233. Face Selectivity of the *Diels-Alder* Additions of Sulfur-Substituted Dienes and Tetraenes Grafted onto 7-Oxabicyclo[2.2.1]heptanes[1][2])

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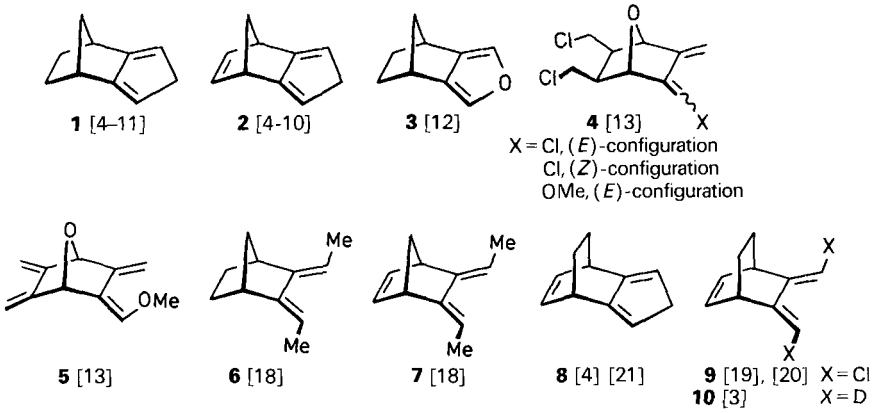
Dedicated to Prof. Dr. *Tino Gäumann* on the occasion of his 60th birthday

(10.V.85)

Stereoselective synthesis of 2-methylidene-3-[(*Z*)-(2-nitrophenylsulfenyl)methylidene]-7-oxabicyclo[2.2.1]-heptane (**16**), 1,4-epoxy-1,2,3,4-tetrahydro-5,8-dimethoxy-2-methylidene-3-[(*Z*)-(2-nitrophenylsulfenyl)methyl-idene]anthracene (**18**), and 1,4-epoxy-1,2,3,4-tetrahydro-5,8-dimethoxy-2-methylidene-3-[(*Z*)-(phenylsulfenyl)-methylidene]anthracene (**19**) are presented. The *Diels-Alder* additions of these S-substituted dienes and those of 2,5-dimethylidene-3,6-bis{[(*Z*)-(2-nitrophenyl)sulfenyl]methylidene}-7-oxabicyclo[2.2.1]heptane (**17**) have been found to be face selective and *'ortho'* regiospecific. The face selectivity depends on the nature of the dienophile. It is *exo*-face selective with bulky dienophiles such as ethylene-tetracarbonitrile (TCNE) and 2-nitro-1-butene and *endo*-face selective with methyl vinyl ketone, methyl acrylate, and 3-butyn-2-one. In the presence of a *Lewis* acid, the face selectivity of the *Diels-Alder* reaction can be reversed. The addition of the first equivalent of a dienophile to tetraene **17** is at least 100 times faster than the addition of the second equivalent of the same dienophile to the corresponding mono-adduct. The X-ray structure of the crystalline bis-adduct **43**, a 7-oxabicyclo[2.2.1]hepta-2,5-diene system annellated to two cyclohexene rings, resulting from the successive additions of methyl acrylate and methyl vinyl ketone to tetraene **17** is presented. Only one of the two endocyclic double bonds of the 7-oxabicyclo[2.2.1]hepta-2,5-diene deviates from planarity, the substituents bending towards the *endo* face by 5.7°.

Introduction. – The face selectivity of the *Diels-Alder* additions of compounds **1**–**10** and of substituted derivatives of **1** and **2** has been studied extensively [3–22]. It depends on

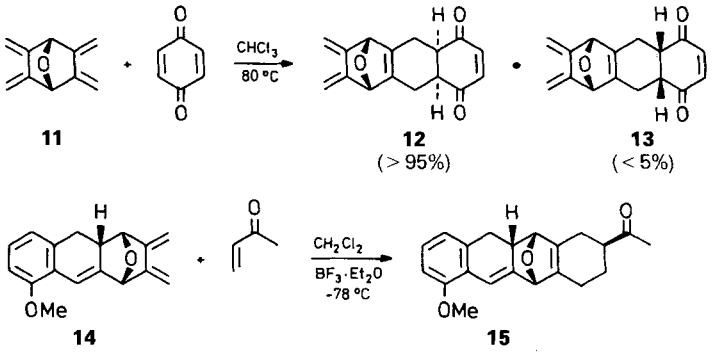


1 [4–11] **2** [4-10] **3** [12] **4** [13] X = Cl, (*E*)-configuration; Cl, (*Z*)-configuration; OMe, (*E*)-configuration

5 [13] **6** [18] **7** [18] **8** [4] [21] **9** [19], [20] X = Cl; **10** [3] X = D

[1]) Interaction between non-conjugated chromophores, Part 23; Part 22, see [1].

[2]) Part of the Ph. D. thesis of *Jean-Marc Tornare*, University of Lausanne, February 1985. For a preliminary communication of a part of this work, see [2].

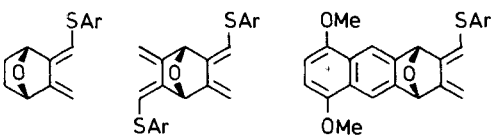


11 **12** (> 95%) **13** (< 5%)

14 **15**

the nature of the bridges that constitute the bicyclic part of the molecule and on the nature of the dienophile.

We have found that the *Diels-Alder* additions of olefinic dienophiles to dienes grafted onto 7-oxabicyclo[2.2.1]heptane systems (*e.g.* **11** and **14**) [23] [24] are highly stereoselective, in the sense that the β-adducts (*e.g.* **12** and **15**, resp.) are generally preferred over the α-isomers (*e.g.* **13**). Can this be attributed to an attractive effect of the oxa bridge on the dienophile which would favour the *exo*-face attack and *endo-Alder*-rule orientation [25]? The *exo*-face selectivity observed for the cycloadditions of the oxanorbornane derivatives **4** and **5** to strong dienophiles was consistent with this hypothesis. We have now prepared the S-substituted dienes **16–19**. The S-substituent is not only a useful stereochemical



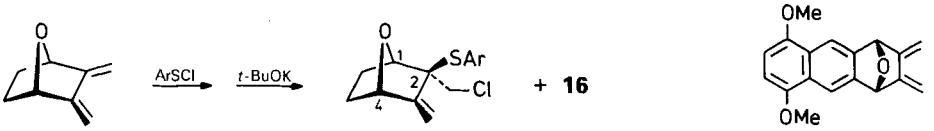
16 **17** **18** Ar = 2-NO_2-C_6H_4 **19** Ar = C_6H_5

probe but also renders the s-*cis*-butadiene moiety much more reactive than that in the Cl- and MeO-substituted analogs **4**. Thus, the dienes **16**, **18**, and **19** and tetraene **17** are versatile compounds for *Diels-Alder* reactivity studies intended to approach answers to the following questions: (*a*) does the face selectivity of the cycloadditions of exocyclic s-*cis*-butadiene moieties grafted onto 7-oxabicyclo[2.2.1]heptanes at C(2), C(3) depend on the nature of the dienophile and (*b*) does the face selectivity depend on the nature of the bridge at C(5), C(6) (*i.e.*, saturated *vs.* unsaturated)?

Results and Discussion. – The (arenesulfenyl)diene **16** was prepared from the known 2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane (**20**) [26]. The addition of one mol-equiv. of 2-nitrobenzenesulfenyl chloride to **20** in MeCN (20 °C) gave a mixture of unstable adducts which was directly treated with an excess of *t*-BuOK in anh. THF leading to a 1:3.5 mixture of adduct **21** and S-substituted diene **16**. The two compounds were separated by column chromatography on silica gel. The structures of **16** and **21** were deduced from their ^{1}H- and ^{13}C-NMR spectra and with the help of double-irradiation experiments.

For **16**, irradiation at the ^{1}H-NMR signal of *H*–C–SAr at 6.3 ppm led to a NOE at 5.29 ppm (H of CH_2 = C(2) *cis* with respect to C(2),C(3)). No NOE was observed for the adjacent bridgehead proton H–C(4) at 5.30 ppm. Irradiation at 5.04 ppm (H of CH_2=C(2) *trans*) led to NOE's at 4.92 ppm (H–C(1)) and 5.29 ppm. The signals of the bridgehead protons H–C(1) and H–C(4) were easily recognized by their vicinal coupling with H*exo*–C(6) and H*exo*–C(5), respectively (^3J(H,H) ≈ 5 Hz) [27].

No trace of the (*E*)-isomer of **16** was detected, thus suggesting that **16** was formed under conditions of thermodynamic control from a [1,2]- or/and [1,4]-arenesulfenyl chloride adduct of the *'Markovnikoff'* type' [28]. Adduct **21** corresponds to a *'anti-Markovnikoff'* type of addition which is not capable to eliminate HCl. The *endo* position of the chloromethyl group in **21** was given by the analysis of the vicinal coupling constants in the ^{13}C-NMR spectrum between the C-atom of the CH_2Cl group and the adjacent bridgehead proton H–C(1) (^3J(C,H) < 1 Hz) [29].



20 **21** **22**

The preparation of tetraene **17** has been described elsewhere [2] [30][3]). The S-substituted diene **18** was obtained in 35% yield on treating diene **22** [23b] with 1 mol-equiv. of 2-nitrobenzenesulfenyl chloride (AcOH, LiCl) and then with *t*-BuOK in THF. Similarly, the treatment of **22** with *N*-chlorosuccinimide and thiophenol in CH_2Cl_2 followed by HCl elimination (*t*-BuOK, THF) [31] afforded the phenylthio-substituted diene **19** in 44% yield. The structures of **18** and **19** were deduced from their mode of formation and from their spectral data. The (*Z*)-configuration of the arylthio-substituted double bond was established by NOE measurements in the 360-MHz-^{1}H-NMR spectra, in an analogous way as in the case of diene **16**.

Our results on the thermal *Diels-Alder* additions of several strong dienophiles to the S-substituted dienes **16**–**19** are summarized in *Table 1*. All the reactions gave good yields of the corresponding adducts whose structures were derived from their spectral data (see *Exper. Part*) and more specifically, from their 360-MHz-^{1}H-NMR spectra with the help of double irradiation experiments. The ^{1}H-NMR characteristics of **23**–**38** are summarized in *Tables 2* and *3*.

In **23**–**29**, the signals of the bridgehead protons H–C(1) and H–C(8) were recognized by their vicinal coupling constants with the adjacent H*exo*–C(9) and H*exo*–C(10). The signals of the olefinic CH_2 groups of **30**–**38** were assigned by NOE measurements. Irradiation of the signals attributed to H–C(10') (*trans* to C(9),C(10)) led to NOE's at the signals attributed to H–C(1). The α *vs.* β (*endo* vs. *exo*) configuration of the arylthio substituent in the adducts **23**–**40** was given by the homoallylic coupling constants measured between H–C(3) (H–C(1) in **39** and **40**) and the bridgehead proton H–C(8) (H–C(5) in **39** and **40**). For several other cyclohexenes annellated to 7-oxabicyclo[2.2.1]heptane systems, it has been demonstrated [13] [32] that ^5J(H–C(8),H_α–C(3)) < 0.2 Hz, whereas ^5J(H–C(8),H_β–C(3)) varies between 0.5 and 1.8 Hz. The signals of H_β–C(6) in **23**–**38** and of H_β–C(4) in **39** and **40** were readily identified by the long-range transannular and intraannular coupling constants with the corresponding homoallylic protons. In all cases (**23**–**38**), we found that ^5J(H_α–C(3),H_β–C(6)) > ^5J(H_α–C(3),H_α–C(6)) or ^5J(H_β–C(3),H_α–C(6)) > ^5J(H_β–C(3),H_β–C(6)), in agreement with expectations [32]. The position α *vs.* β of the

[3]) This compound allows to prepare anthracyclinones *via* regiospecific tandem *Diels-Alder* reactions, see *e.g.* [30].

Table 1. *Face Selectivities of the* Diels-Alder *Additions of* **16–19** *to Strong Dienophiles.* Isolated yields are shown in parentheses[a]).

Addition	Face selectivity *exo*- vs. *endo*-attack
16 + TCNE, 50 °C, acetone → **23** (46%) + **24** (25%)	1.8:1
16 + O_2N, 100 °C, PhH/*t*-BuOH → **25** (22%)[b]) + **26** (29%)[b]) + **27** (37%)[b])	2:1
16 + MVK, 100 °C, PhH → **28** (29%) + **29** (67%)	1:2.3
17 + TCNE, 50 °C, acetone → **30** (81%)	> 10:1
17 + O_2N, 100 °C, PhH/*t*-BuOH → **31** (30%)[b]) + **32** (30%)[b]) + **33** (15%)[b])[d])	1.5:1
17 + MVK, 100 °C, PhH → **34** (9%) + **35** (86%)	1:9.6
17 + OMe, 70 °C[c]) → **36** (19%) + **37** (76%)	1:4
17 + , 100 °C, PhH → **38** (84%)	< 1:10
18,19 + MVK, 100 °C, PhH → **39** (Ar = 2-NO_2-C_6H_4) (91%)	< 1:10
	40 (Ar = C_6H_5) (93%)	< 1:13

[a]) The proportions of the adducts isolated after column chromatography did not differ within experimental error from the proportions measured in the 360-MHz-^{1}H-NMR or/and 15.01-MHz-^{13}C-NMR spectra of the reaction mixture before purification.

[b]) The relative configuration of C(4) is not established unambiguously (no measurable ^3J(C,H) coupling constants for the CH_2 signals of the Et groups in the ^{13}C-NMR spectrum due to line broadening).

[c]) Without solvent.

[d]) This compound was unstable in solution. Its structure has not been determined unambiguously.

side chain (CH_3CO or CH_3OOC) in adducts **28**, **29**, **34–37**, **39**, and **40** was given by the vicinal coupling constants measured for the protons at the site of attachment of the side chain (H–C(4) in **28**, **29** and **34–37**, H–C(2) in **39** and **40**) [33]. Typical values ^3J(H–C(3), H–C(4)) = 10–12 Hz are expected for pseudoaxial/axial vicinal coupling constants in cyclohexenes [34] [35]. For pseudoequatorial/axial vicinal coupling constants, values of 4–6 Hz [34] are typical for cyclohexenes, whereas pseudoequatorial/equatorial coupling constants are usually smaller than 3 Hz [36]. Our data suggest the conformation represented in *Fig. 1* for adducts **28**, **34**, and **36**. This is confirmed by the comparison of their ^{1}H-NMR characteristics with those observed for the bis-adduct **43** presented below, for which the structure was established by X-ray crystallography (compare with data of H–C(5) and H–C(6) in **43**, see *Exper. Part*).

