Rappoport.[24] Solvents were prepared by weight from conductivity water (Millipore Systems) and appropriate organic solvents. Conductivity measurements were performed in sealed, paired cells by using a Hewlett-Packard Model 4274A LCR bridge, providing 5.5-digit precision, interfaced with a Hewlett-Packard Model 3497A multiplexer and a Hewlett-Packard Model 9826 BASIC microcomputer. From 1 to 10 μL (depending on concentration) of a pentane solution of the triflate was utilized (in-cell concentration of triflate was ca. 2×10^{-4} M) for each run. Approximately 200 points at equal changes in percent reaction were collected over the range 5–95% reaction. Rate constants were calculated by using a BASIC version nonlinear least-squares program written for the HP 9826 in our laboratories. Temperature control and measurement were accomplished by using a PRT-regulated proportional temperature controller and Hewlett-Packard quartz thermometer.

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Registry No. 2, 71451-07-5; **3**, 83027-30-9; **6**, 74711-40-3; **7**, 83027-31-0; **8**, 77350-69-7; **9**, 79140-87-7; D_2, 7782-39-0.

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[1,5] Hydrogen Sigmatropy within Isodicyclopentadiene. Cycloadditive Capture of a Fleeting Isomer with Dienophiles of Low Reactivity

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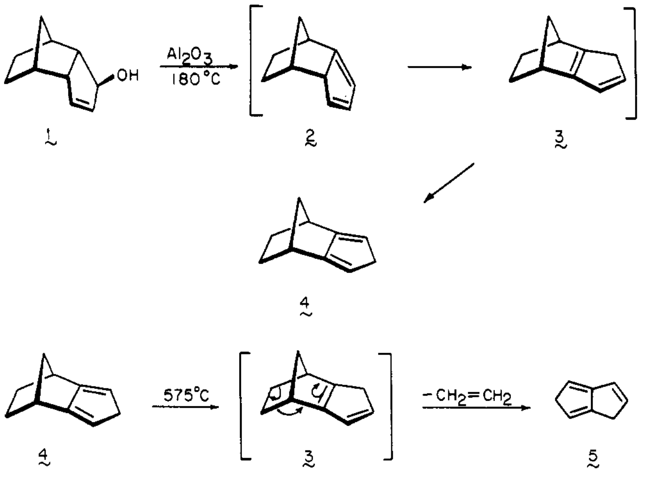
The ability of isodicyclopentadiene (**4**) to experience [1,5] sigmatropic hydrogen migration within its unsaturated five-membered ring has been established by Diels–Alder cycloaddition chemistry. By making recourse to elevated temperatures and dienophiles which react sluggishly with **4**, it becomes possible for one to trap the more reactive isomer **3**, with addition occurring invariably on the exo face. Alternatively, **4** may be preequilibrated with **3** (e.g., at 169 °C) prior to dienophile addition if higher levels of angular adducts are desired with more reactive dienophiles. The dienophiles examined are *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethene (**6**), *trans*-1,2-dichloroethene (**11**), phenyl vinyl sulfide (**13**), phenyl vinyl sulfoxide (**19**), and phenyl vinyl sulfone (**22**). Appropriate chemical transformations of the adducts have given rise to the fused norbornadiene **8** and norbornene **9**. The presence of an *endo*-methyl substituent as in **25** fosters [1,5] hydrogen sigmatropy to give **26**, which, although not spectroscopically detectable, is easily trapped.

Dehydration of tricyclic alcohol **1** over alumina at 180 °C yields the hydrocarbon **4** known as isodicyclopentadiene[2,3] (Scheme I). Since loss of water from **1** cannot lead directly to **4**, this reaction is probably mediated by dienes **2** and **3**, although these isomers have been neither observed nor isolated. The involvement of **3** in the pyrolytic conversion of **4** to dihydropentalene (**5**) and ethylene, the key reaction leading to formation of the pentalenyl dianion, has additionally been claimed by Katz and co-workers.[3] Although no doubt persists that **4** is more thermodynamically favored than **2** or **3**, it remained to detect these less stable isomers or, at a minimum, to gain some reasonable appreciation of the facility for [1,5] hydrogen migration within these systems.[4]

Scheme I



The Diels–Alder reactivity of isodicyclopentadiene has been the subject of intense investigation recently because of the exceptionally high π-facial stereoselectivity exhibited during the course of its cycloaddition reactions. Thus, in the presence of reactive dienophiles, **4** enters into [4 + 2] bonding predominantly, if not exclusively, from its endo surface to produce *syn*-sesquinorbornene derivatives.[5-7] It

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(1) Author to whom inquiries regarding the X-ray crystal structure analysis should be addressed at Hoffmann-La Roche.

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0022-3263/82/1947-4566$01.25/0 © 1982 American Chemical Society

Table I. Final Atomic Parameters for 7 with Standard Deviations in Parentheses

atom	x	y	z	B, Å^2
S	0.3386 (1)	0.5091 (1)	0.6199 (1)	a
Si	0.2771 (1)	0.3495 (1)	0.3099 (1)	a
O(1)	0.4497 (2)	0.5431 (2)	0.6990 (3)	a
O(2)	0.2732 (3)	0.5480 (2)	0.4927 (3)	a
C(1)	0.4194 (3)	0.3417 (2)	0.8433 (3)	a
C(2)	0.4339 (3)	0.3431 (2)	0.7111 (3)	a
C(3)	0.4057 (3)	0.2501 (2)	0.6682 (3)	a
C(4)	0.3565 (3)	0.2099 (2)	0.7550 (4)	a
C(5)	0.4669 (4)	0.1913 (3)	0.8794 (5)	a
C(6)	0.5092 (3)	0.2805 (3)	0.9381 (4)	a
C(7)	0.3102 (3)	0.2875 (2)	0.8052 (3)	a
C(12)	0.3468 (3)	0.3972 (2)	0.5914 (3)	a
C(13)	0.3896 (3)	0.3822 (2)	0.4774 (3)	a
C(14)	0.4907 (3)	0.3179 (2)	0.5457 (3)	a
C(15)	0.4400 (3)	0.2341 (2)	0.5687 (4)	a
C(17)	0.5437 (3)	0.3543 (2)	0.6884 (3)	a
C(21)	0.2539 (3)	0.5169 (2)	0.7136 (4)	a
C(22)	0.3010 (3)	0.5486 (2)	0.8419 (4)	a
C(23)	0.2304 (5)	0.5558 (3)	0.9121 (4)	a
C(24)	0.1179 (5)	0.5323 (3)	0.8538 (6)	a
C(25)	0.0716 (4)	0.5013 (3)	0.7266 (5)	a
C(26)	0.1396 (4)	0.4946 (3)	0.6563 (4)	a
C(27)	0.3452 (3)	0.2847 (3)	0.2198 (4)	a
C(28)	0.2152 (3)	0.4460 (3)	0.2097 (4)	a
C(29)	0.1595 (3)	0.2873 (3)	0.3287 (4)	a
H(1)	0.416	0.400	0.882	5.0
H(4)	0.303	0.160	0.717	6.0
H(5)A	0.450	0.156	0.945	8.0
H(5)B	0.525	0.163	0.855	8.0
H(6)A	0.587	0.292	0.940	6.0
H(6)B	0.512	0.284	1.031	6.0
H(7)A	0.242	0.315	0.733	6.0
H(7)B	0.291	0.274	0.883	6.0
H(12)	0.269	0.371	0.564	4.0
H(13)	0.424	0.437	0.464	4.0
H(14)	0.545	0.311	0.501	5.0
H(15)	0.435	0.179	0.520	5.0
H(17)A	0.609	0.320	0.751	5.0
H(17)B	0.568	0.416	0.691	5.0
H(22)	0.384	0.565	0.884	7.0
H(23)	0.263	0.577	1.006	8.0
H(24)	0.069	0.538	0.905	8.0
H(25)	−0.010	0.484	0.684	8.0
H(26)	0.106	0.473	0.562	7.0
H(27)A	0.287	0.269	0.130	7.0
H(27)B	0.380	0.232	0.272	7.0
H(27)C	0.407	0.320	0.209	7.0
H(28)A	0.156	0.430	0.120	7.0
H(28)B	0.277	0.481	0.198	7.0
H(28)C	0.178	0.483	0.257	7.0
H(29)A	0.101	0.272	0.239	7.0
H(29)B	0.123	0.324	0.376	7.0
H(29)C	0.191	0.235	0.381	7.0

