Addition of Hydrochloric Acid to ASNB. A three-necked, 25-mL round-bottomed flask was flushed with nitrogen for 15 min and charged with ASNB (0.171 g, 0.0011 mol). Anhydrous ether (10 mL) was added and stirring was initiated under an N_2 atmosphere. A gas inlet tube was immersed below the solvent level and dry HCl gas was bubbled through the solution for 10 min. Then the mixture was purged with N_2 for 10 min to remove excess HCl. The ether layer was extracted with 10% $NaHCO_3$ and dried with $MgSO_4$. GC analysis indicated one major product (8): ^1H NMR ($CDCl_3$) δ 2.63–2.26 (br d) 2.20–1.03 (complex multiplet); ^{13}C NMR ($CDCl_3$) δ 88.2, 61.0, 53.0, 44.3, 42.6, 41.9, 37.0, 36.7, 29.4, 28.7, 26.0, 23.3.

Addition of Hydrochloric Acid to SSNB: 7. SSNB (84 mg, 0.5 mmol) was dissolved in ca. 16 mL of ether and treated with a stream of HCl (anhydrous) gas for 1.5 h. The saturated solution was stirred at room temperature for 18 h. After the mixture was neutralized with saturated aqueous $NaHCO_3$, the organic layer was dried with $MgSO_4$ and analyzed by VPC. The major product observed was monochloro compound (7); ^{13}C NMR ($CDCl_3$) δ 91.6, 60.8, 52.0, 47.6, 42.0, 26.0, 23.7 (plus peaks for unreacted SSNB).

Competitive Reaction with Bromine. A solution of ASNB (50 mg) and SSNB (49.8 mg, 0.622 mmol total olefin) in CCl_4 (5 mL) was flushed with nitrogen and cooled to 0 °C. Then, 1.5 mL of 0.0996 M Br_2 (0.269 mmol) in CCl_4 was added to the mixture in one portion. After 15 min at 0 °C (note: the reddish brown bromine color disappeared immediately upon addition to the olefins), the mixture was evaporated in vacuo and the residue analyzed by ^{13}C NMR ($CDCl_3$). The first spectrum indicated approximately 50% disappearance of ASNB and *no* conversion of SSNB to dibromide. Clearly, ASNB had been converted to *anti-cis*-4a,8a-dibromosesquinorbornane (4): ^{13}C NMR ($CDCl_3$) δ 87.84, 56.98, 45.09, 41.97, 34.37, 29.75, 26.11.

The sample was then treated in the same manner with an additional portion (0.5 mL) of 0.0996 M Br_2 in CCl_4. Workup and analysis by ^{13}C NMR showed that 90% of ASNB had been converted to 4 while SSNB remained unreacted. Upon the addition of a third portion of Br_2 (0.5 mL of 0.0996 M solution), all of the ASNB was present as dibromide 4 and a small portion of SSNB had been converted to *syn-exo,cis*-4a,8a-dibromosesquinorbornane (3): ^{13}C NMR ($CDCl_3$) δ 92.0, 55.7, 48.8, 25.9.

Competitive Hydrobromination of ASNB and SSNB. HBr gas from a lecture bottle was bubbled through a solution of ASNB (109.0 mg, 0.68 mmol) and SSNB (111.1 mg, 0.69 mmol) in 2 mL of $CDCl_3$. After a short while the addition of HBr was stopped and ^{13}C NMR showed that only the HBr adduct to ASNB had formed, leaving SSNB and some unreacted ASNB. Successive additions of HBr depleted the anti olefin, while the syn isomer was still present, along with *anti-cis*-4a-hydro-8a-bromosesquinorbornane.

Competitive Hydrochlorination of ASNB and SSNB. A mixture of ASNB (30.2 mg, 0.188 mmol) and SSNB (30.3 mg, 0.189 mmol) in dry ether (5 mL) was flushed with nitrogen and cooled to 0 °C. Then, 0.5 equiv (based on the total amount of olefin) of HCl (0.35 mL of a 0.548 M solution in diethyl ether) was added to the reaction mixture in one portion. The solution was warmed to room temperature over 5 min and then the solvent was evaporated in vacuo.

Residue analysis by ^{13}C NMR ($CDCl_3$) gave peaks at δ 60.8, 53.0, 44.2, 42.8, 41.7, 36.9, 36.6, 29.3, 28.5, 25.9, and 23.2 (note: peak at 88.2 not visible due to low concentration) for *anti-cis*-4a-hydro-8a-chlorosesquinorbornane (7) and peaks at δ 151.6, 50.2, 42.8, and 25.2 for unreacted SSNB.

Preparation of 2-Methoxy-*anti*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodecane (12) Using *p*-Toluenesulfonic Acid. To a solution of ca. 40 mg of ASNB (2) in acetonitrile was added ca. 5 mg of *p*-toluenesulfonic acid and ca. 50 μL of methanol. The mixture was stirred for half an hour, after which injection on VPC showed that no olefin was present. The solvent was removed in vacuo, and the methyl ether 12 was isolated from the residue, by using column chromatography (silica gel, eluent petroleum ether/ether, 1:1, v/v): ^1H NMR ($CDCl_3$) δ 3.1 (s, 3 H), 2.1–2.7 (m, 3 H), 1.0–2.1 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 92.5, 58.0, 51.8, 42.1, 41.0, 39.8, 38.6, 36.9, 36.4, 30.3, 24.4 (2 peaks), 23.7; mass spectrum, *m/e* 192, 164, 160, 67. Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found C, 81.07; H, 10.32.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for support.

Registry No. 1, 73321-28-5; 2, 73679-39-7; 3, 89824-44-2; 4, 89726-60-3; 5, 89824-42-0; 6, 89726-58-9; 7, 89824-43-1; 8, 89726-59-0; 9, 74387-82-9; 10, 89824-46-4; 11, 74387-85-2; 12, 89824-45-3; 13, 670-54-2; 17, 75765-77-4; 18, 89726-61-4; 20, 15872-28-3; 21, 16508-04-6; 22, 19479-86-8; 23, 73654-77-0; 24, 89746-15-6; H_2O, 7732-18-5; MeOH, 67-56-1; *anti*-(*cis*-4a,8a-dicarboxy)sesquinorbornane anhydride, 73654-75-8; *syn*-(*cis*-4a,8a-dicarboxy)sesquinorbornane anhydride, 73679-38-6; hydrogen bromide, 10035-10-6; hydrchloric acid, 7647-01-0; *p*-toluenesulfonic acid, 104-15-4; acetylenedicarboxylic acid, 142-45-0.

Reactions of Tetracyanoethylene (TCNE) with the Three Isodicyclopentadiene Isomers

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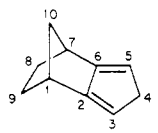
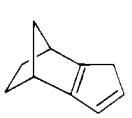
Each of the isodicyclopentadiene isomers 1–3 yields two characteristic cycloadducts with tetracyanoethylene (TCNE). One of these (11) is a (2 + 2) cycloadduct; the other five are reversibly formed Diels–Alder adducts. In the presence of water, TCNE induces a side reaction of hydration of diene isomer 3. TCNE and *N*-phenyltriazolinedione provide unusual examples of initial reaction with diene 1 on its exo face.

