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Diels-Alder Reactions of Sulfur-Substituted Allenecarboxylates An FMO Approach by the PM3-Method[1)]

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The effect of captodative (c,d) substitution of some olefins and allenes has been investigated by MNDO-PM3 calculations. These results are compared with the Diels-Alder reactions of α-sulfur-substituted allenecarboxylates. α-Sulfonyl allenecarboxylates **6** are a new class of stable gem-diacceptor-substituted allenes.

Among the important methods in organic synthesis the Diels-Alder reaction holds an outstanding position[3,4)]. In contrast to the enormous research efforts devoted to the study of Diels-Alder reactions with vinylic or acetylenic dienophiles, little use has been made of allenic dienophiles[5)]. The Diels-Alder reactions using allene as a dienophile might provide a convenient way of synthesizing a variety of methylenecyclohexenes. However, the application of allene to the Diels-Alder reaction has been severly limited[6)] because of its unreactive nature as a dienophile. Recent publications describe a few [4+2] addition reactions involving allene derivatives such as penta-2,3-dienedioic acid, buta-2,3-dienoic acid (and corresponding esters), methyl 2-methyl-buta-2,3-dienoate, or (phenylsulfonyl)allene[7,8)]. The scope of these reactions, however, is limited by one of the fundamental rules of thermal [4+2] cycloadditions according to which a sufficiently high reaction rate is only achieved, if the frontier orbitals of the starting materials (HOMO and LUMO) are energetically close to each other[3,9)]. Such ideal conditions are not always fullfilled, and in the field of olefinic dienophiles there has been no lack of attempts to improve the reactions. Recently, great interest has been devoted to the captodative (c,d) olefins[10)] as dienopiles in Diels-Alder reactions[11,12,13)]. The cycloaddition reactions of captodative allenes[14)] have received less attention compared with these extensive studies. It thus seems to be necessary to check the applicability of Viehe's concept of captodative (c,d) substitution to allenic dienophiles. We now report on our investigations on *gem*-disubstituted allenes, an area which is closely related to our investigations on (c,d) substituted alkenes[12)].

Semiempirical Calculations

Captodative (c,d) olefins, which are defined by a geminal substitution with an electron-acceptor (c) and an electron-donor (d) group are characterized by relatively high HOMO and relatively low LUMO energies[10)]. In order to prove the cd effect we have determined the FMO energies of some model olefins by MNDO-PM3[15)] calculations[16,17)] (Figure 1, Table 1). These results confirm the proposed effect of the different substituents on the vinylic double bond. The substitution by a methylthio and a cyano group as an example of a cd substitution leads to a decrease in HOMO-LUMO distance. The influence of a single methylthio group is remarkable because this substituent alone shows a similar effect and causes a smaller FMO gap.

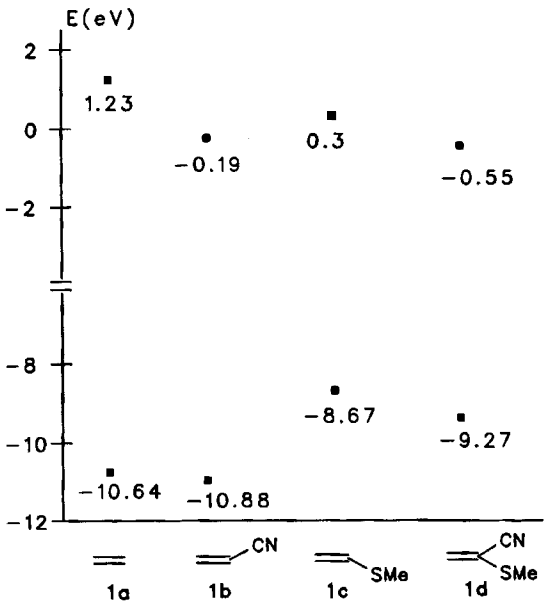

Figure 1. HOMO/LUMO energy levels of ethene derivatives calculated by the MNDO-PM3 method

So far we have only treated olefins. In the case of allenic compounds the influence of substituents is more complicated, because both cumulated double bonds have to be regarded with respect to their interactions in cycloadditions. The PM3-calculations[18)] of 1-methoxyallene (**2b**), 1-(methylthio)allene (**2c**), 1-cyanoallene (**2f**) and 1-cyano-1-(methylthio)allene (**2h**) show comparable results for the FMO of

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Table 1. PM3 HOMO/LUMO energies and heats of formation of cthene derivatives

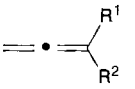
1	R^1	R^2	ΔH_f [kcal/mol]	HOMO [eV]	LUMO [eV]
a	H	H	16.630	-10.64	1.23
b	CN	H	50.168	-10.88	-0.19
c	MeS	H	13.547	-8.68	0.31
d	CN	MeS	51.718	-9.27	-0.55

the 1,2-double bond (Figure 2). The electron-releasing methoxy group mainly increases the HOMO level, whereas the electron-withdrawing cyano group decreases the LUMO energy to a negative level. The methylthio substituent causes an increase of the allene HOMOs, but the LUMO energies are lowered, resulting in a smaller FMO gap as expected for a cd effect. Concerning the 2,3-double bond all calculated substituents lead to a decrease of HOMO and LUMO, effecting an enlarged HOMO-LUMO distance.

