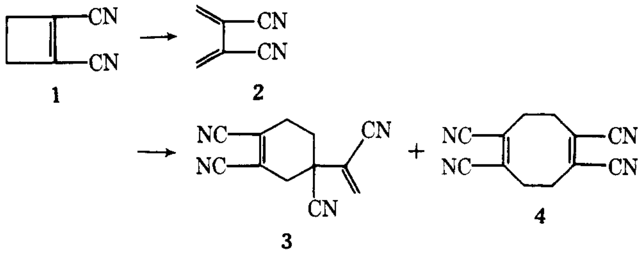


Table I. Dimerization of Butadiene-2,3-dicarbonitrile (2)

Solvent	Reaction conditions		% conversion	% selectivity	
	Temp, °C	Time, h		3	4
Acetonitrile	80	168	100	>95	<5
Benzene	80	336	90	80	15–20
Hexane	120[a]	65	(6)	(60–70)	(30–40)

[a] Used cyclobutene-1,2-dicarbonitrile (1) as an in situ source of 2.

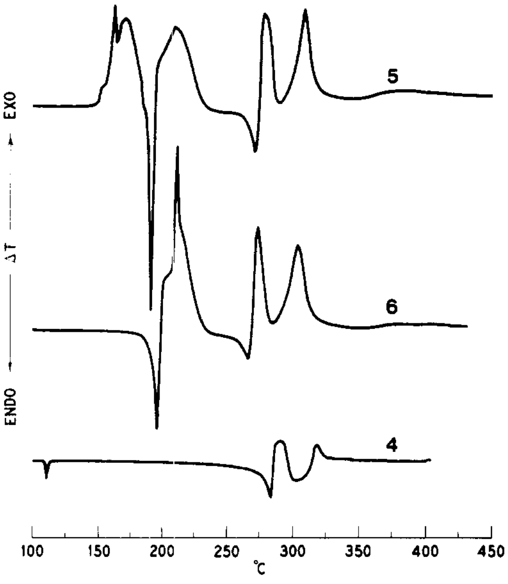
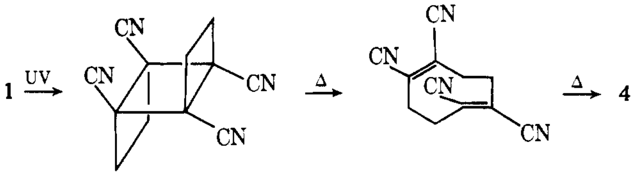


Figure 1. Differential thermal analyses (DTA) of dimers 4, 5, and 6 (ca. 5 mg sample under nitrogen, open pan, 10 °C/min).

below, also), but it was not previously reported as a product of the thermal dimerization of 2.[1a,b] While the relative yields of 3 and 4 were not affected by temperature (nor by starting with either 1 or 2), solvent polarity played a large role in both product distribution and rate of dimerization. Thus, some qualitative observations (Table I) demonstrated that a polar solvent favored both a more rapid dimerization and the formation of 3 (because of the low conversions and solubility problems, the results using hexane are only very approximate).

The VCH dimer 3 might arise by a concerted [2 + 4] Diels–Alder cycloaddition. However, the solvent effect noted suggests that there may be a polar or a charge-separated transition state. The origin of the COD dimer 4 in this thermal process is not so clear; there was no 3 $\rightleftharpoons$ 4 interconversion under these reaction conditions. Because of the large solvent effect on both the rate and the product distribution, it is improbable that the two dimers arise from a common intermediate. COD dimers formed during the thermal dimerization of butadienes are normally considered to arise from an initial [2 + 2] cycloadduct, a *cis*-1,2-divinylcyclobutane. Whether such was involved in this instance is far from certain, since no evidence for such an intermediate (or its trans isomer) could be found. For the present, the origin of 4 in this thermal process remains mechanistically obscure.[5]

Because of ease of polymerization upon irradiation, no interesting photochemistry of diene 2 was found. However, photolytic dimerization of 1 afforded high yields of *anti*-tricyclo[4.2.0.0^{2,5}]octane-1,2,5,6-tetracarbonitrile (5).[1d,7] It has been reported previously that this dimer undergoes a remarkably clean [$_\sigma 2_a$ + $_\sigma 2_s$] cycloreversion to give high yields of *cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile (6).[1d,8] We independently made a study of this latter process, and found that the best method for the preparation of 6 was the prolonged reflux of a suspension of the (insoluble) dimer 5 in benzene, in which 6 has reasonable solubility; under these conditions, there was practically no formation of the isomer 4. Other solvents, such as acetone, tetrahydrofuran (THF), and carbon tetrachloride, were not as satisfactory for this transformation. Indeed, there were indications that acetone and THF took part to some minor extent in formation of byproducts.[9] The 5 → 6 conversion could also be carried out in the solid state,[1d] e.g., by sublimation under high vacuum at 175 °C, but this was not as satisfactory in our hands as the "solution" method. This conversion was sensitive to temperature, as expected, since 6 was thermally unstable and could be converted easily to the stable 4. Thus, while the tricyclooctane 5 gave practically only 6 in hot benzene (in 3 days), refluxing 5 in xylene for 40 h gave 69% of 4, and heating 5 in dichlorobenzene at 175 °C for 40 h gave 4 almost quantitatively.



5 6

Differential thermal and gravimetric analyses (DTA/DGA) of these dimers suggested temperatures at which some of these processes occurred. Thus, DTA revealed that 5 did not melt (no endothermic peak, see Figure 1), but underwent a sharp (exothermic) transformation to 6 at ca. 163 °C, perhaps accompanied by a secondary, slower isomerization to 4 at ca. 170 °C. The dimer 6, after melting at ca. 190 °C (sharp endotherm), was converted to 4 at 200–210 °C, which then melted at 270 °C. The latter, above its melting point, underwent other transformations (at 280, 310, and ca. 375 °C), but these have not been related to any particular process. The pure dimer 6 was stable to 190–195 °C (Figure 1), where it melted; transformations above 200 °C were similar to those noted for 5. The COD dimer 4 underwent an endothermic transformation at 110 °C (Figure 1), which, though intriguing, has neither been rationalized nor studied further.[10] Otherwise, it was stable until it melted at ca. 290–295 °C; this is appreciably higher than the melting point previously reported for 4 (230–231 °C[1d]) and normally observed in this work (ca. 260–270 °C; however, cf. footnote 25). Above this temperature, this dimer exhibited the same exothermic maxima as did 5 and 6. TGA revealed that there were fragmentation processes occurring at higher temperatures. Although the dimers 5 and 6 showed some minor loss of weight below 175 °C or so, they were remarkably free of fragmentation to about 250–275 °C. The nature of the lower temperature fragmentation is unknown, although the dimer 6 released some hydrogen cyanide upon storage. Rapid degradation occurred above 275 °C or so, with total weight loss of ca. 50, 60, and 15%, respectively, for 4, 5, and 6 (the much lower weight loss for 6 is inexplicable). Except as noted below, no discrete products arising from high-temperature degradation could be isolated or characterized. It may be of significance that no phthalonitriles could be de-

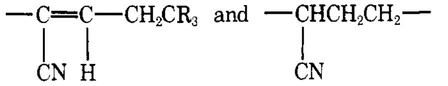
Table II. Irradiation of Dimers 3, 4, and 6

Dimer	Irradiation source[a]	Solvent, sensitizer[b]	Product % yield[c] 2	3	4	8
3	Hg	CH_2Cl_2, BP		96		
4	Sun (Pyrex)	Acetone			>90	+[d]
	Sun (quartz)	CH_2Cl_2			>90	
	Sun (quartz)	Acetone			>55	+[d]
	Hg	Acetone				30
	Hg	CH_3CN, BP		25		6
6	Sun (Pyrex)	Acetone			70	+[d]
	Sun (quartz)	Acetone			54	10
	Hg	Acetone				~30
	Hg	Benzene, BP		12	44	28
	Hg	CH_3CN, BP	12	12		5

[a] Hg is medium-pressure mercury vapor lamp, unfiltered, in quartz apparatus. [b] BP is benzophenone. [c] Isolated yields. [d] Detected but not isolated in a pure state.

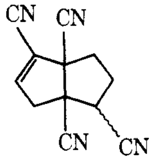
tected (by HPLC) among the thermal decomposition products; in theory, at least, these could have arisen by loss of hydrogen cyanide and acrylonitrile from 4 or 6 (and would approximate the 50% weight loss found by TGA for 4).

Since thermal analyses suggested that other products might be formed at higher temperatures, these processes were studied further. Heating any of the dimers 4, 5, or 6 for a short time under nitrogen at 275 °C, followed by high-vacuum sublimation, gave the product 7, probably as a mixture of epimers. The yield was higher starting from 4 (75% crude yield, vs. 10% or so from 6), so this dimer may be the actual precursor. Based entirely upon spectral data, the structure **7a**, bicyclo[3.3.0]oct-2-ene-1,2,5,6-tetracarbonitrile, rather than the isomeric **7b**, bicyclo[4.2.0]oct-2-ene-1,2,5,6-tetracarbonitrile, has been assigned the product. Of these two possibilities, 270-MHz ^1H NMR (Figure 2)[12] suggests the presence of

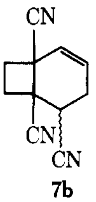


$$-\underset{CN}{C}=\underset{H}{C}-CH_2CR_3 \text{ and } -\underset{CN}{C}HCH_2CH_2-$$

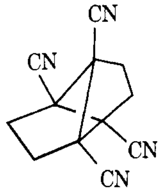
linkages, thus pointing to **7a** rather than **7b**. The vinyl hydrogen (at δ 7.23) consists of a triplet ($J \sim 3$ Hz). The next hydrogen (δ 4.11), due to the HCCN group, is somewhat more complex than might be anticipated, but it is assumed that this may be due to the presence of mixed epimers (this is the asymmetric center in either **7a** or **7b** not "fixed" stereochemically that may give rise to epimers). The "allylic" methylene hydrogens (at δ 3.55) appear as a classical AB quartet pattern with further coupling ($J \sim 3$ Hz) to the vinylic hydrogen; this pattern specifically excludes **7b**, since the corresponding hydrogen in this would be split not only by the vinylic proton but also by that on the sp^3 carbon bearing the cyano group, leading to a far more complicated appearance. The methylene hydrogens in the saturated C_5 ring are split into two complex groups, resonances corresponding to three protons centered at ca. δ 2.6 and that of one (obscured somewhat by the solvent peak) at ca. δ 2.1. No thermal analyses were made of 7; thus, any pattern of its formation or decomposition in the DTA of the dimers 4 or 6 (Figure 1) was not deduced.