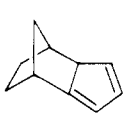
The synthetic possibilities of isodicyclopentadiene have recently been expanded by the discovery that not only the original isomer 1 but also diene isomers 2 and 3 can undergo controlled reactions with dienophiles to produce characteristic tetracyclo ring systems.[1-3] Tetracyanoethylene (TCNE) is of interest not only as one of the most reactive dienophiles[4] but also because under special con-



1



2



3

(1) Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. *J. Org. Chem.* **1982**, *47*, 4491.
(2) Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.
(3) Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

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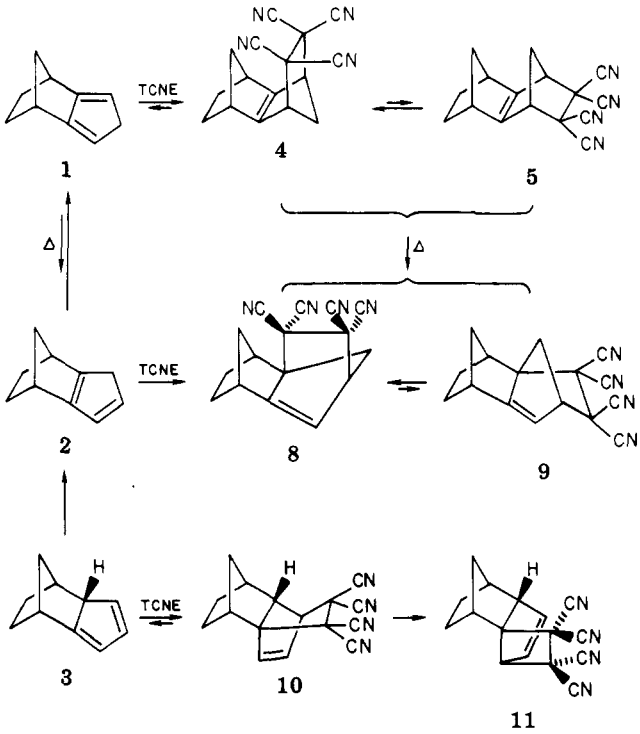
Scheme I



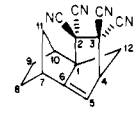
ditions it can react by polar mechanisms[5] and induce polar reactions in olefins.[6]

In this paper we report six addition products of TCNE to the isomeric isodicyclopentadienes, with observations on the rates, stereochemistry, and mechanisms of their formation. We also describe conditions under which TCNE catalyzes addition of water or methanol to diene isomer **3**. A further paper will report a mechanistic study of some ionic reactions of **3** and its derivatives.

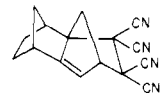
Results

TCNE and Isomers 1 and 2. Reaction of equimolar TCNE and diene **1** in either ether, acetonitrile, or benzene gives one single product **4** (Scheme I) in 90% yield, provided that the reaction and all the later manipulations are performed under 0 °C. NMR evidences[7] and the X-ray crystallographic studies[8] indicate that **4** is the exo adduct. Although **4** is stable at room temperature when dry, in solution it partly rearranges to **5**, the equilibrium ratio of these two compounds in CD_3CN being **4**:**5** = 6.5:1. Compound **5** has the NMR features of an endo adduct[7] and cannot be easily separated from **4** by chromatographic methods. The reversibility of this system was confirmed by adding cyclopentadiene in small excess in CD_3CN to the mixture of **4** and **5**. In 5 min at 0 °C the NMR signals of these isomers were replaced by those of **1** and the TCNE adduct of cyclopentadiene (**6**).

Table I. NMR Spectral Data of TCNE Adducts to 2

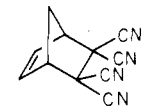


8 (mp 183-184 °C)



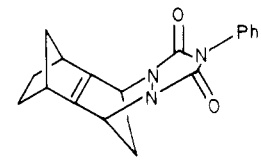
9 (mp 171-172 °C)

^{1}H NMR	
5.85 (d), 1 H, J = 3.0 Hz	5.92 (d), 1 H, J = 3.8 Hz
3.88 (m), 1 H, J = 3.0, 1.5 Hz	3.74 (m), 1 H, J = 3.8, 1.7, 1.4 Hz
3.26 (m), 1 H	3.10 (m), 1 H
2.97 (m), 2 H	2.82 (m), 1 H
2.05 (d), 2 H, J = 1.5 Hz	2.27 (dd), 1 H, J = 10.5, 1.4 Hz
1.2-2.0 (m), 5 H	2.06 (dd), 1 H, J = 10.5, 1.7 Hz
	1.5-2.06 (m), 6 H
^{13}C NMR	
166.3 (s) C_6	163.5 (s) C_6
118.2 (d) C_5	120.0 (d) C_5
112.6 (s) C≡N	112.4 (s) C≡N
112.0 (s) C≡N	111.5 (s) C≡N
74.6 (s) C_1	73.8 (s) C_1
58.4 (d) C_4	55.2 (d) C_4
48.3 (t) C_{12}	53.0 (t) C_{12}
47.9 (s) C_2, C_3	50.7 (s) C_2, C_3
46.9 (s) C_2, C_3	47.1 (s) C_2, C_3
42.0 (t)	43.7 (t) C_{11}
39.6 (d) C_7	40.9 (d) C_7
38.9 (d) C_{10}	38.0 (d) C_{10}
31.5 (t) C_8, C_9	25.1 (t) C_8, C_9
26.1 (t) C_8, C_9	23.9 (t) C_8, C_9



6

The addition of TCNE to **1** at 0 °C represents the first example of a Diels–Alder reaction proceeding essentially entirely on the exo face of this diene. We have also observed the exo addition of *N*-phenyltriazolinedione (PTAD) to diene **1**[9] to yield **7**. This observation, sub-



7

stantiated by X-ray crystallography, is especially surprising in view of the report[10] that *N-methyl*triazolinedione added to **1** on the endo face.

When isomer **1** is added to TCNE in refluxing *m*-dichlorobenzene (conditions of **1** ⇌ **2** equilibration), the resulting brown solution yields two new adduct isomers **8** and **9** (Scheme I) with the properties listed in Table I, in the ratio of 3:1, and none of the direct **1** adducts **4** or **5** observed at low temperature. The total yield under these conditions was only 30% but rose to 90% when the reaction was carried out by direct heating of the mixture of **4** and **5** in *m*-dichlorobenzene.

The general features of these spectra, closely resembling those of other observed adducts of diene **2**, fit well into the picture of adducts to **1** rearranging on heating into adducts of **2**. There is a subtle difference, however, between the TCNE and previous cases. With previously

(4) Middleton, W. J.; Heckert, R. E.; Little, E. L.; Krespan, C. G. *J. Am. Chem. Soc.* **1958**, *80*, 2783.
(5) Huisgen, R.; Schug, R.; Steiner, G. *Angew. Chem., Int. Ed Engl.* **1974**, *13*, 80–81.
(6) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.*, previous paper in this issue.
(7) From our accumulated data on *syn*- and *anti*-sesquinorbornene compounds, these two types of compounds are NMR distinguishable: (a) the ethano carbons in syn compounds (δ 24.5 ± 1.5 ppm) are more shielded than those in the anti ones (26.1 ± 1.0 ppm); (b) the same is true for the methano carbons (for syn, 47.5 ± 2.0 ppm; for anti, 53.2 ± 2.0 ppm); (c) in ^{1}H NMR, the syn compounds usually have two more shielded protons which appeared at below 1 ppm (0.7 ± 0.2 ppm).
(8) Watson, W. H.; Kashyap, R. P.; Bartlett, P. D.; Wu, C. *Acta Crystallogr., Sect. C*, submitted for publication.
(9) Kashyap, R. P.; Watson, W. H.; Bartlett, P. D.; Wu, C. *Acta Crystallogr., Sect. C*, submitted for publication.
(10) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.

studied dienophiles,[1,2] the two isomers obtained at higher temperature have been identified as both being adducts from attack on the exo face of the diene, one in conformity and the other in opposition to Alder's rule, and the absence of any endo addition has been regarded as indicating hindrance to addition on the endo face of **2**. Now TCNE, a symmetrical dienophile, cannot give two adducts on the basis of Alder,anti-Alder orientation, yet two adducts there are. Is TCNE alone capable of adding endo to diene **2**?