Cycloadditions of 2-(Arylthio)allenecarboxylates

Until now only few cd-substituted allenes are known[19,20], and there are no publications on the Diels-Alder reactions of these compounds. Furthermore, the cd allenes, prepared by Viehe's group, cyclodimerize already at room temperature and can only be trapped with cd olefins to form cyclobutane derivatives[14]. So it may be difficult to compare the calculated data with experimental results. In order to get some more information on the cycloadditions of cd allenes, we have studied the reactions of α-sulfur-substituted allenecarboxylates[1] **3**–**6**. We have chosen these allenes because they are readily accessible, more stable against di-

Table 2. PM3 HOMO/LUMO energies and heats of formation of allene derivatives $H_2C=C=C(R^1)R^2$



2	R^1	R^2	ΔH_f [kcal/mol]	C1-C2 HOMO [eV]	C1-C2 LUMO [eV]	C2-C3 HOMO [eV]	C2-C3 LUMO [eV]
a	H	H	47.068	-10.17	1.12	-10.17	1.12
b	MeO	H	11.405	-9.22	1.17	-10.47	1.04
c	MeS	H	44.251	-8.58	0.71	-10.24	0.005
d	PhS	H	80.144	-8.65	0.18	-9.89	-0.38
e	Me_2N	H	43.614	-8.51	1.15	-10.28	1.10
f	CN	H	81.795	-10.43	-0.18	-11.14	0.32
g	COOMe	H	-35.888	-10.57	-0.08	-10.59	0.56
h	CN	MeS	83.562	-9.18	-0.49	-11.11	-0.58
i	CN	MeO	48.569	-10.24	-0.27	-11.34	0.22
j	CN	Me_2N	81.394	-8.95	-0.06	-10.88	0.37
k	COOMe	MeS	-31.341	-10.57	-0.55	-9.08	-0.17
l	COOMe	MeO	-68.831	-9.67	0.01	-10.86	0.50
m	MeSO	H	17.349	-9.07	0.21	-10.16	-0.07
n	PhSO	H	53.401	-8.99	0.07	-10.20	-0.48
o	$MeSO_2$	H	-20.895	-11.09	-0.23	-10.46	-0.08
p	$PhSO_2$	H	16.368	-11.05	-0.46	-10.31	-0.16
q	COOMe	MeSO	-58.989	-11.13	-0.40	-10.51	-0.49
r	COOMe	$MeSO_2$	-96.463	-11.32	-0.57	-11.32	-0.46
s	COOMe	$PhSO_2$	-60.147	-11.29	-0.75	-10.66	-0.33
t	CN	MeSO	56.936	-10.81	-0.74	-9.71	-0.62

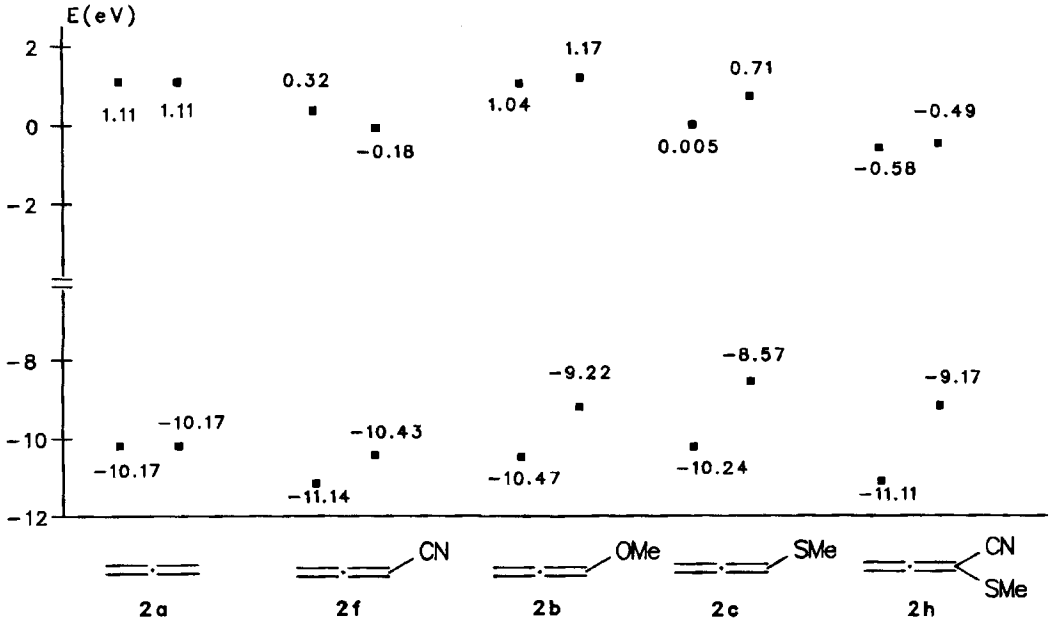
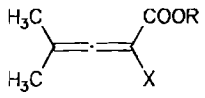


Figure 2. HOMO/LUMO energy levels of allene derivatives calculated by the MNDO-PM3 method

merization, and the sulfur function offers many synthetic possibilities for the cycloadducts.