[a] Anisotropic thermal parameters are given in Table II.

occurred to us that **3** might well be more reactive than **2** and **4** as a 4-π donor because of the norbornene character of one of its double bonds. The substantial kinetic acceleration associated with cycloaddition reactions to norbornenyl compounds, referred to as "factor x" by Huisgen,[8] is now widely recognized.[9] Accordingly, if a reasonable concentration of **3** could be generated in equilibrium with **2** and **4** at more elevated temperatures, the real possibility existed that this unknown isomer might be trapped selectively. For achievement of this end result, it was of course mandatory that the dienophile be sufficiently unreactive that it not be consumed prematurely in bonding to **4** (or **2**). On this basis, we were led to investigate the behavior of **4** toward dienophiles of low reactivity and herein describe capture of **3** by a variety of reagents.

Scheme II

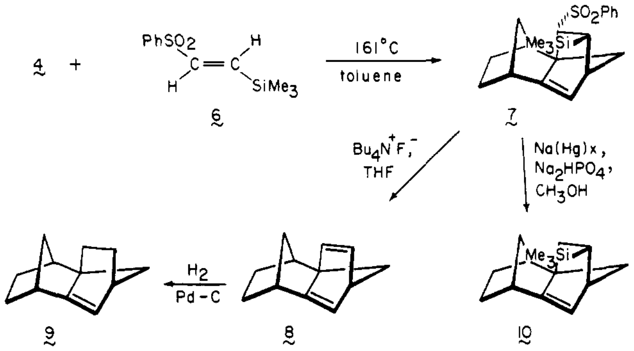

Table II. Final Anisotropic Thermal Parameters (×10^4) for 7 with Standard Deviations in Parentheses[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	125 (1)	33 (1)	113 (1)	3 (1)	68 (1)	3 (1)
Si	78 (1)	49 (1)	80 (1)	−10 (1)	33 (1)	−7 (1)
O(1)	139 (3)	50 (2)	212 (4)	−37 (2)	97 (3)	−33 (2)
O(2)	224 (4)	51 (1)	127 (3)	48 (2)	105 (3)	38 (2)
C(1)	102 (4)	37 (2)	73 (4)	1 (2)	24 (3)	4 (2)
C(2)	62 (3)	34 (2)	75 (4)	−2 (2)	14 (3)	0 (2)
C(3)	81 (3)	33 (2)	97 (5)	1 (2)	28 (3)	2 (2)
C(4)	139 (5)	37 (2)	112 (5)	−12 (2)	48 (4)	2 (3)
C(5)	163 (6)	57 (3)	223 (8)	13 (3)	58 (6)	23 (4)
C(6)	126 (4)	62 (3)	101 (5)	5 (3)	17 (4)	18 (3)
C(7)	109 (4)	53 (2)	102 (5)	−9 (2)	52 (4)	10 (3)
C(12)	66 (3)	30 (2)	80 (4)	−5 (2)	26 (3)	−2 (2)
C(13)	67 (3)	36 (2)	90 (4)	−5 (2)	37 (3)	−3 (2)
C(14)	74 (3)	49 (2)	114 (5)	6 (2)	44 (3)	−1 (3)
C(15)	102 (4)	36 (2)	122 (5)	14 (2)	43 (4)	−1 (3)
C(17)	67 (3)	49 (2)	117 (5)	1 (2)	21 (3)	6 (3)
C(21)	111 (4)	31 (2)	104 (5)	8 (2)	51 (4)	4 (2)
C(22)	147 (5)	45 (2)	123 (6)	−8 (3)	65 (5)	−15 (3)
C(23)	211 (7)	54 (3)	127 (6)	−6 (3)	105 (6)	−15 (3)
C(24)	178 (7)	62 (3)	189 (8)	14 (3)	127 (6)	10 (4)
C(25)	124 (5)	84 (3)	163 (7)	26 (3)	76 (5)	6 (4)
C(26)	110 (5)	66 (3)	120 (5)	26 (3)	48 (4)	3 (3)
C(27)	119 (4)	94 (3)	127 (5)	−17 (3)	54 (4)	−46 (3)
C(28)	124 (4)	78 (3)	112 (5)	−10 (3)	9 (4)	15 (3)
C(29)	109 (4)	75 (3)	111 (5)	−28 (3)	34 (4)	−11 (3)

[a] The anisotropic temperature factor has the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

***trans*-1-(Phenylsulfonyl)-2-(trimethylsilyl)ethene.** A short time ago, we reported that **6**[10] is capable of serving conveniently as a Diels–Alder synthon for acetylene, monosubstituted acetylenes, HC≡CD, and DC≡CD.[11] When toluene solutions of **6** and **4** were heated in sealed ampules at 161 °C for 7.5 days, adduct **7** was obtained in 51% isolated yield as the principal product (Scheme II). Because of the large number of isomeric possibilities for this substance and the minimal diagnostic value of ^{1}H and ^{13}C NMR spectroscopy in this instance, recourse was quickly made to X-ray crystal structure analysis. These

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Table III. Bond Lengths (Å) in 7 with Standard Deviations in Parentheses