7a



7b



8

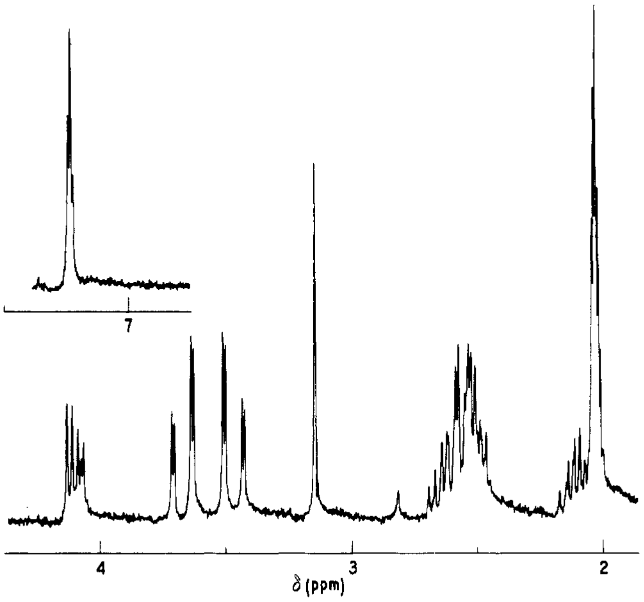
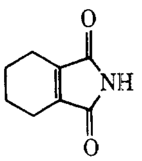


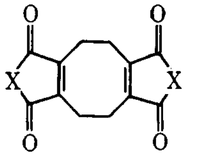
Figure 2. 270-MHz ^1H NMR spectrum of 7 in CD_3CN (saturated solution; measured downfield from internal tetramethylsilane); resonance at δ ca. 2.0 is due to solvent impurity, that at δ ca. 3.15 due to water.

Interesting degradations were also found during investigation of the photolytic behavior of some of these dimers (Table II). The VCH dimer 3 was essentially stable to UV irradiation. However, both of the COD dimers 4 and 6, depending upon the conditions, underwent extensive rearrangement and degradation. The major processes that were recognized included the conversion of 6 into 4 (isolated in good yield when carried out in benzene, in which 4 is insoluble), isomerization of either 4 or 6 to 3, degradation of 6 to the diene 2 (photolytically labile toward polymerization), and isomerization of either of the COD dimers 4 or 6 to a new dimer, tricyclo[3.3.0.0^{2,6}]octane-1,2,5,6-tetracarbonitrile (8) (see below for a more convenient synthesis of 8). There was no evidence for the processes 6 → 5 (the reverse of the thermal cycloreversion), 4 → 5, or 4 → 6, nor for the formation of 7 under any irradiation conditions. As observed for the thermal conversion of 5 to 6, the use of "reactive" solvents (i.e., THF or acetone) for the photolytic reactions resulted in the formation of byproducts incorporating these solvent molecules.[13]

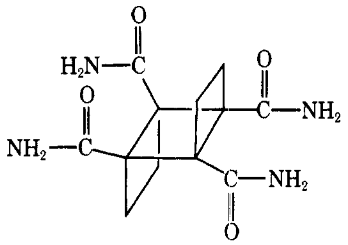
While there was no evidence for the formation of 8 among the thermal transformation products of 4 or 6 just noted,[14] there is ample precedent for the photochemical formation of tricyclo[3.3.0.0^{2,6}]octanes from 1,5-cyclooctadienes.[15] The structure assigned to the dimer 8 was consistent with both its chemical behavior and spectral analyses. It was a remarkably



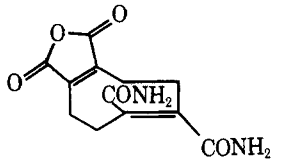
9



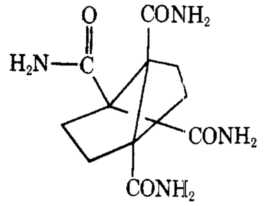
10a, X = NH
b, X = O



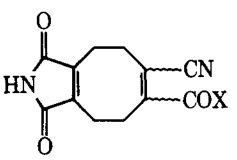
11



12



13



X = OH, NH₂

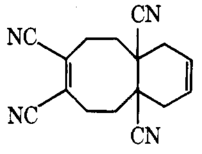
14

stable compound, surviving unchanged for at least 30 min at 300 °C (its tetraamide **13** was stable to 400 °C). Its symmetry was demonstrated by NMR data; in Me_2SO-d_6, its ^1H NMR spectrum consisted of a singlet (δ 2.57), while its ^{13}C NMR spectrum was three lines (at δ 24.62, 53.51, and 112.2 for methylene, quaternary, and cyano carbons, respectively[16]).

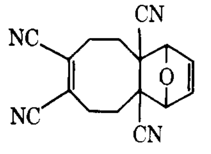
The spatial relationship of the cyano groups in these dimers, as well as a measure of the relative stability of related anhydride or imide structures, was indicated by the results of some hydrolysis studies. Thus, by quenching a sulfuric acid solution of the nitrile with methanol (or ice water), cyclohexene-1,2-dicarbonitrile (as a ring equivalent of the dimer **3**), **4**, **5**,[7] **6**, and **8** gave imide **9**, diimide **10a** (or dianhydride **10b**), tetraamide **11**,[7] diamido anhydride **12**, and tetraamide **13**, respectively. Since the tricyclic dimers gave only amide, existing fused C_4 or C_5 ring systems did not allow formation of another C_5 (imide or anhydride) ring fused onto them. The fused C_6–C_5 and cis,cis C_8–C_5 systems (i.e., imides or anhydrides from **3** and **4**) exhibit little strain. Interestingly, and quite expectedly, the cis,trans dimer **6** gave the "fused" anhydride at the cis and the "open" diamide at the trans double bond (giving a verification of the structure assigned to **6**). With **6**, these hydration studies revealed that one of the (trans) cyano groups was considerably more resistant to hydration than the others; except under prolonged treatment with sulfuric acid, a substantial amount of a partially hydrated product **14** was isolated (cf. footnote 34; see below also). The reasons for this behavior are not readily obvious.

The strain existent in the cis,trans dimer **6** allowed it to undergo a number of reactions which failed with the strain-free isomer **4**. While cycloaddition with furan and cyclopentadiene has been noted,[1d] we independently found that butadiene, furan, and even diene **2** itself react exclusively at the trans-substituted double bond[18a] of **6** under relatively mild conditions to give the cycloadducts bicyclo[6.4.0]dodeca-4,10-diene-1,4,5,8-tetracarbonitrile (**15**), 13-oxatricyclo-[6.4.$1^{9,12}$.0]trideca-4,10-diene-1,4,5,8-tetracarbonitrile (**16**), and bicyclo[6.4.0]dodeca-4,10-diene-1,4,5,8,10,11-hexacarbonitrile (**17**), a $[C_6H_4(CN)_2]_3$, respectively. The adducts **15** and **16** were also prepared by heating the tricyclic dimer **5**, the precursor of **6**, with the diene at 100 °C. The reaction of **6** with furan was especially rapid, being practically complete (by ^1H NMR monitoring) shortly after mixing at room temperature. In contrast to this facile reactivity, the isomer **4** underwent no cycloaddition with these dienes, even under forcing conditions.

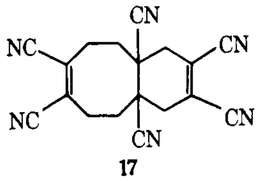
Attempts to confirm these structures by hydrolysis studies were not as satisfactory as with **4** and **6**.[18b] Thus, quenching sulfuric acid solutions of **15** and **17** with ice gave products that contained cyano, amide (or acid), anhydride, and (from **17**) imide groups, suggesting structures **18** and **19**, respectively. Again, the relative inertness of one of the cyano groups is intriguing but inexplicable (cf. **14**).



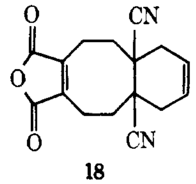
15



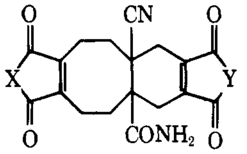
16



17



18



19

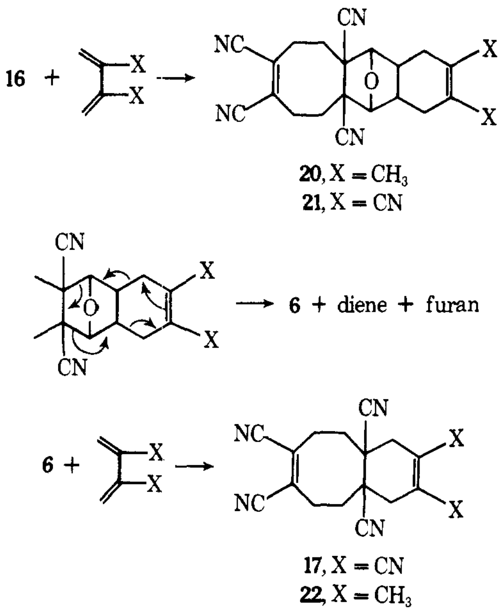
X, Y = O, NH

Investigation of the thermal behavior of these adducts gave some interesting results. That the furan adduct **16** yields only the parent cis,trans "strained" cyclooctadiene **6** upon thermolysis,[1d] demonstrating uniquely the stereospecificity of both the forward and retrograde Diels–Alder processes in this system, was found independently in the present work. Thus, sublimation of **16** under high vacuum, even at 235 °C, gave **6** as the sublimate with no more than traces of the isomeric **4**. In contrast, the butadiene adduct **15** sublimed unchanged at 220 °C, while the adduct **17**, though not sublimed, survived for some time at 250 °C.

The furan adduct **16** was also photolytically labile. Thus, upon irradiation it extruded furan and gave an excellent yield of the dimer **8**. Since the reaction of **6** with furan is rapid, the synthesis of **8** from **6** could be accomplished in high yield simply by irradiation of a solution of **6** and furan in methylene chloride. This finding suggests that the route to **8** may depend upon the geometry present in the cis,trans isomer **6** (i.e., the reaction path may involve **4** → **6** → **8**, rather than **6** → **4** → **8**), and adduction with furan effectively "locks" the geometry at the intermediate stage to allow the desired reaction vs. degradation to **2** or isomerization to **3** or **4**. Alternatively, another reaction path involving a stepwise cycloreversion of the furan adduct **16** may be operable. At any rate, irradiation of the dimer **4** in the presence of furan gave no improvement in the yield of **8** (cf. Table II).