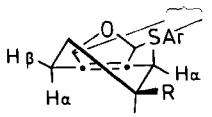


Fig. 1. *Conformation of adducts* **28**, **34**, **43** *(R = COCH$_3$), and* **36** *(R = COOCH$_3$)*

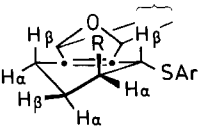
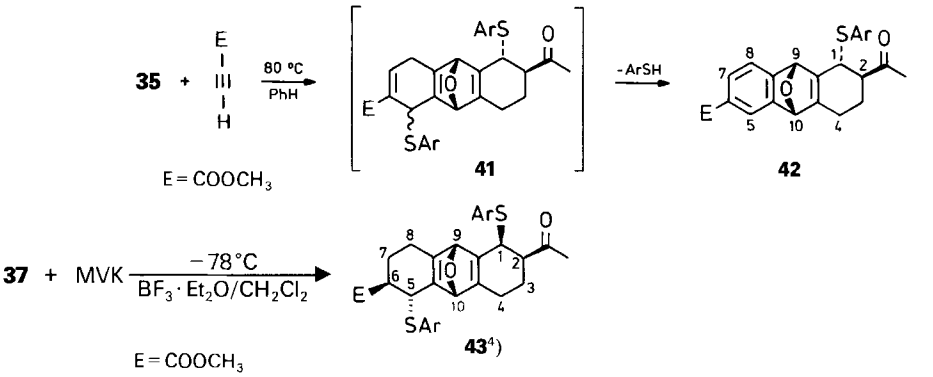


Fig. 2. *Possible conformation of adducts* **29**, **35**, **39**, **40** *(R = COCH$_3$), and* **37**, **43** *(R = COOCH$_3$)*

The fragmentary ^{1}H-NMR data obtained for adducts **29**, **35**, and **37** (see *Tables 2* and *3*) and their comparison with those collected for the bis-adduct **43** were in agreement with the conformation proposed in *Fig. 2* and with the *β* configuration of the acetyl and ester side chains in these molecules. In the case of adducts **39** and **40**, the ^{1}H-NMR data (see *Exper. Part*) were more complete and also suggested structures analogous to that of *Fig. 2*.

As in the case of the unsubstituted tetraene **11** [37], the addition of the first equiv. of dienophile to tetraene **17** is at least 100 times faster than the addition of the second equiv. of dienophile to the corresponding mono-adduct. Only very reactive dienophiles can add to the mono-adducts **30–38** under thermal conditions. For instance, methyl propiolate added to adduct **35** on heating at 80°C for 3 days yielding the benzoate derivative **42** (70%, isolated). The latter derived most probably from the bis-adduct **41** which eliminates one equiv. of 2-nitrothiophenol under the reaction conditions. The ^{1}H-NMR data of **42** confirmed the proposed structures for **38** (and **29**, **37**, **39**, and **40**). Methyl vinyl ketone (MVK) was less reactive than methyl propiolate. It gave bis-adducts under forcing



[4]) The atom numbering of **43** follows the IUPAC rules here. For practical reasons, a different numbering was retained for the description of the crystalline structure of **43**, see below.

Table 2. *360-MHz-^{1}H-NMR Characteristics of Adducts* **23–29**. Chemical shifts in ppm (±0.02 ppm); 30°C;

Adduct	Solvent	Chemical shifts δ_H					
		H–C(1)	H–C(3)	H–C(4)	H_α–C(5)	H_β–C(5)	H_α–C(6)
23	CD_3CN	5.22	4.95 (α^d))	–	–	–	3.43
24	CD_3COCD_3	5.21	5.42 (β^d))	–	–	–	3.49
25	$CDCl_3$	4.89	5.11 (α^d))	–	2.22–2.12	2.07–1.76	2.62–2.56
26	C_6D_6	4.77	4.85 (β^d))	–	2.18–2.05		2.54–2.44
27	$CDCl_3$	5.0	4.5 (α^d))	–		2.40–2.27	
28	$CDCl_3$	4.91	4.59 (α^d))	3.97	*ca.* 2.1	*ca.* 2.0	*ca.* 2.15
29	C_6D_6	4.91	4.94 (β^d))	2.46		2.02–1.07	
	Coupling constants J(H,H)						
	H–C(1),H_{exo}–C(10)		H–C(1),H_β–C(6)		H–C(3),H–C(4)		H–C(3),H_α–C(6)
23	4.4		1.0		–		2.3
24	4.5		1.0		–		3.6
25	4.0		1.0		–		1.4
26	4.3		1.0		–		1.7
27	3.5		[b])		–		[b])
28	3.5		0.8		4.3		1.0
29	4.0		[b])		6.0		[b])

[a]) J's < 0.2 Hz are not reported. [b]) Some J's could not be evaluated due to spectral complexity. [c]) $^3J(H_\alpha\text{–C(5)},H\text{–C(4)}) = 3.0$;

Table 3. *360-MHz-^{1}H-NMR Characteristics of Adducts* **30–38**. Chemical shifts in ppm (±0.02 ppm); 30°C;

Adduct	Solvent	Chemical shifts δ_H						
		H–C(1)	H–C(3)	H–C(4)	H_α–C(5)	H_β–C(5)	H_α–C(6)	H_β–C(6)
30	CD_3COCD_3	4.81	4.32 (α^c))	–	–	–	2.86	3.08
31	$CDCl_3$	5.02	4.90 (α^c))	–	2.19–2.0		2.55–2.45	
32	$CDCl_3$	5.18	5.22 (β^c))	–	*ca.* 2.0	*ca.* 2.2	2.73–2.56	
34	CD_2Cl_2	5.10	4.68 (α^c))	2.96	1.99	1.80	2.09	2.34
35	C_6D_6	5.18	4.99 (β^c))	2.43	1.66	1.53	1.95	
36	$CDCl_3$	5.25	4.77 (α^c))	3.02	2.12	1.96	2.23	2.42
37	$CDCl_3$	5.18	4.90 (β^c))	2.84	2.13	1.20	2.13	2.53
38	$CDCl_3$	5.13	5.45	–	7.07		3.11	3.37
	Coupling constants J(H,H)							
	H–C(1),H_β–C(6)		H–C(3),H–C(4)		H–C(3),H_α–C(6)		H–C(3),H_β–C(6)	H–C(3),H–C(5)
30	0.5		–		1.7 (α^c))		2.7	–
31	1.2				1.0 (α^c))		2.1	1.9[d])
32	1.2		–		2.5 (β^c))		1.5	1.2[e])
34	1.2		4.2		0.7 (α^c))		1.4	< 0.2
35	[f])		6.5		[f]) (β^c))		[f])	< 0.2
36	0.5		4.3		1.0 (α^c))		3.2	< 0.2
37	1.0		4.0		[f]) (β^c))		2.2	< 0.2
38	1.2		–		6.5		6.2	0.7

[a]) J's < 0.2 Hz are not reported. [b]) Compounds **33** and **35** decomposed in solution (see *Exper. Part*). [c]) Relative $^3J(H_\beta\text{–C(5)},H_\alpha\text{–C(6)}) = 6.5$; $^3J(H_\alpha\text{–C(5)},H_\alpha\text{–C(6)}) = 2.5$ Hz. [h]) $^3J(H\text{–C(5)},H_\beta\text{–C(6)}) = 4.7$; $^3J(H\text{–C(5)},H_\alpha\text{–C(6)})$

internal reference: tetramethylsilane (= 0.0 ppm); coupling constants ^nJ(H,H) in Hz (±0.1 Hz)[a]).

H_β–C(6)	H–C(8)	CH_2(9) and CH_2(10) or methylene protons	SAr	Others[b])
3.55	5.08	1.51–1.28	8.12–7.65	
3.89	5.03	1.91–1.39	8.30–7.66	
2.56–2.49	4.73	2.07–1.76; 1.60–1.23	8.08–7.37	0.73 (t, ^3J = 7.2, CH_3)
2.44–2.34	4.75	1.82–1.66 (2 H); 1.36–1.3 (1 H); 1.05–0.99 (1 H)	8.0–7.42	2.0 (q, CH_2); 0.7 (CH_3)
2.40–2.27	4.79	1.93–1.84 (2); 1.77–1.7 (1 H); 1.35–1.27 (1 H)	7.97–7.38	2.1–1.98 (CH_2); 0.87 (CH_3)
ca. 2.32	4.78	1.89–1.75 (2 H); 1.67–1.63 (1 H); 1.32–1.24 (1 H)	8.01–7.33	2.03 (s, CH_3CO)
2.02–1.07	4.68	2.02–1.07 (10 H)	7.76–6.67	1.92 (s, CH_3CO)

H–C(3), H_β–C(5)	H–C(3), H–C(5)	H–C(8), H_{exo}–C(9)	H–C(8), H–C(3)	H–C(5), H–C(5)	H–C(6), H–C(6)
3.5 (α[d]))	–	4.4	< 0.2	–	19.0
2.7 (β[d]))	–	4.5	1.2	–	19.3
2.2 (α[d]))	1.0[e])	4.0	< 0.2	[b])	[b])
0.7 (β[d]))	1.0[f])	4.3	0.5	[b])	[b])
[b])	[b])	3.5	< 0.2	[b])	[b])
2.8 (α[d]))	< 0.2[e])	3.5	< 0.2	[b])	[b])
[b])	< 0.2[b])	4.0	1.4	[b])	[b])

^3J(H_β–C(5), H–C(4)) = 11.0 Hz. [d]) Relative configuration of H–C(3). [e]) ^4J(H_α–C(3), H_α–C(5)). [f]) ^4J(H_β–C(3), H_β–C(5)).

internal reference TMS (= 0.0 ppm); coupling constants ^nJ(H,H) in Hz (±0.1 Hz)[a])[b]).

H–C(8)	HC(SAr)=C(9)	H–C=C(10) *trans* to C(9), C(10)	H–C=C(10) *cis* to C(9), C(10)	SAr	Others
5.09	6.08	4.90	4.74	7.4–6.6	
5.55	6.36	5.46	5.31	8.25–7.3	2.04 (q); 0.72 (t)
5.47	6.41	5.36	4.95	8.28–7.32	2.0 (m); 0.76 (br.)
5.42	6.34	5.27	4.75	8.16–7.24	1.93 (CH_3CO)
5.66	6.24	5.44	5.26	8.02–6.65	1.84 (CH_3CO)
5.53	6.41	5.41	5.09	8.27–7.31	3.37 (CH_3O)
5.52	6.42	5.48	5.24	8.28–7.31	3.68 (CH_3O)
5.57	6.31	5.17	4.65	8.22–7.29	2.40 (CH_3CO)

H–C(4), H_α–C(5)	H–C(4), H_β–C(5)	H–C(8), H–C(3)	H–C(5), H–C(5)	H–C(6), H–C(6)	Others
–	–	< 0.2	–	19.2	
–	–	< 0.2	[f])	[f])	7.2 (CH_3CH_2)
–	–	1.0	[f])	[f])	7.2
2.7	10.6	< 0.2	[f])	[f])	[f])
3.5	8.0	1.0	[f])	[f])	[f])
3.0	11.8	< 0.2	12.5	18.7	[g])
[f])	[f])	0.7	[f])	[f])	[f])
–	–	1.8	–	25	[h])

configuration of H–C(3). [d]) ^4J(H_α–C(3), H_β–C(5)). [e]) ^4J(H_α–C(3), H_α–C(5)). [f]) Could not be determined. [g]) = 2.7 Hz.

conditions with low yields as polymerization became the dominant reaction under thermal conditions. However, MVK precomplexed with $BF_3 \cdot Et_2O$ in CH_2Cl_2 added smoothly to **37** at −78 °C and afforded the bis-adduct **43** (70%, isolated). The latter cycloaddition was highly stereoselective, no trace of isomeric product could be detected in the ^1H- and ^{13}C-NMR spectra of the crude reaction mixture. The structure of **43** was deduced from its 360-MHz-^1H-NMR spectrum (see *Exper. Part*) and was confirmed by single-crystal X-ray diffraction studies (see below). All cycloadditions of the S-substituted dienes **16**, **18**, and **19** and tetraene **17** were *'ortho'* regiospecific as expected [38], no trace of *'meta'* regioisomer could be detected.

Our results demonstrate that the face selectivity of the *Diels-Alder* additions of the S-substituted exocyclic dienes grafted onto 7-oxabicyclo[2.2.1]heptane skeletons varies with the nature of the dienophile and that coordination of the dienophile with the oxa bridge is not the unique factor responsible for the face selectivity of the reactions. With TCNE and 2-nitro-1-butene, the *exo* face is favoured, whereas with dienophiles such as MVK, methyl acrylate, or butynone, the *endo*-face attack is preferred. One should note that the *exo*-face selectivity is in general [13] better for TCNE than for the 2-nitro-1-butene cycloadditions. Furthermore, the *exo*-face selectivity of the TCNE additions to diene **16** (1.8:1) is not as good as for the TCNE additions to **4** (7:3 to > 97:3) or to the tetraenes **5** (85:15) and **17** (> 10:1). The *endo*-face selectivity of the *Diels-Alder* addition of MVK to diene **16** is also slightly smaller than that observed for the cycloadditions of MVK to **17**–**19**. Surprisingly, under conditions of *Lewis*-acid catalysis, the reaction of MVK to the diene moiety of adduct **37** is highly *exo*-face selective.

The results can be interpreted in terms of the competition between at least two factors, *i.e.:* (1) steric hindrance which renders the *exo* face more accessible than the *endo* face, and (2) a stereoelectronic factor which favours *endo* face attack (as in the case of the *Diels-Alder* additions of **1**–**3**, **6**, and **7**) which is related to the non-planarity of the 2-bicyclo[2.2.1]heptene double bond [39][5]) and to the higher stability of *syn- vs. anti*-sesquinorbornene [12] [22] [39].