S-O(1)	1.432 (3)	C(3)-C(15)	1.352 (6)
S-O(2)	1.440 (3)	C(4)-C(5)	1.543 (5)
S-C(12)	1.781 (3)	C(4)-C(7)	1.542 (6)
S-C(21)	1.770 (5)	C(5)-C(6)	1.535 (6)
Si-C(13)	1.890 (3)	C(12)-C(13)	1.570 (5)
Si-C(27)	1.855 (5)	C(13)-C(14)	1.565 (4)
Si-C(28)	1.842 (4)	C(14)-C(15)	1.522 (5)
Si-C(29)	1.864 (5)	C(14)-C(17)	1.542 (5)
C(1)-C(2)	1.534 (5)	C(21)-C(22)	1.380 (5)
C(1)-C(6)	1.531 (5)	C(21)-C(26)	1.379 (6)
C(1)-C(7)	1.536 (5)	C(22)-C(23)	1.404 (9)
C(2)-C(3)	1.523 (5)	C(23)-C(24)	1.364 (8)
C(2)-C(12)	1.579 (4)	C(24)-C(25)	1.366 (7)
C(2)-C(17)	1.528 (6)	C(25)-C(26)	1.377 (8)
C(3)-C(4)	1.475 (6)	C(15)-C(15)A	1.486 (33)

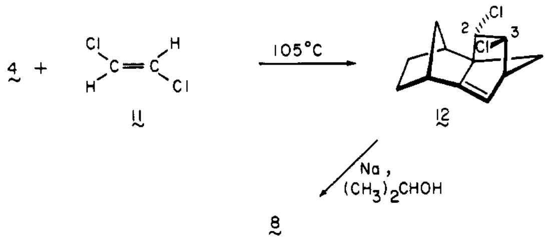
Table IV. Bond Angles (deg) in 7 with Standard Deviations in Parentheses

O(1)-S-O(2)	118.5 (2)
O(1)-S-C(12)	110.8 (2)
O(1)-S-C(21)	108.0 (2)
O(2)-S-C(12)	107.1 (1)
O(2)-S-C(21)	106.4 (2)
C(12)-S-C(21)	105.2 (2)
C(13)-Si-C(27)	109.2 (2)
C(13)-Si-C(28)	109.6 (2)
C(13)-Si-C(29)	111.2 (2)
C(27)-Si-C(28)	107.9 (2)
C(27)-Si-C(29)	110.2 (2)
C(28)-Si-C(29)	108.7 (2)
C(2)-C(1)-C(6)	108.0 (3)
C(2)-C(1)-C(7)	101.0 (3)
C(6)-C(1)-C(7)	101.0 (3)
C(1)-C(2)-C(3)	100.1 (3)
C(1)-C(2)-C(12)	118.8 (3)
C(1)-C(2)-C(17)	128.5 (2)
C(3)-C(2)-C(12)	104.6 (2)
C(3)-C(2)-C(17)	100.1 (3)
C(12)-C(2)-C(17)	100.8 (3)
C(2)-C(3)-C(4)	108.3 (3)
C(2)-C(3)-C(15)	108.2 (3)
C(4)-C(3)-C(15)	143.5 (3)
C(3)-C(4)-C(5)	100.2 (4)
C(3)-C(4)-C(7)	102.8 (3)
C(5)-C(4)-C(7)	100.1 (3)
C(4)-C(5)-C(6)	104.0 (3)
C(1)-C(6)-C(5)	103.8 (3)
C(1)-C(7)-C(4)	95.3 (3)
S-C(12)-C(2)	116.6 (2)
S-C(12)-C(13)	110.5 (2)
C(2)-C(12)-C(13)	103.2 (3)
Si-C(13)-C(12)	116.3 (2)
Si-C(13)-C(14)	116.7 (2)
C(12)-C(13)-C(14)	101.4 (3)
C(13)-C(14)-C(15)	107.8 (3)
C(13)-C(14)-C(17)	101.0 (3)
C(15)-C(14)-C(17)	100.9 (3)
C(3)-C(15)-C(14)	105.8 (3)
C(2)-C(17)-C(14)	93.9 (2)
S-C(21)-C(22)	120.1 (3)
S-C(21)-C(26)	119.8 (3)
C(22)-C(21)-C(26)	120.1 (5)
C(21)-C(22)-C(23)	118.4 (4)
C(22)-C(23)-C(24)	120.4 (4)
C(23)-C(24)-C(25)	121.0 (6)
C(24)-C(25)-C(26)	119.2 (5)
C(21)-C(26)-C(25)	120.9 (4)
C(3)-C(15)-C(15)A	121.5 (14)
C(14)-C(15)-C(15)A	108.9 (14)

Table V. Torsion Angles (deg) in 7 with Standard Deviations in Parentheses

C(6)-C(1)-C(2)-C(3)	63.4 (3)
C(1)-C(2)-C(3)-C(4)	11.4 (3)
C(2)-C(3)-C(4)-C(5)	−79.6 (3)
C(3)-C(4)-C(5)-C(6)	70.1 (5)
C(4)-C(5)-C(6)-C(1)	0.4 (5)
C(5)-C(6)-C(1)-C(2)	−70.9 (4)
C(7)-C(1)-C(2)-C(3)	−42.1 (3)
C(1)-C(2)-C(3)-C(4)	11.4 (3)
C(2)-C(3)-C(4)-C(7)	23.3 (3)
C(3)-C(4)-C(7)-C(1)	−47.7 (3)
C(4)-C(7)-C(1)-C(2)	55.5 (3)
C(7)-C(1)-C(6)-C(5)	34.6 (5)
C(1)-C(6)-C(5)-C(4)	0.4 (5)
C(6)-C(5)-C(4)-C(7)	−35.0 (5)
C(5)-C(4)-C(7)-C(1)	55.2 (4)
C(4)-C(7)-C(1)-C(6)	−55.5 (3)
C(12)-C(2)-C(3)-C(15)	70.7 (3)
C(2)-C(3)-C(15)-C(14)	−0.3 (3)
C(3)-C(15)-C(14)-C(13)	−71.8 (3)
C(15)-C(14)-C(13)-C(12)	66.6 (3)
C(14)-C(13)-C(12)-C(2)	2.9 (3)
C(13)-C(12)-C(2)-C(3)	−69.4 (3)
C(2)-C(3)-C(15)-C(14)	−0.3 (3)
C(3)-C(15)-C(14)-C(17)	33.6 (3)
C(15)-C(14)-C(17)-C(2)	−51.0 (3)
C(14)-C(17)-C(2)-C(3)	50.2 (3)
C(17)-C(2)-C(3)-C(15)	−33.4 (3)
C(17)-C(2)-C(12)-C(13)	34.2 (3)
C(2)-C(12)-C(13)-C(14)	2.9 (3)
C(12)-C(13)-C(14)-C(17)	−38.8 (3)
C(13)-C(14)-C(17)-C(2)	59.7 (3)
C(14)-C(17)-C(2)-C(12)	−57.0 (3)
C(12)-S-C(21)-C(22)	116.0 (3)
C(2)-C(12)-S-C(21)	−78.4 (3)

Scheme III



studies unambiguously provided the indicated structural assignment and revealed several important stereochemical features of the molecule. First, the angular character of the carbon skeleton and the position of the double bond established that addition had indeed occurred to 3, with bonding taking place on its exo surface in an anti-Alder fashion. Furthermore, the phenylsulfonyl substituent must control the regioselectivity of this process, since it is ultimately positioned adjacent to the more highly substituted terminal diene carbon in 3.