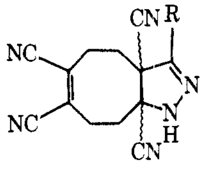
The adduct **16** exhibited some other interesting chemistry. Thus, the remaining double bond in the furan portion of the molecule underwent reaction with selected dienes. With furan itself, while **16** was by far the major product when the dimer **5** was heated with excess furan, there was evidence that further reaction occurred to give a product $(C_{12}H_3N_2)\cdot 2(C_4H_4O)$.[19] Reaction of **16** with 2,3-dimethylbutadiene occurred readily at room temperature with extrusion of furan to give the diene adduct of **6** itself, 10,11-dimethylbicyclo[6.4.0]dodeca-4,10-diene-1,4,5,8-tetracarbonitrile

Scheme I

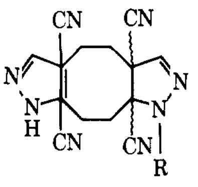


(22). On the other hand, reaction of **16** with diene **2** at room temperature gave the adduct **21** retaining the furan moiety, 17-oxatetracyclo[8.6.1^{2,9}.0.0^{3,8}]heptadeca-5,13-diene-1,5,6,10,13,14-hexacarbonitrile. However, when the reaction of **16** with **2** was carried out at 80 °C, furan extrusion again occurred to give the adduct **17** analogous to **22**. While no further study of these processes was made, a plausible explanation for this diverse behavior is outlined in Scheme I. An NMR study of the reaction of **16** with 2,3-dimethylbutadiene at room temperature gave no evidence for the intermediacy of **20** itself, showing only the direct formation of **22** and furan[20] at the expense of **16** and the diene. Why cyano groups lend stability to this system (i.e., **21**) is not clear; this same trend was evident also in the order of stability of the adducts, **17** > **15** (≫ **16**).

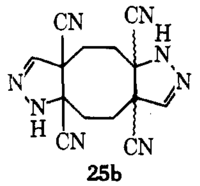
In addition to [4 + 2] Diels–Alder processes, **6** underwent [3 + 2] cycloadditions with diazoalkanes. The reaction with ethereal diazomethane was almost instantaneous to give a high yield of 9,10-diazabicyclo[6.3.0]undeca-4,10-diene-1,4,5,8-tetracarbonitrile (**23**), the "hydrazone" tautomer of an initially formed 1-pyrazoline. With excess diazomethane over a prolonged period, a second cycloaddition occurred, along with a methylation, to give what was apparently 12-methyl-6,7,12,13-tetraazatricyclo[9.3.1^{4,8}.0]pentadeca-5,13-diene-1,4,8,12-tetracarbonitrile (**24**), or an isomer (cf. **25**). The dimer **4** underwent very slow cycloaddition with diazomethane to give the normethyl analogue of **24**; in this instance, however, ^{1}H NMR data, showing double singlet resonances for both the nitrogen and olefinic hydrogens, suggested that the product may have been a mixture of isomers (e.g., **25a** and **25b**[21]). The dimer **6** also underwent reaction with ethyl diazoacetate to give **26**, ethyl 9,10-diazo-1,4,5,8-tetracyanobicyclo[6.3.0]-undeca-4,10-diene-11-carboxylate (again the "hydrazone" tautomer of an initially formed 1-pyrazoline). No attempt was made to ascertain the relative positions of the cyano groups in these derivatives. No thermal cycloaddition reactions occurred with either tetracyanoethylene or dimethyl acetylenedicarboxylate and **6**.



23, R = H
26, R = $CO_2C_2H_5$

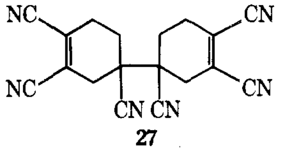


24, R = CH_3
25a, R = H

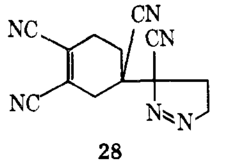


25b

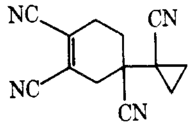
For comparison, the reactivity of the VCH dimer **3** toward cycloaddition was also assessed. With the diene **2**, reaction occurred slowly with **3** at 130–140 °C to give a low yield of what is thought to be **27**, 3,3′-bicyclohexenyl-1,1′,3,3′,4,4′-hexacarbonitrile, another $[C_4H_4(CN)_2]_3$ (cf. **17**). With diazomethane, **3** underwent facile reaction at the exocyclic double bond to give epimers (i.e., erythro and threo) of 3-(3-cyclohexenyl)pyrazoline-1′,3,3′,4′-tetracarbonitrile (**28**), which lost nitrogen thermally to give epimers of 4-cyclopropyl-1-cyclohexene-1,1′,2,4-tetracarbonitrile (**29**).



27

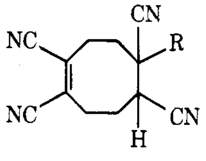


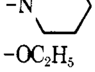
28

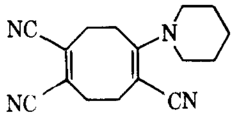


29

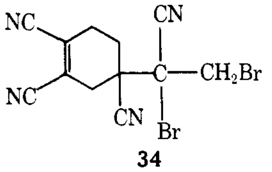
A number of other reagents underwent reaction at the trans double bond of **6** under conditions which the dimer **4** was essentially inert. Thus, piperidine, ethanol in the presence of a base, and hydrogen (over palladium) added to **6** to give 6-(1-piperidino)-1-cyclooctene-1,2,5,6-tetracarbonitrile (**30**), 6-ethoxy-1-cyclooctene-1,2,5,6-tetracarbonitrile (**31**), and 1-cyclooctene-1,2,5,6-tetracarbonitrile (**32**), respectively. Interestingly, the piperidine adduct **30** lost hydrogen cyanide at its melting point (165 °C) to give apparently the cyanoenamine[23] **33**, 6-(1-piperidino)-1,5-cyclooctadiene-1,2,5-tricarbonitrile. This behavior is similar to that found for the addition products of amines with **1**.[24] On the other hand, **6** gave little brominated product upon treatment with bromine. Rather isomerization occurred rapidly to give **4** in practically quantitative yield. Only catalytic amounts of bromine were required, and isomerization resulted similarly under conditions favoring either radical or ionic addition, e.g., under normal light, or in a polar, aprotic solvent in the presence of large amounts of lithium bromide. Iodine also effected isomerization, but at a somewhat slower rate. This conversion,



30, R = -N 
31, R = $-OC_2H_5$
32, R = H
35, R = $-OSO_2CF_3$



33



34

Table III. Combustion Analyses

Registry no.	Compd	Formula	Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
41793-19-5	**3**	$C_{12}H_8N_4$	69.22	3.87	26.90	69.35	4.05	26.15
53399-95-4	**4**	$C_{12}H_8N_4$	69.22	3.87	26.90	68.87	3.82	26.54
53399-94-3	**6**	$C_{12}H_8N_4$	69.22	3.87	26.90	68.85	3.82	26.13
62198-24-7	**10a**	$C_{12}H_{10}N_2O_4$	58.54	4.09	11.37	54.24	4.21	11.32
62198-25-8	**12**	$C_{12}H_{12}N_2O_5$	54.54	4.54	10.60	55.06	4.65	10.60
62198-26-9	**13**[a]	$C_{12}H_{16}N_4O_4$	51.42	5.75	20.00	50.45	6.85	19.83
62198-27-0	**15**	$C_{16}H_{14}N_4$	73.26	5.38	21.36	73.14	4.86	20.61
62198-28-1	**17**	$C_{18}H_{12}N_6$	69.22	3.87	26.90	69.13	3.97	26.80
62198-29-2	**18**[b]	$C_{16}H_{15}NO_5$	63.78	5.02	4.65	62.82	5.79	5.83
62198-30-5	**19**	$C_{18}H_{15}N_3O_6$	58.54	4.09	11.38	58.11	4.09	11.01
62198-31-6								
62198-32-7	**21**	$C_{22}H_{16}N_6O$	69.46	4.24	22.09	68.96	4.58	21.45
62198-33-8	**25**	$C_{14}H_{12}N_8$	57.53	4.14	38.33	56.92	4.36	37.84
62198-34-9								

[a] On the crude reaction product. [b] See footnote 37.

complementing the thermal and photolytic **6** → **4** isomerization processes (vide supra), is probably the best procedure for the preparation of **4**. Thus, addition of a little bromine (or iodine) to a benzene solution of **6**, prepared in this solvent from **5** (vide supra), caused rapid and nearly quantitative precipitation of the insoluble dimer **4**. In the same manner, treatment of **5** (the precursor of **6**) with bromine in hot benzene gave **4**. In related work, the VCH dimer **3** added a molecule of bromine only under irradiation to give 4-(1,2-dibromoethyl)-1-cyclohexene-1,1′,2,4-tetracarbonitrile (**34**).

A limited study was made of the reactions of **4** and **6** with transition metal reagents. The cis,trans isomer **6** readily formed complexes of the type (*cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)bis(triphenylphosphine)M(0) (M = Ni, Pd) when treated with tetrakis(triphenylphosphine)-nickel(0) and -palladium(0), respectively. The nickel complex slowly decomposed in air, while the palladium complex exhibited reasonable air stability. The IR spectra did not reveal the nature of the hydrocarbon–metal bonding, but a simple coordination of the trans double bond to the metal seems most probable. With tetrakis(triethylphosphine)nickel(0), **6** gave a product thought to be (*μ-cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)tetrakis(triethylphosphine)dinickel(0), very sensitive to air and handling. When the cis,cis dimer **4** was treated with tetrakis(triphenylphosphine)nickel(0), a brown, insoluble product was formed that did not lend itself to characterization. In contrast, **4** afforded a bright red-orange solid (otherwise uncharacterized) with cuprous chloride, while **6** was apparently unreactive. With **4**, silver trifluoromethanesulfonate gave what is thought to be **35**; formally, triflic acid added across one of the double bonds.[25] Under slightly different conditions, **6** gave an ill-defined, insoluble product containing (by IR) two types of nitrile groups and (probably) a sulfonate group (at 2230, 2180, and 1250, 1185 cm^{-1}, respectively).