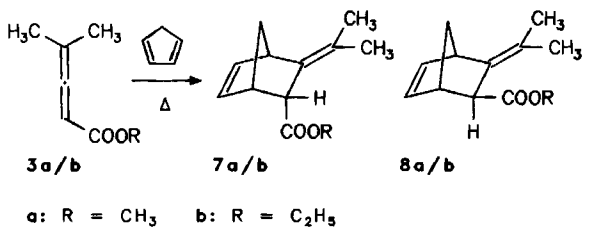
	X		X
3	H	**5b**	SOC_6H_4Cl-(4)
4a	SPh	**6a**	SO_2Me
4b	SC_6H_4Cl-(4)	**6b**	SO_2Ph
5a	SOPh	**6c**	$SO_2C_6H_4Cl$-(4)

The cd allenes methyl 4-methyl-2-(phenylthio)penta-2,3-dienoate (**4a**) and 2-(4-chlorophenylthio)-4-methylpenta-2,3-dienoate (**4b**) are nearly inert in a cycloaddition with cyclopentadiene (only traces of cycloadducts after several days at 120°C). The inverse Diels-Alder reaction with acrolein or hexachlorocyclopentadiene has been unsuccessfull also. This low reactivity is surprising, because the LUMO energy of 1-(methoxycarbonyl)-1-(methylthio)allene (**2k**) is lowered relative to the unsubstituted allenecarboxylate. Regarding the Diels-Alder reactions of α-(alkylthio)acrylates with cyclopentadiene Stella and Boucher[11c,d] have found similar results. The cd substitution causes no rate enhancement; even a decrease of the rate by a factor of 4 relative to methyl acrylate is observed. On the other hand, *tert*-butyl acrylate reacts by a factor of 9 slower. It is obvious that steric effects may have a greater influence on the reactivity than cd substitution. Thus, the stability and hence low reactivity of the allenes **4** can be explained by steric effects of the aryl group. This behavior of **4a** and **4b** is in contrast to the observation made by Gundermann and Röhrl[21] concerning the fast dimerization of α-(alkylthio)acrylonitrile. Furthermore, the PM3 data of 1-(phenylthio)allene (**2d**) indicate that the introduction of a phenylthio group causes a stronger lowering of the LUMO energy level and an increase of the HOMO energy as compared to 1-(methylthio)allene (**2c**) (cf. Table 2). Hitherto, this effect has been paid less attention during the investigation of the Diels-Alder reactions of cd dienophiles. In order to get more information on this point we have started to investigate the influence of the aryl group on allenic sulfoxides and sulfones.

Cycloadditions of 2-(Arylsulfinyl)allenecarboxylates

The most important feature of vinyl sulfoxides is that they can be prepared in optically active form. However, there are cases in which the sulfoxide moiety has been used only as an activating function[22]. In the case of vinylic sulfoxides, if the carbon bearing the sulfoxide function carries a further electron-withdrawing group, the reactivity is higher and similar to that observed for the captodative vinyl sulfides[23].

Scheme 1



3a/b **7a/b** **8a/b**

a: R = CH_3 b: R = C_2H_5

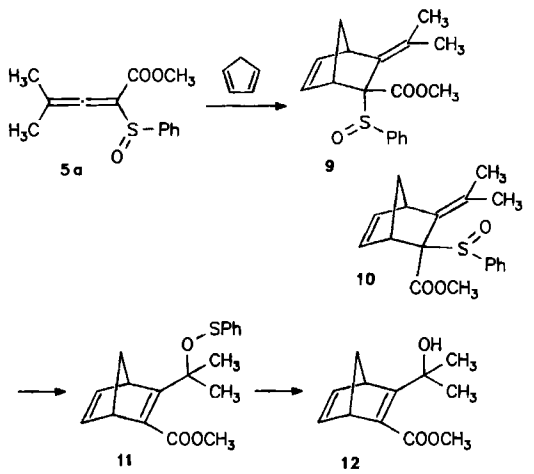
Table 3. Diels-Alder reactions of allene dienophiles with cyclopentadiene

	Reaction Conditions	Yield	endo : exo[a]
3a	70 °C, 24 h,	48 %	83 :17
3a	25 °C, $Eu(fod)_3$, 24 h	78 %	89 :11
3b	80 °C, benzene, 10 h	no reaction[b]	
3b	25 °C, $Eu(fod)_3$, 6 h	60 %	90 : 10[b]
5a	25 °C, 36 h	69 %	74 : 26
6a	-30 °C, 20 h[c]	74 %	63 : 37
6a	25 °C, 12 h[c]	88 %	72 : 28
6a	-30 °C, $Ti(OiPr)_2Cl_2$, 20 h[c]	70 %	83 : 17
6a	-30 °C, ZnI_2, 24 h[c]	83 %	72 : 28
6b	120 °C, 4 h	96 %	87 : 13
6c	120 °C, 4 h	67 %	83 : 17
6c	25 °C, 66 h	64 %	80 : 20

[a] Ratios were determined by ^1H- or ^{13}C-NMR analysis. — [b] From ref.[8]. — [c] Solvent CH_2Cl_2.

In the reaction with cyclopentadiene at 25°C methyl 4-methyl-2-(phenylsulfinyl)penta-2,3-dienoate (**5a**) exhibits a slightly higher reactivity than the unsubstituted 4-methylpenta-2,3-dienoate **3**, which reacts only in the presence of a Lewis acid or at a higher temperature (Scheme 2). The activating phenylsulfinyl group leads to a decrease in the *endo*-selectivity[24] with regard to the methoxycarbonyl group.

