Regio- and Stereochemical Definition of Silatropic Migration within Trimethylsilyl-Substituted Isodicyclopentadienes[1]

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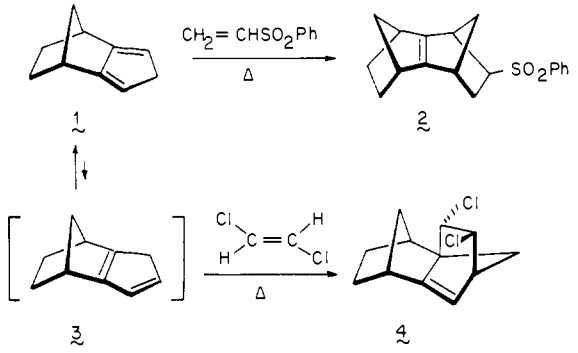
Abstract: Reaction of the anion of isodicyclopentadiene with chlorotrimethylsilane proceeds with predominant below-plane capture of the electrophile (**5**/**6** = 91:9) as expected from long-range stereoelectronic control. To make exo isomer **6** accessible in quantity, this product was deprotonated to generate anion **27** where added electronic interactions with the trimethylsilyl substituent lead to more stereorandom protonation (**5**/**6** = 54:46). Alternatively, silylation of this intermediate delivers **7**. The course of various Diels–Alder cycloadditions to **5**–**7** has been examined with a view to gaining insight into possible silatropic migrations within these systems. Whereas the reactions involving **6** occurred exclusively from the endo direction without evidence of silatropic migration, those involving **5** were more varied. For example, *N*-phenylmaleimide captured only the [1,5]~Si migrated isomer **20** to give **34**. Because dimethyl acetylenedicarboxylate is sterically inhibited from adding to such isomerized dienes, direct addition to **5** occurs in this instance exclusively from the exo direction. Preequilibration of **5** at 140 °C provides a still wider array of cycloadducts such as **35**, **37**–**39**, and **48**. With boron trifluoride catalysis, desilylation occurs. *N*-Methyltriazolinedione and tetracyanoethylene react with **5** by an ene mechanism, the first with retention of the silyl group. In the case of **7**, Diels–Alder reaction proceeds via either **23** or the [1,5]~Si/[1,5]~H isomers **24** and **26**. That sigmatropic migration can advance as far as **61** was demonstrated by independent thermolysis experiments. The various mechanistic implications brought to light by these reactions are discussed.

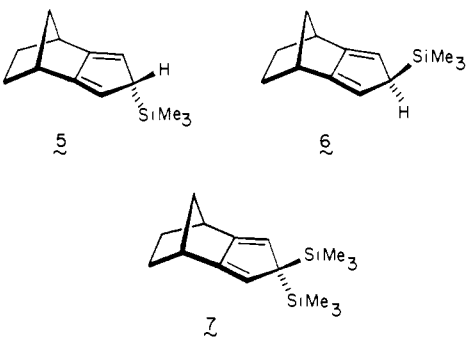
Dienophilic addition to isodicyclopentadiene (**1**) has come to command a special position in the evolution of the Diels–Alder reaction because of the high below-plane stereoselectivity of the process[3–6] and the exceptional double bond deformation in the resulting *syn*-sesquinorbornenes (**2**).[3d,h,7,8] In common with other



1 2 3 4

cyclopentadienes, **1** is capable of [1,5] hydrogen migration. However, the concentration gradients of less stable isomers such as **3** remain so low over a wide temperature range that their presence is not detectable by NMR methods. Nevertheless, as shown recently both in our laboratory[9] and by Bartlett and coworkers,[10] it is possible to trap **3** effectively. The diene system in **3** is more reactive than that in **1** as a consequence of the norbornene double bond. Therefore, the selection of a dienophile which is sufficiently unreactive that it does not enter readily into bonding with **1** can lead to the effective capture by **3** at somewhat elevated temperatures. A host of dienophiles shows this selectivity, and all additions to **3** occur exclusively from above-plane as illustrated by **4**.

These observations have led us to examine the cycloaddition chemistry of trimethylsilyl-substituted isodicyclopentadienes **5**–**7**.



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The choice of Me_3Si groups as probes was founded on the established fact that degenerate [1,5] silatropic rearrangement in 5-(trimethylsilyl)cyclopentadiene (**8**) occurs with a much lower activation energy (≤9 kcal/mol)[11] than the related prototropic shift in cyclopentadiene (25 kcal/mol)[12] or intramolecular methyl transfer within 1,5,5-trimethylcyclopentadiene (>40 kcal/mol).[13]

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(2) Author to whom inquiries concerning the X-ray crystal structure analyses should be directed.

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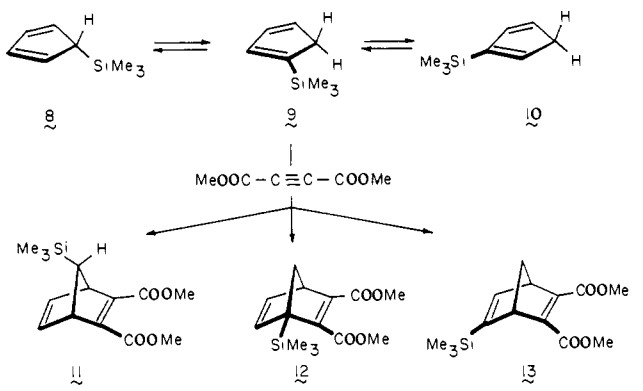
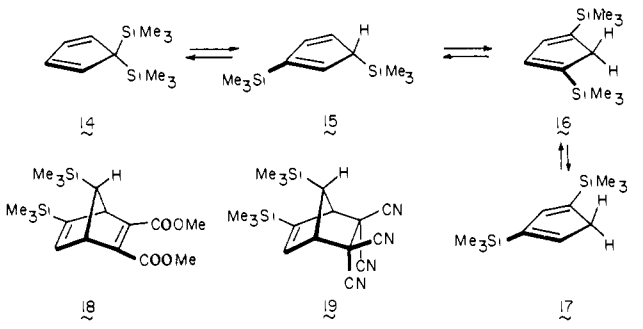


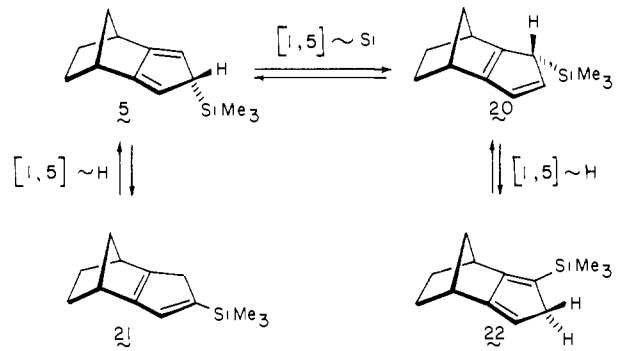
In fact, Ashe's kinetic studies involving **8** have shown hydrogen shifting to occur 10^6 times more slowly than Me_3Si migration.[14-16] Conversion of the thermodynamically favored **8** to **9** and **10** has nevertheless been observed spectroscopically. Although the propensity of **8** for Diels–Alder reaction is intermediate between that of **9** (slowest) and **10** (fastest),[14] 7-substituted norbornenes (e.g., **11**) are major products, at least with more reactive dienophiles.[17,18]

1,1-Bis(trimethylsilyl)cyclopentadiene (**14**) also dominates its



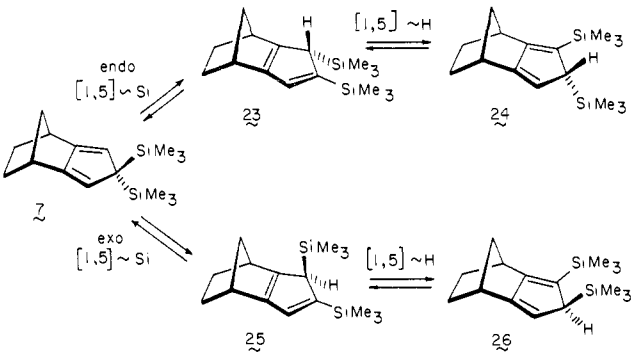
equilibrium with **15–17** (ratio 132:3.6:2.2:1 at −30 °C).[19] The rate of degenerate [1,5] silatropic rearrangement within **15** is again quite facile (E_a = 14.5 kcal/mol) as compared to its conversion to **14** (E_a = 15.8 kcal/mol) or the reverse reaction (E_a = 18.6 kcal/mol). Only above +120 °C does the **16** ⇄ **15** ⇄ **17** interconversion become fast relative to the NMR time scale (E_a(**16** ⇄ **15**) ≈ 21 kcal/mol). Upon reaction of this mixture with tetracyanoethylene or dimethyl acetylenedicarboxylate at 20 °C, only adducts **18** and **19**, which correspond to the trapping of **15**, could be isolated and identified.[19]

The fluxional properties of **5–7** were expected to be more constrained than those of **8** and **14** if the thermodynamic rewards associated with positioning of the isodicyclopentadiene double bonds as in **1** proved controlling. Under the provisions of this assumption, the simplest dynamic alternatives available, for example, to **5** include reversible [1,5] silatropic migration to generate **20** and competing sigmatropic hydrogen shifts which deliver **21** (less favorable) and **22** (highly favorable). Consequently, under reasonably controlled conditions, dienophile capture might well be restricted to the four isomers shown. These considerations gain particular relevance when it is recognized that more advanced isomerization of **21** and **22** could lead to the epimerization of both **5** and **20**. The resulting stereochemical leakage would most



certainly complicate in-depth analysis of the dynamic behavior of **5** (and **6**).

When the same constraints are applied to **7**, the opportunity to define the preferred course of the silatropic shift becomes equally apparent. Differentiation between the upper and lower reaction

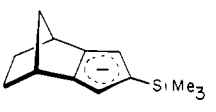


channels is made dependent, at least in part, upon proper identification of Diels–Alder adducts and/or suitable isotopic labeling. The possibility of fully stereocontrolled silatropic isomerization within **7** is of substantive interest in view of the unique features of isodicyclopentadiene pπ orbitals.[4,20] While ψ_2 in **1** is quite normal, strong σ/π interaction causes the terminal lobes within ψ_1 to be disrotatorily tilted. The direction of these deformations is known to be dependent upon the nature of the substituents bonded to the tetrahedral center.[4h,i] Diels–Alder stereoselectivity[3-6] and ^{13}C NMR chemical shifts[4e] are influenced by these effects. However, experiments designed to evaluate possible effects on sigmatropy remained to be documented.

Results

To gain access to **5**, use was made of the exceptional π-facial stereoselectivity and regioselectivity with which the cyclopentadienide anion derived from **1** is captured by electrophiles.[4g] Following treatment with equimolar amounts of *n*-butyllithium and chlorotrimethylsilane at −78 → 20 °C in tetrahydrofuran, **1** was converted into a 91:9 mixture of **5** and **6**. The product distribution was ascertained by integration of the vinyl proton absorptions characteristic of the individual epimers. Whereas **5** exhibits a singlet of area 2 at δ 5.79, the two-proton singlet for **6** appears well separated at δ 5.73 (in $CDCl_3$). The correctness of the configurational assignments was ascertained by ^1H NMR analysis of Diels–Alder adducts, as described below.