Experimental Section[26]

Thermal Dimerization of Butadiene-2,3-dicarbonitrile (2). A solution of 15 g of diene **2** and 0.5 g of hydroquinone in 100 mL of benzene, under 200 psig nitrogen pressure, was heated in a rocking autoclave at 95 °C for 65 h. After cooling and venting, an insoluble product was filtered and washed with tetrahydrofuran (THF) and a little acetone to give 2.80 g of crude dimer **4**, mp 250–260 °C. Recrystallization from boiling acetone, removing 0.06 g of insoluble polymeric **2**, gave the pure dimer **4** as white crystals: mp 268–270 °C dec (lit.[1d] mp 230–231 °C); IR (KBr) 2230 (CN), 1615 cm^{-1} (C=C);[27] UV max (acetonitrile) 225 nm (ε 24 000); ^{1}H NMR (Me$_2$SO-d_6) δ 2.98 (s, CH$_2$);[28] ^{13}C NMR (Me$_2$SO-d_6) δ 127.5 (C=C), 116.9 (CN), 29.0 (CH$_2$); mass spectrum *m/e* (rel intensity) 208 (18), 181 (13), 155 (38), 141 (41), 129 (100). After removal of the insoluble **4**, the solution was stripped under aspirator pressure to a solid residue. This was stirred with boiling ether to give 11.4 g of (insoluble) dimer **3** (another 0.4 g was recovered from the ether), mp 123–125 °C. Recrystallization from a mixture of acetone, ether, and pentane at −70 °C afforded an analytical sample: mp 125–127 °C (lit.[1a,b] mp 124.5–125 °C); IR (KBr) 2270 and 2260 (CN), 1640 cm^{-1} (C=C);[27] UV max (acetonitrile) 204 and 230 nm (ε 16 600 and 12 500) (lit.[1a,b] 229–230 nm, ε 12 800); ^{1}H NMR (acetone-d_6) δ 6.52 (s, CH$_2$=, 2) (a doublet in CDCl$_3$), 3.1–3.3 (m, CH$_2$, 2), 2.8–3.1 (m, CH$_2$, 2), 2.3–2.5 (m, CH$_2$, 2); ^{13}C NMR (acetone-d_6) δ 135.43 (CH$_2$=), 127.0, 122.8, and 115.6 (C=C), 121.7, 118.3, and 115.9 (CN), 39.35 (quaternary C), 35.64, 28.90, and 26.55 (CH$_2$); mass spectrum *m/e* (rel intensity) 208 (14), 104 (100).

A solution of 70.0 g of cyclobutene **1** and 0.4 g of hydroquinone in 600 mL of xylene was stirred under nitrogen under reflux for 8 h. After cooling the insoluble solid product (ca. 28 g) was removed and exhaustively extracted with hot acetone, leaving 1.4 g of insoluble polymeric **2**. The acetone solution, concentrated to a volume of 200 mL, gave 5.6 g of **4**. Further successive concentration gave another 2.7 g of **4**, 4.2 g of a mixture of **3** and **4**, and finally two crops, 7.3 and 5.0 g, of **3**. The xylene solution was stripped under aspirator pressure to give 37 g of an oil. This was taken up in ether, giving 22.0 g of insoluble **3**, mp 123–125 °C; a second crop, 0.8 g, was obtained by chilling the ether filtrate at −70 °C. The ether filtrate was distilled in vacuo to give 11.0 g of unreacted **1**, bp 60 °C (0.5 mm).

***cis,trans*-1,5-Cyclooctadiene-1,2,5,6-tetracarbonitrile (6).** A mixture of 10.0 g of the dimer **5**[1d,7] in 1 L of benzene was stirred under reflux for 20 h. The hot mixture was filtered, removing 0.28 g of insoluble, unreacted **5**. Cooling the benzene solution to room temperature gave 0.54 g of the dimer **4**. After removal of this, the benzene solution was concentrated to a volume of about 500 mL. Cooling in an ice bath gave 3.89 g of **6**. The benzene solvent was removed from the mother liquor, and the residual solid was washed out with ether to give another 5.41 g of **6**. Recrystallization from acetone at −70 °C afforded an analytical sample: mp 188.5–189 °C, the clear melt resolidifying at about 191 °C, and this melting at ca. 260 °C dec (lit.[1d] mp 192–193 °C); IR (KBr) 2220 cm^{-1} (CN);[27,29] UV max (acetonitrile) 231–239 nm (ε 13 000);[31] ^{1}H NMR (acetone-d_6) δ 2.7–3.3 (m); ^{13}C NMR (acetone-d_6) δ 130.5 and 132.2 (C=C), 116.3 and 117.1 (CN), 31.6 and 35.3 (CH$_2$); mass spectrum *m/e* (rel intensity) 208 (19), 181 (10), 155 (25), 143 (16), 141 (44), 105 (100), 77 (57), 64 (36), 52 (37). This dimer could also be purified by sublimation under high vacuum at ca. 170 °C.

Conversion of 5 to 4. A suspension of 1.0 g of **5** in 50 mL of *o*-dichlorobenzene was stirred under reflux for 40 h. The solid product was filtered and washed with ether to give 0.94 g of **4**, mp 261–263 °C (from acetone). Dilution of the dichlorobenzene filtrate with the ether wash gave another 0.05 g of **4**.

Bicyclo[3.3.0]oct-2-ene-1,2,5,6-tetracarbonitrile (7). The dimer **4** (0.50 g), in a sublimation apparatus, was heated under a nitrogen atmosphere (at atmospheric pressure) in an oil bath at 280–290 °C for 5 min. Vacuum was then applied to sublime the volatile products. This sequence was repeated twice more on a 0.25-g scale. The combined sublimate was washed with ether to give 0.77 g of crystalline solid. This was resublimed at 170–180 °C under a high vacuum to give an almost white solid, mp 184–186 °C. Recrystallization twice from acetone at −70 °C afforded **7** as small, white crystals: mp 201–202 °C;

IR (KBr) 3070 (HC=), 2250 and 2235 (CN), 1630 (C=C), 1445, 1422, 1320, 1300, 1280, 900 cm^{-1}; ^{1}H NMR (acetonitrile-d_3), see Discussion, Figure 2; ^{13}C NMR (acetone-d_6) δ 151.1 (HC=), 117.3 (C=), 61.8 and 53.2 (quaternary Cs), 41.5 (methine C), 44.5, 37.5, and 29.9 (methylene Cs); mass spectrum *m/e* (rel intensity) 208 (15), 181 (11), 154 (20), 141 (18), 130 (20), 129 (100), 128 (15).

Photochemical Isomerizations and Degradations of Dimers 3, 4, and 6. These studies were carried out in quartz tubes (for studies utilizing irradiation from the sun), or in a glass–quartz reactor with an immersion-type medium-pressure mercury vapor lamp described previously.[7] The results are summarized in Table II.

A. Irradiation of VCH Dimer 3. A solution of 5.0 g of 3 and 2.0 g of benzophenone in methylene chloride was irradiated with the mercury vapor lamp for 4 days at room temperature in a slow nitrogen sweep. After removal of 0.05 g of an insoluble, amorphous material, the solvent was removed in vacuo. The residue was recrystallized from a mixture of acetone and ether at −70 °C to give, in two crops, 4.80 g of recovered, unreacted 3.

B. Irradiation of COD Dimer 4. A solution of 1.0 g of 4 and 0.25 g of benzophenone in acetonitrile was irradiated as described under A for 40 h. After filtration of 0.08 g of an insoluble solid, and removal of the solvent in vacuo, the residue was taken up in THF. Concentrating the solution to a volume of 10 mL gave ca. 0.07 g of an unsaturated nitrile [IR (KBr) 2230, 1665 cm^{-1}] otherwise uncharacterized. The THF mother liquor was chilled at −70 °C to give 0.06 g of 8 (see below). The solvent was removed from the filtrate; recrystallization of the residue from a mixture of THF and ether at −70 °C gave 0.25 g of 3.

A solution of 0.75 g of 4 in 100 mL of acetone was allowed to stand in the sunlight (quartz tube) for 18 days. The resulting yellow solution was concentrated to a volume of 10 mL; unreacted 4 (0.12 g) was removed. Chilling the filtrate at −70 °C gave 0.16 g of a crystalline solid which proved (by IR) to be a mixture of 4 and 8. Further crystalline crops (ca. 0.50 g) were essentially unchanged 4.

C. Irradiation of COD Dimer 6. A solution of 0.75 g of freshly sublimed 6 in acetone was irradiated as described under A for 5 days. Solvent was removed from the resulting yellow solution, and the residue was taken up in a little THF. An insoluble solid, 0.25 g, was removed and recrystallized twice from THF to give **tricyclo[3.3.0.0^{2,6}]octane-1,2,5,6-tetracarbonitrile (8)**, as white crystals: mp 300 °C; IR (KBr) 2270 cm^{-1} (CN);[27] NMR, see Discussion; mass spectrum *m/e* (rel intensity) 208 (8), 181 (16), 156 (100), 155 (11), 143 (24), 105 (36).

A solution of 0.80 g of 6 and 0.5 g of benzophenone in benzene was irradiated in the same manner for 2 days. Insoluble dimer 4 gradually precipitated and was removed (0.35 g). The benzene solution was stripped in vacuo. Recrystallization of the residue from a mixture of THF and ether gave, in two crops, a total of 0.22 g of 8. Evaporation of the THF–ether mother liquor at room temperature gave ca. 0.10 g of the VCH dimer 3.

A solution of 2.0 g of 6 and 0.5 g of benzophenone in acetonitrile was irradiated in the same manner for 2 days. After removal of a small amount of an insoluble material, the solvent was removed in vacuo. The residue was taken up in 10 mL of THF, giving 0.10 g of insoluble 8. Dilution of the THF filtrate with 10 mL of ether and chilling at −70 °C gave 0.24 g of diene 2. Dilution of the mother liquor with more ether gave, at −70 °C, 0.18 g of a solid, unsaturated nitrile (by IR) not further characterized. Adding pentane to the filtrate gave 0.25 g of the VCH dimer 3.

Hydrolysis of Cyclohexene-1,2-dicarbonitrile and Dimers 4, 6, and 8. A solution of the nitrile in sulfuric acid was allowed to stand for several days at room temperature, and was then poured into either a limited amount of ice water or into a large volume of methanol. Insoluble products were filtered, while soluble products were isolated by conventional solvent-removal and/or extraction methods.

A. Cyclohexene-1,2-dicarbonitrile (0.50 g) in 5 mL of sulfuric acid, quenched after 24 h with 25 mL of ice water, gave 0.15 g of an insoluble, partially hydrolyzed product, and, by extraction of the aqueous solution with methylene chloride, cyclohexene-1,2-dicarboximide (9):[32] mp 171–173 °C (from a mixture of THF and ether); IR (KBr) 3230 (NH), ca. 1730 cm^{-1} (broad and strong imide carbonyl).

B. COD Dimer 4 (0.5 g) in 5 mL of sulfuric acid was quenched after about 5 days by pouring into 150 mL of methanol. After the solution was heated under reflux for 24 h, the solvent was removed in vacuo. Pouring the residue into 200 mL of ice and water gave the diimide **10a**: mp 321–325 °C (from THF and ether at −70 °C); IR (KBr) 3280 (NH), 1790 (w), and 1700 cm^{-1} (strong imide carbonyl).