An important consequence of the transoid relationship of the functional groups in 7 is seen in the responsiveness of this adduct to fluoride ion induced elimination.[12] However, because the phenylsulfonyl and trimethylsilyl substituents are rigidly held in a dihedral angle relationship somewhat less than conducive to antiplanar elimination, extended reaction times were required to arrive at the structurally unusual norbornadiene 8. By means of selective catalytic hydrogenation, 8 could readily be converted to 9. The purpose of this experiment was to make both 8 and 9 available as relay compounds for establishing unambiguously the three-dimensional topologies of adducts to be formed subsequently. As anticipated from earlier precedent,[13,14] reductive desulfonylation[15] of 7 proceeded

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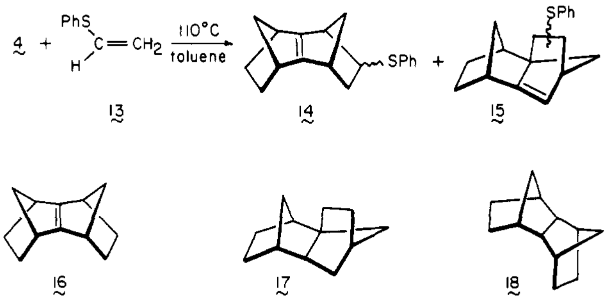
Scheme IV



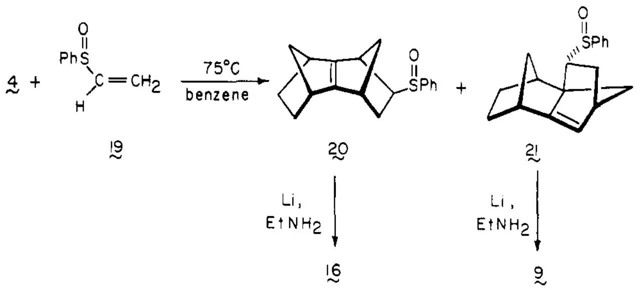
with retention of the trimethylsilyl group to provide stereochemically well-defined homoallyl silane **10**.

***trans*-1,2-Dichloroethene.** Since the reactivity level of *trans*-1,2-dichlorethene (**11**) also appeared to be well suited to our purposes, this dienophile was heated with **4** for 6.5 days at 105 °C. Under these conditions, there was obtained the single adduct **12** in 38% yield (Scheme III). In this instance, the arrangement of the chlorine atoms about the newly formed norbornenyl ring was quite apparent from the ^{1}H NMR spectrum. While H_2 appears as a narrow doublet (J = 2.3 Hz), requiring it to be trans to H_3, the latter is seen as a doublet of doublets (J = 4.0 and 2.3 Hz). A spin–spin interaction of this magnitude with the adjacent bridgehead proton can only be manifested if H_3 is oriented exo to the newly formed norbornene system.[16] The remaining question of π-facial stereoselectivity was resolved by subjecting **12** to dehalogenation with sodium in hot isopropyl alcohol.[17] Since **8** was cleanly produced under these conditions, **11** must also add to **3** from above the diene π plane. Structural assignement to **12** can consequently be made with full confidence. Once again, it is seen that the substituent at C_2 has positioned itself in a manner which avoids the highly crowded region located on the endo surface of this carbon atom.

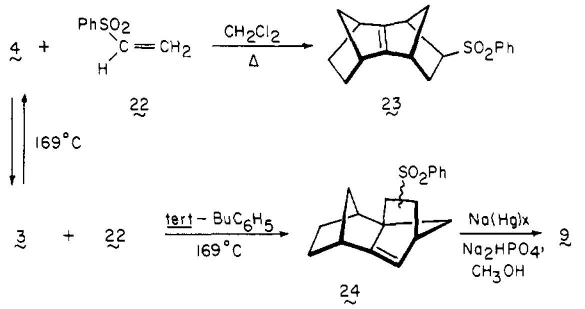
Phenyl Vinyl Sulfide. Because **13** is a monosubstituted dienophile which enjoys somewhat higher reactivity than either **6** or **11**, our attention was next directed to its behavior toward **4**. Under conditions where benzene solutions of **4** and **13** were heated at 110 °C for 3 days, there was produced in good yield a 3:0.5:0.5 mixture of three adducts. Although the major component (**14**, Scheme IV) could be chromatographically separated from the other two, the difficulties encountered in obtaining **15a** and **15b** in a pure state caused us to subject this mixture directly to reductive cleavage of the phenylthio group with lithium in ethylamine at −78 °C.[18] At short reaction times, **14** was smoothly converted to **16**, and **15a**/**15b** gave exclusively **9**, clearly demonstrating that exo π-facial stereoselectivity had been followed in producing the angular adduct. Overreduction occurs during more extended exposure to the reducing agent to give the saturated hydrocarbons **18** and **17**, respectively.

On this basis, it is evident that **13** is capable of adding to both **3** and **4**, as expected from its somewhat increased dienophilic character relative to **6** and **11**. The *syn*-sesquinobornene nature of linear adduct **14** follows from the well characterized nature of its reduction products **16** and **18**.[6] The stereochemical disposition of the phenylthio substituent could not be unequivocally defined by careful ^{1}H NMR spectral analysis. These considerations apply also to the pair of angular adducts **15a** and **15b**. Furthermore, in this instance there would appear to be less than reasonable assurance that the SPh group fully controls the regioselectivity of the cycloaddition process, although excessive steric interactions will likely continue to be avoided. For these reasons, no positional or stereochemical descriptors are assigned to these products at this time, although it is quite clear that both indeed possess the *anti*-tetracyclo$[4.4.0.1^{1,4}.1^{7,10}]$dodec-5-ene skeleton.

Scheme V



Scheme VI



Phenyl Vinyl Sulfoxide. As a sequel to the above, it was of interest to study the behavior of **19** which, because of the higher oxidation state of the sulfur atom, has more pronounced dienophilicity. The utilization of phenyl vinyl sulfoxide as an acetylenic synthon in Diels–Alder cycloadditions has previously been described.[19] A mixture of **4** and **19** reacted upon being heated in benzene at 110 °C for 4 days to give a mixture of **20** and **21** (77% yield) in a ratio of 11:1 (Scheme V). The two adducts could be obtained in pure form by medium-pressure liquid chromatography. The major component was identified as the exo-substituted *syn*-sesquinobornene **20** through a combination of ^{1}H NMR spectroscopy and reductive desulfurization to **16**. The less prevalent isomer, considered to be the anti-Alder adduct **21**, was similarly reduced to **9**.