The *endo* approach of TCNE to dienes **1**–**3**, **4**, **5**, **16**–**19** cannot avoid the steric repulsions between the C(5),C(6) bridge and the CN group as shown in *Fig. 3*, thus making the *exo* attack the preferred mode *(Fig. 4)*. In the case of 2-nitro-1-butene, the

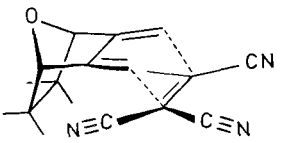


Fig. 3.

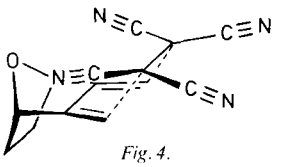


Fig. 4.

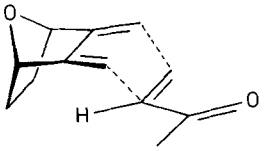


Fig. 5.

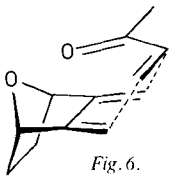


Fig. 6.

[5]) We thank Professor *K. N. Houk* for a preprint of his calculations related to this factor.

same steric effect intervenes although less strongly as only one end of the dienophile is substituted. This could explain the lower face selectivity observed for the cycloadditions of 2-nitro-1-butene compared with those of TCNE [13]. With MVK and methyl acrylate, the steric factor is less important for the *endo* attack since the dienophile can approach the diene in an *anti-Alder*-rule [25] fashion, as observed (see *Fig. 5*). In the case of the cycloaddition of butynone to **17**, the steric factor is negligible, and the reaction is dominated by the stereoelectronic factor favouring the *endo*-face attack.

It is interesting to note that the *exo* mode of addition of MVK and acrylic ester occurs following the *Alder* rule *(Fig. 6)*. When coordinated to BF_3, MVK is a bulkier reagent than in its native form. This might explain the *exo*-face selectivity of the *Lewis*-acid-catalyzed cycloaddition of MVK to **37**. Alternatively, one can invoke a co-coordination of the dienophile and O-bridge of the 7-oxabicyclo[2.2.1]heptane system to the *Lewis* acid that favours the *exo*-face attack following the *Alder* rule *(Fig. 6)*.

Crystal Structure Determination of Bis-adduct 43. – The bis-adduct **43** crystallized as yellow plates from hexane/AcOEt 1:1. The crystal used for data collection was cleaved from a larger plate in order to have sufficient thickness.

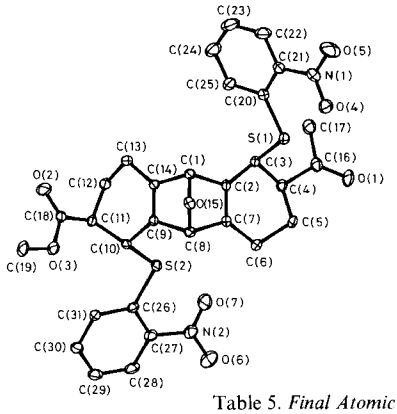
X-Ray intensity data collection was carried out at room temperature with a *Syntex P2$_1$* automatic diffractometer. The crystal data, intensity collection, structure solution, and refinement methods are summarized in *Table 4*. The measured intensities were corrected for absorption as before [40], and the variances of the intensities were derived from counting statistics and the fluctuations of three periodically measured check reflections.

Table 4. *Crystal Data, Intensity Measurements, Structure Solution, and Refinement for Bis-adduct* **43**

Formula	$C_{30}H_{38}N_2O_8S_2$	Radiation	Cu-$K\alpha$
Molecular weight	618.76	λ [Å]	1.54178
Crystal dimensions [mm]	0.30 × 0.18 × 0.04	μ [cm^{-1}]	12.1
Crystal system	Triclinic	Scan method	2θ–θ
a [Å]	7.7382(7)	$(\sin\theta/\lambda)_{max}$	0.55
b [Å]	9.381(1)	No. of unique reflections	3906
c [Å]	20.346(2)	No. of reflections $< 3\sigma$	564
α [°]	83.680(8)	No. of observations/No of variables	
β [°]	82.951(7)		8.3/7.8[a])
γ [°]	78.200(8)	Structure solution	MULTAN and *Fourier*
U [Å^3]	1429.3(3)	Refinement method	Blocked matrix least squares
Z	2	Function minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
$d_{obs.}$ [g·cm^{-3}]	1.42	w	$1/\sigma^2$
$d_{calc.}$ [g·cm^{-3}]	1.41	R	0.059
F_{000}	636	R_w	0.084
Space group	$P\bar{1}$	Goodness of fit	2.73

[a]) Only those reflections with $I < 3\sigma$ with $|Fc| > |Fo|$ were included in the refinement.

The computer programs used for data reduction and structure solution were taken from the XRAY-72 program system [41]. The scattering factors for the neutral non-H-atoms were taken from *Cromer* and *Mann* [42], and for H from *Stewart et al.* [43]. Anomalous dispersion coefficients were taken from *Cromer* and *Liberman* [44]. Starting phases were generated by the program MULTAN [45], the subsequent *E*-map revealing all the non-H-atoms. Refinement by block matrix least squares to $R = 0.089$, followed by a difference-*Fourier* synthesis revealed all H-atoms. Refinement was continued in 4 blocks to $R = 0.059$. In the last cycles, the non-H-atoms were refined anisotropically and H-atoms of the same type constrained to have the same isotropic temp. factor. The final atomic



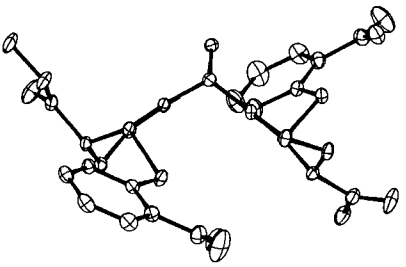


Fig. 7. *ORTEP representations of* **43**. For practical reasons, the atom numbering does not follow the IUPAC rules.

Table 5. *Final Atomic Coordinates for Bis-adduct* **43**[a])

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	0.7667(5)	0.3133(4)	0.7245(2)	0(4)	0.1524(4)	0.1934(3)	0.8732(2)
C(2)	0.7974(4)	0.1683(3)	0.7688(2)	0(5)	–0.0340(5)	0.3487(5)	0.9275(2)
C(3)	0.7466(5)	0.1403(4)	0.8415(2)	0(6)	1.6213(7)	–0.3648(3)	0.6732(2)
C(4)	0.8343(5)	–0.0167(4)	0.8652(2)	0(7)	1.4798(5)	–0.1923(3)	0.7286(2)
C(5)	0.8327(6)	–0.1272(4)	0.8153(2)	0(15)	0.7391(3)	0.2606(3)	0.6630(1)
C(6)	0.9377(6)	–0.0899(4)	0.7493(2)	S(1)	0.5011(1)	0.16281(9)	0.85455(4)
C(7)	0.8818(5)	0.0687(4)	0.7289(2)	S(2)	1.3378(1)	0.07374(9)	0.67727(4)
C(8)	0.9033(5)	0.1547(4)	0.6600(2)	H(1)	0.674(5)	0.397(4)	0.738(2)
C(9)	1.0343(4)	0.2568(3)	0.6636(2)	H(3)	0.785(4)	0.204(3)	0.864(2)
C(10)	1.2220(5)	0.2431(3)	0.6351(2)	H(4)	0.954(5)	–0.010(3)	0.873(2)
C(11)	1.2922(5)	0.3807(4)	0.6451(2)	H(5A)	0.697(5)	–0.142(4)	0.810(2)
C(12)	1.2313(5)	0.4332(4)	0.7147(2)	H(5B)	0.880(5)	–0.217(4)	0.833(2)
C(13)	1.0284(5)	0.4676(4)	0.7298(2)	H(6A)	1.065(6)	–0.118(4)	0.758(2)
C(14)	0.9493(5)	0.3543(3)	0.7053(2)	H(6B)	0.922(5)	–0.152(4)	0.716(2)
C(16)	0.7669(6)	–0.0651(4)	0.9364(2)	H(8)	0.910(5)	0.100(4)	0.622(2)
C(17)	0.7480(8)	0.0422(5)	0.9876(2)	H(10)	1.236(4)	0.226(3)	0.594(2)
C(18)	1.2437(5)	0.5004(4)	0.5901(2)	H(11)	1.421(5)	0.355(3)	0.641(1)
C(19)	1.2422(8)	0.5537(5)	0.4733(2)	H(12A)	1.288(5)	0.514(4)	0.727(2)
C(20)	0.4280(5)	0.3400(4)	0.8801(2)	H(12B)	1.270(5)	0.368(4)	0.743(2)
C(21)	0.2477(5)	0.3954(4)	0.8995(2)	H(13A)	0.996(5)	0.471(4)	0.776(2)
C(22)	0.1863(7)	0.5353(5)	0.9190(2)	H(13B)	0.988(5)	0.552(4)	0.710(2)
C(23)	0.3014(9)	0.6258(6)	0.9183(3)	H(17A)	0.745(7)	–0.001(6)	1.031(3)
C(24)	0.4783(8)	0.5788(5)	0.8998(3)	H(17B)	0.816(8)	0.113(6)	0.975(3)
C(25)	0.5418(7)	0.4385(4)	0.8808(2)	H(17C)	0.639(8)	0.115(6)	0.985(3)
C(26)	1.5161(5)	0.0112(4)	0.6188(2)	H(19A)	1.268(8)	0.498(6)	0.435(3)
C(27)	1.6160(5)	–0.1308(4)	0.6252(2)	H(19B)	1.121(8)	0.580(6)	0.473(3)
C(28)	1.7609(6)	–0.1798(5)	0.5803(2)	H(19C)	1.305(7)	0.632(6)	0.476(2)
C(29)	1.8110(6)	–0.0906(5)	0.5275(2)	H(22)	0.055(6)	0.564(4)	0.933(2)
C(30)	1.7126(5)	0.0492(5)	0.5176(2)	H(23)	0.276(6)	0.720(5)	0.921(2)
C(31)	1.5683(5)	0.0995(4)	0.5623(2)	H(24)	0.574(6)	0.638(5)	0.901(2)
N(1)	0.1152(5)	0.3073(4)	0.9007(2)	H(25)	0.669(6)	0.416(5)	0.864(2)
N(2)	1.5697(5)	–0.2362(4)	0.6793(2)	H(28)	1.815(6)	–0.259(5)	0.588(2)
O(1)	0.7328(6)	–0.1838(3)	0.9513(2)	H(29)	1.912(6)	–0.122(4)	0.498(2)
O(2)	1.1890(5)	0.6264(3)	0.5975(1)	H(30)	1.723(6)	0.110(5)	0.482(2)
O(3)	1.2741(4)	0.4501(3)	0.5306(1)	H(31)	1.515(6)	0.191(5)	0.556(2)

[a]) For practical reasons, the atom numbering does not follow the IUPAC rules. The ^{1}H- and ^{13}C-NMR spectra of **43** are described in the *Exper. Part;* there, the atom numbering follows the IUPAC rules (see also formula **43**).

Table 6. *Bond Lengths [Å] and Angles [°] for Bis-adduct* **43** *with Estimated Standard Deviations in Parentheses*[a])

Distances			
C(1)–C(2)	1.539(4)	C(18)–O(2)	1.190(4)
C(1)–C(14)	1.533(5)	C(18)–O(3)	1.325(4)
C(1)–O(15)	1.449(4)	C(19)–O(3)	1.446(5)
C(2)–C(3)	1.493(4)	C(20)–S(1)	1.757(4)
C(2)–C(7)	1.321(4)	C(20)–C(21)	1.409(5)
C(3)–C(4)	1.542(5)	C(20)–C(25)	1.403(7)
C(3)–S(1)	1.856(4)	C(21)–C(22)	1.385(6)
C(4)–C(5)	1.532(6)	C(22)–C(23)	1.348(9)
C(4)–C(16)	1.531(5)	C(23)–C(24)	1.369(8)
C(5)–C(6)	1.527(6)	C(24)–C(25)	1.387(7)
C(6)–C(7)	1.489(5)	C(26)–S(2)	1.756(3)
C(7)–C(8)	1.548(5)	C(26)–C(27)	1.398(5)
C(8)–C(9)	1.542(5)	C(26)–C(31)	1.409(5)
C(8)–O(15)	1.444(4)	C(27)–C(28)	1.390(6)
C(9)–C(10)	1.482(5)	C(28)–C(29)	1.355(6)
C(9)–C(14)	1.333(4)	C(29)–C(30)	1.382(6)
C(10)–C(11)	1.541(5)	C(30)–C(31)	1.387(5)
C(10)–S(2)	1.835(3)	N(1)–C(21)	1.439(6)
C(11)–C(12)	1.537(5)	N(1)–O(4)	1.226(5)
C(11)–C(18)	1.519(5)	N(1)–O(5)	1.221(5)
C(12)–C(13)	1.536(6)	N(2)–C(27)	1.458(5)
C(13)–C(14)	1.487(6)	N(2)–O(6)	1.206(5)
C(16)–C(17)	1.501(7)	N(2)–O(7)	1.208(5)
C(16)–O(1)	1.195(5)		
Angles			
C(2)–C(1)–C(14)	106.6(3)	C(4)–C(16)–C(17)	117.2(4)
C(2)–C(1)–O(15)	100.1(3)	C(4)–C(16)–O(1)	121.8(4)
C(14)–C(1)–O(15)	100.4(2)	C(17)–C(16)–O(1)	120.9(4)
C(1)–C(2)–C(3)	129.0(3)	C(11)–C(18)–O(2)	125.7(3)
C(1)–C(2)–C(7)	105.5(3)	C(11)–C(18)–O(3)	112.1(3)
C(3)–C(2)–C(7)	125.4(3)	O(2)–C(18)–O(3)	122.2(3)
C(2)–C(3)–C(4)	109.3(3)	C(18)–O(3)–C(19)	118.0(3)
C(2)–C(3)–S(1)	107.6(2)	C(3)–S(1)–C(20)	104.5(2)
C(4)–C(3)–S(1)	110.3(3)	S(1)–C(20)–C(21)	121.9(3)
C(3)–C(4)–C(5)	112.7(3)	S(1)–C(20)–C(25)	123.1(3)
C(3)–C(4)–C(16)	113.4(3)	C(21)–C(20)–C(25)	114.9(3)
C(5)–C(4)–C(16)	113.5(3)	C(20)–C(21)–C(23)	93.3(3)
C(4)–C(5)–C(6)	110.9(3)	C(20)–C(21)–N(1)	121.2(3)
C(5)–C(6)–C(7)	108.9(3)	C(23)–C(21)–N(1)	145.5(3)
C(6)–C(7)–C(2)	125.2(3)	C(21)–N(1)–O(4)	119.5(3)
C(6)–C(7)–C(8)	130.2(3)	C(21)–N(1)–O(5)	119.7(4)
C(2)–C(7)–C(8)	104.5(3)	O(4)–N(1)–O(5)	120.8(4)
C(7)–C(8)–C(9)	107.6(3)	C(21)–C(22)–C(23)	119.6(5)
C(7)–C(8)–O(15)	100.3(2)	C(22)–C(23)–C(24)	120.3(5)
C(9)–C(8)–O(15)	99.4(3)	C(23)–C(24)–C(25)	120.8(6)
C(8)–C(9)–C(10)	129.2(3)	C(24)–C(25)–C(20)	121.5(4)
C(8)–C(9)–C(14)	104.9(3)	C(10)–S(2)–C(26)	103.6(2)
C(10)–C(9)–C(14)	125.5(3)	S(2)–C(26)–C(27)	122.0(3)
C(9)–C(10)–C(11)	110.2(3)	S(2)–C(26)–C(31)	122.7(2)
C(9)–C(10)–S(2)	104.8(2)	C(27)–C(26)–C(31)	115.3(3)
C(11)–C(10)–S(2)	114.3(3)	C(26)–C(27)–C(28)	122.4(3)
C(10)–C(11)–C(12)	112.1(3)	C(26)–C(27)–N(2)	120.9(3)
C(10)–C(11)–C(18)	110.7(3)	C(28)–C(27)–N(2)	116.7(3)

Table 6 (cont.)