A known distinction of TCNE is its ability to add upon occasion to a diene in the (2 + 2) fashion. There are three conceivable (2 + 2) adducts of TCNE to the exo face of diene isomer **1** or **2**, but all three of these hypothetical compounds lack a feature common to the actual rearrangement products of **4** and **5**: they have no single vinylic proton coupled to only a single neighboring allylic proton. We conclude that neither new compound is a (2 + 2) cycloadduct to either **2** or **1**, and it follows that these are the facial isomers **8** and **9** and TCNE is providing the first example of a Diels–Alder addition on the endo face of isodicyclopentadiene **2**. These structures of **8** and **9** have been confirmed by X-ray crystallographic examination.[11] Not only is the structure **9** viable in the case of TCNE but it represents 27% of the mixture when **4**, **5**, or **8** is equilibrated by heating in *m*-dichlorobenzene at 170 °C for 5 h.

TCNE and Isomer 3. The reaction of **3** with TCNE goes readily at room temperature in acetonitrile, yielding a single adduct whose NMR assignments require the structure of the (2 + 4) cycloadduct **10**. The exo addition of TCNE is revealed by the close resemblance in NMR spectra of **10** with those of the well-studied exo cycloadduct of maleic anhydride and **3**.[12] This compound (**10**) is stable at room temperature when dry but decomposes rapidly at 130 °C. In solution in a polar solvent such as acetonitrile it readily rearranges into **11**, shown to be the (2 + 2) adduct by comparison of its decoupled ^1H and ^{13}C NMR spectra with those of **10** and by X-ray crystallographic structure determination.[13] The thermal stabilities of **10** and **11** are different: adduct **10** decomposed readily upon heating to 130 °C, whereas **11** is stable enough to pass through a GC column at 250 °C.

The sequence **3** → **10** → **11** was observed both in concentrated solution, where the initially formed product precipitated out, and in dilute solution where no precipitation occurred.

The reversibility of the formation of **10** is further shown by the fact that equivalent amounts of **1** or of cyclopentadiene react at room temperature with **10** (but not with **11**) in deuteriochloroform to yield diene **3** and the corresponding TCNE adduct of the added diene (**4**, **5**, or **6**).

The Question of a Polar Mechanism with TCNE. The formation of **10** appears to be about 50 times as fast in acetonitrile as in benzene; the conversion of **10** to **11** was complete in about 24 h in acetonitrile, 12 h in acetone, and 4 h in dimethyl sulfoxide (Me_2SO). A solvent effect of this order might merely reflect mild charge-transfer character in the transition state for concerted cycloaddition. On the other hand, since dipolar intermediates have been detected in (2 + 2) additions to olefins,[5] evidence was sought for the involvement of either dipolar ions or ion radicals in the present reactions.

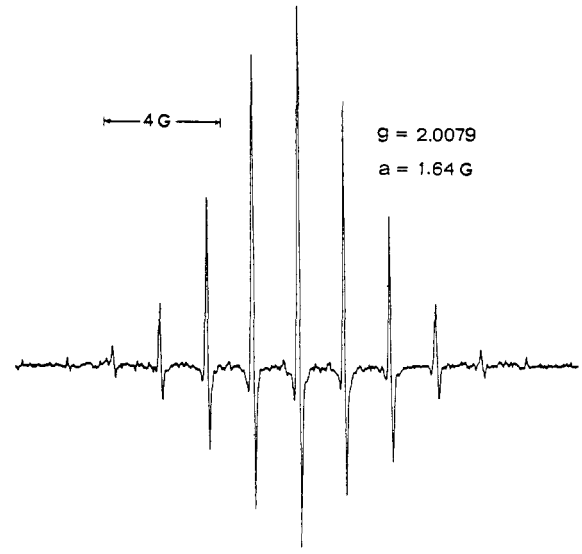


Figure 1. The ESR signal observed in the 10–Me_2SO system.

When **10** was dissolved in Me_2SO, a deep brown color developed and **11** was rapidly formed; at the same time the solution showed a symmetrical ESR signal of 13 lines as seen in Figure 1: $g = 2.0079$, $a = 1.64$ G. This signal lasted for about 6 h. The signal was identical with that reported[14-16] for the TCNE radical anion when TCNE was dissolved in such electron-donating solvents as Me_2SO or dimethoxyethane. No ESR signal was seen on solution of **10** in benzene, chloroform, nitromethane, acetonitrile, or acetone.

These observations alone do not implicate $(TCNE)^{-\cdot}$ in the formation of either the (2 + 4) or the (2 + 2) adduct to **3**, since the observed electron donation could be a side reaction between TCNE and Me_2SO. In the hope of achieving some specific trapping of a dipolar intermediate as in ref 5, the effect of added water or alcohol on the TCNE–diene reactions was investigated.

Rearrangement of 10 to 11 in the Presence of Water and Me_2SO. When **10** was stirred with excess water in Me_2SO at room temperature for 40 h, all the starting **10** disappeared, as shown by GCMS analysis. The analysis indicated three components in the resulting brown solution: the (2 + 2) adduct **11**, 35%; isodicyclopentadiene **3**, 20%; and a product with m/e 150, amounting to 40%. This principal product, 18 mass units heavier than the diene, proved indeed to be the alcohol **12**. It and **11** were isolated by column chromatography using 2:1 ether–pentane as eluent.

