Articles

Synthesis and Reactions of α-Methylene-β-keto Sulfones†

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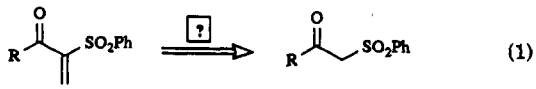
Modified Jones oxidation of 2-(benzenesulfonyl)-2-alken-1-ols and rapid nonnucleophilic workup below 0 °C yields a variety of α-methylene-β-keto sulfones **4**, including crystalline parent **4a** and also **e–h**, which can be stored at −20 °C without change. In the absence of nucleophiles, the new compounds are stable (heating in benzene) toward dimerization and polymerization. Thus, selective cross-reactions are feasible. With alcohols, including sterically hindered tertiary alcohols and also with 2-(ethoxycarbonyl)cyclopentanone, the compounds function as efficient Michael acceptors, even in the absence of base catalysis. In moist ether, 2-(benzenesulfonyl)-1-penten-3-one (**4b**) suffers rearrangement to 2-(benzenesulfonyl)ethyl propanoate (**9**). Sulfonylated alcohol **7** and strained α-hydroxyoxetane **8** are assumed as intermediates. Toward electron-rich aromatics and heteroaromatics, α-methylene-β-keto sulfones **4** behave as electrophiles in Friedel–Crafts-type functionalizations. The new compounds are also dienophilic: of the two groups (acetyl and benzenesulfonyl) attached to the ethylenic terminus in **4a**, benzenesulfonyl has been found to preferentially adopt the endo position in cycloadditions of cyclopentadiene and also cyclohexadiene. Prototype 3-(benzenesulfonyl)-3-buten-2-one (**4a**) is a crystalline methyl vinyl ketone (MVK) equivalent which, unlike MVK, undergoes controlled free-radical additions with nucleophilic radicals. In hetero-Diels–Alder reactions, **4a** serves as a 1-oxa-1,3-butadiene unit, combining with a wide range of alkenes of graded nucleophilicity. Electron deficient **4a** also reacts as an enophile toward 1,1-dialkylated ethylenes. In the presence of $ZnCl_2$·OEt_2, the ene reaction with β-pinene can be suppressed completely in favor of cycloaddition, giving a robustadial building block in 85% yield. In further applications to natural products chemistry, the synthesis of frontalin and novel oxatricyclics are described.

Introduction

The benzenesulfonyl group is a versatile and flexible functionality that enjoys increasing popularity as a temporary control element and activating group in organic synthesis.[1-8] The group can be removed reductively and also oxidatively with formation of ketones.[9] It stabilizes adjacent carbanions,[10] useful in carbon–carbon bond forming reactions. Benzenesulfinate anion also serves as a leaving group with S_N1-reactive substrates[11,12] and, given sufficient intramolecular nucleophilic pressure, in the formation of cyclopropanes[13] ("chemical chameleon"[1] or Umpolung). Elimination to olefins can be accomplished also,[14] as, for example, in the second step of the Julia alkene synthesis.[7] Vinylic sulfones have been cross-coupled with Grignard reagents[15] and used widely in cycloadditions.[16-18] Significantly, bulky benzenesulfonyl has recently been shown to be useful for acyclic stereocontrol.[18b]

Results

We here report the synthesis and reactions of α-methylene-β-keto sulfones. Previously, Michael acceptors containing a 1,1-diactivated ethylenic unit have frequently been obtained by methylenation of the corresponding C–H acid. While introduction of an alkylidene group is often

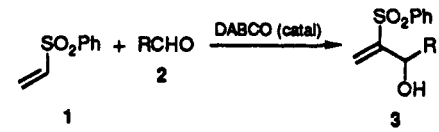


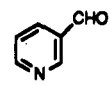
(1)

straightforward (e.g., enal **5** below), simple *methylenation* proved difficult. The desired methylenated sulfones were assumed to be too reactive, and this premise turned out to be correct.

†Dedicated to Professor Michael Hanack, Tübingen, with good wishes on his forthcoming 60th birthday.