C(12)–C(11)–C(18)	112.3(3)	C(27)–N(2)–O(6)	118.8(4)
C(11)–C(12)–C(13)	113.0(3)	C(27)–N(2)–O(7)	119.2(3)
C(12)–C(13)–C(14)	110.1(3)	O(6)–N(2)–O(7)	122.0(4)
C(13)–C(14)–C(1)	130.0(3)	C(27)–C(28)–C(29)	120.8(4)
C(13)–C(14)–C(9)	125.0(3)	C(28)–C(29)–C(30)	119.0(4)
C(1)–C(14)–C(9)	104.8(3)	C(29)–C(30)–C(31)	120.6(4)
C(1)–O(15)–C(8)	94.3(2)	C(30)–C(31)–C(26)	121.7(3)
Torsion angles			
H(3)–C(3)–C(4)–H(4)	– 36.9(3)	H(10)–C(10)–C(11)–H(11)	– 75.4(3)
H(4)–C(4)–C(5)–H(5A)	175.2(3)	H(11)–C(11)–C(12)–H(12A)	53.4(3)
H(4)–C(4)–C(5)–H(5B)	64.8(3)	H(11)–C(11)–C(12)–H(12B)	– 56.8(3)
H(5A)–C(5)–C(6)–H(6A)	–158.2(3)	H(12A)–C(12)–C(13)–H(13A)	– 65.0(3)
H(5A)–C(5)–C(6)–H(6B)	– 44.3(3)	H(12A)–C(12)–C(13)–H(13B)	54.5(3)
H(5B)–C(5)–C(6)–H(6A)	– 46.6(3)	H(12B)–C(12)–C(13)–H(13A)	41.5(3)
H(5B)–C(5)–C(6)–H(6B)	67.3(3)	H(12B)–C(12)–C(13)–H(13B)	161.0(3)

[a]) See *Footnote* of *Table 5*.

coordinates are reported in *Table 5*. Calculated bond lengths and angles are reported in *Table 6*. Perspective drawings of the molecule prepared by the program ORTEP [46] are shown in *Fig. 7*. The H-atoms are omitted for clarity. A list of the observed and calculated structure factors as well as tables of temperature factors are available as supplementary material. For torsion angles, see bottom of *Table 6*.

The out-of-plane deviations of the substituents at the endocyclic double-bond centres of the 7-oxabicyclo[2.2.1]hepta-2,5-diene system of **43** are given in *Fig. 8* (angles between mean planes). Unexpectedly, one of the double bond (C(2),C(7)) is planar ($\alpha_1 = -0.7°$, unsignificant out-of-plane deformation towards the *exo* face), whereas the other double bond (C(9),C(14)) presents an average out-of-plane deformation of the substituents towards the *endo* face of $\alpha_2 = 5.7°$.

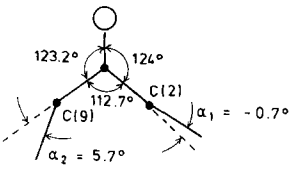
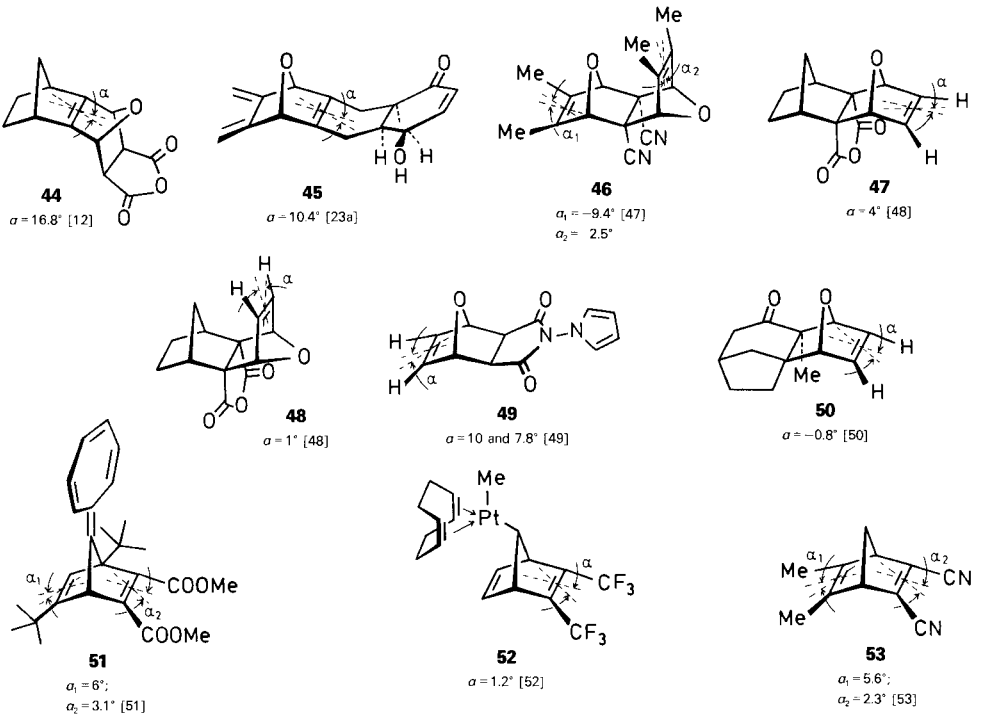


Fig. 8. *Values of angles between mean planes of the bicyclic skeleton of* **43**

The non-planarity of the bicyclo[2.2.1]hept-2-ene double bond has been demonstrated [54]. MO calculations at the *ab-initio* STO 3G level [55] suggested that out-of-plane deviations toward the *endo* face of the substituents at C(2),C(3) of 7-oxabicyclo-[2.2.1]hept-2-enes should also exist, in agreement with experimental data collected for compounds **44**–**49**. The out-of-plane deviations toward the *exo* face reported for the CH_3 groups in **46** ($\alpha_1 = -9.4°$) [47] can be attributed to repulsive interactions between the *endo* CN groups and these CH_3 substituents (see also the 'tortured' structure **50** [50]). Our MO calculations [54] suggested, however, that the pyramidalization of the olefinic C-atom in 7-oxabicyclo[2.2.1]hept-2-enes should be somewhat smaller than for the bicyclo[2.2.1]-hept-2-ene analogs (*Bartlett*'s repulsion effect between the *syn* H–C(7) and the π-electrons [56]) for which an average value of $\alpha = 7°$ was obtained from a statistical analysis of the structures in the *Cambridge Crystallographic Data File* [54]. The MO calculations also suggested the olefinic C-atom pyramidalization should be smaller in bicyclo[2.2.1]hepta-



2,5-dienes and 7-oxabicyclo[2.2.1]hepta-2,5-dienes than in bicyclo[2.2.1]hept-2-enes and 7-oxabicyclo[2.2.1]hept-2-enes, respectively. The number of experimental data available today (**43**–**53**) is not sufficient to tell whether the MO predictions are founded or not. It is interesting to note, however, that the out-of-plane deviations α_1 and α_2 in **43** appear to be smaller than the α value reported for the analogous system **45** (α = 10.4° [23a]). The limited number of experimental data on bicyclo[2.2.1]hepta-2,5-dienes (**51**–**53**) support the hypothesis that the π-anisotropy in the dienes (α = 1.2 to 6°) is smaller than in the corresponding monoolefins (α = 7°, averaged). The observation of two different α_1 and α_2 values for **43**, although the bicyclic diene has the local C_{2v} symmetry, is a surprise. If there should be a repulsive interaction between the *endo* ArS group at C(10) and the methylene H-atoms at C(6) (atom numbering used in *Fig. 7*), it should affect both α_1 and α_2 values in a similar fashion; in other words, the two α_1 and α_2 values should be nearly the same. We thus must admit that lattice effects of the crystals are quite important on the out-of-plane deviations of the substituents at the olefinic centres of bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]hepta-2,5-diene systems.

Conclusions. – The face selectivity of the thermal cycloadditions of S-substituted s-*cis*-butadiene moieties grafted onto 7-oxabicyclo[2.2.1]heptanes depend on the nature of the dienophile. For bulky dienophiles such as TCNE and 2-nitro-1-butene, the *exo* face is favoured, whereas the *endo* face is preferred for the *Diels-Alder* additions of the less bulky dienophiles such as methyl vinyl ketone, methyl acrylate, or butynone. This demonstrates that at least two factors intervene and compete to render the cycloadditions face selective. The nature (saturated *vs.* unsaturated) of the ethano bridge homoconju-

gated with the exocyclic diene does not affect the face selectivity in a dramatic fashion. In the presence of a *Lewis* acid, the face selectivity of the *Diels-Alder* additions of methyl vinyl ketone can be reversed compared with that of the reaction under thermal conditions. All the cycloadditions were found to be *'ortho'* regiospecific.

We thank *Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for generous support. We thank also Prof. *J. Lauterwein* and Mr. *M. Rey* for their help in the 360-MHz-^{1}H-NMR measurements. We are grateful to Prof. *T. Gäumann* and Dr. *D. Stahl*, EPFL, for measurements of absolute masses by high resolution mass spectrometry. We thank Mr. *O. Giordano* for technical assistance.

Experimental Part

General. See [54]. 360-MHz-^{1}H-NMR spectra: *Bruker WH 360 FT* with *Aspect 2000*, 32 K memory space, deuterium signal of the solvent as lock signal, internal tetramethylsilane as reference (= 0.0 ppm). 90.55-MHz-^{13}C-NMR spectra: *Bruker WH 360 FT*, δ_C of the solvent as internal reference.

2-Methylidene-3-[(Z)-(2-nitrophenylsulfenyl)methylidene]-7-oxabicyclo[2.2.1]heptane (**16**). A soln. of 2-nitrobenzenesulfenyl chloride (777 mg, 4.1 mmol) in anh. MeCN (60 ml) was added slowly to a stirred soln. of 2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane (**20**; 500 mg, 4.1 mmol) in anh. MeCN (60 ml) at 20°. After stirring at 20° for 90 min, the solvent was evaporated and the residue taken up in CH_2Cl_2 (50 ml). After washing with H_2O (50 ml, 3 times) and drying ($MgSO_4$), the solvent was evaporated. The residue was dissolved in anh. THF (50 ml) and cooled to −70° under N_2. *t*-BuOK (920 mg, 8.2 mmol) was added portionwise, and the mixture was stirred and allowed to warm up to 20°. After stirring at 20° for 12 h, H_2O (50 ml) and then CH_2Cl_2 (50 ml) were added. The org. layer was separated, washed with H_2O (50 ml, 3 times), and dried ($MgSO_4$). After evaporation, the residue was purified by column chromatography on silica gel (30 g; AcOEt/hexane 1:3). The 1st fraction contained 127 mg (10%) of **21** (see below); the 2nd fraction gave, after recrystallization from CH_2Cl_2/hexane 9:1, 396 mg (35%) of **16**, yellow crystals, m.p. 109–110°. UV (MeCN): 243 (15000), 292 (13500), 381 (5000). IR (KBr): 3100, 3090, 3020, 3000, 2960, 2910, 2890, 1595, 1570, 1515, 1465, 1455, 1340, 1320, 1310, 1285, 1270, 1260, 1255, 1190, 1125, 1110, 1060, 1050, 1020. ^{1}H-NMR ($CDCl_3$): 8.22–7.28 (*m*, 4 arom. H); 6.30 (*s*, H–C–S); 5.3 (*d*, ^3J(H–C(4),H_{exo}–C(5)) = 5, H–C(4)); 5.29 (*s*, H of CH_2=C(2) *cis* to C(2),C(3)); 5.04 (*s*, H of CH_2=C(2) *trans* to C(2),C(3)); 4.92 (*d*, ^3J(H–C(1),H_{exo}–C(6)) = 5, H–C(1)); 2.01–1.62 (*m*, CH_2(5),CH_2(6)). ^{13}C-NMR ($CDCl_3$): 150.3, 148.1, 145.8, 136.6 (4 br. *s*, C(2),C(3), C (arom.)); 133.6, 128.6, 125.9, 125.6 (4*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, HC (arom.)); 107.2 (*d*, ^1J(C,H) = 175, *C*H=C(3)); 101.7 (*t*, ^1J(C,H) = 158, CH_2=C(2)); 81.1 (*dt*, ^1J(C,H) = 165, C(4)); 78.9 (*dt*, ^1J(C,H) = 165, C(1)); 29.1, 28.2 (2*t*, ^1J(C,H) = 137, CH_2(5), CH_2(6)). MS (70 eV): 276 (18), 275 (100, M^+), 246 (8), 212 (9), 201 (9), 200 (9), 153 (9). Anal. calc. for $C_{14}H_{13}NO_3S$ (275.322): C 61.07, H 4.76; found: C 61.22, H 4.61.