Phenyl Vinyl Sulfone. Previously, we reported that phenyl vinyl sulfone (**22**), a versatile ethylene and terminal olefin dienophile equivalent,[20] adds smoothly to **4** in refluxing dichloromethane solution to produce adduct **23** in 91% yield[21] (Scheme VI). This behavior is considered to be a direct consequence of the still more enhanced dienophilicity of **22** and the virtual absence of **3** in equilibrium with **4** at these low temperatures. To gain support for these conclusions, we preequilibrated solutions of **4** in *tert*-butylbenzene for 30 min at the reflux temperature (169 °C) prior to the addition of **22**. Such reactions gave mixtures of four adducts now containing only low levels of **23** (7%). The remaining three sulfones (23%, 27%, and 31% isolated yields, respectively) were determined to share

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(16) (a) Trecker, D. J.; Henry, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 3204. (b) Davis, J. C.; van Auken, T. V. *Ibid.* **1965**, *87*, 3900. (c) van Auken, T. V.; Rick, E. A. *Tetrahedron Lett.* **1968**, 2709.

(17) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193.

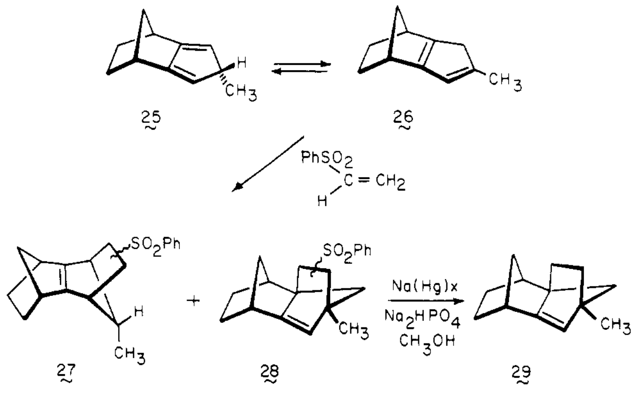
(18) Nederlof, P. J. R.; Moolenaar, M. J.; De Waard, E. R.; Huisman, H. O. *Tetrahedron* **1977**, *33*, 579.

(19) Paquette, L. A.; Moerck, R.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597.

(20) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853.

(21) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

Scheme VII



in common the carbocyclic framework of 24, since individual reduction with phosphate-buffered sodium amalgam furnished only 9 in each instance. Thus, phenyl vinyl sulfone clearly prefers to add to 3 when its concentration gradient is made sufficiently high to allow competitive capture to be made. However, these findings must be viewed as neither a measure of the actual 4 ⇄ 3 equilibrium constant nor an indication of the relative rate constants of the competing cycloadditions.

Addition of Phenyl Vinyl Sulfone to *endo*-4-Methylisodicyclopentadiene (25). Unlike the equilibrium between 4 and 3 which results in structural interconversion between two dialkyl-substituted butadienes, the analogous isomerization of 25[22] would give rise to 26 (Scheme VII) whose diene unit is now trisubstituted. If the usual thermodynamic considerations apply here, then conversion to 26 might well occur at lower temperatures than those applicable to 4. In an effort to gain preliminary information on this question, we first allowed 25 to react with 22 under mild conditions (CH_2Cl_2, 20 °C, 18 days). A mixture of 27 (38%) and 28 (28%) was produced, a result in striking contrast to the behavior of 4 under analogous conditions. At higher temperatures (toluene, 107 °C, 2 days), the proportion of 28 in the mixture (50%) was significantly increased (33% of 27). Desulfonylation of 28 resulted in formation of 4-methyl-*anti*-tetracyclo[$4.4.0.1^{1,4}.1^{7,10}$]dodec-5-ene (29).

Although the proportion of 26 in equilibrium with 5 would appear to be higher than the level of 3 present alongside 4, variable-temperature ^{1}H NMR analysis ($CDCl_3$ solutions) of 25 in the −30 to +60 °C temperature range provided no evidence for significant spectral changes. Accordingly, the absolute concentration level of 26 at these temperatures still remains below the spectroscopically detectable limit.

Summary. The preceding results reveal that isodicyclopentadiene (4) does experience [1,5] sigmatropic hydrogen shifting to give, at more elevated temperatures, low concentrations of the previously unknown and less thermodynamically stable isomer 3 (not directly observable by ^{1}H NMR). As a direct result of the greater inherent reactivity of the diene moiety in 3, this hydrocarbon can readily enter into Diels–Alder reaction with somewhat unreactive dienophiles, while 4 does so more sluggishly. As a result, it is possible to demonstrate the presence of 3 in the equilibrium mixture. Upon completion of this work, we learned that Bartlett and co-workers independently arrived at the identical conclusion through use of other weakly dienophilic reagents.[23]

Through suitable chemical transformations, the various adducts have been converted to the structurally unusual norbornene 9 and norbornadiene 8.

The presence of a 4-*endo*-methyl substituent on 4 as in 25 seemingly provides for a greater concentration gradient of 26 (although still not spectroscopically detectable to 60 °C), as gauged by its cycloaddition behavior toward phenyl vinyl sulfone.

Experimental Section

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian EM-390, Bruker WP-200, and Bruker WM-300 spectrometers. Carbon spectra were recorded with Bruker WP-80 and WP-200 spectrometers. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***exo*-2-(Phenylsulfonyl)-*endo*-3-(trimethylsilyl)-*anti*-tetracyclo[$4.4.0.1^{1,4}.1^{7,10}$]dodec-5-ene (7).** A solution of 4 (0.50 g, 3.8 mmol) and 6 (1.0 g, 1.1 equiv) in toluene (5 mL) was sealed in a heavy-walled glass tube and heated at 161 °C for 7.5 days. The solvent was evaporated in vacuo, and the crude product was purified by MPLC on silica gel (elution with 10% ethyl acetate in hexane). Although several minor adduct isomers were seen, the major component by far proved to be 7: 714 mg (51%); mp 123–124 °C (from petroleum ether); ^{1}H NMR ($CDCl_3$) δ 7.93–7.89 (m, 2 H), 7.61–7.54 (m, 3 H), 5.53 (d, J = 2.3 Hz, 1 H), 3.22 (m, 1 H), 2.93 (br s, 2 H), 2.73 (br s, 1 H), 1.75–1.36 (m, 9 H), −0.19 (s, 9 H); ^{13}C NMR ($CDCl_3$) 162.58, 133.34, 129.26, 128.90, 120.91, 66.65, 48.22, 47.86, 41.69, 38.47, 38.30, 32.04, 30.35, 24.70, −1.4 ppm (two quaternary C's were not observed); mass spectrum, calcd (M^+) m/e 372.1579, obsd 372.1587.

Anal. Calcd for $C_{21}H_{28}O_2SSi$: C, 67.86; H, 7.59. Found: C, 67.50; H, 7.64.

Single-Crystal X-ray Analysis of 7. The crystals of 7 were monoclinic, space group $P2_1/a$, with a = 12.749 (1) Å, b = 15.586 (2) Å, c = 10.969 (1) Å, β = 113.73 (1)°, and d_{calcd} = 1.240 g cm^{-3} for Z = 4 ($C_{21}H_{28}O_2SSi$, M_r = 372.60). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.12 × 0.30 mm; the data were corrected for absorption (μ = 20.3 cm^{-1}). A total of 1880 independent reflections were measured for $\theta < 48°$, of which 1636 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[24] and was refined by full-matrix least-squares methods. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were R = 0.038 and R_w = 0.044 for the 1636 observed reflections. The final difference map had no peaks greater than ±0.2 A^{-3}.