Table I. 2-(Benzenesulfonyl)-3-hydroxyalkenes (3α–h)



aldehyde[a] RCHO (2)	reaction time (days)	product no.	isolated yield (%)
$(CH_2O)_n$	2	**3α**	33
CH_3CHO	10	**3a**	81
CH_3CH_2CHO	11	**3b**	66[b]
$CH_3(CH_2)_2CHO$	28	**3c**	60
$(CH_3)_2CHCH_2CHO$	77	**3d**	65
PhCHO	21	**3e**	44
	1	**3f**	46
$Ph(CH_2)_2CHO$	21	**3g**	46[c]
$Ph(CH_2)_3CHO$	15	**3h**	63

[a] 1–5 equiv of aldehyde **2** were used with respect to phenyl vinyl sulfone. [b] Refers to 50% conversion of **1**. [c] Refers to 78% conversion of **1**.

As a more promising approach, we investigated the oxidation of allylic alcohols **3**, which were prepared from

(1) Recent overview: Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.
(2) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.
(3) Schank, K. *Methoden der Organischen Chemie*, (Houben-Weyl) 4th ed.; Thieme: Stuttgart, 1985; Vol. E 11, p 1129.
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(5) *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; pp 1–1210.
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(7) For an excellent review on sulfone-based olefination reactions (Julia olefination), see: Kocienski, P. *Phosphorus Sulfur Relat. Elem.* **1985**, *24*, 97–127. See also: Julia, M.; Paris, J.-M. *Tetrahedron Lett.* **1973**, 4833. Hird, N. W.; Lee, T. V.; Leigh, A. J.; Maxwell, J. R.; Peakman, T. M. *Tetrahedron Lett.* **1989**, *30*, 4867.

0022-3263/91/1956-4098$02.50/0

Table II. α-Methylene-β-keto Sulfones (4a–h) Prepared by eq 2

4	R	isolated yield (%)	mp (°C)
a	Me	59	47[a]
b	Et	49[c]	oil[b]
c	n-Pr	38[c]	oil[b]
d	CH_2CHMe_2	36[c]	oil[b]
e	Ph[d]	71	98[a]
g	$(CH_2)_2Ph$	56	88[a]
h	$(CH_2)_3Ph$	51	63[a]

[a] Needles. [b] bp > 50 °C (0.03 Torr) dec. [c] Decomposition on chromatography (silica gel). [d] Compound 4e has been prepared by a Russian group; see ref 52.

phenyl vinyl sulfone (1) and aldehydes (2) (Table I). For example, the reaction of ethanal (2a) with 1 in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO)[19] could be scaled up and gave 3a in 20-g quantities. Isolation of 3a was simplified by Kugelrohr distillation. The distillate, previously obtained as an oil by chromatography,[19] solidified (mp 34–36 °C) at −20 °C. Compared with other Michael acceptors such as methyl acrylate,[20] methyl vinyl ketone,[21a] and acrylonitrile,[21b,22] phenyl vinyl sulfone (1) reacted less readily with aldehydes. Isaacs has reported that high pressure accelerates a number of DABCO-catalyzed coupling reactions.[23] In general, this was not observed for 1 (probably because the solubility of sulfone 1 in the reaction mixture is decreased by increasing pressure). However, 200 atm instead of 7 kbar was a good compromise in the case of propanal (2b), which is known to produce 3b with difficulty under normal conditions.[19] At 200 atm, the formation of 3b was cleaner and fewer side reactions were observed, allowing spectroscopic identification of 3b for the first time.

Scheme I. α-Cleavage of α-Benzenesulfonyl-β-hydroxy Ketone 7

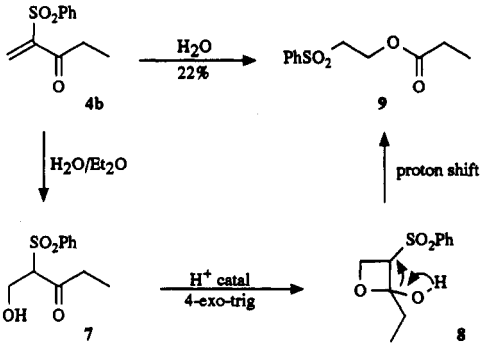

Table III. Michael Additions of Various Alcohols

6	R	reaction time (h)	yield (%)
a	Me	1	quant
b	Et	1	90
c	t-Bu	24	86
d	Thex (Me_2CHCMe_2)	18	81
e	H	72[a]	51

[a] Aqueous acetone used.