*2-*endo*-Chloromethyl-3-methylidene-2-*exo*-(2-nitrophenyl)sulfenyl-7-oxabicyclo[2.2.1]heptane* (**21**). Yellow crystals (CH_2Cl_2/hexane 9:1), m.p. 139–140°. UV (MeCN): 364 (1500), 276 (sh, 2850), 242 (9100), 220 (sh, 12550). IR (KBr): 3100, 3030, 3010, 2990, 2970, 2940, 2900, 2890, 1570, 1530, 1475, 1450, 1435, 1365, 1305, 1290, 1275, 1255, 1230, 1200, 1150, 1140, 1055, 1020. ^{1}H-NMR (C_6D_6): 7.92–7.35 (*m*, 4 arom. H); 4.9, 4.4 (2*s*, CH_2=C(3)); 3.93, 3.56 (2*d*, J_{gem} = 12.5, CH_2Cl); 2.10–1.44 (*m*, CH_2(5), CH_2(6)). ^{13}C-NMR ($CDCl_3$): 155.6, 152.6 (2*s*); 140.5 (*dd*, ^1J(C,H) = 166, ^3J(C,H) = 5); 130.9, 130.1 (2*dd*, ^1J(C,H) = 165, ^3J(C,H) = 8); 125.2 (*s*); 123.3 (*ddd*, ^1J(C,H) = 168, ^3J(C,H) = 8); 107.0 (*t*, ^1J(C,H) = 159); 84.4 (*dm*, ^1J(C,H) = 161); 81.7 (*dm*, ^1J(C,H) = 161); 65.4 (*s*); 49.4 (*t*, ^1J(C,H) = 154); 30.7, 24.7 (2*t*, ^1J(C,H) = 136). MS (70 eV): 313 (1.3), 311 (4.5, M^+), 276 (4), 175 (10), 173 (30), 155 (11), 149 (12), 139 (10), 77 (100). Anal. calc. for $C_{14}H_{14}ClNO_3S$ (311.78): C 53.93, H 4.52; found: C 53.72, H 4.66.

1,4-Epoxy-1,2,3,4-tetrahydro-5,8-dimethoxy-2-methylidene-3-[(Z)-(2-nitrophenylsulfenyl)methylidene]anthracene (**18**). A soln. of 1,4-epoxy-1,2,3,4-tetrahydro-5,8-dimethoxy-2,3-dimethylideneanthracene [23b] (**22**; 200 mg, 0.71 mmol) in anh. AcOH (3 ml; degassed) was added dropwise to a stirred mixture of LiCl (300 mg, 7.07 mmol) and 2-nitrobenzenesulfenyl chloride (280 mg, 1.47 mmol) in anh. and degassed AcOH (6 ml). After stirring at 20° for 14 h, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (15 ml). The soln. was washed successively with aq. sat. $NaHCO_3$ soln. (10 ml, 3 times) and with H_2O (10 ml, 2 times) and dried ($MgSO_4$). After evaporation, the residue was dissolved in anh. THF (30 ml) and cooled to −78°. *t*-BuOK (500 mg, 4.45 mmol) was added portionwise under N_2. After stirring at 20° for 12 h, H_2O (10 ml) was added, and the mixture was extracted with CH_2Cl_2 (20 ml, 3 times), filtered through silica gel (15 g, AcOEt/hexane 1:3), and the residue recrystallized

from CH_2Cl_2/hexane 9:1 yielding 108 mg (35%) of yellow crystals, m.p. 227–228°. UV (MeCN): 210 (49500), 262 (32000), 298 (15500), 339 (6300). IR (KBr): 3000, 2960, 2940, 2900, 2830, 1590, 1560, 1500, 1450, 1330, 1300, 1255, 1215, 1160, 1130, 1100, 1070, 1050, 950, 920. ^{1}H-NMR ($CDCl_3$): 8.27–7.3 (*m*, 4 arom. H); 8.16 (*s*, H–C(10)); 8.15 (*s*, H–C(9)); 6.75 (*s*, H–C(6), H–C(7)); 6.42 (*s*, H–C–SAr); 6.24 (br. *s*, H–C(4)); 5.81 (br. *s*, H–C(1)); 5.42 (*s*, H of CH_2=C(2) *cis* to C(2),C(3)); 5.35 (*s*, H of CH_2=C(2) *trans* to C(2),C(3)); 3.97 (*s*, CH_3O–C(8)). ^{13}C-NMR ($CDCl_3$): 150.1, 149.8, 147.1, 147.0, 145.8, 144.7, 141.1, 140.0, 136.4, 125.7 (10*s*); 133.6, 128.8, 125.9, 125.6 (4*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8); 113.2, 112.6 (2*d*, ^1J(C,H) = 166); 109.7 (*d*, ^1J(C,H) = 176); 104.2 (*t*, ^1J(C,H) = 162); 104.2, 104.1 (2*d*, ^1J(C,H) = 159); 83.9, 81.5 (2*dm*, ^1J(C,H) = 167); 55.7, 55.1 (2*q*, ^1J(C,H) = 144). MS (70 eV): 433 (100, M^+), 279 (48), 261 (54). Anal. calc. for $C_{24}H_{19}NO_5S$ (433.486): C 66.50, H 4.41; found: C 66.42, H 4.44.

1,4-Epoxy-1,2,3,4-tetrahydro-5,8-dimethoxy-2-methylidene-3-[(Z)-(2-phenylsulfenyl)methylidene]anthracene (**19**). *N*-Chlorosuccinimide (1.6 g, 12 mmol) was dissolved in anh. CH_2Cl_2 (22 ml) and then cooled to 0°. Thiophenol (1.2 ml, 12 mmol) was added dropwise under N_2 and stirring. After stirring at 20° for 20 min, the mixture was cooled to −78° and **22** (3.37 g, 12 mmol) dissolved in anh. CH_2Cl_2 (33 mol) was added dropwise. The mixture was stirred and allowed to reach 20° within *ca.* 90 min. After washing with sat. aq. NaCl soln. (30 ml, 2 times) and drying ($MgSO_4$), the solvent was evaporated and the residue dissolved in anh. THF (100 ml). After cooling to −78°, *t*-BuOK (13 g, 0.12 mol) was added portionwise. The mixture was stirred under N_2 and allowed to reach 20°. Stirring was continued for 12 h, then H_2O (30 ml) was added and the mixture extracted with CH_2Cl_2 (20 ml, 3 times). After filtration on silica gel (AcOEt/hexane 1:3) and evaporation, the residue was recrystallized from CH_2Cl_2/hexane 9:1 yielding 2.05 g (44%), white crystals, m.p. 170–171°. UV (MeCN): 213 (54000), 259 (49000), 323 (5500), 336 (5800). IR (KBr): 2940, 2900, 2830, 1605, 1585, 1460, 1440, 1385, 1330, 1260, 1225, 1170, 1140, 1080, 1055. ^{1}H-NMR ($CDCl_3$): 8.16 (*s*, H–C(10)); 8.15 (*s*, H–C(9)); 7.41–7.16 (*m*, C_6H_5S); 6.6 (*s*, H–C(6), H–C(7)); 6.49 (*s*, H–C–S); 6.13 (*s*, H–C(4)); 5.76 (*s*, H–C(1)); 5.23 (*s*, H of CH_2=C(2) *cis* to C(2),C(3)); 5.21 (*s*, H of CH_2=C(2) *trans* to C(2),C(3)); 3.98 (*s*, CH_3O–C(5)); 3.97 (*s*, CH_3O–C(8)). ^{13}C-NMR ($CDCl_3$): 150.1, 150.0, 144.9, 142.0, 140.7, 139.9, 135.5 (7*s*): 129.4 (*ddd*, ^1J(C,H) = 164, ^3J(C,H) = 6); 129.1 (*dd*, ^1J(C,H) = 162; ^3J(C,H) = 8); 126.9 (*ddd*, ^1J(C,H) = 168, ^3J(C,H) = 7); 125.9, 125.8 (2*s*); 114.3 (*d*, ^1J(C,H) = 174); 112.7 (*d*, ^1J(C,H) = 164); 104.1 (*d*, ^1J(C,H) = 159); 102.1 (*t*, ^1J(C,H) = 160); 84.1, 81.6 (2*dm*, ^1J(C,H) = 168); 55.8 (*q*, ^1J(C,H) = 143). MS (70 eV): 388 (78, M^+), 311 (31), 295 (12), 281 (13), 280 (28), 279 (100), 265 (11), 264 (12), 253 (11), 252 (19), 251 (66), 249 (27), 236 (24).

(1RS,3SR,8SR)-3-(2-Nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (**23**). A mixture of **16** (290 mg, 1.05 mmol) and freshly sublimed TCNE (135 mg, 1.05 mmol) in anh. acetone (5 ml) was stirred at 50° for 6 h. After filtration on silica gel (AcOEt/petroleum ether 3:7), **23** and **24** (see below) were separated by fractional crystallization from CH_2Cl_2/hexane 9:1. Adduct **23** crystallized first yielding 196 mg (46%), colourless crystals, m.p. 166–167°. UV (MeCN): 196 (22500), 214 (sh, 18500), 244 (sh, 10000), 336 (2500). IR (KBr): 3010, 2980, 2950, 2900, 1600, 1575, 1540, 1475, 1460, 1435, 1365, 1255, 1230, 1160, 1000, 940, 880, 860. ^{1}H-NMR: *Table 2*. ^{13}C-NMR (CD_3COCD_3): 141.1, 137.0, 136.0, 134.1 (4*s*, C(2), C(7), C (arom.)); 136.4, 134.7, 131.7, 126.7 (4*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, CH (arom.)); 112.3, 112.0, 110.4, 110.3 (4 br. *s*, CN); 81.2, 80.0 (2*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C(1), C(8)); 49.8 (*d*, ^1J(C,H) = 153, C(3)); 47.8, 41.7 (2*s*, C(4), C(5)); 30.5 (*t*, ^1J(C,H) = 132, C(6)); 25.6, 24.3 (2*t*, ^1J(C,H) = 138, C(9), C(10)). MS (70 eV): 249 (1.6, $M^+ - SC_6H_4NO_2$), 221 (27), 194 (12), 167 (22), 154 (32), 139 (100). Anal. calc. for $C_{20}H_{13}N_5O_3S$ (403.422): C 59.54, H 3.25; found: C 59.55, H 3.28.

(1RS,3RS,8SR)-3-(2-Nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (**24**). Evaporation of the mother-liquor of the crystallization of **23** yielded a crystalline product which was recrystallized from CH_2Cl_2/hexane 9:1 yielding 105 mg (25%) of colourless crystals, m.p. 215–216°. UV (MeCN): 196 (22000), 218 (sh, 17000), 246 (sh, 10000), 334 (2500). IR (KBr): 3000, 2960, 2940, 2880, 1590, 1570, 1510, 1460, 1430, 1340, 1310, 1255, 1220, 1175, 1150, 1105, 1070, 1040, 1000, 955, 930, 870, 820. ^{1}H-NMR: *Table 2*. ^{13}C-NMR (CD_3COCD_3): 141.1, 136.8, 128.3 (3 br. *s*, C(2), C(7), C (arom.)); 135.1, 134.9, 131.1, 126.7 (4*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, C (arom)); 112.2, 111.6 (2 C), 110.2 (3 br. *s*, CN); 81.6, 80.5 (2*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, C(1), C(8)); 49.8 (*d*, ^1J(C,H) = 158, C(3)); 48.1, 40.9 (2*s*, C(4), C(5)); 31.0 (*t*, ^1J(C,H) = 132, C(6)); 26.5, 24.8 (2*t*, ^1J(C,H) = 138, C(9), C(10)). MS (70 eV): 403 (1.3, M^+), 249 (3.5), 221 (26), 194 (7), 167 (11), 166 (13), 154 (26), 139 (100), 138 (53), 106 (27). Anal. calc. for $C_{20}H_{13}N_5O_3S$ (403.422): C 59.54, H 3.25; found: C 59.68, H 3.25.

(1RS,3RS,4RS or 4SR,8SR)-4-Ethyl-4-nitro-3-(2-nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (**25**). A mixture of **16** (300 mg, 1.09 mmol), 2-nitro-1-butene (770 mg, 7.6 mmol), and benzene/*t*-BuOH 2:1 (3 ml) was degassed, sealed under vacuum in a *Pyrex* tube, and heated to 100° for 24 h. After cooling, the solvent evaporated. The residue was purified by column chromatography on silica gel (30 g; AcOEt/hexane 1:1) and yielded a 1st fraction containing 90 mg of **25** and 120 mg of **26**. The 2nd fraction contained 150 mg of **27**. The adducts **25** and **26** were separated by HPLC (*Dupont Instruments, 830* liquid chromatograph) on silica gel

(AcOEt/hexane 1:4). **25**: Yellow crystals, recrystallized from CH_2Cl_2/hexane 9:1, m.p. 176–177°. UV (MeCN): 196 (25500), 246 (13000), 273 (sh, 6200), 358 (2600). IR (KBr): 3090, 2990, 2980, 2950, 2880, 1580, 1520, 1460, 1435, 1380, 1350, 1285, 1255, 1220, 1195, 1170, 1115, 1050, 990, 945, 920. ^{1}H-NMR: *Table 2.* ^{13}C-NMR ($CDCl_3$): 148.6, 145.3, 137.1, 133.6 (4 br. *s*, C(2), C(7), C (arom.)); 133.4, 130.0, 126.8, 125.8 (4*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, C (arom.)); 94.8 (*s*, C(4)); 80.3, 79.8 (2*d*, ^1J(C,H) = 164, C(1), C(8)); 47.7 (*d*, ^1J(C,H) = 149, C(3)); 30.4 (*t*, ^1J(C,H) = 131); 27.1 (*t*, ^1J(C,H) = 136); 26.9 (*t*, ^1J(C,H) = 129, CH_3CH_2); 7.6 (*q*, ^1J(C,H) = 126, CH_3CH_2). MS (70 eV): 330 (78, $M^+ - NO_2$), 302 (100), 210 (78), 276 (96). Anal. calc. for $C_{18}H_{20}N_2O_5S$ (376.434): C 57.43, H 5.35; found: C 57.71, H 5.21.