***anti*-Tetracyclo]$4.4.0.1^{1,4}.1^{7,10}$]dodeca-2,5-diene (8).** A magnetically stirred solution of 7 (0.10 g, 0.27 mmol) and tetra-*n*-butylammonium fluoride (1 mL of a 1 M solution in THF) in tetrahydrofuran (3 mL) was heated at the reflux temperature for 9 days. After the second day, an additional 1 mL of the fluoride salt solution was added. The cooled reaction mixture was poured into water, the product was extracted with dichloromethane, and the combined extracts were washed with water (three times), dried, and evaporated carefully. There was recovered a quantitative amount of an oil (50% of 8 by ^{1}H NMR) which was purified further for analysis by preparative VPC (12 ft × 0.25 in. column, 15% SE-30 on Chromosorb G 180 °C: ^{1}H NMR ($CDCl_3$) δ 6.73 (dd, J = 5, 3 Hz, 1 H), 6.47 (d, J = 5 Hz, 1 H), 5.82 (d, J = 2.3

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[22] Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R., submitted for publication.

[23] Subramanyam, R.; Bartlett, P. D.; Watson, W. H.; Galloy, J. submitted for publication in *J. Org. Chem.*

[24] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, *A27*, 368.

Hz, 1 H), 3.51 (br s, 1 H), 2.81 (m, 1 H), 2.51 (m, 1 H), 1.8–1.2 (m, 8 H); ^{13}C NMR ($CDCl_3$) 168.70, 143.70, 143.55, 122.85, 73.26, 71.85, 53.35, 43.01, 38.40, 37.77, 31.02, 24.12 ppm; mass spectrum, calcd (M^+) *m/e* 158.1095, obsd 158.1100.

***anti*-Tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene (9).** A solution of **8** (0.10 g, 0.63 mmol) in ethyl acetate (3 mL) was treated with 15 mg of 10% palladium on charcoal and subjected to atmospheric-pressure hydrogenation. After 30 min, the mixture was filtered and the filtrate evaporated to provide 90 mg (90%) of **9** which was purified for analysis by preparative VPC as above: ^{1}H NMR ($CDCl_3$) δ 5.23 (d, J = 3.0 Hz, 1 H), 2.77 (m, 1 H), 2.70 (m, 1 H), 2.32 (m, 1 H), 2.20–0.62 (series of m, 12 H); ^{13}C NMR ($CDCl_3$) 172.73, 116.12, 61.70, 48.84, 46.02, 42.48, 39.85, 38.88, 32.23, 26.50, 26.16, 25.09 ppm; mass spectrum, calcd (M^+) *m/e* 160.1252, obsd 160.1256.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.56; H, 10.16.

***endo*-3-(Trimethylsilyl)-*anti*-tetracyclo]4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene (10).** A 78.5-mg (0.21 mmol) sample of **7** was added to a stirred slurry of 6% sodium amalgam (410 mg, 5 equiv of Na) and disodium hydrogen peroxide (270 mg, 9 equiv) in dry methanol (8 mL), and reaction was allowed to proceed under a nitrogen atmosphere for 18 h. Petroleum ether was added, and the organic phase was decanted off. The residual solids were leached several more times, and the combined solutions were washed with water, saturated sodium bicarbonate solution, and water prior to drying. Solvent evaporation left a residue which was purified by chromatography on basic alumina (elution with petroleum ether). There was isolated 9.4 mg (20%) of **10** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.23 (d, J = 2.5 Hz, 1 H), 2.91 (br s, 1 H), 2.72 (m, 1 H), 2.28 (br s, 1 H), 2.0–1.1 (series of m, 11 H), –0.10 (s, 9 H); mass spectrum, calcd (M^+) *m/e* 232.1647, obsd 232.1653.

***exo*-2,*endo*-3-Dichloro-*anti*-tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene (12).** A mixture of **4** (0.50 g, 3.5 mmol) and freshly distilled *trans*-1,2-dichloroethene (3 mL, 39 mmol) was sealed in a thick-walled glass tube and heated at 105 °C for 6.5 days. Preparative TLC purification on silica gel (elution with petroleum ether) furnished 326 mg (38%) of **12** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.45 (d, J = 2.3 Hz, 1 H), 4.30 (dd, J = 4.0, 2.3 Hz, 1 H), 3.72 (m, 1 H), 3.10 (br s, 1 H), 2.8 (m, 1 H), 2.5 (m, 1 H), 1.88–1.2 (m, 9 H); ^{13}C NMR ($CDCl_3$) 161.57, 116.81, 68.07, 67.63, 52.82, 45.59, 41.46, 38.98, 37.24, 31.46, 23.84 ppm; mass spectrum, calcd (M^+) *m/e* 228.0473; obsd 228.0479.

Dechlorination of 12. To a refluxing solution of **12** (246 mg, 1.1 mmol) in isopropyl alcohol (25 mL) was added portionwise sodium metal (0.25 g, 10 equiv) with stirring. Heating was continued until all of the sodium was consumed (2.5 h). The cooled reaction mixture was poured into water and extracted with dichloromethane. The combined extracts were washed with water, dilute hydrochloric acid, and water prior to drying and solvent evaporation. There was obtained a quantitative yield oof ca 95% pure **8**, the spectra of which after VPC purification were identical with those of the diene isolated above.

Addition of Phenyl Vinyl Sulfide to 4. Into a heavy-walled Pyrex tube were placed 10.1 g (74 mmol) of freshly distilled **13**, 3.0 g (23 mmol) of **4**, and 12 mL of toluene. The tube was flushed with argon, evacuated, sealed, and heated at 110 °C for 5 days. The solvent was evaporated, and hydrocarbon material was removed by chromatography on Florisil. There was obtained 4.2 g (69%) of a 3:0.5:0.5 mixture of **14**, **15a**, and **15b**. The two sets of isomers could be separated only by careful preparative TLC on silica gel (pentane elution) and were obtained individually as colorless oils.

For **14**: ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 5 H), 3.19–3.08 (m, 1 H), 3.07–26.3 (m, 4 H), 2.18–0.95 (m, 10 H); mass spectrum, calcd (M^+) *m/e* 268.1296, obsd 268.1291.

Anal. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51. Found: C, 80.39; H, 7.43.

For **15a/15b**: ^{1}H NMR ($CDCl_3$) δ 7.39–7.08 (m, 5 H), 5.46 (d, J = 2.6 Hz, 1 H), 5.35 (d, J = 2.6 Hz, 1 H), 3.3–2.75 (m, 2 H), 2.1.0.9 (series of m, 11 H); mass spectrum, calcd (M^+) *m/e* 268.1296, obsd 268.1293.

Anal. Calcd for $C_{18}H_{10}S$: C, 80.54; H, 7.51. Found: C, 80.43; H, 7.50.