In preliminary experiments, a number of oxidizing agents including $BaMnO_4$,[24] pyridinium dichromate,[25] pyridinium chlorochromate,[26] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,[27] tetrapropylammonium perruthenate (TPAP)/4-methylmorpholine N-oxide (NMO)[28] and CrO_3/t-BuOOH[29] were tried unsuccessfully. However, it became clear later that the conditions for working up the reaction mixtures were not compatible with the high sensitivity of the activated sulfones (see also Table III).

A modified Jones oxidation at low temperature was successful (eq 2 and Table II). Defined conditions of workup (nonnucleophilic), temperature (−20 °C), and the amount of ether used were essential for rapid crystallization of the products. On prolonged standing of the mother liquor *without* crystallization, yields of 4 dropped due to

(8) Connective synthesis of acetylenes via β-oxo sulfones: Lythgoe, B.; Waterhouse, I. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2429.

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(15) Cross-coupling of vinylic sulfones with Grignard reagents: Fabre, J.-L.; Julia, M.; Verpeaux, J.-N. *Tetrahedron Lett.* **1982**, *23*, 2469. Alvarez, E.; Cuvigny, T.; Hervé du Penhoat, C.; Julia, M. *Tetrahedron* **1988**, *44*, 111, 119.

(16) Sulfonyl dienes: Padwa, A.; Harrison, B.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.* **1989**, *54*, 4232. Bäckvall, J. E.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 5347. Bäckvall, J. E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396. Chou, T. S.; Hung, S. C. *J. Org. Chem.* **1988**, *53*, 3020. Chou, T. S.; Hung, S. C.; Tso, H. H. *Ibid.* **1987**, *52*, 3394. Cuvigny, T.; Hervé du Penhoat, C.; Julia, M. *Tetrahedron* **1986**, *42*, 5329. Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *J. Am. Chem. Soc.* **1983**, *105*, 6335. Eisch, J. J.; Galle, J. E.; Hallenbeck, L. E. *J. Org. Chem.* **1982**, *47*, 1608.

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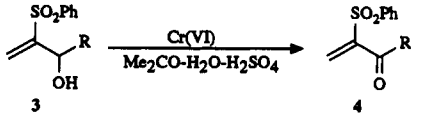
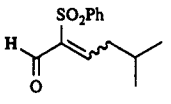
(29) Muzart, J. *Tetrahedron Lett.* **1987**, *28*, 2133.

consecutive reactions (cf. eq 3 and Scheme I).



3 4 (2)

In nearly all cases, small amounts of the corresponding sulfonylated enals could be observed as byproducts of the oxidation. The enal derived from **3d** was isolated readily (cf. **5**). Enal **5** containing a bulky alkylidene group instead

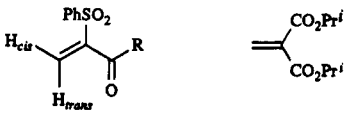


5

of a methylene group is kinetically more stable. Presumably, the formation of enals is due to acid-catalyzed rearrangement of **3** to the primary allylic alcohol and oxidation.

The low-temperature oxidation procedure was applied to all allylic alcohols except **3α** and **3f** (Table II). α-Methylene-β-keto sulfones **4a,e–h** were crystalline (needles) and gave accurate microanalyses. They could be stored for prolonged periods at −20 °C. The comparative high yield (71%) of **4e** (cf. also Table II, footnote *d*) is due to benzenoid resonance and ease of crystallization (mp 98 °C). The compounds were sensitive to water (cf. Scheme I) and, of course, to other nucleophiles. The oily **4b,c** were thermally sensitive, turning dark around 50 °C on attempted further purification by distillation. All compounds **4** decomposed readily on TLC (silica gel, alumina)!