The one previously known related allylic alcohol **13** (Table III), an intermediate in the preparation of **1**, was directly compared by ^1H and ^{13}C NMR and shown to be different. The differentiation of **12** from its possible isomers was accomplished by (1) preparing the alcohol, starting with the specifically deuterated **3**-D6 in the first step and H_2O–Me_2SO in the second and (2) using D_2O–Me_2SO in the hydration step separately on the deuterated and the undeuterated **3** derivative. It turned out that the position of the entering deuterium on carbon from the D_2O hydration was 90% specific, so this method provided alcohols **12**-D6, **12**-D5, and **12**-D5,D6 (Table II). It was easily verified by the ^{13}C NMR that the OH was on the tertiary position 2, that the D from D_2O was at the allylic

(11) Watson, W. H.; Kashyap, R. P.; Wu, C., Bartlett, P. D. *Acta Crystallogr., Sect. C*, submitted for publication.
(12) Watson, W. H.; Galloy, J.; Wu, C.; Bartlett, P. D. *Acta Crystallogr., Sect. C*, submitted for publication.
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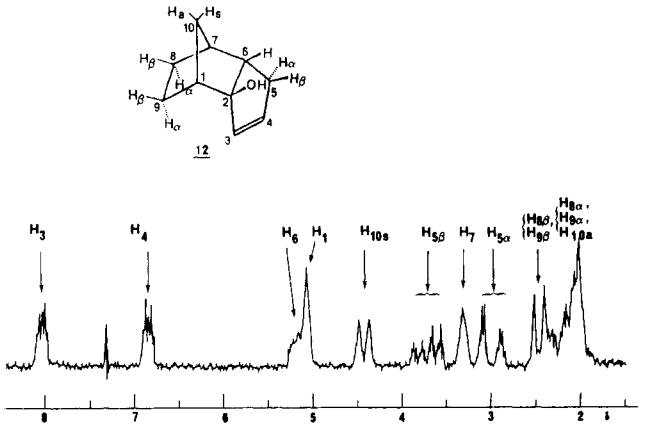


Figure 2. ^{1}H NMR spectrum of nondeuterated **12** extended by Eu(fod)$_3$: **12**, 25 mg; Eu(fod)$_3$, 45 mg; $CDCl_3$, 500 μL.

Table II. ^{13}C NMR Data of Labeled 12

	12	12-D5	12-D6	12-D5,D6
C_3	134.0 (d)	134.0 (d)	133.9 (d)	133.9 (d)
C_4	133.7 (d)	133.7 (d)	133.7 (d)	133.7 (d)
C_2	95.3 (s)	95.3 (s)	95.1 (s)	95.1 (s)
C_6	53.6 (d)	53.5 (d)	53.4 (t), J_{C-D} = 19.2 Hz	53.4 (t), J_{C-D} = 19.2 Hz
C_1[a]	46.3 (d)	46.3 (d)	46.2 (d)	46.2 (d)
C_7[a]	40.7 (d)	40.7 (d)	40.5 (d)	40.5 (d)
C_{10}	39.2 (t)	39.2 (r)	39.2 (t)	39.2 (t)
C_5	31.3 (t)	30.9 (t), J_{C-D} = 19.5 Hz	31.1 (t)	30.9 (t), J_{C-D} = 19.7 Hz
C_8[a]	25.9 (t)	25.8 (t)	25.8 (t)	25.8 (t)
C_9[a]	20.3 (t)	20.3 (t)	20.3 (t)	20.3 (t)

[a] An exo hydroxyl substituent at the C_2 position usually deshields the bridgehead carbon C_1 relative to C_7 and shields the ethane carbon C_9 relative to C_8, both at the same side of the hydroxyl.[17]

position, 5, vicinal to the original D at position 6, and accordingly, that the double bond was at C3–C4.

The NMR characterization was made more precise by the use of the lanthanide shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$. The proton spectra were then studied by spin decoupling. The numerical data are shown in Table III and expanded spectra plotted in Figure 2 for the undeuterated and Figure 3 for the doubly deuterated alcohol.

Not only is the expanded LIS spectrum definitive of **12** as the structure of the alcohol, but comparison of Figures 2 and 3 shows that the incoming deuteron in the D_2O hydration went to the α face of the diene system, trans to the location of the europium reagent. The H5α signal is missing, and the H5β signal is a broad peak in the 5-deuterated alcohol instead of the d-d-t pattern with $J_{5\alpha-5\beta}$ = 7.2 Hz, $J_{5\beta-6}$ = 3.6 Hz, $J_{5\beta-4}$, $J_{5\beta-3}$ = 1.1 Hz. The H-5α is less coupled to H-6 because of the large dihedral angle (100°).

p-Toluenesulfonic acid also catalyzes the addition of water to **3**; in this case the reaction at 0 °C led to a mixture of the alcohols **12** and **13** in a ratio of 7.4:1.

Two addition reactions of diene **3** show a special reactivity at position 2, which illustrates the relation between reactivity and release of strain. In **3** the junction between the norbornane and cyclopentadiene rings is made up of one sp^3- and one sp^2-hybridized carbon atom, twisting both

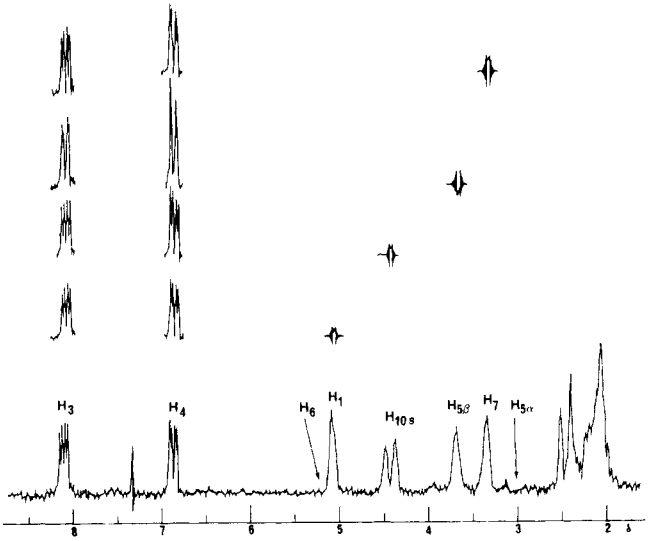


Figure 3. ^{1}H NMR spectrum of dideuterated **12** extended by Eu(fod)$_3$: **12**-D5,D6, 25 mg; Eu(fod)$_3$, 40 mg; $CDCl_3$, 500 μL.

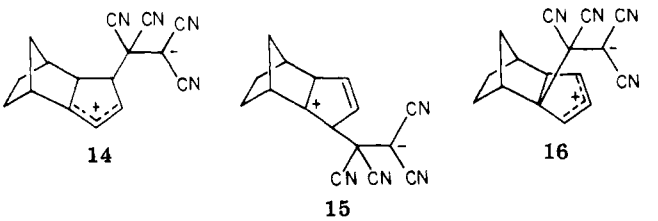
Table III. ^{1}H NMR Spectral Data and ΔEu Shifts for Alcohols 12 and 13

assignment	12 δ	12 ΔEu	13 δ	13 ΔEu
H-1	2.23	9.5	2.37	3.5
H-2	1.63 (OH)	~98	2.37	10.4
H-3	5.80	7.7	4.70	16.0
H-4	5.64	3.5	5.87	8.8
H-5β	2.23	5.3	6.00	4.2
H-5α	2.23	3.2		
H-6	2.23	9.8	3.20	4.9
H-7	2.23	3.5	2.37	2.3
H-8,9β	1.17	3.6	1.23	2.2
H-8,9α	1.17	2.8	1.23	2.2
H-10s	1.90	7.9	1.51	3.1
H-10a	1.32	3.2	1.51	1.2

[a] ΔEu values are $\Delta\delta$ values extrapolated to 1:1 molar ratio of Eu(fod)$_3$ and substrates.

rings and substantially increasing the strain in this ring system. In acid-catalyzed hydration it is highly probable that the initiating step is terminal protonation of the diene to form the more substituted allylic cation. In the choice between the two positions for the hydroxyl group, the ring junction position 2 is energetically preferable, since it converts the ring junction to the less strained one of **12** in which both carbons are saturated.