In order to arrive at preparatively useful quantities of **6**, this mixture was deprotonated as before to generate anion **27**, which



was subsequently quenched by addition to wet tetrahydrofuran

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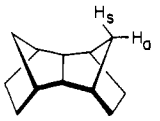
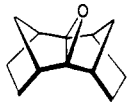
Table I. Chemical Shifts of Methano Bridge Protons ($CDCl_3$ solution, 300 MHz)[a]



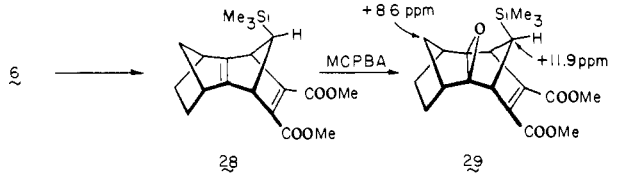
Compd pairs	chemical shifts, δ		Δδ[a]	
	H_s	H_a	H_s	H_a
	1.39	1.05		
	1.88	0.59	−0.49	+0.46
30	—	1.10		
31	—	0.44	—	+0.56
28	—	2.50		
29	—	1.77	—	+0.73
57	—	2.61		
58	—	1.87	—	+0.74
59	—	2.04		
60	—	1.79	—	+0.25

[a] Shielding is described as positive.

at −78 °C. The expectation was that those electronic interactions occurring between the filled cyclopentadienide π orbitals and empty d orbitals on silicon would short-circuit "normal" stereoelectronic control and give rise by more random protonation to a closely balanced distribution of isomers.[21] In fact, a 54:46 ratio of **5** and **6** was obtained. The pure substances were isolated following medium pressure liquid chromatography (MPLC) on silica gel.

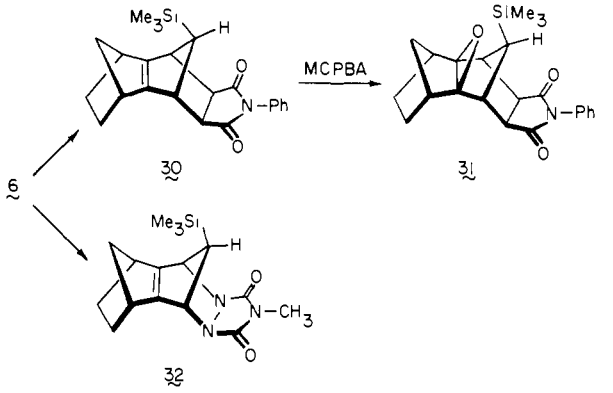
To arrive at **7**, **27** was captured with chlorotrimethylsilane. In line with our prior observations, condensation of **27** with $(C-D_3)_3SiCl$ led to an approximately 1:1 mixture of gem-disilylated stereoisomers. This virtually complete loss of stereoelectronic control precluded us from undertaking potentially diagnostic isotopic labeling studies.

When chloroform solutions of **6** and dimethyl acetylenedicarboxylate (DMAD) were allowed to stir overnight at room temperature, adduct **28** was obtained as the only observable



product in 77% yield after chromatographic purification. The *syn*-sesquinorbornadiene nature of **28** and the configuration of its silyl-substituted apical carbon were deduced simultaneously by conversion to **29** with *m*-chloroperbenzoic acid. Epoxidation occurs syn to the methano bridges[4] and causes *both* of the apical carbon atoms to experience upfield shifting (see formula). At the same time, the proton geminal to the trimethylsilyl substituent in **29** is *shielded* by 0.73 ppm relative to its chemical shift position in **28** (Table I). These effects are particularly diagnostic of the indicated proximities of these atoms to the oxirane ring.[4,22,23] In particular, reversed positioning of the trimethylsilyl group would necessitate that its geminal proton experience substantial deshielding in the course of the **28** → **29** conversion.[4]

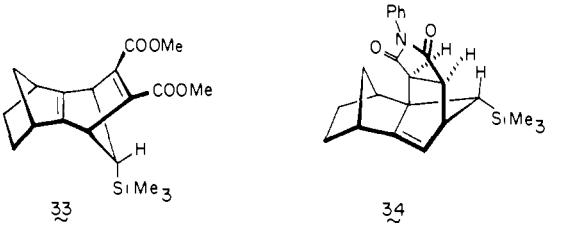
Similarly, *N*-phenylmaleimide added to **6** at room temperature with high below-plane stereoselectivity to give **30**. To more fully



characterize this adduct, its conversion to epoxide **31** was also undertaken. In complete agreement with precedent, *both* apical carbons of **31** become strongly shielded (also see Table I). Additionally, the negligible coupling constant between the tetrahedral α-carbonyl and bridgehead protons in **30** and **31** implicate an exo orientation for the dienophile moiety.[24]

When **6** was admixed with *N*-methyltriazolinedione in ethyl acetate solution at −78 °C, cycloaddition occurred rapidly to deliver **32**. In this instance, adduct stereochemistry has been assigned by comparison of its ^{13}C NMR spectrum to those of structurally related molecules.[4i]

Where **5** is concerned, good reactivity was exhibited by DMAD at room temperature, and the linear adduct **33** was isolated as



the principal product. Structural assignment to **33** follows from its low reactivity toward peracids and its ^1H and ^{13}C NMR spectra, which reveal the molecular C_s symmetry. The first phenomenon is characteristic of *anti*-sesquinorbornadienes.[4]

DMAD has previously been shown not to enter into Diels–Alder reaction with isomer **3**.[10] The complicating factor is steric crowding, the linear array of atoms comprising the acetylenic diester being unsuited to proper approach for bond making. Consequently, this dienophile should not be considered as a suitable probe for the presence or absence of **20** and **21**. *N*-Phenylmaleimide does not suffer from this complication and preferably adds to the isomerized substrate **20** at room temperature in chloroform solution. After 3 days, **34** was isolated in 41% yield. The gross features of **34** are apparent from the 19-line ^{13}C NMR spectrum, the presence of an olefinic proton signal of area 1 at δ 5.57, and the appearance of a single new bridgehead proton. The configuration of the imide ring was assigned from ^1H coupling constant data (Table II), from ^{13}C chemical shift correlations (Table III), and by analogy.[9,10] As with **33**, the formation of **34**

(21) A more detailed study of the behavior of **27** toward electrophilic reagents will be reported elsewhere.

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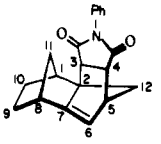
Table II. Selected ^{1}H Chemical Shift and Coupling Constant Data for the *N*-Phenylmaleimide Adducts ($CDCl_3$, 300 MHz)



compd	chemical shift, δ					coupling constants, Hz		
	$H_{1,8}$	H_3	H_4	H_5	H_6	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
				A. Alder Series				
40	2.73 2.85	3.28	3.57	3.45	5.64	7.96	5.21	2.69
37	2.72 2.91	3.26	3.58	3.50		8.00	5.25	
39	2.72 2.83	3.29	3.55		5.45	7.80		
34	2.76	3.30	3.62	3.56	5.58	7.33	*a*	2.43
				B. Anti-Alder Series				
41	2.92 2.98	3.04	2.85	3.39	5.67	6.72	1.51	2.73
38	2.91	2.82	2.76	3.39		7.23	1.19	

[a] Complex multiplicity in this region precluded determination of *J*.

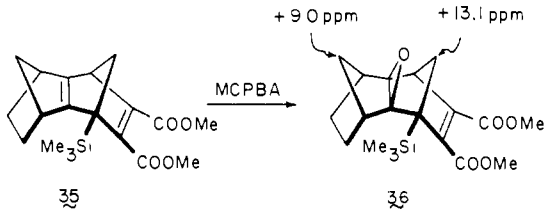
Table III. Selected ^{13}C NMR Shift Data for the *N*-Phenylmaleimide Adducts ($CDCl_3$ solution)[a]

compd	C_2	C_{12}	$C_{1,5,8}$	C_{11}	$C_{3,4}$	$C_{9,10}$
			A. Alder Series			
40	67.37	55.23	48.23	42.33	39.81	32.70
			47.52		37.90	25.97
			46.64			
37	69.06	55.94	50.96	42.49	39.81	32.59
			48.34		38.72	25.98
			46.64			
39	68.55	56.89	50.49	42.56	38.80	33.20
			48.84		38.20	25.87
			47.96			
34	72.82	60.69	50.93	43.31	40.44	31.22
			50.68		37.38	26.46
			50.54			
			B. Anti-Alder Series			
41	65.83	50.31	49.65	47.19	39.26	31.34
		43.91	42.05		36.58	24.34
38	67.20	52.33	48.83	45.71	39.97	31.77
		42.54	42.16		36.75	24.50

[a] See Figure 1 for numbering scheme.

may arise as the result of steric approach control, although electronic contributions from the trimethylsilyl moiety cannot be disregarded. The Alder configuration of the imide ring is clearly discernible from the existence of spin–spin coupling between the α-carbonyl and bridgehead protons (Table II).[24]

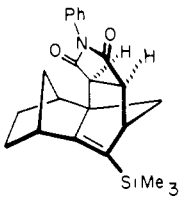
At this point, it was of interest to examine the consequences of preequilibrating **5** prior to introduction of the dienophile. Therefore, a solution of the diene in xylene was heated at the reflux temperature (140 °C) for 30 min. When DMAD was introduced at this point, there was produced a mixture of the three adducts **28** (51%), **33** (10%), and **35** (34%). The isolation of **35** provided



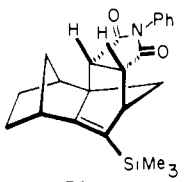
35 36

the first definitive indication that **20** can proceed forward to **22** by [1,5] hydrogen sigmatropy. Although diester **35** clearly lacked symmetry, its *syn*-sesquinorbornene nature was established through epoxidation in customary fashion. The shieldings experienced by both bridging methano carbons in **36** again conform to expectation.[4]

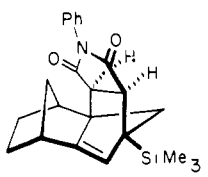
Addition of *N*-phenylmaleimide to a comparably equilibrated solution of **5** afforded the three previously unidentified angular adducts **37** (48%), **38** (31%), and **39** (20%). These isomers were



37



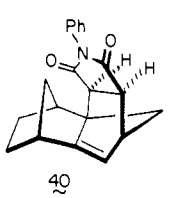
38



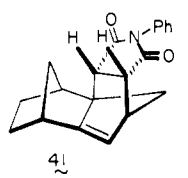
39

readily separated by medium-pressure liquid chromatography and their structures deduced by spectral analysis. As seen in Tables II and III, their NMR spectra parallel closely the data obtained for related molecules. The endo/exo stereochemistry which distinguishes **37** from **38** is apparent from the observed α-carbonyl/bridgehead proton coupling constants (5.25 Hz for **37** and 1.19 Hz for **38**). Whereas **37** and **38** have no olefinic proton, that in **39** appears as a narrow multiplet at δ 5.45 (in $CDCl_3$). The latter substance is considered to be an Alder rule product chiefly on the basis of its ^{13}C NMR spectrum (Table III).

Two interesting points emerge from this aspect of the study. The isolation of **39** reveals that **5** can indeed undergo isomerization to **21**. Also, the 1.5:1 ratio of products **37** and **38** is seen to be somewhat lower than the distribution of **40** (62%) and **41** (28%)



40



41

that arises upon addition of *N*-phenylmaleimide to preequilibrated (169 °C, *tert*-butylbenzene solution) isodicyclopentadiene (**1**), perhaps because of steric contributions from Me_3Si. The highly distinctive portions of the 300-MHz ^{1}H NMR spectra of these archetypal adducts are illustrated in Figure 1.