*(1*RS,*3*SR,*4*RS *or 4*SR,*8*SR*)-4-Ethyl-4-nitro-3-(2-nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-3(7)-ene* (**26**) was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 151–152°. UV (MeCN): 196 (26000), 244 (12000), 273 (sh, 5600), 356 (2300). IR (KBr): 3080, 2990, 2985, 2950, 2920, 2880, 1580, 1560, 1500, 1435, 1330, 1310, 1290, 1255, 1220, 1170, 1125, 1100, 1050, 1035, 1000, 950. ^{1}H-NMR: *Table 2.* ^{13}C-NMR ($CDCl_3$): 150.4, 144.1, 137.6, 131.2 (4 br. *s*, C(2), C(7), C (arom.)); 133.1, 132.8, 127.9, 125.2 (4*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, C (arom.)); 96.1 (*s*, C(4)); 79.9, 79.0 (2*dd*, ^1J(C,H) = 164, ^3J(C,H) = 8, C(1), C(8)); 45.6 (*d*, ^1J(C,H) = 148, C(3)); 31.2 (*t*, ^1J(C,H) = 129); 26.8 (*t*, ^1J(C,H) = 132); 24.7 (*t*, ^1J(C,H) = 136); (*q*, ^1J(C,H) = 128, CH_3CH_2). MS (70 eV): 376 (24, M^+), 348 (67), 330 (40), 302 (100), 296 (22), 274 (29), 254 (34), 222 (53). Anal. calc. for $C_{18}H_{20}N_2O_5S$ (376.434): C 57.43, H 5.35; found: C 57.55, H 5.26.

*(1*RS,*3*RS,*4*RS *or 4*SR,*8*SR*)-4-Ethyl-4-nitro-3-(2-nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene* (**27**) was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 184–185°. UV (MeCN): 244 (sh, 12000), 268 (6200), 356 (2800). IR (KBr): 3100, 3080, 3020, 3000, 2980, 2950, 2850, 1590, 1570, 1530, 1465, 1445, 1365, 1350, 1330, 1310, 1290, 1265, 1255, 1245, 1220, 1180, 1150, 1120, 1100, 1055, 1010, 990, 965, 930. ^{1}H-NMR: *Table 2.* ^{13}C-NMR ($CDCl_3$): 144.7, 137.4, 131.2 (3 br. *s*, C(2), C(7), C (arom.)); 132.7, 132.6, 127.8, 125.0 (4*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, C (arom)); 94.0 (*s*, C(4)); 80.3, 80.2 (2*dd*, ^1J(C,H) = 163, ^3J(C,H) = 8, C(1), C(8)); 51.0 (*d*, ^1J(C,H) = 150, C(3)); 29.1 (*t*, ^1J(C,H) = 130); 24.0 (*t*, ^1J(C,H) = 136); 19.8 (*t*, ^1J(C,H) = 130, CH_3CH_2); 8.5 (*q*, ^1J(C,H) = 125, CH_3CH_2). MS (70 eV): 376 (0.5, M^+), 330 (4), 302 (7), 252 (2), 176 (13), 175 (19), 164 (11), 163 (45), 158 (16), 157 (11), 154 (11), 149 (10), 148 (69), 147 (100). Anal. calc. for $C_{18}H_{20}N_2O_5S$ (376.434): C 57.43, H 5.35; found: C 57.38, H 5.37.

*(1*RS,*3*SR,*4*RS,*8*RS*)-[3-(2-Nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl] Methyl Ketone* (**28**). A mixture of **16** (200 mg, 0.726 mmol) and MVK (506 mg, 7.26 mmol) in anh. benzene (1 ml) was heated to 100° under stirring for 13 h. After evaporation, the residue was purified by column chromatography on silica gel (15 g; AcOEt/petroleum ether 3:2). The 1st fraction contained 168 mg of **29**, the 2nd one 72 mg of **28** as a yellow oil. UV (MeCN): 248 (12500), 272 (sh, 6000), 366 (2500). IR (film): 2990, 2950, 2870, 1700, 1585, 1560, 1510, 1445, 1420, 1335, 1300, 1265, 1210, 1165, 1095, 1050, 1000. ^{1}H-NMR: *Table 2.* ^{13}C-NMR ($CDCl_3$): 207.5 (*s*, CO); 149.7, 145.0, 138.9, 133.7 (4 br. *s*, C(2), C(7), C (arom.)); 132.8, 131.4, 126.7, 125.3 (4*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom)); 80.4 (*d*, ^1J(C,H) = 164, C(1)); 80.1 (*d*, ^1J(C,H) = 162, C(8)); 52.0 (*q*, ^1J(C,H) = 128, CH_3CO); 26.8 (*t*, ^1J(C,H) = 136); 24.5 (*t*, ^1J(C,H) = 135); 21.7 (*t*, ^1J(C,H) = 150); 20.4 (*t*, ^1J(C,H) = 128). CI-MS (CH_4): 346 (0.8, $M^+ + 1$), 220 (3), 207 (2), 198 (3), 191 (100). Anal. calc. for $C_{18}H_{19}NO_4S$ (345.421): C 62.59, H 5.54; found: C 62.47, H 5.48.

*(1*RS,*3*RS,*4*RS,*8*RS*)-[3-(2-Nitrophenyl)sulfenyl-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl] Methyl Ketone* (**29**) was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 159–160°. UV (MeCN): 196 (22500), 248 (17000), 274 (sh, 6000), 368 (3500). IR (KBr): 3100, 3080, 3060, 3000, 2980, 2950, 2910, 2870, 1690, 1590, 1565, 1510, 1455, 1445, 1360, 1340, 1305, 1270, 1255, 1220, 1205, 1175, 1165, 1105, 1060, 1040, 1020, 1010, 965. ^{1}H-NMR: *Table 2.* ^{13}C-NMR ($CDCl_3$): 208.3 (*s*, CO); 147.7, 144.7, 137.9, 135.0 (4*s*, C(2), C(7), C (arom.)); 133.5, 128.7, 125.8 (2 C) (3*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8); 80.5 (*d*, ^1J(C,H) = 164, C(1)); 79.9 (*d*, ^1J(C,H) = 162, C(8)); 52.7 (*d*, ^1J(C,H) = 130, C(4)); 40.6 (*d*, ^1J(C,H) = 148, C(3)); 29.0 (*q*, ^1J(C,H) = 128, CH_3CO); 27.0, 24.7 (*t*, ^1J(C,H) = 134); 24.1 (*t*, ^1J(C,H) = 132); 20.2 (*t*, ^1J(C,H) = 129). MS (70 eV): 345 (0.5, M^+), 207 (12), 191 (16), 173 (10), 163 (28), 155 (20), 149 (39), 148 (12), 147 (23), 145 (14), 139 (10), 138 (20), 132 (12), 131 (100). Anal. calc. for $C_{18}H_{19}NO_4S$ (345.421): C 62.59, H 5.54; found: C 62.76, H 5.76.

Tosylhydrazone of **29**. A mixture of **29** (595 mg, 1.72 mmol) and tosylhydrazine (645 mg, 3.48 mmol) in anh. THF (5 ml) was stirred at 20° for 24 h. After addition of CH_2Cl_2 (5 ml) and H_2O (5 ml), the layers were separated, and the aq. phase was extracted with CH_2Cl_2 (5 ml, 2 times). The org. phases were united, washed with H_2O (5 ml, 2 times), and dried ($MgSO_4$). After evaporation and purification on silica gel (AcOEt/hexane 1:1), the crude product was recrystallized from CH_2Cl_2/hexane 9:1 yielding 795 mg (90%) of yellow crystals, m.p. 169–170°. UV (MeCN): 211 (20000), 229 (23000), 247 (sh, 18500), 275 (sh, 6000), 373 (3000). IR (KBr): 3220, 3100, 3080, 2990, 2980, 2960, 2930, 2885, 2880, 1585, 1560, 1520, 1445, 1420, 1395, 1330, 1300, 1245, 1155, 1095. ^{1}H-NMR ($CDCl_3$): 8.11–7.18 (*m*, 9 H); 4.72, 4.63 (2*d*, ^3J = 4, 2 H); 4.68 (br. *s*, 1 H); 2.76 (*m*, 1 H); 2.39 (*s*, 3 H); 2.16–1.93 (*m*, 4 H); 1.82

(*s*, 3 H); 1.77–1.68 (*m*, 2 H); 1.57–1.48 (*m*, 1 H); 1.31–1.13 (*m*, 1 H). CI-MS (CH_4): 514 (3.2, $M^+ + 1$), 497 (7), 398 (9), 360 (100), 341 (32). Anal. calc. for $C_{25}H_{27}N_3O_5S_2$ (513.627): C 58.46, H 5.29; found: C 58.37, H 5.28.

(1RS,3SR,8RS)-10-Methylidene-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (**30**). A mixture of **17** [2] [30] (300 mg, 0.66 mmol) and TCNE (85 mg, 0.66 mmol; freshly sublimed) in anh. acetone (8 ml) was stirred at 50° for 14 h. After evaporation, the residue was purified on silica gel (15 g; AcOEt/hexane 3:7) and recrystallized from CH_2Cl_2/hexane 9:1 yielding 311 mg (81%) as yellow crystals, m.p. 207–208°. UV (MeCN): 196 (39000), 219 (sh, 36300), 238 (sh, 31500), 288 (18100), 366 (9000). IR (KBr): 3080, 3020, 2930, 2360, 1590, 1565, 1510, 1455, 1430, 1340, 1305, 1270, 1255, 1110, 1060, 1045, 990, 940, 900. ^{1}H-NMR: *Table 3*. ^{13}C-NMR (CD_3COCD_3): 152.7, 147.2, 143.3, 142.5 (2 C), 141.3, 138.9 (6 br. *s*, C(2), C(7), C(9), C(10), C(arom.)); 137.0, 135.2, 135.0, 132.2, 130.0, 127.4, 126.9, 126.8 (8*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom.)); 113.3 (*d*, ^1J(C,H) = 166, H–*C*–SAr); 111.8, 111.5, 111.1, 110.1 (4*s*, CN); 107.0 (*t*, ^1J(C,H) = 162, CH_2=C(10)); 84.6, 83.7 (2*dm*, ^1J(C,H) = 173, C(1), C(8)); 49.8 (*d*, ^1J(C,H) = 154, C(3)); 47.5, 45.8 (2*s*, C(4), C(5)); 31.0 (*t*, ^1J(C,H) = 140, C(6)). CI-MS (CH_4): 581 (100, $M^+ + 1$), 563 (97), 426 (56), 376 (71), 324 (74), 222 (37), 221 (56). Anal. calc. for $C_{28}H_{16}N_6O_5S_2$ (580.604): C 57.92, H 2.77; found: C 57.85, H 2.82.

(1RS,3RS,4RS or 4SR,8RS)-4-Ethyl-10-methylidene-4-nitro-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (**31**). A mixture of **17** (500 mg, 1.1 mmol), 2-nitro-1-butene (1.4 g, 14.3 mmol), benzene (5 ml), and *t*-BuOH (2.5 ml) was degassed, sealed under vacuum in a *Pyrex* tube, and heated to 100° for 24 h. After cooling, the solvent was evaporated and the residue purified by column chromatography on silica gel (60 g; AcOEt/hexane 3:1). The 1st fraction contained 183 mg (30%) of **31** and 182 mg (30%) of **32**. They were separated by HPLC (*Dupont*, SiO_2, AcOEt/hexane 1:4). The 2nd fraction contained 93 mg (15%) of **33**. Adduct **31** was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 174–175°. UV (MeCN): 196 (42500), 238 (30000), 280 (19000), 370 (8000). IR (KBr): 3100, 3080, 3020, 2990, 2980, 2940, 2910, 2880, 2850, 1590, 1570, 1530, 1520, 1450, 1440, 1390, 1345, 1335, 1310, 1250, 1110, 1055, 1040. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 149.8, 146.9, 145.7, 144.8, 141.7, 139.8, 136.9, 129.9 (8 br. *s*, C(2), C(7), C(9), C(10), C (arom.)); 134.0, 133.9, 132.8, 128.6, 128.4, 125.9, 125.5, 125.3 (8*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8, C (arom.)); 108.7 (*d*, ^1J(C,H) = 176, *C*H=C(9)); 104.1 (*t*, ^1J(C,H) = 160, CH_2=C(10)); 95.8 (*s*, C(4)); 83.9, 82.5 (2*dm*, ^1J(C,H) = 168, C(1), C(8)); 45.9 (*d*, ^1J(C,H) = 150, C(3)); 31.0, 26.7 (2*t*, ^1J(C,H) = 131, C(5), C(6)); 19.9 (*t*, ^1J(C,H) = 130, CH_3CH_2); 7.6 (*q*, ^1J(C,H) = 131, CH_3CH_2). MS (70 eV): 443 (5, $M^+ - HN_2O_5$), 324 (71), 303 (86), 209 (100). Anal. calc. for $C_{26}H_{33}N_3O_7S_2$ (553.617): C 56.41, H 4.18; found: C 56.41, H 4.16.

(1RS,2SR,4RS or 4SR,8RS)-4-Ethyl-10-methylidene-4-nitro-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (**32**) was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 161–162°. UV (MeCN): 198 (36000), 242 (27500), 280 (18000), 370 (7500). IR (KBr): 3100, 3020, 2980, 2940, 2880, 2850, 1590, 1570, 1520, 1510, 1450, 1440, 1335, 1305, 1285, 1250, 1105, 1055, 1045, 990. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 149.1, 146.0, 145.0, 143.8 (2 C), 139.8, 136.5, 132.8 (7*s*, C(2), C(7), C(9), C(10), C (arom.)); 133.7, 133.4, 130.1, 128.4, 127.2, 126.0, 125.9, 125.7 (8*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom.)); 108.9 (*d*, ^1J(C,H) = 176, *C*H=C(9)); 104.6 (*t*, ^1J(C,H) = 160, CH_2=C(10)); 94.7 (*s*, C(4)); 84.43, 82.6 (2*dm*, ^1J(C,H) = 168, ^3J(C,H) = 8, C(1), C(8)); 47.9 (*d*, ^1J(C,H) = 150, C(3)); 29.8, 27.4 (*t*, ^1J(C,H) = 130, C(5),C(6)); 19.7 (*t*, ^1J(C,H) = 130, CH_3CH_2); 7.6 (*q*, ^1J(C,H) = 128, CH_3CH_2). MS (70 eV): 507 (30, $M^+ - NO_2$), 479 (29), 478 (18), 477 (45), 369 (29), 368 (39), 352 (100). Anal. calc. for $C_{26}H_{33}N_3O_7S_2$ (553.617): C 56.41, H 4.18; found: C 56.30, H 4.30.