A similar sulfuric acid solution of 4, after 7 days, was poured into 25 mL of crushed ice. The resulting solid, 0.46 g, was recrystallized twice from boiling methanol[33] to give the dianhydride **10b**: mp 263–265 °C (no depression when mixed with authentic[34] **10b**; lit.[35] mp 265–268 °C); IR (KBr) 1850 (w) and 1785 (anhydride C=O), 1670 cm^{-1} (C=C).

C. COD Dimer 6 (1.0 g, resublimed) in 8 mL of sulfuric acid was quenched after 1 week by pouring into 30 mL of crushed ice. The solution was extracted several times with methylene chloride, during which a crystalline solid began to appear in the aqueous phase. Stripping of the extracts gave 0.18 g of **14** as a white solid, mp 171–179 °C (from THF containing a little ether), apparently a mixture of 5-carboxy-6-cyano-1,5-cyclooctadiene-1,2-dicarboxylic anhydride and the 5-carbamoyl analogue:[36] IR (KBr) 3460 and 3350 (OH and NH), 2220 (CN), 1850 (w) and 1760 (anhydride C=O), 1670 (C=O), 1600, 1265, and 1220 cm^{-1} (C–O). The aqueous residue was cooled in ice to give 0.94 g of **12**, 5,6-dicarbamoyl-1,5-cyclooctadiene-1,2-dicarboxylic anhydride:[33] mp 216–218 °C dec (from hot water); IR (KBr) 3450 and 3200 (NH$_2$), 1840 (w) and 1760 (anhydride C=O), 1670 (s) and 1560–1610 cm^{-1} (m) (amide C=O).

D. Dimer 8 (0.06 g) in 5 mL of sulfuric acid was quenched after 1 week by pouring into 200 mL of methanol. The fine white solid which precipitated slowly was collected and washed with methanol and ether to give tricyclo[3.3.0.0^{2,5}]octane-1,2,5,6-tetracarboxamide (**13**): mp ca. 405 °C dec; IR (KBr) 3230 and 3120 (NH$_2$), 1690 and 1610 cm^{-1} (CONH$_2$).

Bicyclo[6.4.0]dodeca-4,10-diene-1,4,5,8-tetracarbonitrile (15). A mixture of 2.0 g of **6**, 0.5 g of hydroquinone, 50 g of butadiene, and 50 mL of benzene was heated in an autoclave at 100 °C for 3 days. After cooling, 2.35 g (93%) of **15** was removed as an insoluble white solid: mp 267–270 °C dec (from boiling acetone); IR (KBr) 3080 (HC=), 2270 and 2250 (CN), 1635 cm^{-1} (C=C); ^{1}H NMR (hexafluoroacetone deuterate) δ 5.85 (s, HC=, 2), 2.7–3.2 (m, CH$_2$, 4), 2.58 (s, CH$_2$, 4), 2.2–2.5 (m, CH$_2$, 4).

A similar reaction of 2.0 g of **5**, 0.5 g of hydroquinone, 50 mL of butadiene, and 100 mL of benzene at 100 °C for 2 days gave 2.36 g of **15**.

13-Oxatricyclo[6.4.1^{9,12}.0]trideca-4,10-diene-1,4,5,8-tetracarbonitrile (16). A filtered solution of 5.0 g (24 mmol) of **6** in methylene chloride (100 mL) was mixed with 15 mL of furan, giving a rise in temperature from 24 to 30 °C in 1–2 min (NMR monitoring of a similar reaction in CDCl$_3$ showed that the reaction was complete almost upon mixing). After allowing to stand at room temperature overnight, the solution was chilled at −70 °C to give 2.91 g of **16** (a second crop, 3.83 g, resulted in a quantitative yield), mp 148–152 °C. Recrystallization from acetone or THF afforded an analytical sample: mp 166–168 °C dec (lit.[1d] mp 188–189 °C); IR (KBr) 3140 (HC=), 2250 (CN), 1585 (C=C), 1470, 1450, 1315, 1030, 970, 890, 865 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.85 (AB quartet, HC=, 2), 5.40 and 5.28 (2 s, HCO, 2), 2.4–3.3 (m, CH$_2$, 8); mass spectrum *m/e* (rel intensity) 208 (4.5), 104 (34), 67 (100).

A mixture of 2.0 g of **5**, 25 mL of furan, and 50 mL of benzene was heated in an autoclave at 100 °C overnight. Volatile materials were removed in vacuo from the reaction solution. The residual oil was treated with acetone, giving 0.66 g of an insoluble material; evaporation of the acetone gave 2.38 g of soluble products. The latter was treated with ether for 5 days (Soxhlet extractor). The ether-insoluble residue, mp 155–160 °C dec, was mixed with the acetone-insoluble product and the combined solids were fractionally crystallized from THF. Early crystalline fractions were (insoluble) starting dimer **5**, followed by the COD dimer **4**. The last fractions were the furan adduct **16**. An intermediate fraction, mp 265–270 °C, was leached with benzene, and the soluble portion was chromatographed on silica, eluting with benzene. The major fraction was a white, crystalline solid: IR (KBr) 2250 (CN), 1480, 1470, 1450, 1030, 920, 905, 865, 840 cm^{-1} (see footnote 19).

Bicyclo[6.4.0]dodeca-4,10-diene-1,4,5,8,10,11-hexacarbonitrile (17). A solution of 1.49 g (7.15 mmol) of **6**, 0.75 g (7.2 mmol) of diene **2**, and 0.1 g of hydroquinone in 50 mL of benzene, stirred under reflux, gradually deposited a white solid. After 28 h, the mixture was filtered to give 1.77 g (80%) of **17**, mp 281–284 °C dec; ca. 0.5 g of **2** was recovered from the filtrate. Recrystallization from acetone gave **17** as white crystals: mp 285–288 °C dec; IR (KBr) 2250 (CN), 1640 and 1630 cm^{-1} (C=C); ^{1}H NMR (Me$_2$SO-d_6) δ 2.8–3.2 (m, allylic CH$_2$, 10), ca. 2.5 (m, CH$_2$, 4). The same adduct **17** gradually precipitated from an acetone solution of **2** and **6**, held at room temperature for a few days.

Hydrolysis of adducts 15 and 17 was carried out by quenching sulfuric acid solutions of the adducts with ice as described for the dimers above.

A. Adduct 15 (0.22 g) in 5 mL of sulfuric acid after 1 week was added to 25 mL of ice. Extraction with methylene chloride gave 1-

carboxy-8-cyanobicyclo[6.4.0]dodeca-4,10-diene-4,5-dicarboxylic anhydride (**18**): mp 244–245 °C (from THF and ether at −70 °C); IR (KBr) 2280 (CN), 1890 (w), and 1760 cm^{-1} (anhydride C=O).[37]

B. Adduct 17 (0.50 g) in 10 mL of sulfuric acid after 1 week was added to 75 mL of ice. A white solid which slowly precipitated was collected (0.36 g) and recrystallized twice from boiling THF to give 1-carbamoyl-8-cyanobicyclo[6.4.0]dodeca-4,10-diene-4,5,10,11-tetracarboxylic anhydride imide (**19**) as white crystals: mp 316–318 °C; IR (KBr) 3470, 3400, and 3220 (NH), 2270 (w, CN), 1890 (w), 1850 (w), 1760 (s), 1780 (s), 1670 (s), 1610 cm^{-1} (m) (anhydride, imide, and amide C=O).

Chemistry of the Furan Adduct 16. A. Irradiation. A solution of 1.0 g of the adduct **16** and 0.25 g of benzophenone in methylene chloride was irradiated in the apparatus and in the manner described for the dimers **3**, **4**, and **6** for 24 h. The reaction solution was stripped in vacuo, and the residue was washed with ether to give the insoluble dimer **8** as essentially the only product.

A solution of 1.5 g of the dimer **6**, 0.25 g of benzophenone, 10 mL of furan, and benzene, after allowing to stand for 1 h (a little acetone was added to dissolve a solid that appeared), was irradiated in the same manner. A small amount (0.02 g) of insoluble **8** was removed, and the solvent was evaporated in vacuo. Treatment of the residual solid with methylene chloride gave 0.32 g of insoluble **8**. The methylene chloride solution gave an additional 0.66 g of **8** in several crops (65% total yield).

B. Reaction with 2,3-Dimethylbutadiene. A solution of 0.80 g of the adduct **16** and 3 mL of dimethylbutadiene in 25 mL of methylene chloride was allowed to stand at room temperature for 2 weeks. After removal of volatile materials in vacuo, the residual solid was washed with ether to give 0.99 g of an insoluble solid. This was taken up in 10 mL of acetonitrile, removing a small amount of insoluble **22** (see below). Analysis of the acetonitrile solution by HPLC showed that two materials were present, starting **16** and the product **22**. These were separated by preparative HPLC (on a 4 ft × 1 in. Porasil-packed column, eluting with 10% acetonitrile in chloroform); the adduct **22** eluted first (60–75 min) followed by the starting adduct **16** (90–120 min). The adduct **22**: mp 225–227 °C dec; IR (KBr) 2360 (CN), 1640 cm^{-1} (C=C); ^{1}H NMR (Me$_2$SO-d_6) δ 2.8–3.1 (t, CH$_2$, 4), 2.2–2.6 (m, CH$_2$, 8), 1.65 (s, CH$_3$, 6); ^{13}C NMR (Me$_2$SO-d_6) δ 127.82 and 122.73 (C=C), 119.38 and 117.23 (CN), 42.69, 34.10, 27.58, and 17.68 (four sp^3 carbons; it is presumed that the fifth one is masked by the Me$_2$SO solvent peaks in the same region, δ 36.6–42.9); mass spectrum *m/e* (rel intensity) 290 (14), 275 (6.2), 208 (4.7), 144 (11), 104 (8.7), 82 (100), 67 (36).

C. With Butadiene-2,3-dicarbonitrile (2). A filtered (to remove traces of polymeric **2**) solution of 1.38 g (5 mmol) of **16**, 0.54 g (5 mmol) of **2**, and 0.01 g of hydroquinone in the minimum amount of methylene chloride was allowed to stand at room temperature for 7 weeks as a white solid precipitated gradually. Filtration and washing with methylene chloride gave 1.19 g (59%; a similar reaction mixture, after 19 days, gave 17%) of **21**. The methylene chloride was removed from the filtrate, and the resulting solid was washed with ether to give 0.76 g of solid which, by IR spectral analysis, was largely unreacted **16**. A sample of the crude **21** was dissolved at room temperature in 100 mL of acetone. Addition of ether and chilling at −70 °C gave the adduct **21** as white crystals: mp 320–322 °C dec; IR (KBr) 2240 and 2220 (CN), 1610 (C=C), 922 cm^{-1} (C-O-C); ^{1}H NMR (Me$_2$SO-d_6, poor spectrum because of low solubility) δ ca. 4.5 and 4.7 (HCO), 2.2–3.0 (m, CH and CH$_2$).