Reductive Cleavage of 14 and 15. Into a flame-dried three-necked flask equipped with a stirring bar, serum cap, gas-inlet tube, and dry ice condenser with a gas outlet was placed a 1:1 mixture of **14** and **15** (1.30 g, 4.85 mmol). The flask was cooled to –78 °C and ethylamine (40 mL) was admitted. Lithium wire (200 mg), cut into small pieces, was added all at once, and the solution was stirred at –78 °C until a blue color persisted (10–15 min). The excess lithium was immediately removed, and 0.5 g of solid ammonium chloride was added. The reaction mixture was warmed to 40 °C while the ethylamine was allowed to distil through a short-path distillation head. Pentane (50 mL) and water (10 mL) were added, and the organic layer was carefully neutralized with 5% hydrochloric acid. The dried pentane fraction was slowly distilled through a short-path distillation head to leave 680 mg (88%) of a colorless oil. Preparative VPC purification of the two components (12 ft × 0.25 in. column, 15% SE-30 on Chromosorb G, 160 °C) afforded pure samples of **9** and **16**.

Overreduction of 14 and 15. A 270-mg (1.0 mmol) sample of a **14/15** mixture was reduced at –78 °C with lithium metal (140 mg, 20 mmol) in ethylamine (20 mL). After the blue color persisted, the reaction mixture was stirred at –78 °C for an additional 15 min. A workup in the predescribed manner gave 105 mg (72%) of crude product as a 1:1 mixture of **17** and **18**. VPC separation as before gave the pure hydrocarbons. For **18**, the spectra were identical with those of an authentic sample.

For **17**: ^{1}H NMR ($CDCl_3$) δ 2.23 (br s, 1 H), 2.05 (br s, 1 H), 1.87–0.90 (series of m, 15 H); ^{13}C NMR ($CDCl_3$) 54.86, 52.14, 44.08, 39.96, 38.80 (2C), 38.45, 35.59, 32.96, 29.71, 28.55, 20.921 ppm.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.75; H, 11.07.

Addition of Phenyl Vinyl Sulfoxide to 4. Into a pyridine-rinsed thick-walled glass tube were placed 6.6 g (43 mmol) of **19**, 4.6 g (35 mmol) of **4**, and 3 mL of benzene. The tube was argon flushed, evacuated, sealed, and heated at 110 °C for 96 h. The crude reaction mixture was distilled at 0.4 torr to remove unreacted starting materials. There remained 9.4 g (77%) of a mixture of **20** and **21** (11:1 ratio, ^{1}H NMR analysis). Crystallization from hexane–ethyl acetate afforded pure **20** as transparent cubic crystals: mp 151–152 °C; ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 5 H), 3.59 (br s, 1 H), 3.13 (m, 3 H), 2.40 (ddd, J = 8.0, 4.5, 1.8 Hz, 1 H), 1.85–0.47 (m, 10 H).

Anal. Calcd for $C_{18}H_{20}OS$: C, 75.86; H, 7.07. Found: C, 76.01, H, 7.09.

Medium-pressure liquid chromatography of the mother liquors on silica gel (elution with 37% ethyl acetate in petroleum ether) gave pure **21** (8% yield) as colorless plates: mp 100–100.5 °C (from petroleum ether); ^{1}H NMR ($CDCl_3$) δ 7.73–7.67 (m, 2 H), 7.46–7.42 (m, 3 H), 5.41 (d, J = 2.6 Hz, 1 H), 3.25 (m, 1 H), 2.88–2.83 (m, 1 H), 2.79 (br s, 1 H), 2.75 (br s, 1 H), 2.2 (br d, J = 10 Hz, 1 H), 1.85–1.48 (m, 6 H), 1.31–1.07 (m, 3 H); ^{13}C NMR ($CDCl_3$) 163.24, 134.03, 131.26, 129.14, 125.88, 119.58, 64.08, 46.11, 44.94, 41.95, 38.74, 37.75, 32.32, 30.51, 24.49 ppm (one quaternary C not observed); mass spectrum, calcd (M^+ – 0) *m/e* 268.1286, obsd 268.1293.

Reductive Cleavage of 20 and 21. To a cold (–78 °C), magnetically stirred solution of the **20/21** adduct mixture in ethylamine (45 mL) was added 178 mg of lithium wire in one portion. The reaction mixture was stirred at –78 °C until the blue color persisted, at which point the excess lithium was immediately removed. Workup in the predescribed manner provided 485 mg (86%) of a pale yellow oil. This two-component hydrocarbon mixture was separated into its constituents by preparative VPC at 160 °C. The more prevalent isomer (**16**) was isolated as a waxy white solid (mp 31–33.5 °C), identical in all respects with an authentic sample. The less prevalent isomer was determined by suitable spectral comparisons to be **9**.

Phenyl Vinyl Sulfone Adducts of 3. To a boiling solution of **4** (700 mg, 5.3 mmol) in *tert*-butylbenzene (30 mL) which had been heated at reflux for 30 min was slowly added a solution of phenyl vinyl sulfone (890 mg, 5.3 mmol) in 10 mL of the same solvent. The reaction mixture was heated overnight at the reflux temperature, and the solvent was removed by distillation under reduced pressure. The residue was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). In addition to **23** (7%), there was isolated three phenylsulfonyl-substituted *anti*-tetracyclo[4.4.0.1^{1,4},1^{7,10}]dodec–5–enes (**24**) in yields of 23%, 27%, and 31%.

Isomer A: mp 90–91 °C (from hexanes); ^{1}H NMR (CDCl$_3$) δ 7.92–7.88 (m, 2 H), 7.62–7.50 (m, 3 H), 5.49 (d, J = 3 Hz, 1 H), 3.23–3.13 (m, 1 H), 3.09 (br s, 1 H), 2.88 (br s, 1 H), 2.78 (br s, 1 H), 2.15–1.20 (series of m, 10 H); ^{13}C NMR (CDCl$_3$) 163.56, 141.03, 133.12, 129.09, 128.16, 120.64, 65.88, 62.38, 45.92, 44.61, 42.14, 38.74, 38.20, 32.13, 31.94, 24.71 ppm; mass spectrum, calcd (M$^+$) *m/e* 300.1184, obsd 300.1193.

Isomer B: ^{1}H NMR (CDCl$_3$) δ 8.03–7.80 (m, 2 H), 7.73–7.41 (m, 3 H), 5.45 (d, J = 4 Hz, 1 H), 3.40–3.00 (m, 2 H), 2.80 (br s, 1 H), 2.40 (br s, 1 H), 2.20–1.10 (series of m, 10 H); ^{13}C NMR (CDCl$_3$) 166.91, 140.06, 133.26, 129.18, 128.21, 116.95, 65.73, 62.04, 48.01, 46.02, 42.38, 39.08, 38.88, 31.60, 29.42, 24.90 ppm.