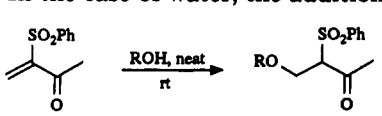
NMR Spectra. The high reactivity of **4** is paralleled by a drastic downfield shift of the terminal methylene protons ($H_\beta cis$ = 7.12–7.18, $H_\beta trans$ = 6.72–6.86 ppm, except for benzene derivative **4e** ($H_\beta trans$ = 6.33 ppm)).



4 **i**

By comparison, a conventional, doubly activated 1,1-diethylene such as a methylenemalonic ester (i) resonates at δ 6.42.[30] Empirical increments for the substituents SO_2R and COR predict[31] that $\delta(H_\beta cis)$ = 7.2 and $\delta(H_\beta trans)$ = 7.3. Presumably, for the new 1,1-disubstituted ethylenes **4**, steric and anisotropic effects cannot be ignored.

Synthetic Applications. From the point of view of chemical reactivity and potential in synthesis, it is important that the α-methylene-β-keto sulfones do *not* dimerize or polymerize, allowing a great variety of cross-reactions in high yield. The unusually high reactivity of parent crystalline **4a** was demonstrated by its Michael-type reactions with alcohols under *neutral* conditions. Even highly hindered tertiary alcohols such as thexyl alcohol reacted without further catalysis at room temperature, giving functionalized ethers **6c,d** in high yield (Table III and eq 3). In the case of water, the addition was rather



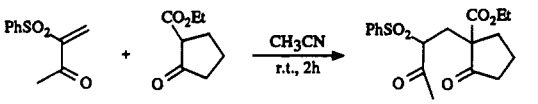
4a **6** (3)

Table IV. Michael Additions with Cyclic Enamines

enamine	R^1, R^2	*n*	reaction time (h)	product	isolated yield (%)	diastereomeric mixture
12a	$-(CH_2)_2O-(CH_2)_2-$	1	2.0	**14**	50	2:1
12b	CH_3, CH_3	1	1.5	**14**	43	2:1
12c	$-(CH_2)_4-$	1	1.0	**14**	38	4:1
13	$-(CH_2)_2O-(CH_2)_2-$	2	2.0	**15**	75	2:1

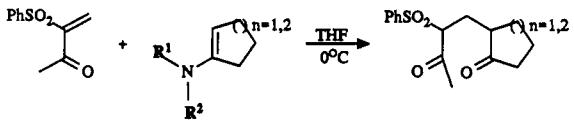
slow, partly explaining the success of the Jones procedure for preparing **4**. Simple aldol **6e** could be purified by rapid column chromatography, but on removal of the solvent the compound was unstable. Structurally related ethyl ketone **4b** rearranged on attempted crystallization of the ether extract (moist) of the mother liquor (Scheme I). Benzenesulfonylated aldol **7** and strained cyclic hemiacetal **8** are rational intermediates en route to ester **9** (22%), which was isolated in addition to unidentified products.

β-Keto ester **10** (pK_a ~11) and **4a** combined to give adduct **11**, containing a quaternary carbon. The mild, neutral conditions probably ensure that **11** suffers neither retro-Michael nor intramolecular aldol reaction (eq 4).



4a **10** **11** 69%, 3:2 diastereomeric mixture (4)

Similarly, enamines **12** and **13** gave 1,5-diketones **14** and **15** after aqueous workup (eq 5, Table IV). The least reactive enamine, i.e., cyclohexenyl derivative **13**, gave the highest yield in this reaction.

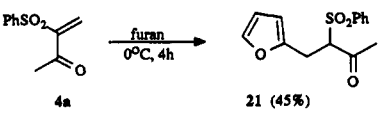


4a **12**, n = 1; **13**, n = 2 **14**, n = 1; **15**, n = 2 (5)

No [2+2] or [2+4] cycloadducts could be observed. However, **12a** reacted to give also [3.2.1]bicycle **20** as byproduct (Scheme II).