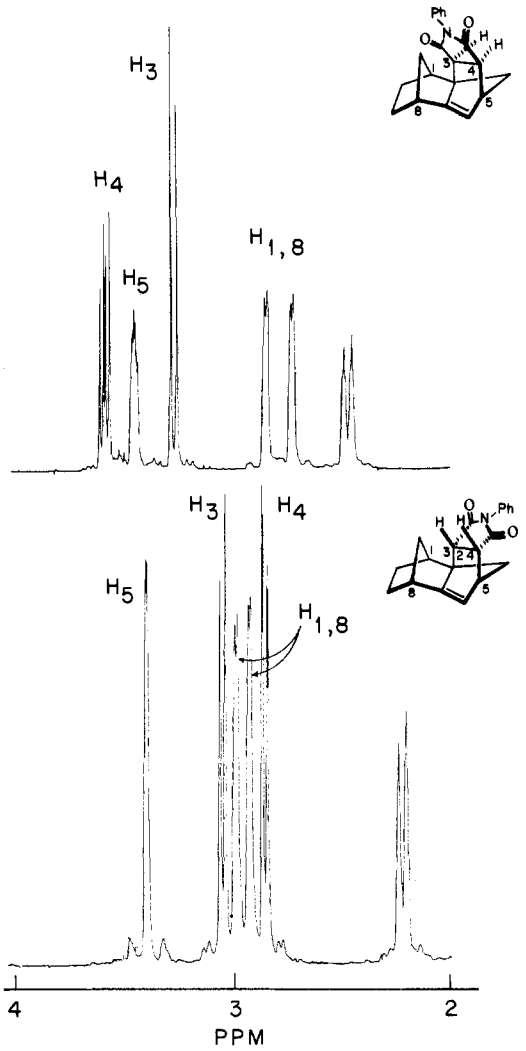


Figure 1. Partial 300-MHz ^{1}H NMR spectra of **40** (top) and **41** (bottom) which allow clear stereochemical distinctions to be made ($CDCl_3$ solutions).

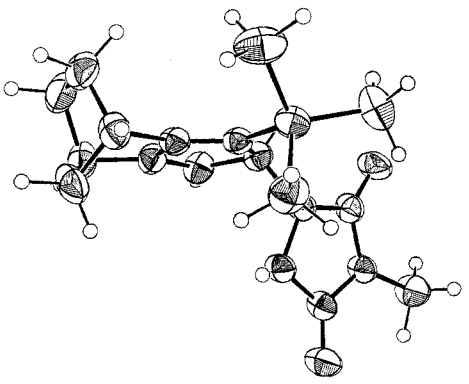


Figure 2. ORTEP drawing of **43**. Non-hydrogen atoms are drawn with 50% probability ellipsoids. Hydrogen atoms have been drawn artifically small.

In view of the heightened dienophilic reactivity of *N*-methyltriazolinedione, reaction with **5** was conducted at −78 °C as before with **6**. Under these conditions, a 1:1 adduct was obtained (23% isolated) that clearly was not the end result of a Diels–Alder process. Rather, the operation of an ene reaction suggested itself, the regio- and stereochemical ramifications of which could not be unequivocally deduced by NMR analysis. Consequently, recourse was made to X-ray structure determination. An ORTEP drawing of **43** is shown in Figure 2 and the associated numbering scheme in Figure 3. Bond lengths and angles are compiled in Table VIII. Other structural details are reported in Tables IV–X.

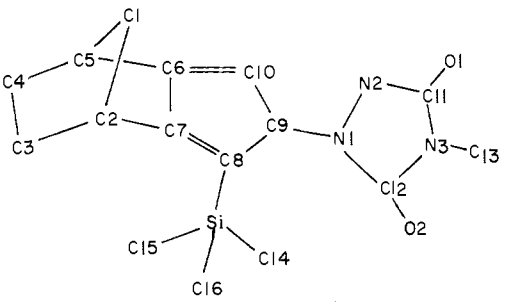


Figure 3. Labeling scheme used for **43**. Hydrogen atoms are named according to the attached carbon or nitrogen atom.

Table IV. Crystallographic Details for 43 and 47

	43	47
formula	$SiO_2N_3C_{16}H_{23}$	$N_4C_{16}H_{12}$
fw	317.47	260.30
space group	$P\bar{1}$-C_i^1	$Pbca$-D_{2h}^{15}
a, Å	8.977 (1)	10.672 (1)
b, Å	11.695 (1)	21.315 (2)
c, Å	8.958 (1)	11.970 (1)
α, deg	110.59 (1)	
β, deg	93.41 (1)	
γ, deg	75.82 (1)	
V, Å^3	853	2723
Z	2	8
density (calcd), g/cm^3	1.235	1.270
radiation	Mo Kα (λ(Kα_1) = 0.709 26 Å), graphite monochromator	same
linear abs coeff, cm^{-1}	1.42	0.74
temp, °C	21 (1)	21 (1)
2θ limits	$4° \leq 2\theta \leq 50°$	$4° \leq 2\theta \leq 55°$
scan speed	variable scan speed from 2.0 to 24.0 deg/min	same
background time/scan time	0.5	0.5
scan range	1.0° below Kα_1 to 1.2° above Kα_2	1.0° below Kα_1 to 1.1° above Kα_2
data collected	$+h, \pm k, \pm l$	$+h, +k, +l$
unique data	3040	3140
unique data, with $F_o^2 > 2\sigma(F_o^2)$	2188	1790
final number of variables	203	182
$R(F)$, for $F_o^2 > 2\sigma(F_o^2)$[a]	0.056	0.056
$R_w(F)$, for $F_o^2 > 2\sigma(F_o^2)$	0.059	0.047
error in observn of unit weight, e	2.52	2.34
isotropic extinction parameter		3.02×10^{-7}

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

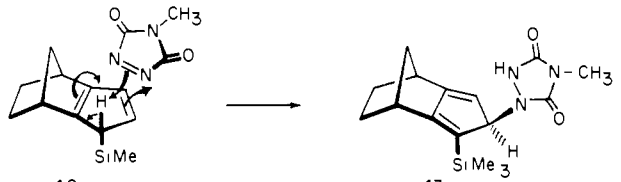
The urazole ring is seen to be exo and distal to the norbornane ring. Although there is no crystallographic symmetry imposed upon this molecule, the norbornane ring contains a pseudo mirror plane which passes through atom C(1) and bisects bonds C(3)–C(4) and C(6)–C(7). The geometry of the norbornane ring is the same as previously reported,[25] with the exception of three bond lengths, C(2)–C(7), C(5)–C(6), and C(6)–C(7). These three bonds are significantly shorter than the other C–C single bonds in this fragment. Especially short is the C(6)–C(7) bond length of 1.463(5) Å, owing to its incorporation within an unsaturated five-membered ring.

(25) (a) Baker, R.; Wood, J. S. *J. Chem. Soc., Perkin Trans. 2* **1978**, 971. (b) Fratini, A. V.; Britts, K.; Karle, I. L. *J. Phys. Chem.* **1967**, *71*, 2482. (c) Albinati, A.; Zocchi, M. *Cryst. Struct. Commun.* **1973**, *2*, 585.

Table IX (supplementary material) contains several least-squares planes through various parts of the molecule. The five-membered ring containing atoms C(6), C(7), C(8), C(9), and C(10) is essentially planar. Furthermore, this ring is almost coplanar with the plane defined by C(5), C(6), C(7), and C(2), the dihedral angle between the planes being 178.8(1)°.

Figure 4 illustrates the molecular packing in the unit cell. There exists an intermolecular hydrogen bond between the N(2) and O(1) atoms of neighboring urazole rings. This N(2)--O(1) distance is 2.782 (4) Å with an N(2)—H(N2)--O(1) angle of 157 (3)°.

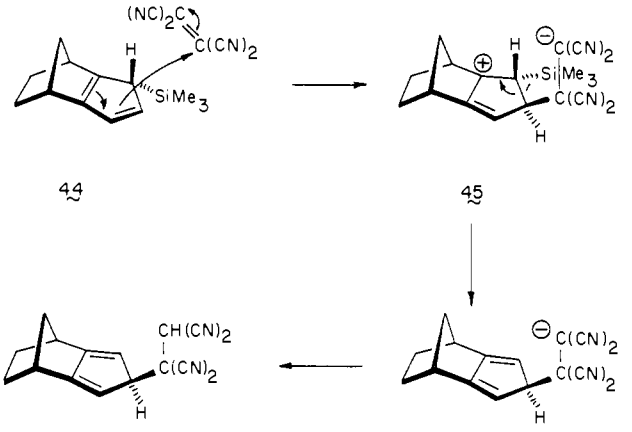
In light of these data, we conclude that [4 + 2] cycloaddition to either face of **5** is kinetically retarded relative to ene reaction involving **20**. As seen in **42**, this process entails electronic re-



42 43

organization within the entire cyclopentadiene ring. The reaction proceeds stereospecifically because the silatropic rearrangement is necessarily relegated to the endo surface. The requisite hydrogen atom consequently resides only on the exo face. The presence of **20** at the low temperature of the reaction suggests that isomerization is very rapid or that the dienophile is somehow promoting the rearrangement.

A related type of reaction occurs when **5** is allowed to react with tetracyanoethylene (TCNE) in ethyl acetate solution at room temperature. The lone adduct isolated in 57% yield was found to possess C_s symmetry and to lack the trimethylsilyl group. Accordingly, the distal carbon in **20** again comes under attack (see **44**). Perhaps because the negative charge terminus of



44 45

47 46

zwitterion **45** is highly stabilized, proton transfer does not occur rapidly or concertedly as in **42**.[26,30] This being the case, the trimethylsilyl group responds in well-precedented fashion to the nearby positive charge.[27] The ultimate fate of the Me_3Si residue is not known.

An alternative possible cause for this series of mechanistic events has its basis in stereochemistry. Should the TCNE approach **20** preferably from below plane, no hydrogen atom lies in adequate

(26) For other examples of this behavior, see: (a) Paquette, L. A.; Broadhurst, M. N.; Read, L. K.; Clardy, J. *J. Am. Chem. Soc.* **1973**, *95*, 4639. (b) Paquette, L. A.; Ley, S. V.; Broadhurst, M. J.; Truesdell, D.; Fayos, J.; Clardy, J. *Tetrahedron Lett.* **1973**, 2943.

(27) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

(28) Katz, T. J.; Rosenberger, M.; O'Hara, L. K. *J. Am. Chem. Soc.* **1964**, *86*, 249.

(29) Roush, W. R.; D'Ambra, T. E. *J. Org. Chem.* **1981**, *46*, 5045.

(30) Huisgen, R.; Ortega, J. P. *Tetrahedron Lett.* **1978**, 3975.

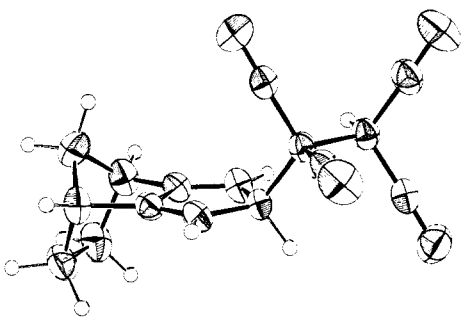


Figure 5. ORTEP drawing of **47**. Non-hydrogen atoms are drawn with 50% probability ellipsoids. Hydrogen atoms have been drawn artifically small.