Scheme 2



5a **9** **10** **11** **12**

If the phenylsulfinyl group is substituted by a 4-chlorophenylsulfinyl group, the allene is strongly deactivated. This effect is found in the reactions of methyl 2-(4-chlorophenylsulfinyl)-4-methylpenta-2,3-dienoate (**5b**) and 1-(4-chlorophenylsulfinyl)-3-methylbuta-1,2-diene, which undergo no Diels-Alder reaction with cyclopentadiene at room temperature. Several attempts to perform these reactions under Lewis acid catalysis conditions or at enhanced temperatures have failed. This may be due to the instability of the allenic sulfoxides at higher temperatures[25]. Heating of **5b** with cyclopentadiene for six hours in refluxing benzene gives only

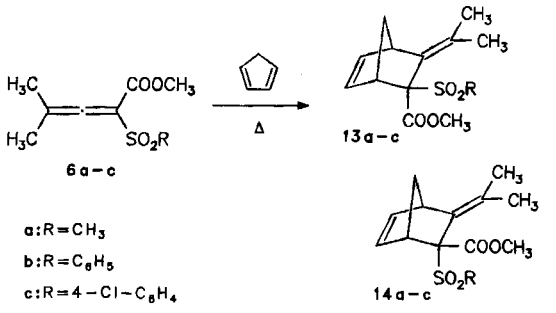
some decomposition products. Furthermore, the Diels-Alder adducts are not stable against sulfoxide-sulfenate rearrangement (Scheme 2), which is typical of allylic sulfoxides[26]. Trying to purify the crude product (**9**/**10**) obtained by the reaction of **5a** with cyclopentadiene by HPLC, we have isolated the norbornadiene derivative **12**, formed by hydrolysis of the sulfenate ester **11**. Because of this rearrangement we have been unable to decide, whether **5b** reacts with cyclopentadiene at higher temperature, followed by rapid rearrangement, or the decomposition of **5b** is the first step. These side reactions limit the scope of the Diels-Alder reaction with allenic sulfoxides because higher temperatures or the use of Lewis acids can accelerate the rearrangement and decomposition of the sulfoxide. On the other hand, this reaction offers a new synthetic approach to norbornadiene derivatives.

Cycloadditions of 2-Sulfonylallenecarboxylates

Allenic sulfones are known to be suitable dienophiles, and several examples[18,27] have been published in view of the utility of the adducts. Depending on the diene, the reaction may be highly stereo- and regioselective. The MNDO-PM3 calculations of 1-(methylsulfonyl)-1,2-propadiene (**2o**) or 1-(phenylsulfonyl)-1,2-propadiene (**2p**) indicate that the introduction of a sulfonyl group causes a remarkable lowering of the LUMO energy level compared with allene (ΔE = −1.35 resp. −1.58 eV) and even with allenecarboxylates. This suggests that sulfonylallenes are more reactive than allenecarboxylates in Diels-Alder reactions, due to the more effective $LUMO_{allene}$-$HOMO_{diene}$ interactions. The introduction of a second electron-withdrawing group lowers the LUMO energy even more and enhances the reactivity towards the [4+2] cycloaddition to dienes.

Some allenes with *gem*-electron-attracting groups have been described which are very reactive and in their reactivity comparable to ketenes. Because of their high reactivity in situ preparation of such allenes at low temperature[28] or by flash pyrolysis[29] is necessary. Now we have found that α-sulfonylallenecarboxylates represent stable 1,1-diacceptor-substituted allenes which do not dimerize even at higher temperature. These allenic compounds are suitable dienophiles with an enhanced reactivity in the Diels-Alder reaction with cyclopentadiene.

The sulfone **6a** is treated with an excess of cyclopentadiene at room temperature. After 12 hours the Diels-Alder adducts **13a** and **14a** are isolated in 88% yield. An NMR analysis reveals that the two isomeric adducts have been formed in a ratio of 72:28. The methylsulfonyl group lowers the *endo* selectivity of the dienophile (with regard to methoxycarbonyl), but the effect is weaker than the influence of an alkyl substituent α to the ester function[30]. This is remarkable, because both the methoxycarbonyl and the sulfonyl group are *endo*-directing substituents[27a,c]. Experiments catalysed by Lewis acids ($AlCl_3$, $BF_3 \cdot Et_2O$, $EtAlCl_2$, 2-bromo-1,3,2-benzodioxaborol) do not show any improvement because we have only isolated complex mixtures of several addition products. Much better results are obtained when the reaction with cyclopentadiene is carried out in the presence of $TiCl_2(OiPr)_2$ or ZnI_2 as catalysts at −30°C to give the adducts **13a** and **14a** in good yields and with a higher *endo* selectivity (**13a**:**14a** = 83:17 resp. 72:28).



The α-arylsulfonyl derivatives **6b** and **6c** display a somewhat lower reactivity in the Diels-Alder reaction with cyclopentadiene. One reason could be the stronger steric effect of the aryl groups. But there is a slightly increased reactivity compared to the unsubstituted 1-(phenylsulfonyl)-allene[27a,b,31]. The *endo* selectivity of these dienophiles is higher than that of the methyl derivative **6a**.

Our results demonstrate, as expected, that α-sulfonylallenecarboxylates are efficient dienophiles. This is in accord with the MNDO-PM3 calculations performed on several allenic compounds. On the other hand there is a discrepancy between calculated and experimental results for α-sulfinylallenecarboxylates and α-thioallenecarboxylates. The former show a moderate reactivity, but decomposition of starting compounds and products becomes the main reaction if forced conditions are necessary. Furthermore, the substituent at the arylsulfinyl group has an influence on the allene moiety. The cd-substituted allenes show nearly no reactivity in the Diels-Alder reaction with cyclopentadiene, though according to PM3 data these compounds should be moderate dienophiles. This discrepancy may be caused by steric factors, because in the case of sulfonylallenes the reactivity decreases with the size of the substituent at the sulfur atom.