The OH proton of **20** appeared as a sharp singlet (δ 3.75) in the ^1H NMR spectrum, even in $CDCl_3$ solvent, suggesting slow proton exchange and consistent with an exo-oriented OH group bonded intramolecularly to the carbonyl oxygen or to the neighboring benzenesulfonyl group. The bulky benzenesulfonyl group[32] adopts an equatorial position ($^3J_{3,4_{ax}}$ = 12 Hz). The formation of bicyclic **20** suggests zwitterion **16**[33] as an intermediate. Hypothetical cycloadduct **17** contains a vinylogous benzenesulfonyloxy group (see the following text), which facilitates ring opening.

Friedel–Crafts Type Reactions. 3-(Benzenesulfonyl)-3-buten-2-one (**4a**) and an excess of furan reacted at 0 °C, giving **21**, whereas anisole required heating at 120 °C, giving predominantly para isomer **22A** (eqs 6 and 7).



4a **21** (45%) (6)

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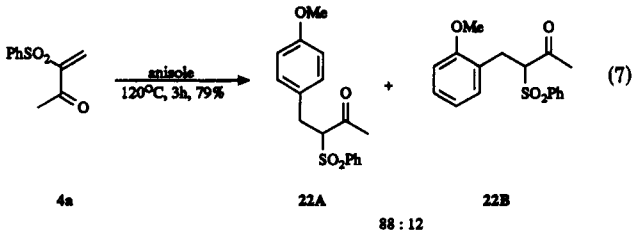
(32) The *A* value of $PhSO_2$ is 2.50 ± 0.05. See: Eliel, E. L.; Kandasamy, D. *J. Org. Chem.* **1976**, *41*, 3899, Table IV, ref d.

(33) Eaton, P. E.; Bunnelle, W. H. *Tetrahedron Lett.* **1984**, *25*, 23. Eaton, P. E.; Bunnelle, W. H. *Can. J. Chem.* **1984**, *62*, 2612. Bunnelle, W. H.; Meyer, L. A. *J. Org. Chem.* **1988**, *53*, 4038.



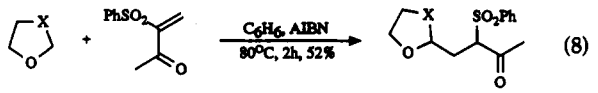
(7)

4a 22A 22B

88 : 12

These electrophilic substitutions were run in the *absence* of catalysts. Less reactive aromatics such as *tert*-butylbenzene failed to react.

Free-Radical Additions. Another aspect of the special reactivity of **4a** is the formation of α-functionalized ethers **23** and **24**, which were isolated from the reaction with cyclic ethers in the presence of AIBN, in a preparatively simple manner (eq 8).



(8)

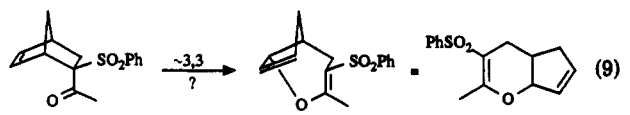
4a

23 X = CH_2
24 X = O

While related adducts have been obtained with methyl vinyl ketone itself,[34] the addition of the nucleophilic radical required special conditions in this case (*t*-BuOOH/2$TiCl_3$). Apparently, by virtue of the benzenesulfonyl group, **4a** becomes markedly *radicophilic* and enters into a controlled radical chain reaction, giving the observed 1:1 adducts without special precautions. Polymerization is suppressed.

Pericyclic Reactions. Because of their high reactivity and dense functionality, compounds **4** could be expected to be versatile partners in cycloaddition reactions. This was tested with crystalline compound **4a** as prototype. Crossed Diels–Alder reactions (Table V) occurred with conjugated dienes, giving [4+2] adducts in good yields under mild conditions (cf. **25**–**28**).