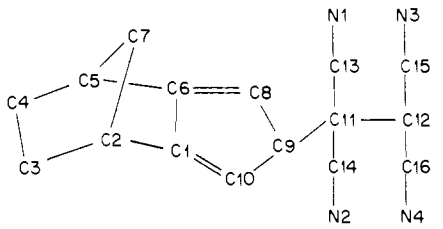
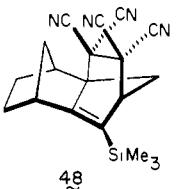


Figure 6. Numbering scheme used for **47**. Hydrogens are labeled according to the attached carbon atom.

proximity to the carbanion site to permit charge annihilation with preservation of the trimethylsilyl functionality. Accordingly, the stereochemistry of **47** becomes particularly relevant, since the exo or endo nature of its tetracyanoethyl moiety is necessarily interlinked with initial C–C bond formation. For these reasons, **47** was also subjected to X-ray analysis. In the ORTEP drawing of this molecule (Figure 5; associated numbering scheme in Figure 6) the tetracyanoethyl group is clearly seen to reside on the upper face of the molecule, syn to the methano bridge. Interestingly, the cyclopentadiene ring is essentially planar despite the presence of this ponderal substituent. A stereodrawing of the unit cell of **47** is provided in Figure 7; other structural details can be found in Tables XI–XVI (supplementary material).

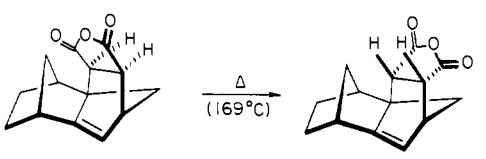
Unlike the room temperature reaction, TCNE adds smoothly to preequilibrated **5** to produce **48** in 51% yield. No other adduct was detected.



48

The ability of Lewis acids to accelerate certain Diels–Alder reactions is well-known. The potential for catalysis in the present context was explored in three examples by addition of 10 equiv of boron trifluoride etherate at 0 °C in anhydrous ether as solvent. Two series of events were expected to gain importance at the molecular level. Coordination of BF_3 to the dienophile is, of course, one of these. The second phenomenon, specific to molecules such as **5**, **6**, and their isomers, was interaction with the dienylsilane moiety. The eventual fate of these isodicyclopentadienes would consequently depend upon the extent of the latter interaction.

In the maleic anhydride example, the desilylated product **49**



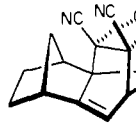
49 50

was obtained exclusively. When heated independently in *tert*-

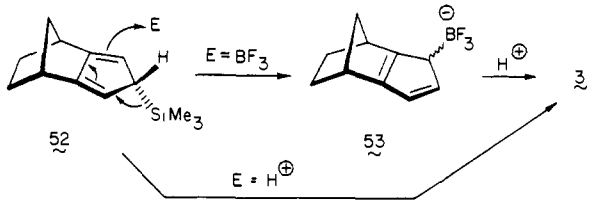
butylbenzene solution for 9 h, **49** experienced complete conversion to the known[10] isomer **50**. The ^{1}H NMR spectra of **49** and **50** are as distinctive and characteristic as those illustrated in Figure 1.

Similar reaction with *N*-phenylmaleimide led to the isolation of **40** (56%) and **41** (10%). Unlike **49**, **40** did not experience postequilibration with **41** on being heated at 169 °C for 12 h.

Desilylation was also observed in the catalyzed addition of TCNE to **5**. The minor product (38%) was identified as **47** and the major product (62%) as **51**. Evidently, the heightened reactivity of TCNE is adequate to allow direct reaction with **20**. On the other hand, the formation of **40**, **41**, **49**, and **51** appears to be triggered either by direct Lewis acid attack on **5** (see **52**, no stereoselectivity implied) followed by protonolysis (**53**), or by



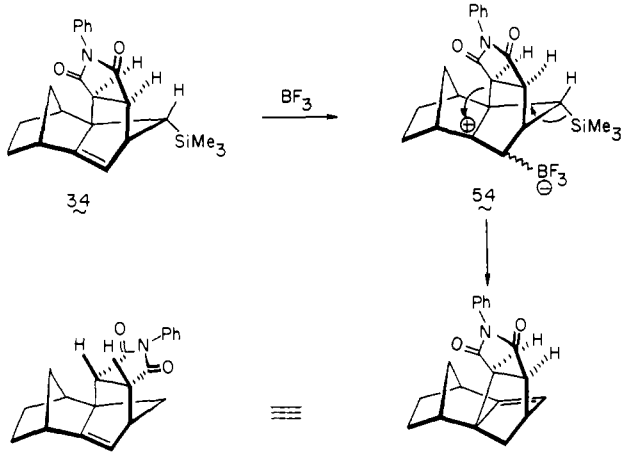
51



52 53 3

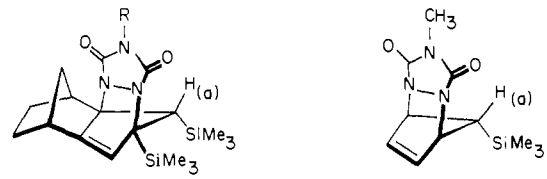
direct protonolysis arising from the presence of adventitious moisture. *In either event, there arises a most expedient method for generating* **3** *virtually free of* **1** *under very mild conditions.* Previously, access to low concentrations of **3** could be gained only by thermolysis of **1**.[9,10,28] The conditions presently uncovered may conveniently allow for the incursion of kinetically controlled cycloadditions to the isomerized diene.

It has been possible to rule out the alternative possibility[18,29] that the desilylated adducts result from subsequent rearrangement of an initially formed silicon-containing product. As detailed in the scheme that follows, attack of boron trifluoride on **34** could induce formation of carbocation **54** and set the stage for Wagner–Meerwein shift and desilylation. This sequence of reactions not only regenerates the carbon framework of the starting material but also leads to reversal (Alder → anti-Alder, or vice versa) of the stereochemical mode of dienophile attachment (e.g., **41**). However, exposure of **34** to 8 molar equiv of boron trifluoride etherate in ether at room temperature for 4 days in an attempt to simulate the original reaction conditions afforded only unchanged reactant. Careful TLC analysis showed no evidence for detectable conversion to **41**.



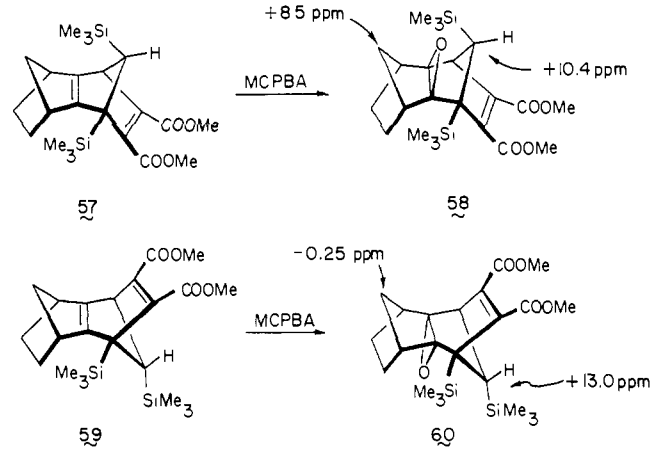
34 54 41

As expected, the reactivity of **7** in Diels–Alder reactions is extremely low. When equimolar amounts of this isodicyclopentadiene and the highly reactive *N*-methyltriazolinedione were allowed to stand in ethyl acetate solution for 2 days, 23% of unreacted **7** was recovered. Additionally, the only product formed (**55a**, 43%) proved to arise not from **7** but from **23**. The stereochemical definition of the silyl-substituted apical carbon in **55a**, the end result of sterically less hindered bonding to the endo-[1,5]-silatropic shift isomer, is based chiefly upon NMR data. Perhaps the most characteristic feature is the singlet arising from $H_{(a)}$ which appears at δ 1.53 in $CDCl_3$ solution. This chemical shift compares favorably to that of $H_{(a)}$ in **56** (δ 1.82), once allowance is made for the additional strain in **55a**. The common projection of these protons above the plane of the urazole ring is thereby signaled. An entirely analogous adduct (**55b**) was isolated from reaction with *N*-phenyltriazolinedione ($\delta_{H_{(a)}}$ 1.61).



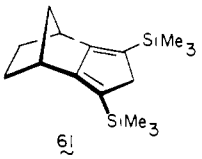
55a, R = CH_3
b, R = C_6H_5 56

Similar considerations carry over to **57** and **59**, the adducts obtained from **7** and DMAD at 140 °C (no reaction at 20 °C) in 65 and 35% yields, respectively. The syn stereochemistry of the more dominant isomer follows from the typical shielding response of the inside ethano bridge protons (δ 0.85) to the proximate maleate ester double bond and the notable upfield shifting of both apical carbons that develops upon conversion to epoxide **58** (see formula). In addition, the other spectral features of **57** and **58** compare very closely to those of **28** and **29** (see, for example, Table I). In contrast, **60** provides evidence for widely different epoxide anisotropy contributions to its two apical carbons (see formula), necessitating an *anti*-sesquinorbornadiene structure for adduct **59**. The same anisotropy effects cause shielding of the proton geminal to the secondary trimethylsilyl group (Table I), a phenomenon requiring that it be positioned exo to the oxygen atom.



57 58 59 60

These findings leave no doubt that **7** can indeed undergo isomerization to **24** and **26** at these more elevated temperatures. The possibility of more advanced silatropic migration within this pair of isodicyclopentadienes remained unanswered, however, because **61** with its two flanking trimethylsilyl substituents attached to primary bonding sites should, like **7**, be a comparatively less reactive diene than **24** and **26** (cf. **14** and **16**). It therefore became relevant to inquire whether **61** could be produced. To this end, benzene solutions of **7** were heated for 4 h at 145 °C in sealed tubes. Following return to room temperature, spectral analysis indicated that 1:1 mixtures of **7** and **61** are formed under



61

these conditions. No signals attributable to other isomers were seen. It soon became obvious that attempts to separate **61** and **7** by various chromatographic means result in its selective destruction. An additional noteworthy observation is the fate of this mixture when *N*-methyltriazolinedione was added. Within 10 min, **61** was completely decomposed and it became possible to reisolate pure **7**.

Since the mixture consists of only two components and the spectra of **7** had earlier been recorded, it was an easy matter to obtain high-quality spectral data for **61** by computer subtraction. Its ^{1}H NMR spectrum is illustrated in Figure 8. The 7-line carbon spectrum conforms to its molecular C_s symmetry.

Discussion

The propensity of simple silyl-substituted cyclopentadienes such as **8** and **14** for [1,5] silatropic migration can be readily followed by observing characteristic changes in NMR spectral line shapes with temperature and subjecting these data to computational analysis. For **6–7**, this has not proven possible because the isodicyclopentadiene arrangement of their conjugated double bonds heavily dominates any equilibria which may exist. Consequently, the concentration levels of [1,5]~Si isomers such as **20**, **23**, and **25** never become adequately elevated to be observed by this method. Previously, procedures were developed to trap **3**, the [1,5]~H isomer of hydrocarbon **1**, in the presence of much larger amounts of **1**.[9,10] By making recourse to dienophiles of sufficiently attenuated reactivity. Diels–Alder cycloadditions can be made to occur preferably with **3** because this diene contains a more reactive norbornene double bond.

This tool has been utilized herein to prove the responsiveness of **5–7** to sigmatropic change. In concordance with the Curtin–Hammett principle, the utilization of [4 + 2] cycloaddition chemistry can hardly be expected to provide a reliable indication of isomer composition. Nonetheless, the technique does serve as a means for detecting the presence of one or more equilibrating isomers whose concentration may be low, but whose reactivity toward a given dienophile is high.

In this context, the differing behavior of **5** and **6** is particularly noteworthy. Substrate **6** having an above-plane trimethylsilyl group enters readily into dienophilic capture without prior migration of any substituent. Only reaction partners of high Diels–Alder reactivity were studied, and endo π-facial stereoselectivity was encountered in each example. Isomer **5** was likewise captured intact by DMAD, although exo bonding to the diene was now clearly evident. However, this reagent is known to be sterically incapable of capturing **3** to provide an angular adduct. Consequently, it is considered unlikely that **20** and **21**, if present, would react under such circumstances. More revealing, therefore, was the finding that *N*-phenylmaleimide condenses preferably with **20** at room temperature to produce **34** as the exclusive adduct. At least two steric contributions could cause this reaction pathway to be the most energetically accessible. The presence of an Me_3Si group on the endo surface of **5** could retard the rate of direct below-plane cycloaddition which is otherwise commonly encountered. Equally important is the configuration of the trimethylsilyl substituent in **20**, which is necessarily below plane and consequently not in position to interfere with favored exo dienophile approach. Where **6** is concerned, the steric situation is reversed on both counts, and the first alternative is followed.