In the (2 + 2) addition of TCNE to **3**, it is obvious that the otherwise probable-looking attack of TCNE at C-5 to form **14** is not the initiating step. One of the two less



14 **15** **16**

expected intermediates **15** or **16** must have been formed. As to **16**, it would be unusual for TCNE to attack the more substituted end of a diene; it would be equally unexpected

that it should disrupt the conjugated system by forming **15**. In the present case, however, we know that whenever **11** is formed, **10** has been formed faster and reversibly, and is there already. If **10** undergoes the likely cleavage to **14**, this process either reverses or leads back to the original reactants. However, when upon occasion **10** gives the reasonable opening to **16**, the process is favored by yielding the unstrained sp^3–sp^3 ring junction, and the facts show that the new reclosure product **11** is the most stable of all.

When the TCNE adduct of **1**—the mixture of **4** and **5**—was dissolved in Me_2SO containing water, there were signs of reversal of the cycloaddition with formation of some diene **1** but no trace of any addition of water to the diene. It appears that the two reactions peculiar to diene **3**—(2 + 2) cycloaddition of TCNE and ionic addition of water—can be observed only because the high reversibility of the Diels–Alder reaction allows these stepwise processes to compete.

Experimental Section

The ^1H NMR spectra were obtained on a Varian EM-390 90 MHz spectrometer. The ^{13}C NMR spectra were determined on a JEOL FX-60 (15 MHz) spectrometer. The IR spectra were recorded on a Perkin-Elmer 197 spectrophotometer. GC was performed on a Perkin-Elmer Sigma-3 chromatograph using a 6-ft column packed with 5% SE-30 on Chromosorb. The GC–MS data were determined on a Finnigan OWA 1020 GC-MS-DS instrument using a 6-ft column packed with 5% SE-30 on Chromosorb; the ionization potential is 70 eV. The ESR spectra were recorded on a Varian E-104 spectrometer. Melting points are uncorrected.

Isodicyclopentadienes **1**, **3**, and **3**-D were prepared as described earlier.[3] exo-Tricyclo[5.2.1.$0^{2,6}$]dec-4-en-3-ol, **13**, was prepared as described elsewhere.[18] TCNE was sublimed 4–5 times before use.

Cycloaddition of 1 with TCNE. A solution of TCNE (100 mg, 0.78 mmol) in dry ether (20 mL) was cooled to 0 °C under argon, and 105 mg (0.79 mmol) of **1** in 2 mL of ether was added via syringe. After being stirred at 0 °C for 0.5 h, the mixture was kept in the freezer (−20 °C) overnight. The mother liquor was removed via syringe at 0 °C, and the crystalline residue, after further washing with 1 mL of ice-cooled ether, was evacuated to 0.01 torr at 0 °C for 12 h to remove any solvents and excess **1**. There was obtained 70 mg of **4** as transparent prisms: mp 157–159 °C dec; ^1H NMR (ppm, $CDCl_3$, 0 °C) 4.03 (t, 2 H, J = 1.5 Hz), 3.18 (q, 2 H, J = 1.5) 2.35 (dq, 1 H, J = 11.4, 1.5), 2.15 (dt, 1 H, J = 10, 2.0), 1.84–2.08 (m, 3 H), 1.53 (dq, 1 H, J = 11.4, 1.5), 1.10–1.30 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$, 0 °C) 156.7 (s), 112.2 (s), 112.4 (s), 56.8 (d), 55.2 (t), 52.6 (t), 48.1 (s), 42.2 (d), 25.9 (t). Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.58; H, 4.96; N, 21.46. Found: C, 73.46; H, 4.80; N, 21.67.

Further concentration of the mother liquor by removal of most of the ether at 0 °C gives 110 mg of crystalline products, the ^{13}C NMR spectrum of which is identical with that of **4**. Total yield of **4** is 88.7%.

Reactions of TCNE with **1** in CH_3CN, benzene, or toluene at 0 °C all give the same product **4**.

Rearrangement of 4 at Room Temperature. To a nitrogen-purged solution of TCNE (50 mg, 0.39 mmol) in 1.0 mL of acetonitrile-d_3 at 0 °C was added 45 mg (0.34 mmol) of **1** in 0.3 mL of the same solvent, and the ^1H and ^{13}C NMR spectra were taken. Compound **4** was formed as the only product with the complete disappearance of **1** right after the addition. At room temperature, a minor compound **5** was developed slowly and its concentration increased with time at the expense of **4**; after 2 h, an equilibrium of **4**:**5** = 6.5:1 is reached. The same equilibrium ratio was reached when pure **4**, obtained by reaction in ether at 0 °C, was redissolved in acetonitrile-d_3. Recrystallization in an ether–pentane mixture or preparative column chromatography failed to separate these two compounds from the equilibrated mixture. The recrystallized mixture consisted of transparent prisms: mp 156–157 °C dec. Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.58; H, 4.96; N, 21.46. Found: C, 73.79; H, 4.75; N, 21.76.

Pure **5** was not obtained. The ^{13}C NMR spectrum of **5** was deduced from the spectra of the mixture and of **4**: (ppm, $CDCl_3$) 157.9 (s), 112.7 (s), 59.5 (d), 54.3 (t), 52.2 (t), 47.2 (s), 43.3 (d), 24.3 (t).

Reaction of a Mixture of 4 and 5 with Cyclopentadiene. To a solution of 60 mg (0.23 mmol) of a mixture of **4** and **5** (recrystallized from ether/pentane) in 0.4 mL of acetonitrile-d_3 was added 20 mg (0.30 mmol) of cyclopentadiene. After 5 min at room temperature, the ^1H NMR signals of **4** and **5** were completely replaced by those of **1** and **6**. After removal of solvent, **1**, and excess cyclopentadiene by evacuation at room temperature and 0.005 torr, 40 mg of **6** was obtained as a yellowish solid, its ^{13}C NMR and ^1H NMR spectra being identical with those of an authentic sample prepared from cyclopentadiene and TCNE.

6: ^1H NMR (CD_3CN, ppm) 6.60 (t, 2 H), 4.10 (t, 2 H), 2.10 (br s, 2 H); ^{13}C NMR (CD_3CN, ppm) 138.8 (d), 114.3 (s), 113.6 (s), 57.2 (d), 48.5 (d), 47.6 (t).

Cycloaddition of 2 with TCNE. (a) From 1 and TCNE. A solution of TCNE (1.0 g, 7.8 mmol) in *m*-dichlorobenzene (15 mL) was brought to reflux under argon and 1.0 g (7.6 mmol) of **1** was added. The reaction mixture turned black upon addition. After refluxing for a total of 30 min., excess **1** and solvent were removed by vacuum distillation. The black reaction mixture was then subjected to flash chromatography (silica gel 230–400 mesh, pentane/ether eluent). Two products, **8** and **9**, in the ratio of 3:1, were isolated in pure form. The total yield was 30%.

2,2,3,3-Tetracyano-*anti*-tetracyclo[4.4.$1^{1,4}$.$1^{7,10}$.0]dodec-5-ene (8): (transparent prisms) mp 183–184 °C; ^1H NMR (ppm, $CDCl_3$) 5.85 (d, 1 H, J = 3.0 Hz), 3.88 (m, 1 H, J = 3.0, 1.5), 3.26 (m, 1 H), 2.97 (m, 2 H), 2.05 (d, 2 H, J = 1.5), 1.2–2.0 (series of m, 5 H); ^{13}C NMR (ppm, $CDCl_3$) 166.3 (s), 118.2 (d), 112.6 (s), 112.0 (s), 74.6 (s), 58.4 (d), 48.3 (t), 47.9 (s), 46.9 (s), 42.0 (t), 39.6 (d), 38.9 (d), 31.5 (t), 26.1 (t). Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.58; H, 4.96; N, 21.46. Found: C, 73.63; H, 4.85; N, 21.93.