Further studies based on these results are under work in order to determine the scope of the cd effect on Diels-Alder reactions. Another aspect of this work is the investigation of the effects caused by different substituents at the sulfur atom[32]. Hitherto, this aspect has been paid less attention.

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Experimental

The dienophiles **4a, b, 5a, b**, and **6a−c** were prepared as described in ref.[1]. Methyl 4-methylpenta-2,3-dienoate (**3a**) was prepared according to the method of Lang and Hansen[33]. All reagents were of commercial quality from freshly opened containers. Diethyl ether was dried with potassium hydroxide and distilled over $LiAlH_4$. Dichloromethane was distilled over calcium hydride. The other sol-

vents were purified by distillation. – ^{1}H and ^{13}C NMR: Varian VXR 300 (300/75 MHz) or Bruker WM 300 (300/75 MHz), TMS internal standard. – IR: Perkin Elmer 257 or Perkin-Elmer 1750. – MS: Varian Mat 212. – Melting points: Büchi 510, uncorrected. – Microanalyses: Mikroanalytisches Laboratorium der Technischen Hochschule Aachen and Analytisches Laboratorium des Organisch-Chemischen Instituts der Universität Münster. – GLC analyses: Siemens Sichromat 3 with 25 m HP Ultra 2. – Silicagel 60 (230–400 mesh): Macherey & Nagel. – Analytical TLC plates: Merck. – HPLC: Kontron HPLC-Pumpe 420, Kontron UV-Detektor 432, RI-Detektor 8110 (Fa. Bischoff), column LiChrosorb Si 60-5 (2 × 25 cm) (Chromatographie-Service). All reactions are performed under argon and monitored by TLC or GC. After the amount of dienophile is constant, the reaction mixtures are worked up as described. In order to establish the ratio of *endo* to *exo* adducts the raw products of the reactions are analyzed by ^{1}H and ^{13}C NMR.

Methyl 3-Isopropylidenebicyclo[2.2.1]hept-5-ene-2-carboxylate (**7a**/**8a**)

a) *With Eu(fod)$_3$ as Catalyst:* To a solution of methyl 4-methylpenta-2,3-dienoate (**3a**) (0.63 g, 5 mmol) in cyclopentadiene (1.65 g, 25 mmol) is added Eu(fod)$_3$ (53 mg, 1 mol-%). After 24 h at room temp. all volatile products are removed in vacuo. The residue is chromatographed (SiO_2, ether/pentane 1:2) to yield 0.75 g (78%) of a colorless oil (**7a**:**8a** = 8:1 from ^{13}C NMR).

b) *Without Catalyst:* **3a** (1.8 g, 14 mmol) and cyclopentadiene (3.0 g, 45 mmol) are heated in a sealed ampoule at 70°C for 24 h. The product is isolated by distillation (b.p. 100°C/16 mbar) to yield 1.3 g (48%) of product (**7a**:**8a** = 5:1, determined by ^{13}C NMR). The two isomers are separated by HPLC (Si 60, ethyl acetate/cyclohexane 5:95, 11 ml/min).

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.97 H 8.39
Found C 74.82 H 8.55

Double irradiation experiments have been carried out to correlate the ^{1}H-NMR signals. Furthermore the NMR data are compared with literature data[7,8].

endo Adduct **7a**: IR (kap): $\tilde{\nu}$ = 3060/2980/2930/2880 cm^{-1} (CH), 1745 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.34 (d, *J* = 10 Hz, 1H, 7-H$_{syn}$), 1.46 (d, *J* = 1.5 Hz, 3H, =CCH$_3$), 1.53 (d/t, *J* = 10/1.7 Hz, 1H, 7-H$_{anti}$), 1.69 (s, 3H, =CCH$_3$), 3.15/3.33 (2 × br. s, each 1H, 1-H/4-H), 3.43 (q, $^4J_{2,7s}$ = 1.6 Hz, 1H, 2-H), 3.56 (s, 3H, CH_3O), 5.89/6.19 (2 × d/d, *J* = 8/3 Hz, each 1H, 5-H/6-H). – ^{13}C NMR ($CDCl_3$): δ = 20.42/21.76 (CH_3), 46.19/46.93/47.51 (C-1/C-2/C-4), 49.11 (C-7), 50.61 (CH_3O), 122.79/132.12 [C-3/=*C*(CH_3)$_2$], 132.30 (C-6), 134.71 (C-5), 172.85 (C=O). – MS (70 eV): *m/z* (%) = 193 (15.3), 192 (100) [M^+].

exo Adduct **8a**: IR (kap): $\tilde{\nu}$ = 3060/2980/2930/2880 cm^{-1} (CH), 1720 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.42 (d/d, *J* = 9/2 Hz, 1H, 7-H$_{syn}$), 1.46/1.68 [2 × s, each 3 H, =C(CH_3)$_2$], 1.90 (d/m, *J* = 9 Hz, 1H, 7-H$_{anti}$), 2.76/3.0/3.41 (3 × br. s, each 1H, 1-H/2-H/4-H), 3.69 (s, 3H, CH_3O), 6.06/6.12 (2 × d/d, *J* = 6/3 Hz, each 1H, 5-H/6-H). – ^{13}C NMR ($CDCl_3$): δ = 20.46/21.07 (CH_3), 40.54/44.50/45.24 (C-1/C-2/C-4), 47.79 (C-7), 50.65 (CH_3O), 131.37/135.23 [C-3/=*C*(CH_3)$_2$], 135.46 (C-6), 134.77 (C-5), 172.95 (C=O).