In an attempt to gain a more quantitative appreciation of the actual steric bulk offered by Me_3Si in **5** and **6**, these substrates were allowed to compete for a limited amount of DMAD at −10 °C. The use of this dienophile was dictated by its previously demonstrated affinity for these diene isomers alone. After a reaction time of 4 days, an 82:12 ratio of **28** and **33** was isolated alongside recovered isodicyclopentadiene which was predominantly

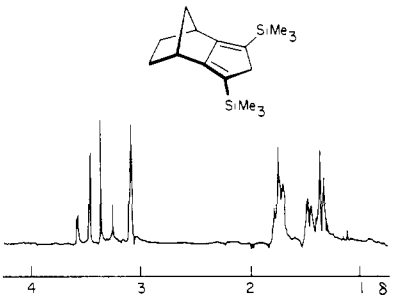
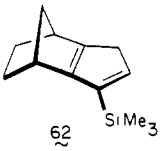


Figure 8. Computer subtracted 300-MHz ^{1}H NMR spectrum of **61** (C_6D_6 solution).

5. Thus, the *exo*-2-(trimethylsilyl) derivative **6** is in fact appreciably more reactive than endo isomer **5**.

The heating of **5** to 140 °C prior to addition of DMAD or *N*-phenylmaleimide has demonstrated that more extensive [1,5] sigmatropic migration is possible in this system. While DMAD captures **22** uniquely, *N*-phenylmaleimide engages in cycloaddition with both **21** and **62**. The latter diene could result from [1,5]~H



62

within **22** in that direction opposite to the one which would return **20**. Interestingly, TCNE is totally selective for **62** in these postequilibration experiments.

It is noteworthy that *N*-methyltriazolinedione and TCNE choose not to cycloadd to **5** (compare **6** → **32**) and to enter instead into ene reaction. In both cases, the application of x-ray crystal structure analysis clearly revealed the occurrence of exo C–C bond formation. The dichotomy between the two reagents is seen in terms of the retention of Me_3Si in **43** and its loss while proceeding to **47**. Both reagents are well-known to be capable of generating zwitterionic intermediates readily[26,30–35] and engaging in ene reaction chemistry.[36–38] Two particularly relevant examples are illustrated by the behavior of **63**[39] and **64**.[40]

Our attempts at Lewis acid catalysis of selected cycloadditions to **5** hold fascination in that the methodology provides a mild and convenient method for generating apparently high concentrations of **3** at room temperature. Previously, access to **3** was possible only by thermal activation of **1**.[9,10]

From the outset, we anticipated that **7** would prove as unreactive as its monocyclic analogue **14** to [4 + 2] cycloaddition. Some

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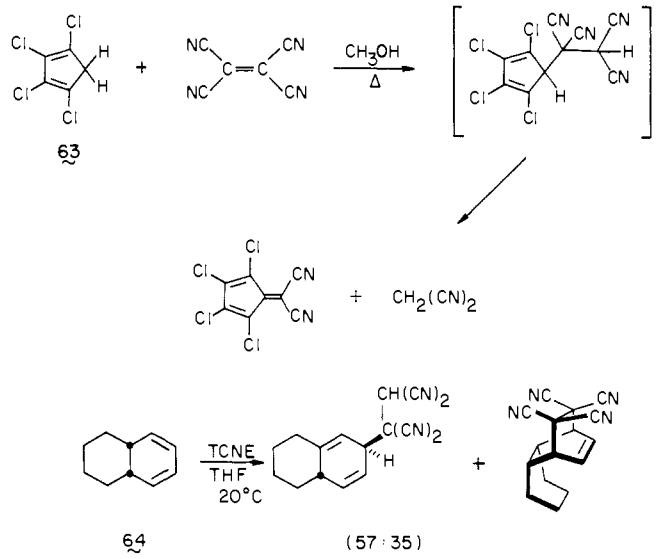
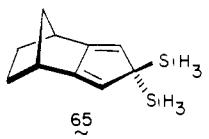


insight into preferred migratory capabilities might therefore be hoped for. Gleiter has analyzed the π orbital network in **65** by



MINDO/3 and INDO.[41] Whereas the first procedure provided evidence for the usual[4,42] disrotatory tilting of the terminal olefinic orbitals in π_1, the second did not. As noted earlier, stereospecific labeling of **7** could not be achieved. However, this failure proved to have lesser consequence when subsequent isolation of the product pair **57**/**59** indicated that both Me_3Si groups enter into silatropic migration. These observations are not dissimilar from those of Bartlett and Wu,[43] who described, following completion of the present study, a kinetic investigation of [1,5] sigmatropic hydrogen/deuterium migration in isodicyclopentadiene (**1**).

Finally, the isolation of **33** indicates that Me_3Si migration from the exo to endo face of **6**, i.e., **6** → **5**, can occur under purely thermal conditions.

Experimental Section

Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. The ^1H NMR spectra were determined with Varian EM-390, Bruker HX-90, and Bruker WM-300 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were obtained with a Bruker WP-80 spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***endo*- and *exo*-4,5,6,7-Tetrahydro-2-(trimethylsilyl)-4,7-methano-2*H*-indenes (5 and 6).** To a cold (−78 °C), magnetically stirred solution of isodicyclopentadiene (**1**, 1.0 g, 7.58 mmol) in freshly distilled tetrahydrofuran (100 mL) was added *n*-butyllithium in hexane (8.1 mL of 1.4 M, 11.4 mmol). After 30 min, the yellow solution was slowly transferred via canula to a cold (−78 °C) solution of chlorotrimethylsilane (1.64 g, 15.2 mmol) in the same solvent (20 mL). The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature during 30 min. Ether (100 mL) was added and the salts were removed by washing with water (4 × 100 mL). The organic phase was dried and evaporated to leave an oil (1.1 g) which was composed of 91:1 mixture of **5** and **6** (^1H NMR analysis; see text).

This substance was redissolved in anhydrous tetrahydrofuran (100 mL) and the above deprotonation sequence was repeated. After 30 min at −78 °C, the yellow solution was transferred via canula to a cold (−78 °C), magnetically stirred solution of water (1 mL) in distilled tetrahydrofuran (20 mL). The reaction mixture was allowed to warm to room temperature during 30 min, at which point it was processed as before to give 1.2 g of a yellow oil which was subjected to MPLC on silica gel (elution with petroleum ether).

The first isomer to elute was **6** (264 mg, 24%), a colorless oil: ^1H NMR ($CDCl_3$) δ 5.73 (s, 2 H), 3.21 (s, 1 H), 3.07 (br s, 2 H), 1.88 (d, J = 7.1 Hz, 2 H), 1.76 (d, J = 8.8 Hz, 1 H), 1.67 (d, J = 8.8 Hz, 1 H), 1.44 (d, J = 7.1 Hz, 2 H), −0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 155.01, 115.21, 52.99, 48.84, 38.99, 28.77, −2.06; *m/e* (M^+) calcd 204.1334, obsd 204.1305.

Endo isomer **5** (330 mg, 28%) eluted subsequently, a colorless oil, mp 15.5–16.5 °C: ^{H} NMR ($CDCl_3$) δ 5.79 (s, 2 H), 3.34 (s, 1 H), 3.12 (br s, 2 H), 1.84 (d, J = 6.7 Hz, 2 H), 1.77 (d, J = 9.0 Hz, 1 H), 1.62 (d, J = 9.0 Hz, 1 H), 1.24 (d, J = 7.3 Hz, 2 H), −0.5 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 154.05, 115.84, 84.52, 52.72, 46.85, 83.94, 28.84, −1.99; *m/e* (M^+) calcd 204.1334, obsd 204.1339.

Dimethyl Acetylenedicarboxylate Addition to 6. A solution of **6** (450 mg, 2.21 mmol) and DMAD (314 mg, 2.21 mmol) in chloroform (20 mL) was stirred overnight at room temperature. Following solvent removal, the yellow residue was purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 590 mg (77%) of **28** as a pale yellow oil. No other products were seen.

For **28**: ^1H NMR ($CDCl_3$) δ 3.73 (s, 6 H), 3.71 (s, 2 H), 3.01 (br s, 2 H), 2.50 (m, 1 H), 1.66–1.38 (m, 3 H), 1.13 (d, J = 9.4 Hz, 1 H), 0.50 (d, J = 8.1 Hz, 2 H), −0.08 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 166.23, 158.65, 153.60, 79.42, 54.95, 51.94, 48.30, 42.77, 22.28, −0.58; *m/e* (M^+) calcd 346.1600, obsd 346.1607.

Epoxidation of 28. A solution of *m*-chloroperbenzoic acid (93 mg, 0.54 mmol) in dichloromethane (10 mL) was added to a solution of **28** (156 mg, 0.45 mmol) in the same solvent (15 mL) at room temperature. The reaction mixture was then heated at the reflux temperature for 24 h, cooled, and evaporated. The solid residue was purified by MPLC on silica gel (elution with 7% ethyl acetate in petroleum ether) to give 130 mg (80%) of **29** as a colorless solid, mp 104.5–105.5 °C (from hexane); ^1H NMR ($CDCl_3$) δ 3.76 (s, 6 H), 3.40 (s, 2 H), 2.65 (br s, 2 H), 2.10–1.90 (m, 1 H), 1.77 (s, 1 H), 1.60–0.85 (m, 5 H), −0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 165.21, 151.90, 67.53, 66.07, 52.18, 51.17, 39.71, 39.42, 25.05, −0.34; *m/e* (M^+ − 15) calcd 347.1315, obsd 347.1322.

Anal. Calcd for $C_{19}H_{26}O_5Si$: C, 62.96; H, 7.23. Found: C, 63.03; H, 7.26.

***N*-Phenylmaleimide Addition to 6.** A solution of **6** (200 mg, 0.98 mmol) and *N*-phenylmaleimide (170 mg, 0.98 mmol) in chloroform (30 mL) was stirred at room temperature for 36 h. The solvent was evaporated and the solid residue was recrystallized from ether to give 210 mg of **30** as a white crystalline solid. The filtrate was evaporated and subjected to preparative TLC on silica gel (elution with 10% ethyl acetate in petroleum ether). There was isolated an additional 40 mg (total yield 68%) of **30**, mp 167–168 °C (from hexane). No other adducts were seen.

For **30**: ^1H NMR ($CDCl_3$) δ 7.5–7.41 (m, 3 H), 7.25–7.22 (m, 2 H), 3.53 (s, 2 H), 3.10 (s, 2 H), 2.80 (s, 2 H), 1.70 (d, J = 7.5 Hz, 2 H), 1.49 (d, J = 8.3 Hz, 1 H), 1.19 (d, J = 8.4 Hz, 1 H), 1.10 (s, 1 H), 0.88 (d, J = 7.6 Hz, 2 H), −0.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 177.15, 154.13, 132.04, 129.25, 128.65, 126.41, 50.14, 49.92, 44.95, 42.71, 25.32, −0.31; *m/e* (M^+) 377 too small for accurate mass measurement.

Anal. Calcd for $C_{23}H_{27}NO_2Si$: C, 73.17; H, 7.21. Found: C, 72.97; H, 7.24.