2,2,3,3-Tetracyano-*syn*-tetracyclo[4.4.$1^{1,4}$.$1^{7,10}$.0]dodec-5-ene (9): (transparent needles), mp 174–175 °C; ^1H NMR (ppm, $CDCl_3$) 5.92 (d, 1 H, J = 3.8 Hz), 3.74 (m, 1 H, J = 3.8, 1.7, 1.4), 3.10 (m, 1 H), 2.82 (m, 1 H), 2.27 (dd, 1 H, J = 10.5, 1.4), 2.06 (dd, 1 H, J = 10.5, 1.7), 1.5–2.06 (series of m, 6H); ^{13}C NMR (ppm, $CDCl_3$) 163.5 (s), 120.0 (d), 112.4 (s), 111.5 (s), 73.8 (s), 55.2 (d), 53.0 (t), 50.7 (s), 47.1 (s), 43.7 (t), 40.9 (d), 38.0 (d), 25.1 (t), 23.9 (t).

(b). From the Rearrangement of a Mixture of 4 and 5 at 150 °C. The solution of 1.0 g of a mixture of **4** and **5** (ratio 6.5:1) in *m*-dichlorobenzene (6 mL) was heated at 150 °C under argon for 0.5 h. The resulting yellow solution was composed of **8** and **9** in a molar ratio of 70.7:29.3, as calculated from the intensity of δ 3.88 and 3.74 peaks in ^1H NMR, with complete disappearance of the starting material. The reaction mixture was then worked up as stated above. The combined yield of **8** and **9** is 91%.

Rearrangement of 8. Pure **8** (60 mg) was dissolved in 0.4 mL of *m*-dichlorobenzene under argon. Rearrangement from **8** to **9** was observed when the solution was heated at 170 °C and its composition was traced by ^1H NMR. The spectrum is a superposition of those of **8** and **9**. An equilibrium ratio of **8**:**9** = 73:27 was reached after 5 h.

Cycloaddition of 3 with TCNE: 11,11,12,12-Tetracyanotetracyclo[4.3.$2^{1,4}$.$1^{6,9}$.0]dodec-2-ene (10). To an ice-cooled solution of 0.80 g (6.2 mmol) of repeatedly multisublimed TCNE in CH_3CN (5 mL) was added 0.80 g (6.1 mmol) of **3** under argon. A blue color formed during the addition but faded away immediately upon stirring. The mixture became thick due to precipitation shortly after the addition. After stirring for 0.5 h, 10 mL of ether was added and the mixture was filtered. The precipitate was washed with 2 mL of cold ether. The dried product weighed 1.16 g (72% yield) and consisted of only one compound as indicated by ^1H and ^{13}C NMR.

10: mp 132–133 °C dec; ^1H NMR ($CDCl_3$) δ 6.50 (d, 1 H, J = 6 Hz), 6.29 (dd, 1 H, J = 6, 2.8 Hz), 4.15 (m, 1 H, J = 2.8 Hz), 2.89 (m, 1 H), 2.47 (m, 1 H), 2.32 (m, 1 H), 1.25–1.98 (m, 6 H); ^{13}C NMR (CD_3NO_2, 0 °C) δ 138.7 (d), 132.9 (d), 114.2 (s), 114.0 (s), 113.6 (s), 112.9 (s), 75.4 (s), 68.9 (d), 57.9 (d), 48.9 (s), 47.3 (s), 46.7 (t), 41.0 (d), 38.2 (d), 28.7 (t), 23.0 (t); MS, m/e 260 (M^+),

(17) Grutzner, J. R.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107.

(18) Alder, K.; Flock, F. H.; Janssen, R. *Chem. Ber.* **1956**, *89*, 2689.

132 (3^+), 128 ($TCNE^+$), 117, 104, 91, 76, 65, 55. Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.53. Found: C, 73.87; H, 4.56; N, 21.66.

Similar results were obtained when benzene was used as solvent, but the reaction is slower than in the CH_3CN case. TCNE and **3** reacted in benzene at 0 °C, giving the following results: 1 h, yield <5%; 22 h, yield 76%.

Rearrangement of 10 into 11. Compound **10** rearranges when dissolved. A sample of 50 mg (0.19 mmol) of **10** was dissolved in CD_3CN (2 mL) at room temperature in an NMR tube and monitored by ^{13}C NMR. After 24 h, all signals of **10** had vanished. The ^1H and ^{13}C NMR spectra indicated that only one product was present in the solution. The yellow solution was quickly passed through a pipet which was filled with alumina and rotary evaporated under vacuum to give a white crystalline solid **11** (30 mg, 60% yield).

2,2,3,3-Tetracyanotetracyclo[4.3.2^{1,4}.1^{8,11}.0]dodec-5-ene (11): mp 157–158 °C; ^1H NMR ($CDCl_3$) δ 6.33 (m, 1 H), 5.77 (m, 1 H), 3.93 (m, 1 H), 3.58 (m, 1 H), 2.80 (m, 1 H), 2.60 (m, 1 H), 0.90–1.77 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.1 (d), 127.4 (d), 110.5 (s), 109.6 (s), 108.9 (s), 61.5 (d), 60.3 (s), 53.5 (d), 44.7 (s), 44.1 (d), 40.2 (d), 39.3 (t), 23.1 (t), 22.4 (t); GC–MS (*m/e*) 260 (M^+), 232, 205, 165, 141, 132, 128, 117, 104, 91, 78, 77, 67, 65, 51. Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.53. Found: C, 73.86; H, 4.62; N, 21.60.

In an argon-flushed ESR tube was placed 5 mg of **10** and 100 μL of Me_2SO. The tube was placed in the ESR probe and a symmetrical ESR signal, $g = 2.0079$, was observed immediately. This signal, which consists of 13 lines having $a_H = 1.649$, reached its maximum intensity after about 2–3 h and lasted for about 6 h. This signal is identical with the one observed upon dissolving TCNE crystals in degassed Me_2SO in an argon-flushed ESR tube (without shaking) and is consistent with literature values.[9-11]

Reaction of 10 with 1. A sample of 60 mg (0.23 mmol) of **10** was dispersed in 400 μL of CD_3CN in an NMR tube. After the ^1H NMR spectrum was taken, the tube was cooled in an ice bath and 30 μL (0.23 mmol) of **1** was added. The remaining solid dissolved immediately. The ^1H NMR spectrum became a superposition of **3** and **4** with complete disappearance of that of **10**.

Reaction of 10 with Cyclopentadiene. **10** (60 mg, 0.23 mmol) was dispersed in 400 μL of CD_3CN in an NMR tube. After the ^1H NMR spectrum was taken, 20 μL (0.30 mmol) of cyclopentadiene was added. The remaining solid of **10** dissolved immediately. The ^1H NMR spectrum became a superposition of **3** and **6**. After removal of solvent and **3** by flask-to-flask distillation at room temperature and 0.005 torr, approximately 40 mg of a yellowish crystalline solid **6** was obtained; its ^1H NMR and ^{13}C NMR spectra are identical with those of an authentic sample prepared from cyclopentadiene and TCNE.