Isomer C: mp 119–120 °C (from hexanes); ^{1}H NMR (CDCl$_3$) δ 7.90–7.84 (m, 2 H), 7.63–7.50 (m, 3 H), 5.38 (d, J = 2.6 Hz, 1 H), 3.75–3.62 (m, 1 H), 3.07 (br s, 1 H), 2.89 (d, J = 2.5 Hz, 1 H), 2.28 (d, J = 3 Hz, 1 H), 2.00–1.18 (series of m, 10 H); ^{13}C NMR (CDCl$_3$) 163.90, 140.64, 133.16, 129.04, 128.16, 111.85, 65.44, 62.43, 49.90, 49.03, 42.33, 39.42, 38.83, 31.45, 29.80, 24.66 ppm; mass spectrum, calcd (M$^+$) *m/e* 300.1184, obsd 300.1193.

Desulfonylation of the Phenyl Vinyl Sulfone Adducts 24. The general 6% sodium amalgam reduction procedure described above was applied independently to isomers A–C. Each of these reactions delivered only olefinic hydrocarbon **9** in isolated yields of 25%, 20%, and 87%, respectively.

Phenyl Vinyl Sulfone Addition to 25 ⇄ 26. A mixture of **25** (0.50 g, 3.42 mmol), phenyl vinyl sulfone (0.58 g, 3.45 mmol), and toluene (3 mL) was placed in a sealed heavy-walled Pyrex tube and heated at 107 °C for 2 days. The solvent was evaporated, and the residue was subjected to MPLC purification (elution with 10% ethyl acetate in petroleum ether). There was isolated 0.35 g (33%) of linear adduct **27** and 0.54 g (50%) of angular adduct **28**.

For **27**: mp 128–129.5 °C (from hexanes); ^{1}H NMR (CDCl$_3$) δ 8.00–7.80 (m, 2 H), 7.67–7.40 (m, 3 H), 3.10–2.63 (m, 6 H), 2.40–2.10 (m, 1 H), 1.90–1.03 (series of m, 7 H), 0.63 (d, J = 6 Hz, 3 H); ^{13}C NMR (CDCl$_3$) 155.65, 150.36, 140.45, 133.32, 129.24, 128.22, 66.85, 56.46, 55.35, 49.33, 46.75, 41.27, 40.93, 31.61, 25.49, 25.25, 11.75 ppm; mass spectrum, calcd (M$^+$) *m/e* 314.1340 obsd 314.1349.

Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.46; H, 7.08.

For **28**: mp 107–108 °C (from hexanes); ^{1}H NMR (CDCl$_3$) δ 7.87–7.83 (m, 2 H), 7.63–7.50 (m, 3 H), 5.19 (s, 1 H), 3.50 (dd, J = 9.6, 5.1 Hz, 1 H), 2.79 (d, J = 3.6 Hz, 1 H), 2.19 (d, J = 3.6 Hz, 1 H), 1.87–1.90 (m, 2 H), 1.80–1.64 (m, 2 H), 1.62–1.54 (m, 1 H), 1.39 (s, 3 H), 1.47–1.21 (m, 5 H); ^{13}C NMR (CDCl$_3$) 163.12, 141.37, 133.12, 128.99, 128.41, 116.95, 70.10, 60.93, 57.79, 57.63, 41.95, 39.47, 38.74, 34.13, 31.51, 24.61, 19.32 ppm; mass spectrum, calcd (M$^+$) *m/e* 314.1340, obsd 314.1346.

4-Methyl-*anti*-tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene (29). By use of the general procedure described above, reduction of **28** (300 mg, 0.95 mmol) gave 40 mg (24%) of **29** after preparative VPC purification (12 ft × 0.25 in. column, 15% SE-30, 170 °C) together with 200 mg (67%) of recovered starting material.

For **29**: ^{1}H NMR (CDCl$_3$) δ 5.12 (s, 1 H), 2.73 (br s, 1 H), 2.24 (br s, 1 H), 1.98 (td, J = 10, 2 Hz, 1 H), 1.25 (s, 3 H), 1.74–1.02 (series of m, 11 H); ^{13}C NMR (CDCl$_3$) 162.40, 120.55, 62.29, 54.86, 53.70, 41.99, 40.10, 38.74, 32.14, 29.28, 25.05, 20.05 ppm; mass spectrum, calcd (M$^+$) *m/e* 174.1408, obsd 174.1413.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.68; H, 10.36.

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Registry No. 3, 75725-33-6; **4**, 6675-72-5; **6**, 64489-06-1; **7**, 83134-44-5; **8**, 83134-45-6; **9**, 83134-46-7; **10**, 83134-47-8; **11**, 156-60-5; **12**, 83134-48-9; **13**, 1822-73-7; **14**, 83134-49-0; **15a**, 83134-50-3; **15b**, 83134-51-4; 16, 73321-28-5; **17**, 83134-52-5; **18**, 53862-33-2; **19**, 20451-53-0; **20**, 83134-53-6; **21**, 83134-54-7; **22**, 5535-48-8; **23**, 73321-26-3; **24A**, 83134-55-8; **24B**, 83134-56-9; **24C**, 83198-37-2; **25**, 83134-57-0; **26**, 83134-58-1; **27**, 83134-59-2; **28**, 83151-98-8; **29**, 83134-60-5.

Dimethyl 1,1-Dicyanoethene-2,2-dicarboxylate, a New Electrophilic Olefin

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Dimethyl 1,1-dicyanoethene-2,2-dicarboxylate (DDED), a new electrophilic tetrasubstituted olefin, was synthesized via a Knoevenagel condensation. DDED spontaneously copolymerizes with electron-rich olefins such as styrene and *p*-methylstyrene. In the copolymerization, the bulky growing styryl radicals add to the dicyano-bearing carbon of DDED. Cyclobutane adducts are obtained in thermal reactions with styrene, *p*-methylstyrene, *p*-methoxystyrene, and vinyl ethers via a tetramethylene intermediate. Bond formation occurs at the diester end of DDED due to the greater stabilization provided by the dicyano group and the minimal steric requirements of the attacking methylene.

In our continuing study of the reactions of electron-poor and electron-rich olefins, we reported the spontaneous thermal copolymerization of dimethyl dicyanofumarate and styrenes.[1] This was a rare case of a (nonfluorinated) tetrasubstituted olefin capable of undergoing copolymerization. The lower energy barrier for cross-propagation of an electron-poor radical with an electron-rich monomer, and vice versa, may be enough to overcome the steric hindrance which usually prevents such reactions. Recently Vogl and co-workers[2] reported the copolymerization of dimethylmaleic anhydride and vinyl ethers, and we have described the copolymerization of bis(carbomethoxy)maleic anhydride and styrene.[3]

We postulate that spontaneous reactions between electrophilic and electron-rich olefins involve bond formation between the β-positions of the olefins, generating a tetramethylene intermediate which acts as a resonance hybrid of a zwitterion and a biradical structure.[4] If derived from polymerizable olefins, and depending on which character is predominant in the hybrid, the tetramethylene intermediate can initiate either cationic or anionic homo-

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