Epoxidation of 30. Treatment of **30** (100 mg, 0.27 mmol) with *m*-chloroperbenzoic acid (60 mg, 0.35 mmol) in dichloromethane (10 mL) as before (reflux, 9 days) returned 70 mg of unreacted adduct and 25 mg (24%) of **31** after preparative TLC on silica gel (elution with 15% ethyl acetate in petroleum ether); colorless solid, mp 187–188 °C: ^1H NMR ($CDCl_3$) δ 7.52–7.42 (m, 3 H), 7.20–7.7 (m, 2 H), 3.61 (s, 2 H), 3.33 (s, 2 H), 2.88 (s, 2 H), 2.01 (d, J = 9.2 Hz, 1 H), 1.77 (d, J = 12 Hz, 2 H), 1.69 (d, J = 12 Hz, 2 H), 0.81 (d, J = 9.2 Hz, 1 H), 0.44 (s, 1 H), −0.03 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 177.21, 131.42, 129.37, 128.93, 126.42, 58.90, 48.51, 47.47, 40.64, 39.27, 35.44, 26.91, −0.15; *m/e* (M^+) calcd 393.1760, obsd 393.1727.

***N*-Methyltriazolinedione Addition to 6.** A solution of *N*-methyltriazolinedione (111 mg, 0.98 mmol) in ethyl acetate (10 mL) was syringed into a cold (−78 °C), magnetically stirred solution of **6** (200 mg, 0.98 mmol) in the same solvent (50 mL). After 15 min, the solvent was evaporated and the solid residue was redissolved in ether (50 mL) with no external heating. The ether was slowly evaporated under vacuum to a volume of ca. 15 mL and cooled to give 125 mg (40%) of **32**, colorless crystals, mp 121–122 °C (dec) (from ether). NMR (^1H and ^{13}C) analysis of the remaining material showed no additional Diels–Alder adducts to be present; ^1H NMR (C_6D_6) δ 4.90 (s, 2 H), 2.74 (br s, 2 H), 2.53 (s, 3 H), 1.57 (s, 1 H), 1.38 (d, J = 7.2 Hz, 2 H), 1.23 (d, J = 8.3 Hz, 1 H), 0.95 (d, J = 5 Hz, 2 H), 0.81 (d, J = 8.4 Hz, 1 H), −0.3 (s, 9 H); ^{13}C NMR (C_6D_6) ppm 159.16, 153.15, 67.92, 53.48, 51.08, 42.33,

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25.65, 24.72, −1.35; *m/e* (M^+) calcd 317.1559, obsd 317.1558.

Anal. Calcd for $C_{16}H_{23}N_3O_2Si$: C, 60.36; H, 7.28. Found: C, 60.52; H, 7.41.

Dimethyl Acetylenedicarboxylate Addition to 5. A solution of DMAD (71 mg, 0.50 mmol) and **5** (102 mg, 0.50 mmol) in chloroform (20 mL) was stored at −10 °C for 4 days. The solvent was evaporated and the resulting yellow oil was purified by preparative TLC on silica gel (elution with 5% ethyl acetate in petroleum ether). In addition to 50 mg (50%) of recovered **5**, there was isolated 60 mg (70% corrected) of **33** as a colorless oil: ^1H NMR ($CDCl_3$) δ 3.73 (s, 6 H), 3.71 (m, 2 H), 3.00 (br s, 2 H), 2.50 (m, 1 H), 1.66–1.1 (series of m, 4 H), 0.6–0.4 (m, 2 H), −0.07 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 166.23, 158.65, 153.60, 79.42, 54.95, 51.94, 48.30, 42.77, 22.28, −0.58; *m/e* calcd (M^+) 346.1600, obsd 346.1607.

When the same reaction was carried out at room temperature for 18 h, 30 mg (10%) of **5** was recovered and 110 mg (72% corrected) of **33** was isolated.

***N*-Phenylmaleimide Addition to 5.** A solution of **5** (107 mg, 0.52 mmol) and *N*-phenylmaleimide (91 mg, 0.52 mmol) in chloroform (15 mL) was stirred at room temperature for 3 days. The solvent was evaporated and the solid residue was recrystallized from ether to give 120 mg of **34** as colorless crystals, mp 170–171 °C. The mother liquor was concentrated and subjected to preparative TLC on silica gel (elution with 10% ethyl acetate in petroleum ether) to provide an additional 34 mg of **34** (total yield 154 mg, 79%): ^1H NMR ($CDCl_3$) δ 7.48–7.38 (m, 3 H), 7.17–7.14 (m, 2 H), 5.58 (d, J = 2.4 Hz, 1 H), 3.62–3.56 (m, 2 H), 3.30 (d, J = 7.3 Hz, 1 H), 2.76 (br s, 2 H), 2.53 (d, J = 10.9 Hz, 1 H), 1.82–1.78 (m, 2 H), 1.64–1.47 (m, 3 H), 1.21 (s, 1 H), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 177.88, 176.14, 158.37, 132.20, 129.04, 128.41, 126.66, 116.18, 72.82, 60.69, 50.93, 50.89, 50.54, 43.30, 40.44, 37.38, 31.22, 26.46, 0.15; *m/e* (M^+) 377 observed but too small for accurate mass measurement.

Anal. Calcd for $C_{23}H_{27}NO_2Si$: C, 73.17; H, 7.21. Found: C, 72.93; H, 7.27.

Competition Experiment. A cold (0 °C) solution containing **5** (131 mg, 0.64 mmol), **6** (129 mg, 0.63 mmol), and DMAD (90 mg, 0.63 mmol) in chloroform (20 mL) was prepared and stored in a freezer at −10 °C for 4 days. The solvent was evaporated and the residue was separated into its components by preparative TLC on silica gel (triple elution with 5% ethyl acetate in petroleum ether). Three fractions were isolated: (a) 130 mg of recovered isodicyclopentadienes consisting mostly of **5**; (b) 140 mg (64%) of adduct **28**; (c) 30 mg (14%) of adduct **33**. The ratio of endo:exo cycloaddition is therefore 82:18.

Addition to Preequilibrated 5. Dimethyl Acetylenedicarboxylate. A solution of **5** (200 mg, 0.98 mmol) in xylene (20 mL) was heated at the reflux temperature under nitrogen for 30 min and a solution of DMAD (139 mg, 0.98 mmol) in the same solvent (5 mL) was slowly introduced. The reaction mixture was stirred with heating for 30 min and solvent was evaporated under reduced pressure. The yellow oily residue was separated into its components by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether).

The first product to elute was **35** (116.3 mg, 34%) which was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 3.75 (s, 3 H), 3.70 (s, 3 H), 3.03 (br s, 1 H), 2.66–2.03 (m, 2 H), 1.60–1.0 (m, 8 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 168.31, 165.30, 161.52, 161.03, 156.81, 149.09, 71.02, 54.56, 51.85, 51.07, 48.79, 43.11, 42.72, 22.23, −2.23; *m/e* calcd (M^+) 346.1600, obsd 346.1607.

The next component proved to be **28** (174.3 mg, 51%).

The third and final product was **33** (34.3 mg, 10%).

Peracid Oxidation of 35. An ice-cold solution of **35** (115 mg, 0.33 mmol) in dichloromethane (25 mL) was treated dropwise with a solution of *m*-chloroperbenzoic acid (63 mg, 0.37 mmol) in the same solvent (5 mL). The reaction mixture was stirred at 0 °C for 45 min and worked up in the usual manner. The residue was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) and the resulting solid was recrystallized from hexanes to give **36** (102 mg, 85%) as a colorless crystalline solid, mp 87.5–88.0 °C: ^1H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 3.83 (s, 3 H), 3.53 (br s, 1 H), 2.80 (br s, 2 H), 2.30–0.85 (series of m, 8 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 167.14, 164.74, 155.39, 148.23, 69.28, 66.87, 57.91, 52.06, 49.71, 47.41, 40.14, 39.76, 39.59, 25.27, 24.61, −2.44; *m/e* calcd (M^+) 362.1549, obsd 362.1557.

Anal. Calcd for $C_{19}H_{26}O_5Si$: C, 62.96; H, 7.23. Found: C, 62.95; H, 7.25.

Addition to Preequilibrated 5. *N*-Phenylmaleimide. To a 200 mg (0.98 mmol) sample of **5** which had been preequilibrated in hot xylene (20 mL) as before for 30 min was slowly added a solution of *N*-phenylmaleimide (170 mg, 0.98 mmol) in the same solvent (2 mL). After 30 min at the reflux temperature, the solvent was removed under reduced pressure and the residue was subjected to MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether).

The least polar component proved to be **38** (114.5 mg, 31%), colorless crystalline solid, mp 116–117 °C (from hexanes): ^1H NMR ($CDCl_3$) δ 7.5–7.2 (m, 5 H), 3.47 (br s, 1 H), 3.15–2.80 (m, 3 H), 1.9–1.2 (series of m, 6 H), 0.20 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 178.04, 177.69, 175.78, 132.21, 131.17, 129.09, 128.43, 126.47, 67.20, 52.33, 48.83, 45.71, 42.54, 42.16, 39.97, 36.75, 31.77, 24.50, −0.91; *m/e* (M^+) 377 observed but too small for accurate mass measurement; *m/e* calcd (M^+ − 15) 362.1576, obsd 362.1584.

The second fraction was identified as **39** (74.5 mg, 20%), colorless crystals, mp 149–150 °C (from hexanes): ^1H NMR ($CDCl_3$) δ 7.35–7.20 (m, 3 H), 7.15–7.12 (m, 2 H), 5.45 (s, 1 H), 3.55 (d, J = 7.8 Hz, 1 H), 3.29 (d, J = 7.8 Hz, 1 H), 2.83 (d, J = 3.7 Hz, 1 H), 2.72 (d, J = 3.5 Hz, 1 H), 2.45 (d, J = 10.5 Hz, 1 H), 1.89–1.30 (m, 7 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 178.12, 176.42, 165.01, 132.29, 129.09, 128.41, 126.80, 117.48, 68.55, 56.89, 50.49, 48.84, 47.96, 42.56, 39.80, 38.20, 33.20, 25.85, −2.57; *m/e* calcd (M^+) 377.1811, obsd 377.1819.

Anal. Calcd for $C_{23}H_{27}NO_2Si$: C, 73.17; H, 7.21. Found: C, 72.90; H, 7.17.

The third and final constituent was **37** (177.5 mg, 48%), colorless crystalline solid, mp 129–130 °C (from hexanes): ^1H NMR ($CDCl_3$) δ 7.48–7.37 (m, 3 H), 7.15–7.12 (m, 2 H), 3.58 (dd, J = 8.0 and 5.3 Hz, 1 H), 3.50 (d, J = 5.2 Hz, 1 H), 3.26 (d, J = 8.0 Hz, 1 H), 2.91 (d, J = 4.0 Hz, 1 H), 2.72 (d, J = 4.2 Hz, 1 H), 2.50 (d, J = 8.9 Hz, 1 H), 1.95–1.85 (m, 1 H), 1.74–1.50 (m, 5 H), 1.30–1.23 (m, 1 H), 0.07 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 178.19, 176.44, 174.30, 132.26, 129.86, 129.04, 128.38, 126.79, 69.06, 55.94, 50.96, 48.34, 46.64, 42.49, 39.81, 38.72, 32.59, 25.98, −0.69, *m/e* (M^+) 377 observed but too small for accurate mass measurement; *m/e* calcd (M^+ − 15) 362.1576, obsd 362.1584.

Anal. Calcd for $C_{23}H_{27}NO_2Si$: C, 73.17; H, 7.21. Found: C, 73.05; H, 7.16.