Reaction of 10 with Water in Dimethyl Sulfoxide. A solution of 0.5 mL (28 mmol) of water (or D_2O) in dimethyl sulfoxide (5 mL) was added to 500 mg (1.9 mmol) of **10** at room temperature and under nitrogen. The mixture was stirred for 40 h to give a brown solution that contained 20% diene, 35% **11** and 40% **12** (GC/MS). To this solution was added 30 mL of ether and 5 mL of H_2O and the two layers were separated. The aqueous layer was further twice extracted with 10 mL of ether. The combined ether layers were dried over $MgSO_4$ and passed through a short SiO_2 column to remove the color. After the ether was evaporated, the residue was worked up with 5 mL of pentane–ether (3:1) to give a solution and a solid portion. From the solid there was obtained 150 mg (30%) of **11**, which was further purified by recrystallization in ether. The solution was separated by column chromatography using 40–200-mesh SiO_2 as adsorbant and pentane–ether (3:1) as eluent. There was obtained 110 mg (38% yield) of **12** as a semisolid.

Alcohol **12** (from **10** and H_2O): ^{13}C NMR ($CDCl_3$) δ 134.0 (d), 133.7 (d), 95.3 (s), 53.6 (d), 46.3 (d), 40.7 (d), 39.2 (t), 31.3 (t), 25.9 (t), 20.3 (t); ^1H NMR ($CDCl_3$) δ 5.80 (1 H, dt, J = 6.0, 2.4 Hz), 5.64 (1 H, dt, J = 6.0, 1.8 Hz), 1.80–2.25 (5 H, series of m, 1 H is exchangeable with deuterium upon D_2O addition), 1.63 (1 H, br s), 1.0–1.50 (6 H, series of m); IR (cm^{-1}, neat) 3340, 3040, 2950, 2870, 1725, 1605, 1450, 1430, 1350, 1320, 1260, 1060, 995, 895, 790, 745; GC–MS, *m/e* 150 (M^+), 135, 132, 121, 108, 104, 95, 91, 82, 77, 67, 55, 41, 39. Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.60; H, 9.64.

12-D5 (from **3** and D_2O): ^{13}C NMR ($CDCl_3$) δ 134.0 (d), 133.7 (d), 95.3 (s), 53.5 (d), 46.3 (d), 40.7 (d), 39.2 (t), 30.9 (t, $^1J_{C-D}$ = 19.5 Hz), 25.8 (t), 20.3 (t); ^1H NMR ($CDCl_3$) δ 5.84 (1 H, dd, J = 6.0, 1.8 Hz), 5.70 (1 H, dd, J = 6.0, 2.1 Hz), 2.15–2.50 (4 H, series of m), 1.96 (1 H, dt, J = 8.4, 2.4 Hz), 1.67 (1 H, br s), 1.03–1.53 (5 H, series of m); GC–MS *m/e* 151 (M^+), 150, 136, 122, 108, 105, 96, 92, 83, 77, 67, 55, 41, 39.

12-D6 (from **3**-D and H_2O): ^{13}C NMR ($CDCl_3$) δ 133.9 (d), 133.7 (d), 95.1 (s), 53.4 (t, $^1J_{C-D}$ = 19.2 Hz), 46.2 (d), 40.5 (d), 39.2 (t), 31.1 (t), 25.8 (t), 20.3 (t); ^1H NMR ($CDCl_3$) δ 5.83 (1 H, dt, J = 6.0, 2.0 Hz), 5.68 (1 H, dt, J = 6.0, 2.1 Hz), 2.08–2.58 (4 H, series of m), 1.94 (1 H, dt, J = 8.4, 2.4 Hz), 1.74 (1 H, br s), 1.05–1.51 (5 H, series of m).

12-D5,D6 (from **3**-D and D_2O): ^{13}C NMR ($CDCl_3$) δ 133.9 (d), 133.7 (d), 95.1 (s), 53.4 (t, $^1J_{C-D}$ = 19.2 Hz), 46.2 (d), 40.5 (d), 39.2 (t), 30.9 (t, $^1J_{C-D}$ = 19.7 Hz), 25.8 (t), 20.3 (t); ^1H NMR ($CDCl_3$) δ 5.83 (1 H, dd, J = 6.0, 1.8 Hz), 5.68 (1 H, dd, J = 6.0, 2.4 Hz), 2.10–2.43 (3 H, series of m), 1.94 (1 H, dt, J = 9.0, 2.4 Hz), 1.67 (1 H, br s), 1.03–1.60 (5 H, series of m).

Cycloadduct 7 from PTAD and 1. A solution of PTAD (200 mg, 1.14 mmol) in 40 mL of dry ether was cooled to 0 °C under nitrogen, and 160 mg (1.21 mmol) of **1** in 2 mL of ether was added via syringe. After being stirred at 0 °C for 10 min, the mixture was kept in the freezer (−20 °C) overnight. The mother liquor was removed by syringe at 0 °C and the solid product, after washing with 1 mL of cooled ether, was evacuated to 0.01 torr at 0 °C for 12 h. There was obtained 300 mg (86% yield) of colorless crystals **7**: mp 180 °C dec; ^1H NMR (ppm, $CDCl_3$, room temperature): 7.31 (m, 5 H), 5.09 (t, 2 H, J = 1.8 Hz), 3.03 (m, 2 H), 2.40 (dt, 1 H, J = 8.1, 1.8), 1.80 (m, 3 H), 1.33 (br s, 2 H), 1.15 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 159.5 (s), 151.4 (s), 131.6 (s), 129.2 (d), 128.3 (d), 125.1 (d), 65.0 (d), 55.3 (t), 55.2 (t), 41.4 (d), 25.7 (t). Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.68; O, 10.41. Found: C, 70.12; H, 5.68; N, 13.76.

The same product was obtained when the reaction was performed at −20 °C as evidenced by its NMR spectra. Although the adduct can be kept indefinitely in its crystal form, it did decompose in solution. After standing at room temperature for 24 h, a solution in chloroform-d_1 was completely decomposed into an orange substance, which was not yet identified.

For the X-ray crystallographic study of **7**, see ref 9.

LIS Experiments on the Alcohols 12 and 13 (Table III). The LIS reagent used was tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$ (from Aldrich). Shifts of peaks were followed on stepwise addition of LIS reagents to the test $CDCl_3$ solution up to 0.2:1 of reagent:substrate mol ratio, the δEu values are Δδ values extrapolated to 1:1 mol ratio. Assignments and the coupling constants were on the basis of the spin-decoupling spectra, which were extended by LIS reagents.