Methyl 3-Isopropylidene-2-(phenylsulfinyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**9**/**10**): Methyl 4-methyl-2-(phenylsulfinyl)penta-2,3-dienoate (**5a**) (1.5 g, 6.0 mmol) in CH_2Cl_2 (8 ml) is treated with cyclopentadiene (2.0 g, 30 mmol) at room temp. After 36 h dicyclopentadiene is removed by filtration over silica gel (pentane/ether). The product (**9**:**10** = 2.9:1 from ^{13}C NMR) is eluated with ethyl acetate to yield 1.3 g (69%) of a yellow oil. Attempts to purify the crude product by HPLC (Si 60, ethyl acetate/hexane 40:60, 10 ml/min) have been unsuccessful, because the product showed decomposition, giving the norbornadiene derivative **12**. – IR (kap): $\tilde{\nu}$ = 3055/2966/2860 cm^{-1} (CH), 1710 (C=O).

endo Adduct **9**: ^{1}H NMR ($CDCl_3$): δ = 1.29 (d/t, *J* = 7/1 Hz, 1H, 7-H$_{syn}$), 1.92/1.94 [2 × s, each 3H, =C(CH_3)$_2$], 2.23 (d, *J* = 7 Hz, 1H, 7-H$_{anti}$), 2.80 (br. s, 1H, 1-H), 3.55 (s, 3H, CH_3O), 3.67 (s, 1H, 4-H), 5.81/6.45 (2 × d/d, *J* = 5/3.5 Hz, each 1H, 5-H/6-H), 7.51 (m, 3H, 3′-, 4′-, 5′-H), 7.85 (m, 2H, 2′-, 6′-H). – ^{13}C NMR ($CDCl_3$): δ = 22.6/24.85 (2 × CH_3), 45.12 (C-7), 46.16/52.06 (C-1/C-4), 51.55 (CH_3O), 79.52 (C-2), 126.53 (C-2′/C-6′), 128.53 (C-3′/C-5′), 130.48/131.54 [C-3/=*C*(CH_3)$_2$], 131.15 (C-4′), 134.54/141.76 (C-5/C-6), 141.66 (C-1′), 170.79 (C=O).

exo Adduct (**10**): ^{1}H NMR ($CDCl_3$): δ = 1.42 (d/m, *J* = 8 Hz, 1H, 7-H$_{syn}$), 1.92/1.94 [2 × s, each 3H, =C(CH_3)$_2$], 2.92 (br. s, 1H, 1-H), 3.61 (s, 3H, CH_3O), 5.81/6.4 (2 × d/d, *J* = 5/3.5 Hz, each 1H, 5-H/6-H), 7.51 (m, 3H, 3′-, 4′-, 5′-H), 7.85 (m, 2H, 2′-, 6′-H). – ^{13}C NMR ($CDCl_3$): δ = 23.42/24.88 (2 × CH_3), 45.78 (C-7), 48.3/51.8 (C-1/C-4), 52.27 (CH_3O), 80.71 (C-2), 126.66 (C-2′/C-6′), 128.45 (C-3′/C-5′), 130.18/132.5 [C-3/=*C*(CH_3)$_2$], 131.8 (C-4′), 133.84/140.8 (C-5/C-6), 138.2 (C-1′), 167.84 (C=O).

Methyl 3-(1-Hydroxy-1-methylethyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**12**): ^{1}H NMR ($CDCl_3$): δ = 1.26/1.50 [2 × s, each 3H, C(CH_3)$_2$], 1.94 (d/d, *J* = 5/1.5 Hz, 1H, 7-H), 2.06 (d/d, *J* = 5/1.5 Hz, 1H, 7-H), 3.64 (br. s, 1H, 4-H), 3.78 (s, 4H, CH_3O and OH), 3.94 (br. s, 1H, 1-H), 6.74 (d/d, *J* = 5/3 Hz, 5-H or 6-H), 6.89 (d/d, *J* = 5/3 Hz, 5-H or 6-H). – ^{13}C NMR ($CDCl_3$): δ = 26.29/28.77 (2 × CH_3), 51.48 (C-1), 51.55 (CH_3O), 55.23 (C-4), 69.98 (C-7), 71.10 [=*C*(CH_3)$_2$], 136.40 (C-2), 140.23/143.31 (C-5/C-6), 167.25 (C=O), 180.90 (C-3).