Addition to Preequilibrated 1. *N*-Phenylmaleimide. A solution of **1** (200 mg, 1.52 mmol) in *tert*-butylbenzene (25 mL) was heated at the reflux temperature under nitrogen for 30 min. To this solution was added *N*-phenylmaleimide (236 mg, 1.36 mmol) dissolved in the same solvent (5 mL). The stirred reaction mixture was heated at reflux for 18 h and the *tert*-butylbenzene was removed by distillation under reduced pressure. The residue was subjected to MPLC on silica gel (elution with 15% ethyl acetate in petroleum ether).

The more rapidly eluted component was **41** (155 mg, 32%), colorless solid, mp 166–168 °C (from hexanes): ^1H NMR ($CDCl_3$) δ 7.57–7.40 (m, 3 H), 7.38–7.28 (m, 2 H), 5.67 (d, J = 2.7 Hz, 1 H), 3.39 (br d, 1 H), 3.04 (d, J = 6.2 Hz, 1 H), 2.98 (d, J = 3.25 Hz, 1 H), 2.92 (d, J = 3.25 Hz, 1 H), 2.85 (dd, J = 7.2 and 1.5 Hz, 1 H), 2.06 (d, J = 10.3 Hz, 1 H), 1.86–1.28 (m, 7 H); ^{13}C NMR ($CDCl_3$, ppm) 176.98, 165.28, 129.09, 128.49, 126.47, 118.59, 65.83, 49.49, 48.83, 46.04, 42.87, 42.11, 39.21, 36.91, 31.66, 24.45; *m/e* calcd (M^+) 305.1416, obsd 305.1427.

The less rapidly eluted adduct was **40** (255 mg, 62%), colorless solid, mp 182–183 °C (from ether): ^1H NMR ($CDCl_3$) δ 7.50–7.37 (m, 3 H), 7.19–7.15 (m, 2 H), 5.64 (d, J = 2.7 Hz, 1 H), 3.57 (dd, J = 7.9 and 5.2 Hz, 1 H), 3.47–3.44 (m, 1 H), 3.28 (d, J = 8.0 Hz, 1 H), 2.85 (d, J = 3.8 Hz, 1 H), 2.73 (d, J = 3.5 Hz, 1 H), 2.47 (d, J = 10.6 Hz, 1 H), 2.85 (d, J = 3.8 Hz, 1 H), 2.73 (d, J = 3.5 Hz, 1 H), 2.47 (d, J = 10.6 Hz, 1 H), 1.91–1.34 (m, 7 H); ^{13}C NMR ($CDCl_3$, ppm), 177.91, 176.60, 163.37, 132.21, 128.98, 128.38, 126.68, 115.91, 67.37, 55.28, 48.23, 47.52, 46.64, 42.33, 39.81, 37.90, 25.92; *m/e* calcd (M^+) 305.1416, obsd 305.1427.

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27. Found: C, 78.61; H, 6.32.

***N*-Methyltriazolinedione Addition to 5.** A cold (−78 °C), magnetically stirred solution of **5** (500 mg, 2.45 mmol) in ethyl acetate (20 mL) was treated dropwise with a 0.1 M solution of *N*-methyltriazolinedione in the same solvent until the pink color persisted. The reaction mixture was evaporated to dryness and the residue was twice recrystallized from ether to give 100 mg of **43**. Further purification of the mother liquors by MPLC on silica gel (elution with 40% ethyl acetate in petroleum ether) afforded an additional 80 mg of **43** (total yield 23%) as a colorless, crystalline solid, mp 158–159 °C dec (from ether): ^1H NMR ($CDCl_3$) δ 5.66 (m, 2 H), 3.13 (m, 3 H), 3.03 (s, 3 H), 1.93–1.60 (m, 4 H), 1.40–1.20 (m, 2 H), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 167.63, 156.72, 153.85, 152.01, 126.32, 117.15, 70.88, 42.53, 39.28, 37.97, 27.82, 25.00, −0.63; *m/e* calcd (M^+) 317.1559, obsd 317.1567.

Anal. Calcd for $C_{16}H_{23}N_3O_2Si$: C, 60.52; H, 7.36. Found: C, 60.53; H, 7.30.

Tetracyanoethylene Addition to 5. A solution of **5** (200 mg, 0.9, mmol) and TCNE (115 mg, 0.90 mmol) in ethyl acetate (20 mL) was stirred at room temperature for 18 h and evaporated. The solid residue was recrystallized from ether to give 144 mg (57%) of **47**. The mother liquor contained additional quantities of **47** (^1H NMR analysis), but all attempts at chromatographic purification resulted in destruction of this

adduct. Further recrystallization from ether furnished analytically pure **47** as colorless crystals, mp 159–160 °C: ^{1}H NMR ($CDCl_3$) δ 5.80 (m, 2 H), 4.30 (s, 1 H), 4.03 (m, 1 H), 3.25 (m, 2 H), 2.10–1.3 (series of m, 6 H); ^{13}C NMR ($CDCl_3$, ppm) 162.55, 111.38, 107.55, 59.16, 44.68, 40.79, 38.77, 29.91, 27.56; *m/e* calcd (M^+) 260.1062, obsd 260.1067.

Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65. Found: C, 73.77; H, 4.72.

Addition to Preequilibrated 5. Tetracyanoethylene. To the xylene solution (20 mL) of preequilibrated diene **5** (200 mg, 0.98 mmol) (reflux, 30 min, N_2) was added TCNE (115 mg, 0.90 mmol) in the same solvent (5 mL). The reaction mixture was stirred with heating for 30 min and the solvent was evaporated under reduced pressure. Purification of the residue by MPLC on silica gel (elution with 8% ethyl acetate in petroleum ether) gave 165 mg (51%) of **48** as a colorless solid, mp 139–140 °C (from hexanes): ^{1}H NMR ($CDCl_3$) δ 4.00 (m, 1 H), 3.30–2.83 (m, 3 H), 2.2–1.23 (series of m, 7 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$, ppm) 175.11, 134.04, 112.68, 111.95, 75.10, 61.51, 48.84, 47.67, 46.60, 42.04, 40.14, 38.64, 31.41, 26.02, –1.11; *m/e* calcd (M^+) 332.1457, obsd 332.1465.

Anal. Calcd for $C_{19}H_{20}N_4Si$: C, 68.84; H, 6.06. Found: C, 68.83; H, 6.13.

Lewis Acid Promoted Reactions of 5. Maleic Anhydride. A stirred solution of maleic anhydride (96 mg, 0.98 mmol) in anhydrous ether (20 mL) was treated slowly with boron trifluoride etherate (1.2 mL, 9.8 mmol) at 0 °C. After 30 min, **5** (200 mg, 0.98 mmol) in the same solvent (10 mL) was introduced. The reaction mixture was stirred at 0 °C for 30 min, washed with water, dried, and evaporated. Purification of the residue by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) and recrystallization of the only component from hexanes gave 80 mg (35%) of **49** as a colorless solid, mp 110–111 °C: ^{1}H NMR ($CDCl_3$) δ 5.63 (d, J = 2.9 Hz, 1 H), 3.42 (dd, J = 2.8 and 1.2 Hz, 1 H), 3.17 (d, J = 7.6 Hz, 1 H), 2.97 (dd, J = 7.5 and 1.7 Hz, 1 H), 2.91 (br s, 2 H), 2.10 (d, J = 10.5 Hz, 1 H), 1.86–1.28 (m, 7 H); ^{13}C NMR ($CDCl_3$, ppm) 172.55, 171.46, 164.46, 116.73, 68.19, 55.56, 49.60, 48.01, 47.57, 42.22, 39.17, 38.17, 32.37, 25.98; *m/e* calcd (M^+) 230.0943, obsd 230.0952.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.83; H, 6.19.

Thermal Isomerization of 49. A solution of **49** (60 mg, 0.26 mmol) in *tert*-butylbenzene (20 mL) was heated at the reflux temperature for 9 h. The solvent was removed under vacuum and the white solid residue was recrystallized from hexanes to give **50** (50 mg, 83%), mp 125–126 °C (lit.[10] mp 124–125 °C): ^{1}H NMR ($CDCl_3$) δ 5.65 (d, J = 2.8 Hz, 1 H), 3.76 (dd, J = 8.5 and 5.3 Hz, 1 H), 3.45–3.42 (m, 1 H), 3.40 (d, J = 8.5 Hz, 1 H), 2.87 (d, J = 3.92 Hz, 1 H), 2.69 (d, J = 3.6 Hz, 1 H), 2.35 (d, J = 10.8 Hz, 1 H), 1.90–1.30 (m, 7 H); ^{13}C NMR ($CDCl_3$, ppm) 172.23, 171.57, 164.95, 118.54, 66.76, 50.31, 49.65, 47.19, 43.91, 42.05, 39.26, 36.58, 31.34, 24.34; *m/e* calcd (M^+) 230.0943, obsd 230.0952.

Lewis Acid Promoted Reactions of 5. Tetracyanoethylene. A stirred solution of TCNE (125 mg, 0.98 mmol) in anhydrous ether (20 mL) was treated slowly with boron trifluoride etherate (1.2 mL, 9.8 mmol) at 0 °C. After 30 min, **5** (200 mg, 0.98 mmol) in the same solvent (10 mL) was introduced and the reaction mixture was stirred for an additional hour prior to washing with water (2 × 50 mL), drying, and evaporation of solvent. The residue was subjected to recrystallization from ether (chromatography was destructive), and 110 mg of a mixture of **47** and **51** (43% yield) was obtained in a ratio of 38:62 (^{1}H NMR analysis). The ^{13}C NMR spectrum of **51** was obtained by subtraction: ($CDCl_3$, ppm) 166.13, 118.13, 112.55, 111.84, 111.46, 110.34, 74.61, 58.32, 48.26, 47.87, 46.86, 42.00, 39.45, 38.83, 31.42, 25.95.

4,5,6,7-Tetrahydro-2,2-bis(trimethylsilyl)-4,7-methano-2*H*-indene (7). A cold (–78 °C), magnetically stirred solution of dienes **5**/**6** (91:1) (2.0 g, 9.8 mmol) in dry tetrahydrofuran (100 mL) was treated slowly via syringe with *n*-butyllithium in hexane (10.5 mL of 1.5 M, 15.7 mmol). After 30 min, the slightly yellow reaction mixture was transferred to a cold (–78 °C), magnetically stirred solution of chlorotrimethylsilane (2.5 mL, 19.6 mmol) in the same solvent (15 mL). After an additional 30 min, the solution was allowed to warm to room temperature and was partitioned between water (100 mL) and ether (100 mL). The ether layer was washed with water (2 × 100 mL), diluted with petroleum ether (100 mL), and washed again with water (2 × 100 mL). After drying and concentration, the product was eluted (pentane) through a neutral alumina column (1 × 10 cm). There was isolated 1.8 g (67%) of **7** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.80 (s, 2 H), 3.13 (br s, 2 H), 2.10–1.20 (series of m, 6 H), –0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 155.25, 118.89, 56.70, 49.08, 39.37, 29.78, –0.58, –0.77; *m/e* (M^+) calcd 276.1729, obsd 276.1741.

***N*-Methyltriazolinedione Addition to 7.** A solution of **7** (200 mg, 0.72 mmol) and *N*-methyltriazolinedione (81 mg, 0.72 mmol) in ethyl acetate (10 mL) was stirred at room temperature for 2 days. The solvent was evaporated and the oily residue was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). The first fraction consisted of unreacted **7** (57 mg, 28% recovery). Subsequently, there was obtained 120 mg (60% corrected yield) of **55a**, a colorless oil, as the only identifiable product: ^{1}H NMR ($CDCl_3$) δ 5.73 (s, 1 H), 2.96 (s, 3 H), 3.10–2.70 (m, 3 H), 2.00–1.20 (series of m, 5 H), 1.53 (s, 1 H), 0.33 (s, 9 H), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 165.01, 154.79, 119.63, 90.27, 73.43, 61.35, 43.58, 38.88, 36.48, 31.72, 25.54, 25.40, –0.04, –1.40; *m/e* (M^+) calcd 389.1955, obsd 389.2020.