A similar solution of 5 mmol each of **2** and **16**, with 0.10 g of hydroquinone, in 50 mL of benzene, was stirred under reflux for 24 h. The resulting mixture was filtered hot to give 0.54 g (35%) of insoluble **17**, mp 283–285 °C dec. Removal of benzene from the filtrate and washing the residue with ether gave 0.96 g (3.5 mmol) of unreacted furan adduct **16**.

Reaction of Dimer 6 with Diazoalkanes. A. With Diazomethane. Ethereal diazomethane was added via a buret to a solution of 1.04 g (5 mmol) of **6** in THF until the yellow color persisted. After the solution was allowed to stand (at room temperature) for 30 min, the volatile materials were removed in vacuo. The residue was dissolved in 20 mL of THF, removing and discarding a small amount of an insoluble material. The solution was chilled at −70 °C to give 0.93 g (74%) of **23**: mp 216–218 °C dec (from THF and ether); IR (KBr) 3310 (NH), 3070 (HC=), 2240 and 2230 (CN), 1590 (C=C), 1560 cm^{-1} (C=N, disappeared upon standing); ^{1}H NMR (acetone-d_6) δ 8.14 (s, NH, 1), 7.00 (s, HC=, 1), 2.4–3.2 (m, CH$_2$, 8); mass spectrum *m/e* (rel intensity) 223 (3), 196 (2), 27 (100).

A solution of 1.0 g of **6** in 50 mL of THF was allowed to stand with a threefold excess of ethereal diazomethane at room temperature for 11 days. After stripping in vacuo at room temperature, the residue was taken up in THF and reprecipitated by addition of ether to give 0.58 g of a solid; another 0.65 g was recovered from the mother liquor. This product was recrystallized twice from acetone to give white, crystalline **24**: mp ca. 300 °C dec; IR (KBr) 3280 (NH), 2260 (CN), 1650 cm^{-1} (C=N?); mol wt (mass spectrum) 306.

B. With Ethyl Diazoacetate. A solution of 1.04 g (5 mmol) of **6** and 0.60 g (5 mmol) of ethyl diazoacetate in 50 mL of THF was allowed to stand at room temperature for several weeks. The solvent was removed in vacuo, and the residual solid was washed with ether to give 1.59 g (97%) of **26**: mp 133–135 °C dec (from THF); IR (KBr) 3330 (NH), 2250 (CN), 1725 (C=O), 1590 cm^{-1} (C=N); ^{1}H NMR (acetone-d_6) δ 9.10 (s, NH, 1), 4.38 (quartet, ethyl CH$_2$, 2), 2.4–3.5 (m, CH$_2$, 8), 1.33 (t, CH$_3$, 3).

Reaction of Dimer 4 with Diazomethane. The COD dimer **4** (1.0 g) in THF was allowed to stand with a threefold excess of ethereal diazomethane at room temperature for 11 days. After removal of 0.11 g of precipitated **4**, the solution was evaporated in vacuo. The residual solid, ca. 2 g, was taken up in THF, removing another 0.16 g of insoluble, unreacted **4**. Chilling the solution at −70 °C gave a little more of **4** which was removed. The mother liquor was concentrated to a volume of about 5 mL; chilling the solution at −70 °C gave 0.36 g of **25**; another 0.32 g was recovered from the mother liquor. Recrystallization from THF and then from acetone afforded **25** as white crystals: mp 227–229 °C dec; IR (KBr) 3330 (NH), 3130 (HC=), 2260 (CN), 1600 cm^{-1} (C=N); ^{1}H NMR (acetone-d_6) δ 8.20 and 7.90 (s, NH, 2), 7.10 and 6.96 (s, HC=, 2), 2.2–3.2 (m, CH$_2$, 8).

Reactions of VCH Dimer 3. A. With Butadiene-2,3-dicarbonitrile (in Situ from Cyclobutene-1,2-dicarbonitrile). A mixture of 10.0 g of **3** and 5.0 g of **1** (4.8 mmol each) was heated in an oil bath at 140 °C for 8 h and then at 120 °C for 12 h. The viscous melt was poured into THF, removing 0.42 g of an insoluble product. The THF filtrate was mixed with 300 mL of ether, yielding another 4.87 g of a solid. These two solid portions were digested well with THF (ca. 20 °C). The insoluble portion was recrystallized twice from acetonitrile to give ca. 0.10 g (7%) of white crystals tentatively assigned the structure **27**: mp 295–297 °C; IR (KBr) 2250 and 2230 (CN), 1623 cm^{-1} (C=C).

B. With Diazomethane. A solution of 5.4 g (26 mmol) of **3** in THF was treated with a slight excess of ethereal diazomethane. The resulting solution was allowed to stand at room temperature for 30 min. The volatile materials were then removed in vacuo at room temperature. The tacky, yellow residue was taken up in methylene chloride and ether was added to the solution to the cloud point. Chilling at −70 °C gave 2.10 g of an off-white solid. Recrystallization twice from methylene chloride at −70 °C gave the pyrazoline **28** (probably threo): mp 107–109 °C dec; IR (KBr) 2260 and 2240 (CN), 1620 (C=C), 1565 cm^{-1} (N=N?); ^{1}H NMR (acetone-d_6) δ 4.95–5.30 (m, CH$_2$N=N, 2), 2.2–3.3 (m, CH$_2$, 8); mass spectrum *m/e* (rel intensity) 222 (77), 207 (13), 194 (35), 180 (14), 170 (33), 118 (100), 117 (50), 105 (34), 91 (58). After removal of this isomer of **28**, the filtrate was evaporated. The residue was recrystallized twice from a mixture of THF and ether, and then twice from acetone to give the isomeric pyrazoline **28** (probably erythro): mp 115–117 °C dec; IR (KBr) 2240 and 2260 (CN), 1625 (C=C), 1555 cm^{-1} (N=N?); ^{1}H NMR (acetone-d_6) δ 4.98–5.33 (m, CH$_2$N=N, 2), 2.3–3.4 (3 m, CH$_2$, 8); mass spectrum *m/e* (rel intensity) 222 (27), 207 (5), 194 (13), 180 (7), 170 (13), 118 (100), 105 (37), 91 (74).

The (presumed) threo adduct **28** (1.0 g) in toluene was heated at 100 °C (steam bath) for about 2 h. Removal of the toluene and recrystallization of the residue three times from a mixture of THF and ether gave the cyclopropane **29**: mp 144–146 °C; IR (KBr) 3120 (cyclopropane CH?), 2270 and 2250 (CN), 1635 cm^{-1} (C=C); ^{1}H NMR (acetone-d_6) δ 2.2–2.5 (m, CH$_2$, 2), 2.7–3.2 (m, CH$_2$, 4), 1.49 (s, cyclopropane CH$_2$, 4); ^{13}C NMR (CDCl$_3$) sp and sp^2 carbons at δ 125.99, 121.55, ca. 119.5, ca. 117.6, 114.41, and 114.21, quaternary sp^3 carbons at δ 39.21 (in C$_6$ ring) and 16.27 (in C$_3$ ring), and methylene sp^3 carbons at δ 35.71, 28.49, and 26.51 in the C$_6$ ring and at δ 12.30 and 12.10 in the C$_3$ ring; mass spectrum *m/e* (rel intensity) 222 (33), 207 (5), 194 (13), 180 (6), 170 (26), 129 (14), 118 (100), 105 (26), 91 (57). Treatment of the (presumed) erythro **28** in the same manner gave a crystalline isomer of **29**: mp 117–118 °C; IR (KBr) virtually identical with that of the isomer, mp 144–146 °C (not characterized further).

C. With Bromine. A solution of 1.04 g (5 mmol) of **3** in 25 mL of methylene chloride in a Pyrex flask was stirred while 0.80 g (5 mmol) of bromine was added; there was no reaction. The solution was transferred to a quartz tube, and the bromine color faded rapidly (in normal, fluorescent light). After standing for a few days, a small amount of an insoluble solid was removed, and solvent was removed from the filtrate. The residue was triturated with ether, recovering 1.53 g (83%) of **34**. Recrystallization afforded white crystals: mp

158–160 °C; IR (KBr) 2250 (CN), 1640 cm^{-1} (C=C); ^{1}H NMR (acetone-d_6) δ 4.40 (AB quartet with "doubling" caused by diastereomers, CH_2Br, 2), 2.2–3.5 (CH_2, 6); ^{13}C NMR (Me_2SO-d_6) δ 125.7 (C=C), 121.7 and 119.3 (BrCCN in 2 isomers), 116.3 and 114.7 (CN), 53.6 (BrCCN), 44.8 (CCN), 37.8, 33.9, 27.6, and 25.3 (CH_2); mass spectrum *m/e* (rel intensity) 208 (25), 193 (15), 179 (14), 154 (13), 129 (15), 104 (100), 79–82 (4 strong peaks, Br) (spectrum is similar to that of a mixture of 3 and bromine).

Other Reactions of Dimer 6. A. With Piperidine. A solution of 1.04 g (5 mmol) of **6** in 100 mL of methylene chloride was mixed with 0.42 g (5 mmol) of piperidine. The amber-colored solution was allowed to stand at room temperature for 1 week, and then the solvent was stripped in vacuo. The residue, recrystallized twice from THF, gave a nearly quantitative yield of **30:** mp 163–164 °C dec; IR (KBr) 2270 and 2250 (CN), 1620 cm^{-1} (C=C); ^{1}H NMR (acetone-d_6) δ 3.7–4.1 (m, HCCN, 1), 2.3–3.0 (m, CH_2, 12), 1.5–1.7 (m, CH_2, 6); mass spectrum *m/e* (rel intensity) 266 (15), 162 (24), 128 (12), 27 (100). A sample of the adduct **30**, held at its melting point for 15 min, gave crude **33** as an oil:[23] IR (neat) 2250 and 2180 (CN), 1635 and 1570 cm^{-1} (C=C).