The δ values, ΔEu values (in parentheses), multiplicities, coupling constants, and assignments of ^1H NMR spectrum of **12** are respectively: δ 5.80 (7.7), dt, J_{3-4} = 6.0 Hz, $J_{3-5\alpha} = J_{3-5\beta}$ = 2.4 Hz, H_3; 5.64 (3.5), dt, J = 6.0, 2.4 Hz, H_4; 2.23 (9.8), m, H_6; 2.23 (9.5), m, H_1; 2.23 (5.3), ddt, $J_{5\alpha-5\beta}$ = 18 Hz, $J_{5\beta-6}$ = 9.0 Hz, $J_{5\beta-4} = J_{5\beta-3}$ = 2.1 Hz, $H_{5\beta}$; 2.23 (3.5), m, H_7; 2.23 (3.2), dq, J = 18, 2.4 Hz, $H_{5\alpha}$; 1.90 (7.9), dm, J = 9.0 Hz, H_{10s}; 1.63 (98), br s, OH; 1.32 (3.2), m, H_{10a}; 1.17 (3.6) dm, J = 2.1 Hz, $H_{8\beta}$ and $H_{9\beta}$; 1.17 (2.8), m, $H_{8\alpha}$ and $H_{9\alpha}$.

In **12**-D6, H_6 is missing, $H_{5\beta}$ becomes a broad doublet (J = 9.0 Hz) and $H_{5\alpha}$ becomes a dt (J = 9.0, 1.5 Hz). In **12**-D5,D6, H_6 and $H_{5\alpha}$ are missing and $H_{5\beta}$ becomes a broad singlet. The ratio of $H_{5\beta}/H_{5\alpha}$ is >90:10.

For **13**, the related values are as follows: δ 6.00 (4.2), dt, J_{4-5} = 6.0 Hz, $J_{4-3} = J_{4-6}$ = 1.8 Hz, H_4; 5.87 (8.8), dt, J = 6.0, 1.8 Hz, H_3; 4.70 (16.0), br s, H_3; 3.20 (4.9), m, H_6; 2.37 (10.4), dd, J = 9.0, 4.5 Hz, H_2; 2.37 (3.5), m, H_1; 2.37 (2.3), m, H_7; 1.51 (3.1), dm, J = 9.0 Hz, H_{10s}; 1.51 (1.2), dt, J = 9.0, 1.5 Hz, H_{10a}; 1.23 (approximately 2.2), m, H_8 and H_9.

Acid-Catalyzed Addition of Water to 3: Formation of 12 and 13. To a stirred solution of 5.2 mg (0.03 mmol) of *p*-TsOH·2H_2O and 20 mg (1.1 mmol) of water in 1.5 mL of acetonitrile with external cooling (ice-bath) was added 250 mg (1.9 mmol) of **3** under nitrogen. After 1 h, all peaks of **3** disappeared as the reaction was traced by ^1H NMR. The product was composed of two components, **12** and **13**, in a ratio of 7.4:1; both have the same molecular ion *m/e* 150 in their mass spectra. The

identities of these two compounds were proved by comparing the ^{13}C NMR spectra with those of the authentic compounds and by the coinjection of each of the authentic pure compounds **12** and **13**. Pure **12** from this reaction mixture was obtained by flash chromatography, using silica gel (230–400 mesh) as adsorbant and pentane/ether (2:1) as eluent, and two subsequent Kugelrohr distillations at 100 °C and 0.2 torr; the yield of **12** was 80%.

Reaction of the 1-TCNE Cycloadduct with Water in Dimethyl Sulfoxide. A solution of 1 mL (56 mmol) of water in Me_2SO (5 mL) was added to 300 mg (1.1 mmol) of the cycloadduct of **1** with TCNE (a 6.5:1 mixture of the exo and endo adduct) at 0 °C and under nitrogen. The mixture was stirred at room temperature for 40 h; no formation of any allylic alcohol (m/e 150) was detected by GC–MS. (Since the cycloadduct itself undergoes decomposition under GC conditions, the only detectable component of this mixture is isodicyclopentadiene.) To this mixture was added 30 mL of ether and 5 mL of H_2O. The aqueous layer was further twice extracted by 10 mL of ether. The combined ether layers were passed through a short SiO_2 column to remove the dark color. Upon evaporation of ether, there was obtained 90 mg (30% recovery) of a solid which was proved identical with the starting material by ^1H and ^{13}C NMR.

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Registry No. **1**, 6675-72-5; **2**, 75725-33-6; **3**, 89689-33-8; **4**, 89772-13-4; **5**, 89689-34-9; **6**, 6343-21-1; **7**, 89689-35-0; **8**, 87556-20-5; **9**, 89771-45-9; **9**-D, 89689-36-1; **10**, 89689-37-2; **11**, 89689-38-3; **12**, 89689-39-4; **12**-D5, 89689-40-7; **12**-D6, 89689-41-8; **12**-D5,D6, 89689-42-9; **13**, 58616-86-7; TCNE, 670-54-2; PTAD, 4233-33-4; cyclopentadiene, 542-92-7.

Ring-Opening Polymerization of Norbornene Substituted with Amine and Ammonium Groups

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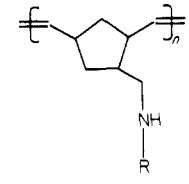
Norbornene substituted with amine groups gives rise to ring-opening polymerization, with $W(CO)_5(CPh_2)$ or $W(CO)_3$(mes) (mes = mesitylene) associated with $C_2H_5AlCl_2$ and molecular oxygen. With a 1:1 mixture of the exo and endo isomers, turnover of ca. 350 mol of monomer/mol of W are observed. The polymer obtained, which is almost insoluble in most organic solvents, is soluble in polar media (water, alcohols) after quaternization of the amine group. They can also be more soluble if a molecular weight regulator such as 1-pentene is used. The cis/trans ratio of double bonds in the polymer is close to unity, indicating a statistical coordination of the monomer to the metallocarbene fragment. It is also possible to obtain a copolymer between the functionalized norbornene and norbornene or cyclopentene. With norbornene it is possible to incorporate up to 90% of functionalized norbornene in the copolymer. With cyclopentene a 1:1 copolymer is obtained. No higher incorporation of cyclopentene can be achieved probably for steric reasons.

Introduction

One of the main reasons for the limitation of the development of the olefin metathesis reaction in organic and in polymer synthesis is the high reactivity of most catalytic systems with functional groups bearing heteroatoms.[1-4] In some particular cases it was possible to carry out metathesis of functionalized olefins by using an excess of Lewis acid cocatalyst which could complex to the heteroatoms and thus allow the catalytic reaction to proceed.[5] For example metathesis of acyclic olefinic amines is possible with the catalyst $W(CO)_3$(arene) associated with a large excess of organoaluminum compounds and molecular oxygen. The resulting compound is a telechelic compound with two amine groups at both ends.[5]

$$NR_2(CH_2)_nCH{=}CH(CH_2)_nNR_2$$

We wish to report here that metathesis of norbornene substituted with amine groups leads to the expected functionalized polymer shown. If the amine group is



R = H, CH_3, $CH(CH_3)_2$

quaternized by HCl, the resulting polymer is obtained with specific solubilities in polar media (e.g., water) and potential ion exchange properties.

Results and Discussion

A. Metathesis of 2-(Aminomethyl)bicyclo[2.2.1]-hept-5-ene (1:1 of Mixture Endo–Exo). Two catalytic systems were found to be active in metathesis of norbornene substituted with amine groups. They include zero valent complexes of tungsten (a) $W(CO)_3$(mes), (b) $W(CO)_5(CPh_2)$, associated with a large excess of organoaluminum compound, and molecular oxygen (Table I). In the absence of organoaluminum compound, the reaction does not proceed (with $W(CO)_5(CPh_2)$ the substitution of the carbene ligand by the amine ligand produces the new

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