(1RS, 3SR, 4RS, 8RS)-[10-Methylidene-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl] Methyl Ketone (**34**). A mixture of **17** (300 mg, 0.66 mmol) and MVK (464 mg, 6.6 mmol) in anh. benzene (1 ml) was stirred at 100° for 2½ h. After evaporation, the mixture was purified by column chromatography on silica gel (15 g, AcOEt/petroleum ether 1:1). The 1st fraction contained 296 mg (86%) of **35** (see below), the 2nd fraction 33 mg (9%) of **34**. The latter was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 130–131°. UV (MeCN): 202 (31000), 244 (26000), 280 (17500), 376 (7600). IR (KBr): 3110, 3090, 3000, 2960, 2930, 2870, 2830, 1710, 1590, 1570, 1505, 1450, 1425, 1335, 1305, 1245, 1215, 1175, 1150, 1105, 1060, 1040, 985, 940. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 208.2 (*s*, CO); 146.6, 145.5 (2 C), 143.8, 141.3, 136.9 (5 br. *s*, C(2), C(7), C(9), C(10), C (arom.)); 133.7, 132.7, 133.3, 128.4, 127.3, 126.0, 125.5, 125.3 (8*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom.)); 108.2 (*d*, ^1J(C,H) = 176, *C*H=C(9)); 104.6 (*t*, ^1J(C,H) = 160, CH_2=C(10)); 84.7, 82.7 (2*d*, ^1J(C,H) = 168, C(1), C(8)); 52.1 (*d*, ^1J(C,H) = 128, C(4)); 44.7 (*d*, ^1J(C,H) = 148, C(3)); 28.7 (*q*, ^1J(C,H) = 128); 21.4 (*t*, ^1J(C,H) = 130, C(5),C(6)). MS (70 eV): 368 (3.5, $M^+ - SC_6H_4NO_2$), 353 (14), 324 (20), 252 (15), 250 (11), 216 (19), 215 (100), 214 (14), 213 (20). Anal. calc. for $C_{26}H_{22}N_2O_6S_2$ (522.603): C 59.75, H 4.24; found: C 59.88, H 4.23.

(1RS, 3RS, 4RS, 8RS)-[10-Methylidene-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl] Methyl Ketone (**35**) was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 208–209°. UV (MeCN): 196 (32000), 246 (28000), 282 (18500), 376 (8100). IR (KBr): 3090, 3000, 2960, 2930, 2880, 2840, 1710, 1590, 1560, 1505, 1450, 1335, 1305, 1245, 1155, 1100, 1040, 960, 850. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 208.1 (*s*, CO); 147.6, 146.7, 145.7, 145.1, 143.7, 140.4, 136.6, 134.6 (8 br. *s*, C(2), C(7), C(9), C(10), C (arom.)); 133.7, 133.4, 128.6, 128.4 (2 C), 125.9 (2 C), 125.6 (6*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom.)); 108.2 (*d*, ^1J(C,H) = 175, *C*H=C(9)); 105.1 (*t*, ^1J(C,H) = 160, *C*H$_2$=C(10)); 84.4, 82.8 (2*dm*, ^1J(C,H) = 168, C(1), C(8)); 52.7 (*d*, ^1J(C,H) = 130, C(4)); 40.9 (*d*, ^1J(C,H) = 149, C(3)); 28.8 (*q*, ^1J(C,H) = 128); 24.0, 20.7 (2*t*, ^1J(C,H) = 130, C(5),C(6)). MS (70 eV): 368 (2, $M^+ - SC_6H_4NO_2$), 338 (19), 252 (100), 250 (56), 235 (48), 219 (29), 217 (19), 203 (14), 201 (13), 187 (16), 185 (20), 183 (36), 155 (22), 142 (11), 141 (50), 139 (17). Anal. calc. for $C_{26}H_{22}N_2O_6S_2$ (522.603): C 59.75, H 4.24; found: C 59.84, H 4.24.

Methyl (1RS,3SR,4RS,8RS)-10-Methylidene-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4-carboxylate (**36**). A mixture of **17** (500 mg, 1.1 mmol) and methyl acrylate (860 mg, 10 mmol) was stirred at 70° for 15 h. After evaporation of the excess of methyl acrylate, the residue was purified by column chromatography on silica gel (15 g; AcOEt/petroleum ether 1:3). The 1st fraction contained 447 mg (76%) of **37**, the 2nd fraction 112 mg (19%) of **36** which was recrystallized from CH_2Cl_2/hexane 9:1, yellow crystals, m.p. 180–181°. UV (MeCN): 245 (25500), 282 (17500), 375 (7000). IR (KBr): 3020, 2960, 2910, 2840, 1745, 1595, 1575, 1530, 1505, 1455, 1440, 1360, 1335, 1310, 1250, 1225, 1195, 1175, 1115, 1005, 995, 960, 895, 850. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 171.7 (*s*, CO); 150.5, 146.8, 146.3 (2 C), 146.2, 144.0, 141.1, 137.0 (7 br. *s*, C(2), C(7), C(9), C(10), C (arom.)); 133.7, 132.5, 132.4, 128.4, 127.1, 126.0, 125.6, 125.3 (8*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom.)); 108.2 (*d*, ^1J(C,H) = 166, *C*H=C(9)); 104.7 (*t*, ^1J(C,H) = 161, *C*H$_2$=C(10)); 84.7, 82.7 (2*dm*, ^1J(C,H) = 170, C(1), C(8)); 51.3 (*q*, ^1J(C,H) = 148, *C*H$_3$OOC); 45.2 (*d*, ^1J(C,H) = 148, C(3)); 45.0 (*d*, ^1J(C,H) = 130, C(4)); 21.4, 21.0 (2*t*, ^1J(C,H) = 130, C(5),C(6)). CI-MS (CH_4): 567 (14, $M^+ + C_2H_5$), 539 (17, $M^+ + 1$), 521 (8), 511 (34), 384 (100). Anal. calc. for $C_{26}H_{22}N_2O_7S_2$ (538.601): C 57.98, H 4.11; found: C 57.83, H 4.09.

Methyl (1RS,3RS,4RS,8RS)-10-Methylidene-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4-carboxylate (**37**) was recrystallized from CH_2Cl_2/Et_2O 9:1, yellow crystals, m.p. 188–189°. UV (MeCN): 247 (22000), 282 (13000), 375 (5800). IR (KBr): 3060, 3030, 3000, 2980, 2960, 2920, 2840, 1725, 1590, 1570, 1515, 1455, 1430, 1375, 1305, 1270, 1250, 1201, 1185, 1170, 1100, 1090, 1060, 1040, 985, 970, 935, 910, 900. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 172.6 (CO); 147.1, 146.4 (2 C), 145.4, 143.5, 138.8, 136.6, 134.8 (7 br. *s*, C(2), C(7), C(9), C(10), C (arom.)); 133.6, 128.2, 127.9, 125.8, 125.6, 125.5 (6*dd*, ^1J(C,H) = 177, *C*H=C(9)); 105.1 (*t*, ^1J(C,H) = 161, *C*H$_2$=C(10); 84.3, 82.6 (2*dm*, ^1J(C,H) = 168, C(1), C(8)); 52.1 (*q*, ^1J(C,H) = 148, *C*H$_3$OOC); 44.3 (*d*, ^1J(C,H) = 131, C(4)); 41.7 (*d*, ^1J(C,H) = 147, C(3)); 21.8, 19.6 (2*t*, ^1J(C,H) = 131, C(5),C(6)). CI-MS (CH_4): 567 (7, $M^+ + C_2H_5$), 539 (10, $M^+ + 1$), 521 (10), 511 (12), 384 (100).

(1RS, 3SR, 8RS)-[10-Methylidene-3-(2-nitrophenyl)sulfenyl-9-[(Z)-(2-nitrophenyl)sulfenylmethylidene]-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),4-dien-4-yl] Methyl Ketone (**38**). A mixture of tetraene **17** (300 mg, 0.66 mmol), 3-butyn-2-one (225 mg, 3.31 mmol), and anh. benzene (3 ml) was degassed and sealed under vacuum in a *Pyrex* tube. The tube was heated to 50° for 40 h. After cooling, the solvent and excess of butynone were evaporated. The crude adduct was purified by filtration through silica gel (AcOEt/hexane 1:1) and recrystallized from CH_2Cl_2/hexane 9:1 yielding 288 mg (84%) of yellow crystals, m.p. 132–133°. UV (MeCN): 202 (36000), 241 (22000), 284 (15000), 376 (6400). IR (KBr): 3100, 3060, 3010, 2880, 2840, 2800, 1675, 1665, 1620, 1590, 1570, 1500, 1455, 1410, 1385, 1370, 1330, 1300, 1280, 1260, 1250, 1230, 1210, 1100, 1055, 1040, 965, 900, 865, 850, 835, 775. ^{1}H-NMR: *Table 3*. ^{13}C-NMR ($CDCl_3$): 196.4 (CO); 148.1, 145.8 (2 C), 143.1 (2 C), 141.8, 140.7, 139.4 (6 br. *s*, C(2), C(7), C(9), C(10), C (arom.)); 138.6 (*d*, ^1J(C,H) = 158, C(5)); 131.2 (br. *s*, C(4)); 133.8, 132.8, 129.3, 128.4, 126.0, 125.9, 125.7, 125.6 (8*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8, C (arom.)); 108.5 (*d*, ^1J(C,H) = 170, *C*H=C(9)); 104.5 (*t*, ^1J(C,H) = 160, *C*H$_2$=C(10)); 84.3, 82.3 (2*dm*, ^1J(C,H) = 171, C(1), C(8)); 39.4 (*dd*, ^1J(C,H) = 150, ^3J(C,H) = 6, C(3)); 25.9 (*q*, ^1J(C,H) = 128, *C*H$_3$CO); 25.6 (*t*, ^1J(C,H) = 130, C(6)). MS (70 eV): 366 (37, $M^+ - SC_6H_4NO_2$), 244 (14), 237 (89), 211 (97), 185 (37), 183 (37), 171 (58), 169 (73), 140 (100). Anal. calc. for $C_{26}H_{20}N_2O_6S_2$ (520.587): C 59.98, H 3.87; found: C 59.95, H 3.86.

(1RS, 2RS, 5RS, 12RS)-[5,12-Epoxy-1,2,3,4,5,12-hexahydro-7,10-dimethoxy-1-(2-nitrophenyl)sulfenyl-2-naphthacenyl] Methyl Ketone (**39**). A mixture of **18** (400 mg, 0.92 mmol), MVK (650 mg, 9.2 mmol), and anh. benzene (5 ml) was degassed and selaed under vacuum in a *Pyrex* tube. The tube was heated to 100° for 56 h. After cooling, the solvent and excess of dienophile were evaporated. The residue was filtered through silica gel (20 g; AcOEt/hexane 1:1) and recrystallized from CH_2Cl_2/hexane 9:1 yielding 422 mg (91%) of yellow crystals, m.p. 129–130°. A trace (< 1%) of another isomeric adduct was detected by ^{1}H-NMR (360 MHz) of the mother liquor and by TLC. UV (MeCN): 210 (sh, 41000), 261 (28500), 343 (4500). IR (KBr): 3010, 2970, 2940, 2900, 2840, 1710,

1615, 1595, 1575, 1515, 1475, 1465, 1435, 1390, 1360, 1340, 1330, 1310, 1265, 1245, 1225, 1185, 1160, 1135, 1100, 1080, 1050, 960, 850, 840, 800, 790, 740. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.16–7.25 (*m*, 4 H); 7.98 (*s*, H–C(11)); 7.77 (*s*, H–C(6)); 6.73 (*s*, H–C(8), H–C(9)); 5.61 (br. *s*, $^5J(H_\beta$–C(4),H–C(12)) = 1.2, H–C(12)); 5.55 (br. *s*, $^5J(H_\beta$–C(1),H–C(5)) = 1.0, H–C(5)); 4.88 (*dddd*, $^3J(H_\beta$–C(1),H_α–C(2)) = 7.2, $^5J(H_\beta$–C(1), H_α–C(4)) = 3.1, $^5J(H_\beta$–C(1),H_β–C(4)) = 2.7, $^5J(H_\beta$–C(1),H–C(5)) = 1.0, H_β–C(1)); 3.94 (*s*, CH_3O–C(10)); 3.93 (*s*, CH_3O–C(7)); 3.65 (*ddd*, $^3J(H_\alpha$–C(2),H_β–C(3)) = 9.5, $^3J(H_\beta$–C(1),H_α–C(2)) = 7.2, $^3J(H_\alpha$–C(2), H_α–C(3)) = 3.7, H_α–C(2)); 3.52 (*m*, ^2J = 18.5, $^3J(H_\alpha$–C(3),H_β–C(4)) = 5.0, $^5J(H_\beta$–C(1),H_β–C(4)) = 2.7, $^5J(H_\beta$–C(4), H–C(12)) = 1.2, H_β–C(4)); 2.22 (*s*, CH_3CO); 2.13–2.07 (*m*, ^2J = 18.5, $^5J(H_\beta$–C(1),H_α–C(4)) = 3.1, H_α–C(4)); 2.07–2.02 (*m*, $^3J(H_\alpha$–C(3),H_β–C(4)) = 5.0, ^3J(H–C(2),H_α–C(3)) = 3.7, H_α–C(3)); 1.93–1.81 (*m*, ^3J(H–C(2), H_β–C(3)) = 9.5, H_β–C(3)); signal attributions confirmed by NOE measurements and double-irradiation experiments. ^{13}C-NMR ($CDCl_3$): 208.3, 150.6, 150.4, 149.8, 147.6, 144.8, 144.6, 143.5, 135.1 (9*s*); 133.2, 128.7, 125.9, 125.6 (4*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8); 124.7, 124.1 (2*s*); 113.7, 111.9 (2*d*, ^1J(C,H) = 164); 104.8, 104.6 (2*d*, ^1J(C,H) = 158); 84.2, 83.4 (2*d*, ^1J(C,H) = 166); 56.0, 55.8 (2*q*, ^1J(C,H) = 144); 52.5 (*d*, ^1J(C,H) = 132); 41.4 (*d*, ^1J(C,H) = 148); 29.2 (*q*, ^1J(C,H) = 128); 24.8, 21.8 (2*t*, ^1J(C,H) = 130). MS (70 eV): 503 (42, M^+), 349 (69), 333 (36), 307 (100).