B. With Ethanol. A mixture of 0.5 g of **6** in 5 mL each of ethanol and pyridine was allowed to stand at room temperature. After 4 days, solution was practically complete, the solution was stripped under aspirator pressure. The residual solid was taken up in THF, discarding a small amount of an insoluble material; sequential addition of ether and chilling at −70 °C gave several crops of the ether **31**, mp 157–160 °C. Fractional recrystallization from ethanol, mixtures of acetone and ether, or a mixture of THF and ether gave two isomers, more soluble, mp 169–171 °C, and much less soluble, mp 144–152 °C (still impure) (spectral analyses were almost identical): IR (KBr) 2250 (CN), 1050 cm^{-1} (C–O–C); ^{1}H NMR (acetone-d_6) δ 3.6–4.1 (complex of overlapping m, CH, CH_2O, 3), 2.3–3.0 (m, ring CH_2, 8), 1.33 (t, CH_3, 3); mass spectrum *m/e* (rel intensity) 294 (1), 199 (100), 172 (15), 171 (15), 146 (22), 144 (22), 117 (19), 45 (24).

C. Hydrogenation. A mixture of 0.5 g of **6**, 0.1 g of palladium hydroxide on diatomaceous earth, and 25 mL of acetonitrile was reduced in a Brown[2] hydrogenator. After removal of the catalyst and the solvent, the product solid was recrystallized from a mixture of THF and ether (Norit), then once from methanol (very difficultly soluble) to give **32** as small, yellow crystals: mp 208–210 °C; IR (KBr) 2260 and 2230 (CN), 1620 cm^{-1} (C=C); ^{1}H NMR (Me_2SO-d_6) δ 4.02 (t, HCCN, 2), 2.5–2.8 (m, CH_2, 4), 2.0–2.3 (m, CH_2, 4); mass spectrum *m/e* (rel intensity) 210 (10), 183 (19), 157 (18), 156 (19), 143 (11), 130 (24), 129 (14).

D. With Bromine. A solution of 1.04 g (5 mmol) of **6** in 100 mL of benzene was stirred under nitrogen with heating while a solution of 0.80 g (5 mmol) of bromine in 50 mL of benzene was added over a 90-min period. After the first few drops of bromine solution, the brown color persisted, and a white solid slowly precipitated. The mixture was stirred for another 1 h under reflux, and was then filtered hot to give 1.50 g[38] of the dimer **4**, mp 279 °C. Removal of the solvent from the filtrate gave ca. 0.5 g of a lachrymatory semisolid (containing apparently HBr). Treating this with ether gave another 0.02 g of insoluble **4;** nothing more could be isolated. Similar results were found using only catalytic amounts of bromine or iodine (100 and 65–70% conversion in 2 h at room temperature, respectively).

A stirred solution of 1.04 g of **6** and 25 g of lithium bromide in 150 mL of acetonitrile was treated dropwise over a 1-h period at room temperature with a solution of 0.80 g of bromine in 25 mL of acetonitrile. The resulting golden orange solution, after standing at room temperature overnight, was stripped in vacuo. The solid residue was triturated with 80–100-mL portions of methylene chloride until the solid was colorless; the residue, ca. 26 g, was completely water soluble. The methylene chloride (ca. 600 mL) was evaporated in vacuo. The residue was taken up in 25 mL of THF, removing 0.67 g of insoluble **4**. The solution was stripped, and the residue was taken up in ether, giving another 0.16 g of **4**. Evaporation of the ether gave an oily material from which no other discrete material could be isolated.

A mixture of 5.0 g of the tricyclo dimer **5** in 600 mL of benzene was stirred under reflux for 20 h, giving complete solution. A crystal of iodine was added to the hot solution; crystallization of **4** commenced shortly. After the solution had stood at room temperature for 65 h, 5.47 g[36] of **4** was removed; another 0.12 g of **4** was isolated from the mother liquor. Alternatively, 10.0 g of **5** in 1 L of benzene was stirred under reflux for 65 h. A small amount of insoluble material was filtered from the hot solution. Cooling the filtrate in ice gave 6.90 g of dimer **6**. The benzene filtrate was heated to boiling, and a crystal of iodine was added. Handling of the reaction mixture as described above gave a total of 2.96 g of **4**.

E. With Tetrakis(triphenylphosphine)nickel(0).[39] A solution of 1.11 g (1.0 mmol) of the title Ni(0) reagent and 0.21 g (1.0 mmol) of **6** in 9 mL of benzene was prepared under argon and allowed to stand overnight. Addition of hexane caused a yellow-brown oil to separate. Benzene was slowly added until the solution was homogeneous. Yellow-brown crystals began to form. After cooling at 5–10 °C for 2.5 h, the solid (0.32 g) was removed; two additional crops (0.18 g of red crystals and 0.09 g of orange crystals) were collected from the filtrate, giving a 71% total yield of air-sensitive (*cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)bis(triphenylphosphine)-nickel(0) (containing one-half a molecule of benzene solvate): mp (red crystals) 217–218 °C dec (in argon); IR (KBr) 2230 and 2180 cm^{-1} (CN) (all three crops had identical IR spectra). Anal. Calcd for $C_{48}H_{38}N_4NiP_2 \cdot 0.5C_6H_6$: C, 73.75; H, 4.98; N, 6.75. Found: C, 74.15; H, 4.74; N, 6.85.

F. With Tetrakis(triphenylphosphine)palladium(0).[39] A solution of 0.96 g (0.83 mmol) of the title Pd(0) reagent and 0.20 g (0.96 mmol) of **6** in 20 mL of benzene was allowed to stand over the weekend. After removal of some red-brown solid, the solution was diluted with 20 mL of hexane, causing an oil to separate. Benzene was added to the rapidly stirred mixture in ca. 1-mL increments until the oil had redissolved; a pale yellow solid began to precipitate before solution was complete. After cooling to ca. 0 °C, 0.57 g of (*cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)bis(triphenylphosphine)palladium(0) (again as a benzene solvate) as yellow, air-stable crystals was collected: mp 261–263 °C dec (in argon) (after a single recrystallization from a mixture of benzene and hexane); IR (KBr) 2180 and 2220 cm^{-1} (CN). Anal. Calcd for $C_{48}H_{38}N_4P_2Pd \cdot 0.5C_6H_6$: C, 69.74; H, 4.71; N, 6.38. Found: C, 69.74; H, 4.62; N, 6.36.

G. With Tetrakis(triethylphosphine)nickel(0).[39] A hexane solution of the title nickel reagent, prepared from triethylphosphine and bis(1,5-cyclooctadiene)nickel(0), was mixed with a solution of **6** (ca. 0.2 g) in 5–10 mL of benzene. A brown solid began to precipitate from the initially homogeneous solution. The reaction gave 0.18 gm of (*μ-cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)tetrakis(triethylphosphine)dinickel(0) as brown crystals: mp 235–238 °C dec (sealed in argon); IR (KBr) 2170 cm^{-1} (CN). Anal. Calcd for $[C_{12}H_8N_4][Ni(PEt_3)_2]_2$: C, 54.16; H, 8.58; N, 7.02. Found: C, 54.59; H, 8.02; N, 7.61.

Reaction of Dimer 4 with Silver Trifluoromethanesulfonate. A solution of 1.04 g (5 mmol) of **4** and 0.10 g (0.4 mmol) of the title silver reagent in 150 mL of acetonitrile was allowed to stand at room temperature for 10 days. After solvent was removed from the colorless solution in vacuo, the residual material was taken up in 60 mL of THF, giving 0.92 g of insoluble, unreacted **4**, mp 294–295 °C dec.[25] The THF filtrate was evaporated in vacuo. Washing the residue with ether gave 0.25 g of **35:** mp 220–222 °C dec (from a mixture of acetone and ether); IR (KBr) 2270 and 2240 (CN), 1610 (C=C), 1250 (broad), and 1180 cm^{-1} (SO_2). Anal. Calcd for $C_{12}H_8N_4 \cdot CF_3SO_3H$: C, 43.58; H, 2.53; N, 15.64. Found: C, 44.83; H, 2.61; N, 17.99.

Acknowledgments. We are indebted to Mr. A. N. Widener for his careful attention in carrying out a great deal of the experimental work, and to Professor L. M. Stock for many stimulating discussions and helpful suggestions.

Registry No.—**1,** 3716-97-0; **2,** 19652-57-4; **5,** 53399-93-2; **7a,** 62198-35-0; **8,** 62198-36-1; **9,** 4720-86-9; **10b,** 28885-97-4; **14** (X = OH), 62198-37-2; **14** (X = NH_2), 62198-38-3; **16,** 62249-51-8; **22,** 62237-83-6; **23,** 62198-39-4; **24,** 62198-40-7; **26,** 62198-41-8; **27,** 62198-42-9; *erythro*-**28,** 62198-43-0; *threo*-**28,** 62198-44-1; *erythro*-**29,** 62198-45-2; *threo*-**29,** 62198-46-3; **30,** 62198-47-4; *cis*-**31,** 62198-48-5; *trans*-**31,** 62198-49-6; **32,** 62198-50-9; **33,** 62198-51-0; **34** isomer 1, 62198-52-1; **34** isomer 2, 62198-54-3; **35,** 62198-53-2; hydroquinone, 123-31-9; benzophenone, 119-61-9; cyclohexene-1,2-dicarbonitrile, 52477-67-5; tetrakis(triphenylphosphine)nickel(0), 15133-82-1; (*cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)bis(triphenylphosphine)-nickel(0), 62228-13-1; tetrakis(triphenylphosphine)palladium(0), 14221-01-3; (*cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)bis(triphenylphosphine)palladium(0), 62228-14-2; tetrakis-(triethylphosphine)nickel(0), 52230-29-2; (*μ-cis,trans*-1,5-cyclooctadiene-1,2,5,6-tetracarbonitrile)tetrakis(triethylphosphine)dinickel(0), 62228-15-3; silver trifluoromethanesulfonate, 2923-28-6.

References and Notes

(1) (a) D. Belluš, K. von Bredow, H. Sauter, and C. D. Weis, *Helv. Chim. Acta*, **56**, 3004 (1973); (b) D. Belluš and C. D. Weis, *Tetrahedron Lett.*, 999 (1973); (c) D. Belluš and G. Rist, *Helv. Chim. Acta*, **57**, 194 (1974); (d) D. Belluš, H.-C. Mez, G. Rihs, and H. Sauter, *J. Am. Chem. Soc.*, **96**, 5007 (1974).

(2) J. C. Westfahl and D. S. Sears, U.S. Patent 2 587 558 (1952).

(3) E. Müller, R. Mayer-Mader, and K. Dinges, Abstracts, 163rd National Meeting

of the American Chemical Society, Boston, Mass., April 1972, No. INDE-44.

(4) C. S. Marvel and N. O. Brace, *J. Am. Chem. Soc.*, **71**, 37 (1949).