***N*-Phenyltriazolinedione Addition to 7.** Comparable reaction of **7** (100 mg, 0.36 mmol) with *N*-phenyltriazolinedione (63 mg, 0.36 mmol) returned 10 mg (10%) of unreacted diene and 68 mg (42%) of **55b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.55–7.30 (m, 5 H), 5.88 (s, 1 H), 3.12 (br s, 1 H), 2.90 (m, 2 H), 1.61 (s, 1 H), 1.97–1.55 (m, 5 H), 0.38 (s, 9 H), 0.21 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 165.45, 152.65, 132.37, 129.09, 128.87, 127.72, 125.65, 120.29, 90.55, 73.76, 61.46, 43.80, 38.94, 36.58, 31.68, 24.99, –0.04, –13.5; *m/e* (M^+) calcd 317.1559, obsd 317.1558.

Dimethyl Acetylenedicarboxylate Addition to 7. To a solution of **7** (200 mg, 0.72 mmol) in xylene (20 mL) which had been preequilibrated at the reflux temperature for 30 min was added a solution of DMAD (124 mg, 0.86 mmol) in the same solvent (2 mL). The reaction mixture was maintained at the boiling point for 2 h, the solvent was evaporated, and the oily residue was purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 195 mg (65%) of **57** and 105 mg (35%) of **59**, both as colorless oils.

For **57**: ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 3.69 (d, J = 0.9 Hz, 1 H), 3.66 (s, 3 H), 3.06 (br s, 1 H), 2.93 (br s, 1 H), 2.61 (d, J = 1.2 Hz, 1 H), 1.61–1.36 (m, 4 H), 1.13 (d, J = 8.3 Hz, 1 H), 0.84 (m, 1 H), 0.15 (s, 9 H), –0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 169.65, 164.86, 164.13, 160.55 (2C), 149.80, 84.08, 58.96, 53.68, 51.92, 51.80, 48.34, 43.42, 42.63, 22.24 (2C), 0.52, –0.99; *m/e* (M^+) calcd 418.1996, obsd 418.2009.

For **59**: ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 1 H), 3.76 (s, 3 H), 3.68 (s, 3 H), 2.85 (br s, 2 H), 2.04 (s, 1 H), 1.78–1.22 (series of m, 6 H), 0.09 (s, 9 H), –0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 175.72, 167.40, 164.73, 160.12, 153.45, 134.69, 83.78, 80.99, 60.05, 51.92, 51.55, 44.21, 38.51, 37.90, 29.59, 24.37, –0.26, –0.87; *m/e* (M^+) calcd 418.1996, obsd 418.2009.

Epoxidation of 57. Reaction of **57** (200 mg, 0.48 mmol) with *m*-chloroperbenzoic acid (116 mg, 0.67 mmol) in dichloromethane (25 mL) as before (reflux, 3 days) followed by preparative TLC (silica gel) purification (elution with 10% ethyl acetate in petroleum ether) gave 120 mg (58%) of **58** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 3.72 (s, 3 H), 3.37 (s, 1 H), 2.64 (br s, 1 H), 2.52 (br s, 1 H), 1.96 (d, J = 9.1 Hz, 1 H), 1.87 (s, 1 H), 1.78 (d, J = 11.4 Hz, 1 H), 1.44 (d, J = 8.9 Hz, 2 H), 0.87 (d, J = 8.5 Hz, 2 H), 0.16 (s, 9 H), –0.02 (s, 9 H); *m/e* (M^+) calcd 419.1710, obsd 419.1675.

Epoxidation of 59. Reaction of **59** (105 mg, 0.25 mmol) with *m*-chloroperbenzoic acid (69 mg, 0.40 mmol) in dichloromethane (25 mL) as before (reflux, 18 h) followed by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) gave 70 mg (65%) of **60** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 3.67 (s, 3 H), 3.15 (s, 1 H), 2.61 (br s, 1 H), 2.19 (br s, 1 H), 1.94 (d, J = 10.3 Hz, 1 H), 1.79 (s, 1 H), 1.74–1.56 (m, 5 H), 0.15 (s, 9 H), 0.11 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 166.38, 164.58, 147.96, 138.12, 83.72, 72.62, 70.81, 56.93, 52.33, 52.12, 51.67, 44.46, 38.78, 36.97, 26.09, 24.83, 1.49, –2.17; *m/e* (M^+) calcd 434.1945, obsd 434.2030.

Thermolysis of 7. A benzene solution of **7** was heated at 145 °C in a sealed tube for 4 h, cooled, and evaporated. ^{1}H NMR analysis of the residue indicated it to be a 1:1 mixture of **7** and **61**. Attemps to isolate **61** by various chromatographic methods failed because of the lability of **61** toward these agents. The following NMR spectra were determined by computer subtraction of the features of **7** from the composite: ^{1}H NMR (C_6D_6) δ 3.51 (d, J = 22.6 Hz, 1 H), 3.29 (d, J = 22.6 Hz, 1 H), 3.05 (br s, 2 H), 1.82–1.22 (series of m, 6 H), 0.23 (s, 18 H); ^{13}C NMR ($CDCl_3$) ppm 166.43, 131.17, 53.70, 46.10, 38.83, 28.49, –0.09.

X-ray Crystal Structure Determinations. Clear, colorless platelike crystals of **43** are triclinic, space group $P\bar{1}$ with unit cell constants of dimensions a = 8.977(1) Å, b = 11.695(1) Å, c = 8.958(1) Å, α = 110.59(1) Å, β = 93.41(1)°, and γ = 75.82(1)° at 21 °C. The final full-matrix least-squares refinement on the 2188 unique reflections with $F_0^2 > 2\sigma(F_0^2)$ yielded an R index (on F) of 0.056 for 203 variables (anisotropic thermal motion for non-hydrogen atoms, isotropic thermal motion for hydrogen bonded to N2, and remainder of hydrogen atoms fixed).

Compound **47** crystallizes in space group *Pbca* of the orthorhombic system in a cell of dimensions a = 10.672(1) Å, b = 21.315(2) Å, and c = 11.970(1) Å at 21 °C. The final refinement on the 1790 unique observations with $F_0^2 > 2\sigma(F_0^2)$ gave ann R index (on F) of 0.056 for

182 variables (anisotropic thermal motion for non-hydrogen atoms, hydrogen atoms as fixed contributions, and an isotropic extinction parameter).

Acknowledgment. We thank the National Cancer Institute for their financial support of this research (Grant CA-12115).

Registry No. 1, 6675-72-5; **5**, 87556-04-5; **6**, 87585-15-7; **7**, 87556-05-6; **28**, 87556-06-7; **29**, 87556-07-8; **30**, 87556-08-9; **31**, 87556-09-0; **32**, 87556-10-3; **33**, 87678-00-0; **34**, 87556-11-4; **35**, 87556-12-5; **3l**, 87556-13-6; **3m**, 87556-14-7; **38**, 87585-16-8; **39**, 87556-15-8; **40**, 87556-16-9; **41**, 87585-17-9; **43**, 87556-17-0; **47**, 87556-18-1; **48**, 87556-19-2; **49**, 82950-40-1; **50**, 82918-62-5; **51**, 87556-20-5; **55a**, 87556-21-6; **55b**, 87556-22-7; **57**, 87556-23-8; **58**, 87556-24-9; **59**, 87585-18-0; **60**, 87585-19-1; **61**, 87556-25-0; chlorotrimethylsilane, 75-77-4; dimethyl acetylenedicarboxylate, 762-42-5; *N*-phenylmaleimide, 941-69-5; *N*-methyltriazolinedione, 13274-43-6; tetracyanoethylene, 670-54-2; maleic anhydride, 108-31-6; *N*-phenyltriazolinedione, 4233-33-4.

Supplementary Material Available: Figures 4 and 7 (unit cell stereodrawings of **43** and **47**) and final positional (Table V) and thermal (Table VI) parameters, observed and calculated structure factors (Table VII), bond lengths and angles (Table VIII), least-squares planes (Table IX), and torsional angles (Table X) for **43** and final positional (Table XI) and thermal (Table XII) parameters for non-hydrogen atoms, calculated positional and thermal parameters for hydrogen atoms (Table XIII), bond lengths and angles (Table XIV), least-squares planes (Table XV), torsional angles (Table XVI), and observed and calculated structure factors (Table XVII) for **47** (32 pages). Ordering information is given on any current masthead page.

Syntheses and ENDOR Investigations of ^{13}C-Labeled and Deuterated Phenalenyls. Rearrangement Reactions

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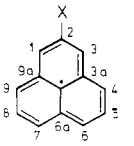
Abstract: Different synthetic routes to obtain ^{13}C-labeled, deuterated, and substituted phenalenyls are described. A rearrangement reaction has been discovered, probably of the Wagner–Meerwein type, that cannot be observed in the case of the unlabeled compound. ESR, ^{1}H, ^{2}H, ^{13}C, and ^{19}F ENDOR and TRIPLE experiments have been performed in fluid solution. Anisotropic hyperfine components have been obtained from liquid-crystal measurements. Relative signs of the hyperfine coupling constants have been determined by general TRIPLE resonance and by the interpretation of cross-relaxation effects observed in the ENDOR spectra. It is shown that the strong cross-relaxation effects of ^{13}C also significantly affect the relaxation properties of the protons.

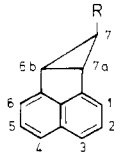
Phenalenyl radical **1a** (perinaphthenyl) has proved to be very suitable in magnetic resonance investigations focusing on the properties of organic free radicals[1,2] or the development of new techniques.[3] This is due to its unique structure, being a planar hydrocarbon neutral radical of threefold symmetry, its stability, and its easy availability via several synthetic routes.[1,4-6] Moreover, phenalenyl is known to achieve high degrees of ordering in liquid-crystalline solutions (nematic and smectic phases).[5,7-10]

The present paper deals with ESR and ENDOR studies of ^{13}C-labeled phenalenyls. Studies of the isotropic and anisotropic ^{13}C hyperfine interactions provide a more detailed insight into the spin density distribution of a molecule than knowledge of the proton hyperfine interactions alone. In favorable cases it is possible to extract information on ^{13}C hyperfine splittings from the positions of natural abundance ^{13}C "satellite lines" observed in the ESR spectra. Actually, for phenalenyl this could be achieved in isotropic[2] as well as in liquid-crystalline solution.[5,7] However, this method usually fails with substituted phenalenyls because of the lowered symmetry decreasing the resolution of the ESR spectra. Attempts to observe ^{13}C ENDOR lines of phenalenyl in natural abundance have not been successful so far. This possibility is

Chart I



1 X = H
2 X = F
3 X = Cl



4 R = $COOC_2H_5$
5 R = COOH
6 R = COCl
7 R = $NH_3^+Cl^-$
8 R = Cl

a unlabelled
b ^{13}C-labelled, **1-3** -1-,3-$^{13}C_2$, **4-8** -6b-^{13}C
c ^{13}C-labelled, **1-3** -2-^{13}C, **8** -7-^{13}C
bc ^{13}C-labelled, **3** -1,2-$^{13}C_2$,
d ^{2}H-labelled, **1** -2-H-d_8, **4-8** -7-H-d_8
e ^{2}H-labelled, **1** -1-H-d_8, **8** -6b-H-d_8

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