Methyl 3-Isopropylidene-2-(methylsulfonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**13a**/**14a**)

a) *Uncatalysed Reaction:* A mixture of methyl 4-methyl-2-(methylsulfonyl)penta-2,3-dienoate (**6a**) (2.0 g, 9.8 mmol) in CH_2Cl_2 (5 ml) and cyclopentadiene (10 g, 150 mmol) is stirred at room temp. for 12 h. Then the volatile compounds are evaporated in the vacuum of an oil pump. The residue is triturated with pentane and filtrated. Yield 2.33 g (88%) of a mixture of the isomers **13a**/**14a** (2.6:1, from ^{1}H NMR), m.p. 138°C.

b) *Reaction Catalyzed with TiCl$_2$(OiPr)$_2$:* A mixture of **6a** (2.0 g, 9.8 mmol) in CH_2Cl_2 (10 ml) and cyclopentadiene (2.5 g, 38 mmol) is chilled to –30°C. At this temp. diisopropoxytitanium dichloride (15 mmol, 15 ml 1 M in CH_2Cl_2) is added during 10 min. After stirring at –30°C for 20 h a saturated solution of $NaHCO_3$ is added in order to hydrolyze the catalyst. The mixture is allowed to warm up, and the upper layer is extracted with CH_2Cl_2 (2 × 50 ml). The combined organic layers are dried with $MgSO_4$, and the solvent is evaporated. The raw product is purified by column chromatography (SiO_2, ethyl acetate/cyclohexane 40:60) to yield 1.85 g (70%) of isomers. The pure *endo* isomer **13a** (0.60 g, 23%) is obtained after crystallization from ethyl acetate/hexane (40:60).

$C_{13}H_{18}O_4S$ (270.35) Calcd. C 57.76 H 6.7
Found C 57.87 H 6.56

endo Adduct **13a**: ^{1}H NMR ($CDCl_3$): δ = 1.54 (d/m, *J* = 9/1.7 Hz, 1H, 7-H$_{syn}$), 1.9 [s, 6H, =C(CH_3)$_2$], 2.11 (d/m, *J* = 9 Hz, 1H, 7-H$_{anti}$), 3.12 (s, 3H, CH_3SO_2), 3.63/3.69 (2 × br. s, each 1H, 1-H/4-H), 3.75 (s, 3H, CH_3O), 5.95 (d/d, *J* = 5.6/3 Hz, 1H, 6-H), 6.48 (d/d, *J* = 5.6/3 Hz, 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 23.18/24.84 (2 × CH_3), 40.68/48.09 (C-1/C-4), 45.04 (C-7), 52.88

(CH_3O), 54.01 (CH_3SO_2), 82.3 (C-2), 126.91/134.55 [C-3/=$C(CH_3)_2$], 132.13/141.47 (C-5/C-6), 167.56 (C=O). – MS (70 eV): *m/z* (%) = 270 (7.8) [M^+], 131 (100).

exo Adduct **14a**: ^{1}H NMR ($CDCl_3$): δ = 1.89 [s, 6H, =$C(CH_3)_2$], 2.88 (s, 3H, CH_3SO_2), 3.84 (s, 3H, CH_3O). – ^{13}C NMR ($CDCl_3$): δ = 22.99/24.26 (2 × CH_3), 41.62/49.32 (C-1/C-4), 47.75 (C-7), 53.39 (CH_3O), 54.48 (CH_3SO_2), 83.88 (C-2), 126.57/133.07 [C-3/=$C(CH_3)_2$], 133.7/139.33 (C-5/C-6), 167.5 (C=O).

Methyl 3-Isopropylidene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**13b**/**14b**): A solution of methyl 4-methyl-2-(phenylsulfonyl)penta-2,3-dienoate (**6b**) (0.50 g, 1.9 mmol) and cyclopentadiene (2.0 g, 30 mmol) in benzene (4 ml) is heated in a sealed ampoule at 120°C. After 4 h the ampoule is cooled to room temp., and all volatile compounds are removed by evaporation. The residue is washed with pentane to give 0.60 g (96%) of Diels-Alder adducts **13b** and **14b** in a ratio of 7:1 (from ^{13}C NMR); m.p. 156°C. Recrystallisation from ether/pentane (1:2) yields 340 mg of the pure *endo* adduct **13b**. – IR (KBr): $\tilde{\nu}$ = 3090/3060/3005/2958/2877 cm^{-1} (CH), 1752 (C=O), 1682/1582/1480 (C=C).

$C_{18}H_{20}O_4S$ (332.4) Calcd. C 65.04 H 6.07
Found C 64.87 H 6.04

endo Adduct **13b**: ^{1}H NMR ($CDCl_3$): δ = 1.39 (d/t, *J* = 8.7/1.3 Hz, 1H, 7-H_{syn}), 1.95/2.05 [2 × s, each 3H, =$C(CH_3)_2$], 2.17 (d, *J* = 8.7 Hz, 1H, 7-H_{anti}), 2.74 (br. s, 1H, 1-H), 3.69 (s, 1H, 4-H), 3.72 (s, 3H, CH_3O), 5.75 (d/d, *J* = 5.5/3 Hz, 1H, 6-H or 5-H), 6.41 (d/d, *J* = 5.5/3 Hz, 1H, 6-H or 5-H), 7.54–7.68 (m, 3H, 3′-, 4′-, 5′-H), 7.95–7.99 (m, 2H, 2′-, 6′-H). – ^{13}C NMR ($CDCl_3$): δ = 23.34/25.17 (2 × CH_3), 45.15 (C-7), 48.06/54.72 (C-1/C-4), 52.46 (CH_3O), 83.75 (C-2), 127.19/135.15 [C-3/=$C(CH_3)_2$], 128.61 (C-2′/C-6′), 130.19 (C-3′/C-5′), 132.32/141.55 (C-5/C-6), 133.71 (C-4′), 138.76 (C-1′), 167.78 (C=O).