*(1*RS,*2*RS,*5*RS,*12*RS*)-5,12-Epoxy-1,2,3,4,5,12-hexahydro-7,10-dimethoxy-1-phenylsulfenyl-2-naphthacenyl] Methyl Ketone* (**40**). A mixture of **19** (180 mg, 0.46 mmol), MVK (325 mg, 4.6 mmol), and anh. benzene (2 ml) was degassed and sclaed under vacuum in a *Pyrex* tube. The tube was heated to 100° for 12 h. After cooling, the solvent was evaporated. The crude adduct was purified by filtration through silica gel (15 g; AcOEt/hexane 1:1) and recrystallized from CH_2Cl_2/hexane 9:1 yielding 197 mg (93%) of yellow crystals, m.p. 166–167°. UV (MeCN): 214 (30000), 262 (26000), 310 (4000), 327 (3500), 342 (3000). IR (KBr): 3060, 3000, 2960, 2900, 2840, 1700, 1610, 1585, 1470, 1460, 1440, 1385, 1355, 1330, 1260, 1220, 1180, 1155, 1130, 1080, 1045, 960, 930, 895, 835. ^{1}H-NMR ($CDCl_3$): 8.08 (*s*, H–C(11)); 8.0 (*s*, H–C(6)); 7.44–7.21 (*m*, C_6H_5); 6.75 (*s*, H–C(8),H–C(9)); 5.71 (br. *s*, $^5J(H_\beta$–C(4), H–C(12)) = 1.2, H–C(12)); 5.52 (br. *s*, $^5J(H_\beta$–C(1),H–C(5)) = 1.2, H–C(5)); 4.65 (*dddd*, $^3J(H_\beta$–C(1), H_α–C(2)) = 7.1, $^5J(H_\beta$–C(1),H_α–C(4)) = 3.1, $^5J(H_\beta$–C(1),H_β–C(4)) = 2.7, $^5J(H_\beta$–C(1),H–C(5)) = 1.2, H_β–C(1)); 3.97 (*s*, CH_3O–C(10)); 3.95 (*s*, CH_3O–C(7)); 2.58 (*ddd*, $^3J(H_\alpha$–C(2),H_β–C(3)) = 8.5, $^3J(H_\beta$–C(1),H_α–C(2)) = 7.2, $^3J(H_\alpha$–C(2),H_α–C(3)) = 4.0, H_α–C(2)); 2.49 (*m*, ^2J = 18.5, $^5J(H_\beta$–C(1),H_β–C(4)) = 2.7, $^5J(H_\beta$–C(4), H–C(12)) = 1.2, H_β–C(4)); 2.11 (*s*, CH_3CO); 2.10–2.0 (*m*, ^2J = 18.5, $^5J(H_\beta$–C(1),H_α–C(4)) = 3.1, H_α–C(4)); 1.94–1.82 (*m*, CH_2(3)); signal attributions confirmed by double-irradiation experiments (NOE measurements). ^{13}C-NMR ($CDCl_3$): 208.6, 150.4, 150.0, 149.5 (2 C), 146.0, 145.2, 144.1, 135.2 (8*s*); 131.3 (*dt*, ^1J(C,H) = 162, ^3J = 8); 129.1 (*dd*, ^1J(C,H) = 160, ^3J(C,H) = 8); 127.1 (*dt*, ^1J(C,H) = 162, ^3J(C,H) = 8); 124.6, 124.2 (2*s*); 113.7, 111.8 (2*d*, ^1J(C,H) = 164); 104.6, 104.4 (2*d*, ^1J(C,H) = 158); 84.2, 83.5 (2*d*, ^1J(C,H) = 166); 55.9, 55.8 (2*d*, ^1J(C,H) = 144); 53.2 (*d*, ^1J(C,H) = 130); 43.9 (*d*, ^1J(C,H) = 148); 29.1 (*q*, ^1J(C,H) = 128); 24.3, 21.6 (2*t*, ^1J(C,H) = 130). MS (70 eV): 458 (35, M^+), 349 (36), 307 (100), 291 (27). MS (HR): 458.1493 ($C_{28}H_{26}O_4S$, calc. 458.1552).

*Methyl (1*RS,*2*RS,*9*RS,*10*RS*)-[2-Acetyl-9,10-epoxy-1,2,3,4,9,10-hexahydro-1-(2-nitrophenyl)sulfenyl-anthracene-6-carboxylate]* (**42**). A mixture of **35** (300 mg, 0.662 mmol), methyl propynoate (556 mg, 6.62 mmol), two crystals of hydroquinone, and anh. benzene (3 ml) was degassed and sealed under vacuum in a *Pyrex* tube. The tube was heated to 80° for 72 h. After cooling, the solvent was evaporated. The residue was purified by column chromatography on silica gel (15 g; AcOEt/petroleum ether 1:1) and recrystallization from CH_2Cl_2/hexane 9:1 yielding 208 mg (70%) of yellowish crystals, m.p. 190–191°. UV (MeCN): 230 (34500), 248 (sh, 28000), 268 (sh, 15000), 364 (4000). IR (KBr): 3095, 3030, 3010, 2960, 2910, 2850, 1740, 1590, 1565, 1510, 1450, 1435, 1365, 1355, 1335, 1310, 1290, 1265, 1245, 1185, 1160, 1100, 1080, 1060, 1045, 995, 970, 960, 940, 875. ^{1}H-NMR (C_6D_6): 8.20 (*dd*, ^4J(H–C(5),H–C(7)) = 1.3, ^5J(H–C(5),H–C(8)) = 0.7, H–C(5)); 8.06 (*dd*, ^3J(H–C(7),H–C(8)) = 7.3, ^4J(H–C(5),H–C(7)) = 1.3, H–C(7)); 7.82, 7.53 (2*dd*, ^3J = 8.1, ^4J = 1.5, 2 H, ArS); 7.25 (*dd*, ^3J(H–C(7), H–C(8)) = 7.3, ^5J(H–C(5),H–C(8)) = 0.7, H–C(8)); 6.95, 6.09 (*dt*, ^3J = 8.1, ^4J = 1.5, 2 H, ArS); 5.56 (*s*, H–C(9)); 5.32 (*s*, H–C(10)); 4.99 (*m*, H–C(1)); 3.70 (*s*, CH_3O); 2.17 (*m*, H–C(1), H–C(2)); 2.04 (*m*, H_β–C(4)); 1.98 (*m*, H_α–C(4)); 1.80 (*s*, CH_3CO); 1.60 (*m*, H_β–C(3)); 1.50 (*m*, H_α–C(3)); signal attributions confirmed by NOE measurements. ^{13}C-NMR ($CDCl_3$): 208.2 (br. *s*, CO); 166.9 (br. *s*, COO); 154.7, 151.9, 148.0, 147.7, 145.1, 134.3 (6 br. *s*, C(5a), C(8a), C(9a), C(10a), C–S, C–NO_2); 133.4 (*dm*, ^1J(C,H) = 163); 128.8 (*dd*, ^1J(C,H) = 165, ^3J(C,H) = 8); 128.5 (*dd*, ^1J(C,H) = 162, ^3J(C,H) = 4); 127.3 (*d*, ^3J(C,H) = 6); 126.0 (*dm*, ^1J(C,H) = 168); 125.8 (*dm*, ^1J(C,H) = 168); 120.6 (*d*, ^1J(C,H) = 164, C(5)); 119.9 (*dd*, ^1J(C,H) = 166, ^3J(C,H) = 8); 84.1 (*dd*, ^1J(C,H) = 168, ^3J(C,H) = 7, C(9)); 83.5 (*dd*, ^1J(C,H) = 168, ^3J(C,H) = 7, C(10)); 52.7 (*d*, ^1J(C,H) = 132, C(2)); 51.9 (*q*, ^1J(C,H) = 146, CH_3O); 41.8 (*dd*, ^1J(C,H) = 148, ^3J(C,H) = 6, C(1)); 29.1 (*q*, ^1J(C,H) = 128, CH_3CO); 24.4, 21.8 (*tm*, ^1J(C,H) = 132, C(3), C(4)). MS (70 eV): 419 (9, $M^+ - CH_3O$), 255 (100), 238 (19), 228 (39), 195 (58), 166 (63). Anal. calc. for $C_{24}H_{21}NO_6S$ (450.502): C 63.84, H 4.68; found: C 63.60, H 5.54.

Methyl (1RS,2SR,5SR,6SR,9SR,10SR)-[2-Acetyl-9,10-epoxy-1,2,3,4,5,6,7,8,9,10-decahydro-1,5-bis(2-nitrophenyl)sulfenyl-2-anthracene-6-carboxylate] (**43**). A mixture of MVK (0.56 ml, 6.62 mmol), $BF_3 \cdot Et_2O$ (0.84 ml, 6.62 mmol), and anh. CH_2Cl_2 (3 ml) was stirred at 20° for 30 min under Ar. After cooling to −78°, a soln. of **37** (595 mg, 1.1 mmol) in anh. CH_2Cl_2 (18 ml) cooled to −78° was added. After stirring at −78° for 120 h, the mixture was poured into a vigourously stirred ice-cold aq. sat. $NaHCO_3$ soln. (10 ml). The org. layer was dried ($MgSO_4$) and the solvent evaporated. The crude adduct was purified by column chromatography on silica gel (20 g; AcOEt/hexane 1:1) and recrystallized from CH_2Cl_2/Et_2O 9:1 yielding 470 mg (70%) of yellow crystals, m.p. 172–173°. UV (MeCN): 248 (22000), 272 (sh, 10000), 365 (3900). IR (KBr): 3070, 3020, 2960, 2940, 2910, 2840, 1610, 1590, 1565, 1505, 1465, 1450, 1370, 1330, 1300, 1260, 1225, 1200, 1190, 1170. ^{1}H-NMR ($CDCl_3$): 8.22–7.31 (*m*, arom. H); 5.12 (br. *s*, $^5J(H_\beta\text{–}C(4), H\text{–}C(9)) = 1.0$, H–C(9)); 5.01 (br. *s*, $^5J(H_\beta\text{–}C(8), H\text{–}C(10) = 1.0$, H–C(10)); 4.88 (*m*, $^3J(H_\beta\text{–}C(5), H_\alpha\text{–}C(6) = 3.9$, $^5J(H_\beta\text{–}C(5), H_\beta\text{–}C(8)) = 3.5$, $^5J(H_\beta\text{–}C(5), H_\alpha\text{–}C(8)) = 1.5$, H_β–C(5)); 4.50 (*ddd*, $^3J(H_\alpha\text{–}C(1), H_\alpha\text{–}C(2)) = 4.5$, $^5J(H_\alpha\text{–}C(1), H_\alpha\text{–}C(4)) = 2.7$, $^5J(H_\alpha\text{–}C(1), H_\beta\text{–}C(4)) = 1.0$, H_α–C(1)); 3.75 (*s*, CH_3O); 2.87 (*m*, $^3J(H_\beta\text{–}C(5), H_\alpha\text{–}C(6)) = 3.9$, H–C(6)); 2.76 (*m*, $^3J(H_\alpha\text{–}C(1), H_\alpha\text{–}C(2)) = 4.5$, H–C(2)); 2.67 (*m*, $^5J(H_\beta\text{–}C(5)$, $H_\beta\text{–}C(8)) = 3.5$, $^5J(H_\beta\text{–}C(8), H\text{–}C(10)) = 1.0$, H_β–(C(8)); 2.53 (*m*, $^2J = 18.5$, $^5J(H_\beta\text{–}C(4)$, H–C(9) = 1.0, $^5J(H_\alpha\text{–}C(1), H_\beta\text{–}C(4)) = 1.0$, H_β–C(4)); 2.43–2.22 (*m*, $^2J = 18.5$, $^5J(H_\alpha\text{–}C(1), H_\alpha\text{–}C(4)) = 2.7$, H_α–C(4)); 2.28–2.12 (*m*, H_α–C(8), CH_2(7)); 2.08–1.93 (*m*, CH_2(3)); 2.0 (*s*, CH_3CO); attributions confirmed by double-irradiation experiments. ^{13}C-NMR ($CDCl_3$): 207.7 (*s*); 172.7 (*s*); 155.6, 154.3, 152.0, 147.1, 146.7, 145.7, 135.1, 130.4 (8 br. *s*); 135.1, 133.7, 132.2, 128.2, 127.9, 126.0, 125.7, 124.7 (8*dd*, ^1J(C,H) = 168, ^3J(C,H) = 8); 86.3, 84.9 (2*dd*, ^1J(C,H) = 168, ^3J(C,H) = 7); 53.6 (*d*, ^1J(C,H) = 133); 52.1 (*q*, ^1J(C,H) = 148); 45.5 (*d*, ^1J(C,H) = 148); 44.6 (*d*, ^1J(C,H) = 133); 42.9 (*d*, ^1J(C,H) = 151); 28.9 (*q*, ^1J(C,H) = 128); 23.8, 22.1, 21.3, 20.8 (4*t*, ^1J(C,H) = 130). MS (70 eV): 299 (11, $M^+ - H(SC_6H_4NO_2)_2$), 287 (14), 283 (12), 281 (16), 271 (29), 257 (21), 255 (12), 254 (12), 252 (25), 250 (11), 239 (45), 197 (45), 195 (39), 181 (60), 169 (100). Anal. calc. for $C_{30}H_{28}N_2O_8S_2$ (608.692): C 59.19, H 4.63; found: C 59.13, H 4.56.

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