(5) Further comments on the processes possibly involved in this dimerization will be made as a part of our findings dealing with the dual reactivity of diene **2** as both a diene and a dienophile in Diels–Alder processes.[6]

(6) R. L. Cobb and J. E. Mahan, to be published.

(7) R. L. Cobb and J. E. Mahan, *J. Org. Chem.*, preceding paper in this issue.

(8) We too arrived at this finding and conclusion independently. We are grateful to Professor L. M. Stock for his help in this interpretation.

(9) For example, THF with **5** (60 h under reflux) gave, in addition to **6** (ca. 70%), a small amount of a crystalline product: mp 160–161 °C (from a mixture of THF and ether); IR (KBr) 2250 (CN), 1075 cm^{-1} (ether); ^{1}H NMR (CDCl$_3$) δ 3.7–4.4 (m, HCO, 3), ca. 3.5 (t, HCX, 2), 2.55 (m, CH$_2$CX, 8–9), 1.8–2.4 (m, CH$_2$CO, 4); mass spectrum *m/e* 280 (parent ion for C$_{12}$H$_8$N$_4$ + C$_4$H$_8$O), 71 (C$_4$H$_7$O$^+\cdot$, base peak).

(10) One possibility is that this endotherm may arise from the formation of a more favorable conformer. With *cis,cis*-1,5-cyclooctadiene itself, conformers are frozen below about −175 °C.[11]

(11) F. A. L. Anet and L. Kozerski, *J. Am. Chem. Soc.*, **95**, 3407 (1973).

(12) We are indebted to Professor L. M. Stock for this data and interpretation.

(13) For instance, irradiation of **6** in THF in the presence of benzophenone gave, by chromatographic separation (SiO$_2$, using benzene-THF as the eluting solvent), a small amount of a crystalline solid: mp 174–178 °C (from THF and ether); IR (KBr) 2250 (CN), 2020 (?), 1450, 1075 cm^{-1} (ether); ^{1}H NMR (CDCl$_3$) δ 3.6–4.3 (m, HCO, 3), 1.7–3.0 (m, CH$_2$, 13); mass spectrum *m/e* (rel abundance) 280 (0.3, M$^+$ for C$_{12}$H$_8$N$_4$ + C$_4$H$_8$O), 182 (3.6, C$_{12}$H$_8$N$_4$ − CN), 71 (100, C$_4$H$_8$O − H$^+\cdot$).

(14) Thermal processes have been used to effect such a transformation with 1,2,5,6-tetrachloro-1,5-cyclooctadiene: K. C. Eberly and R. J. Reid, U.S. Patent 2 626 961 (1953).

(15) (a) R. Srinivasin, *J. Am. Chem. Soc.*, **86**, 3318 (1964); (b) I. Haller and R. Srinivasin, *ibid.*, **88**, 5054 (1966); (c) J. G. Baldwin and R. H. Greeley, *ibid.*, **87**, 4514 (1965); (d) R. G. Salomon, K. Folting, W. E. Streib, and J. K. Kochi, *ibid.*, **96**, 1145 (1974).

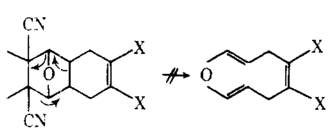
(16) The parent (unsubstituted) tricyclo[3.3.0.0]octane exhibits (^{13}C) resonances[17] at δ 26.8 and 52.2 for methylene and quaternary carbons, very close to those for the sp^3 carbons in **8**. For comparison, the corresponding resonances for **5** (in CF$_3$SO$_3$H) are δ 36.8 and 44.4, respectively.[7]

(17) See footnote 10 of ref 1d.

(18) (a) Other workers have demonstrated the Diels–Alder reactivity of trans vis-a-vis cis cycloalkenes; see, e.g., R. Wheland and P. D. Bartlett, *J. Am. Chem. Soc.*, **95**, 4003 (1973). (b) A comment on the stereochemistry at the bridgehead positions in **15–22** was requested by a referee. The hydrolysis studies did not provide this information. However, the stereospecificity of Diels–Alder reactions and the thermal cycloreversion of **16** to **6**[1d] at least suggest that the cyano groups in the bridgehead positions of **15–17** (and also **21** and probably **22**) are in a trans relationship. The ^{1}H NMR spectrum of **16** (i.e., an AB quartet for the olefinic protons and two singlets for the HCO protons, see Experimental Section) confirms the absence of a plane of symmetry in the molecule and implies a trans fusion of the rings. No further analysis of this was attempted.

(19) While isolation of discrete by-products was extremely difficult, a minute amount of a crystalline material was separated that exhibited (^{1}H NMR) resonances suggesting two types of OCH hydrogens (δ ca. 5.4 and 4.8) and one type of olefinic hydrogen (δ ca. 6.4).

(20) Disregarding kinetic considerations, observance of the direct formation of furan may obviate the possibility of an alternative cycloreversion process leading to an oxacyclononatriene:



(21) The formation of isomeric pairs of adducts such as these has been observed in at least one other diolefinic system.[22] Alternatively, but less likely in our opinion, the "double" resonances may have been due to "scrambling" of the stereochemical positions of the cyano groups.

(22) M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J. Chem. Soc., Perkin Trans. 1*, 1798 (1973).

(23) Evidence for this was intense absorption in the infrared region at ca. 2180 and 1570 cm^{-1} (cf. ref 24).

(24) R. L. Cobb and J. E. Mahan, *J. Org. Chem.*, **42**, 1948 (1977).

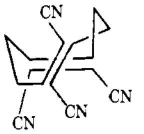
(25) Interestingly, the recovered unreacted **4** from this experiment had the highest melting point observed in this work (294–295 °C dec vs. 268–270 °C dec for an analytical sample; lit.[1d] mp 230–231 °C). This melting point corresponds closely to the endotherm in the DTA indicative of the true melting point (Figure 1). This suggests that the melting point of **4** as ordinarily prepared may be depressed by small amounts of an impurity not easily removed, and that this impurity is the material that actually underwent reaction with silver triflate. It may be noteworthy in this respect also that solutions of **4** (in, e.g., acetone) were often pink; their color gradually faded upon standing.

(26) Melting points (uncorrected) were determined on a Mel-Temp apparatus; IR spectra[27] were recorded on a Perkin-Elmer Model 137 Infracord; NMR spectra were determined (vs. internal Me$_4$Si) on Varian T60, XL100, and CFT 20 instruments; mass spectra were obtained on a CEC 110B instrument (70 eV).

(27) For rapid routine product determination, IR scanning was most helpful. Spectral areas particularly useful follow: for **3**, a closely spaced "triad" at 1450, 1430, and 1410 cm^{-1}, and the strong vinylidene absorption at 980 cm^{-1}; for **4**, two sets of "triads", (strong) at 1490, 1450, and 1430, and (weaker) at 960, 935, and 910 cm^{-1}; for **5**, single strong absorptions at 1450 and 805 cm^{-1}, and "double", somewhat weaker absorptions at 1285 and 1250 cm^{-1}; for **6**, a single strong absorption at 1450 cm^{-1}, and "double" weaker absorptions at 1030 and 1005 cm^{-1}; for **8**, "paired" absorptions at 1470 and 1450, and at 1310 (2 peaks) and 1285 cm^{-1}.

(28) Also a singlet resonance on a 270-MHz instrument.[12]

(29) Especially intriguing in the IR spectrum of **6** was the lack of absorption for C=C stretching vibrations at ca. 1640 cm^{-1}. Such an absorption band would be expected only for the cis substituted (dicyano) ethylene group, since the "stretching" in symmetrical systems (i.e., trans) is very weak and may be undetected. The absence of the absorption anticipated for the "cis" double bond in **6** suggests that there may be an interaction between the two π-electron systems, perhaps enhanced by the cyano groups, that disrupts the normal stretching vibrations.[30,31] A "preferred" conformation for **6** may thus be **6a** as shown, where the π systems are in close proximity and perhaps "overlapping".



6a

(30) We are indebted to Professor Ralph Becker for his aid in this interpretation.

(31) Ordinarily, the ϵ is "additive", i.e., the sum of the ϵ expected for each group at a particular wavelength. For example, the ϵ for **4** is about twice that for **3** (at ca. 230 nm) (or **1**[7]) where there is only a single chromophore. That the ϵ for **6** is not 2 × 12 000 or so suggests also[29] a disruption of some type in the chromophoric π systems.[30]

(32) R. L. Cobb and J. E. Mahan, *J. Org. Chem.*, in press.

(33) The remarkable "stability" of anhydrides of this type toward solvolysis may be related to solubility factors. It was observed generally in this work in both the unsaturated C$_6$ and C$_8$ ring system.

(34) Authentic **10b** was prepared substantially by the literature method,[35] mp 273–275 °C after a final purification by high vacuum sublimation at 200 °C.

(35) B. S. Green, M. Lahav, and G. M. J. Schmidt, *J. Chem. Soc. B*, 1552 (1971).

(36) As an 80:20 mixture of these two products. Anal. Calcd: C, 58.31; H, 3.75; N, 6.82. Found: C, 58.39; H, 4.80; N, 6.74. A similar mixture was the major product when a sulfuric acid solution of **6** was quenched after only a 48-h reaction time.

(37) Combustion analyses of this product were not at all satisfactory (carbon about 1% low and nitrogen about 1% high); the results suggest the presence of the corresponding amide as an impurity, and perhaps further hydration of the anhydride.

(38) The bromine-catalyzed isomerization of **6** to **4** invariably gave 110–150 wt % yields of "crude" **4**, although spectral analyses (IR and ^{1}H NMR) showed that **4** was essentially the only material present. Fractional crystallization of products from reactions run under various conditions yielded only **4**. However, in one reaction where the precursor of **6**, i.e., **5**, was treated with bromine in hot benzene, in addition to a 90% yield of **4**, a trace of a bromine-containing product was obtained by fractional crystallization: white crystals (from THF and ether at −70 °C), mp 181–183 °C; IR (KBr) 2250 (CN), 1495, 1060, 945, 900, 770 cm^{-1}; ^{1}H NMR (THF) δ 5.35 (AB quartet, HCBr?) (other resonances obscured by solvent); mass spectrum *m/e* (rel intensity) 233 (3), 231 (3), 213 (8), 153 (100), 131 and 133 (ca. 9), 126 (14), 80 and 82 (25, HBr), 79 and 81 (12, Br), 75 (26), 72 (22), 71 (18), 52 (52). Anal. Calcd for C$_{12}$H$_8$Br$_2$N$_4$: Br, 43.5. Found: Br, 39.7.

(39) Preparation and handling were carried out under argon in a drybox.