exo Adduct **14b**: ^{1}H NMR ($CDCl_3$): δ = 1.48 (d/t, *J* = 8.7/1.3 Hz, 1H, 7-H_{syn}), 1.89/1.95 [2 × s, each 3H, =$C(CH_3)_2$], 3.88 (s, 3H, CH_3O), 5.82 (d/d, *J* = 5.5/3 Hz, 1H, 6-H or 5-H), 6.37 (m, 1H, 6-H or 5-H), 7.54–7.68 (m, 3H, 3′-, 4′-, 5′-H), 7.95–7.99 (m, 2H, 2′-H/6′-H). – ^{13}C NMR ($CDCl_3$): δ = 23.21/25.07 (2 × CH_3), 48.4 (C-7), 49.6/54.12 (C-1/C-4), 52.8 (CH_3O), 85.09 (C-2), 168.97 (C=O).

Methyl 2-(4-Chlorophenylsulfonyl)-3-isopropylidenebicyclo-[2.2.1]hept-5-ene-2-carboxylate (**13c**/**14c**)

a) A solution of methyl 2-(4-chlorophenylsulfonyl)-4-methylpenta-2,3-dienoate (**6c**) (1.2 g, 4.0 mmol) in CH_2Cl_2 (10 ml) is treated with cyclopentadiene (4.0 g, 60 mmol) at room temp. for 66 h. Filtration over silica gel (pentane/CH_2Cl_2) and crystallization from ether gives 940 mg (64%) of the product; m.p. 201°C; **12c**:**13c** = 83:17 (from ^{1}H NMR).

b) **6c** (0.45 g, 1.5 mmol) and cyclopentadiene (2.0 g, 30 mmol) are heated in a sealed ampoule to 120°C. After 4 h at this temp. the mixture is allowed to cool to room temp. during 2 h. Hereby the white products precipitates. The crude product is washed with ether to give 0.37 g (67%); **13c**:**14c** = 83:17 (from ^{1}H NMR). – IR (KBr): $\tilde{\nu}$ = 3095/3060/2960/2865 cm^{-1} (CH), 1745/1738 (C=O), 1580 (C=C).

$C_{18}H_{19}ClO_4S$ (366.9) Calcd. C 58.93 H 5.22
Found C 58.94 H 5.13

endo Adduct **13c**: ^{1}H NMR ($CDCl_3$): δ = 1.4 (d/t, *J* = 9/1 Hz, 1H, 7-H_{syn}), 1.95/2.03 (2 × s, each 3H, =$C(CH_3)_2$], 2.14 (d, *J* = 9 Hz, 1H, 7-H_{anti}), 2.75 (br. s, 1H, 1-H), 3.71 (t, *J* = 1.5 Hz, 1H, 4-H), 3.73 (s, 3H, CH_3O), 5.76/6.42 (2 × d/d, *J* = 5/3 Hz, each 1H, 5-H/6-H), 7.56 (d, *J* = 9 Hz, 2H, 3′-H/5′-H), 7.91 (d, *J* = 9 Hz, 2H, 2′-H/6′-H).

exo Adduct **14c**: ^{1}H NMR ($CDCl_3$): δ = 1.5 (d/t, *J* = 9/1 Hz, 1H, 7-H_{syn}), 1.95/2.03 [2 × s, each 3H, =$C(CH_3)_2$], 3.23 (br. s, 1H, 1-H), 3.63 (t, *J* = 2 Hz, 1H, 4-H), 3.89 (s, 3H, CH_3O), 5.81/6.39 (2 × d/d, *J* = 5/3 Hz, each 1H, 5-H/6-H), 7.51 (d, *J* = 9 Hz, 2H, 3′-H/5′-H), 7.98 (d, *J* = 9 Hz, 2H, 2′-H/6′-H).

CAS Registry Numbers

1a: 74-85-1 / **1b**: 107-13-1 / **1c**: 1822-74-8 / **1d**: 10568-85-1 / **2a**: 463-49-0 / **2b**: 13169-00-1 / **2c**: 32025-35-7 / **2d**: 1595-38-6 / **2e**: 79415-51-3 / **2f**: 1001-56-5 / **2g**: 18913-35-4 / **2h**: 130884-39-8 / **2i**: 110812-40-3 / **2j**: 130884-40-1 / **2k**: 130884-41-2 / **2l**: 110812-36-7 / **2m**: 104737-24-8 / **2n**: 37605-46-2 / **2o**: 104737-23-7 / **2p**: 2525-42-0 / **2r**: 130884-42-3 / **2s**: 130884-43-4 / **2t**: 130884-44-5 / **3a**: 17039-96-2 / **3b**: 24642-02-2 / **5a**: 130884-26-3 / **6a**: 130884-27-4 / **6b**: 130884-28-5 / **6c**: 130884-45-6 / **7a**: 130884-29-6 / **7b**: 119548-62-8 / **8a**: 130884-30-9 / **8b**: 119548-61-7 / **9**: 130884-31-0 / **10**: 130979-47-4 / **12**: 130884-32-1 / **13a**: 130884- 33-2 / **13b**: 130884-35-4 / **13c**: 130884-37-6 / **14a**: 130884-34-3 / **14b**: 130884-36-5 / **14c**: 130884-38-7 / $TiCl_2(OiPr)_2$: 762-99-2 / Eu(fod)$_3$: 17631-68-4 / cyclopentadiene: 542-92-7

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