The reaction with 2,3-dimethylbutadiene to give **25** was carried out at 80 °C in a sealed tube in order to have a comparison with the reaction of isobutene (Scheme IV). To ensure a reasonable solubility of anthracene in benzene, adduct **28** was prepared at reflux. In the case of cyclopentadiene and cyclohexadiene endo (endo referring to benzenesulfonyl) adducts **26a** and **27a** were formed preferentially. The acetyl group adopted the exo position. Exo adduct **26α** was detected in traces only (^{13}C NMR). Hence, bicyclic dihydropyran **26b** can arise either by a retro-Claisen rearrangement of **26α** (eq 9) or by a direct hetero-Diels–Alder reaction with inverse electron demand. The preferred endo orientation of benzenesulfonyl[35] and methanesulfonyl[36] in Diels–Alder additions with vinyl sulfones has been noted. Our results suggest that this preference persists, even in the presence of the strongly competing acetyl group: Due to the neighboring olefinic



(9)

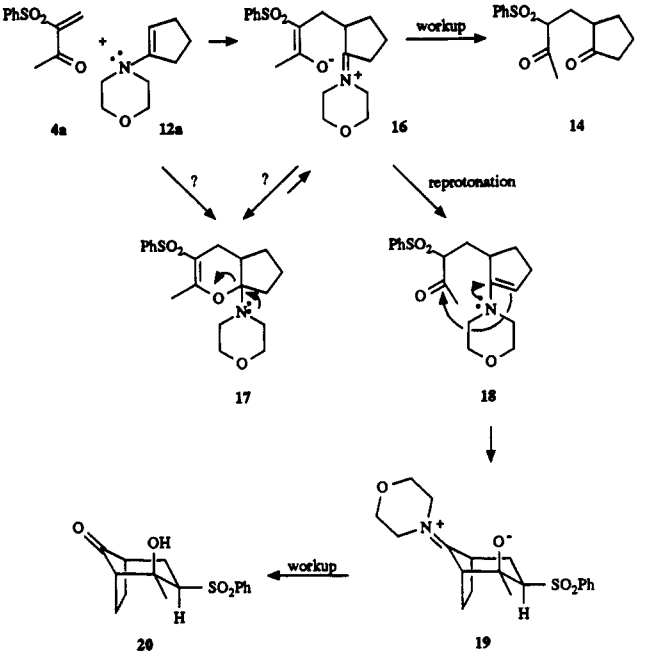
26α 26b

(34) $TiCl_3$ has been suggested to function as initiator and also terminator in this free-radical Michael-type addition. Cf. Citterio, A.; Arnoldi, A.; Griffini, A. *Tetrahedron* **1982**, *38*, 393. Cf. also Ogura, K.; Yanagisawa, A.; Fujino, T.; Takahashi, K. *Tetrahedron Lett.* **1988**, *29*, 5387. Inomata, K.; Sahara, H.; Kinoshita, H.; Kotake, H. *Chem. Lett.* **1988**, 813.

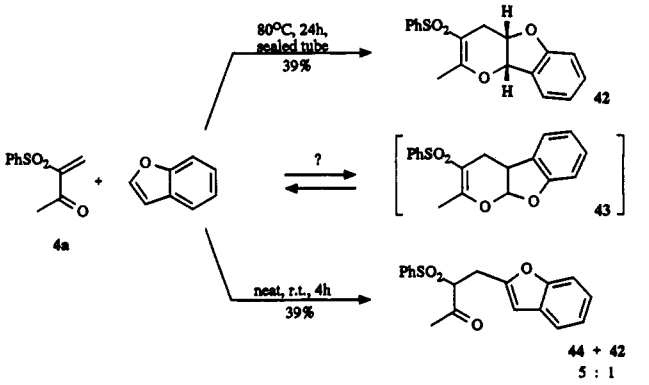
(35) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853. Maccagnani, G.; Montanari, F.; Taddei, F. *J. Chem. Soc. B* **1968**, 453.

(36) Philips, J. C.; Oku, M. *J. Org. Chem.* **1972**, *37*, 4479.

Scheme II. Formation of Bicyclic Keto Alcohol 20



Scheme III. Reactions of 4a with Benzo[*b*]furan



π bond, the endo position of norbornene is less encumbered than the exo position.

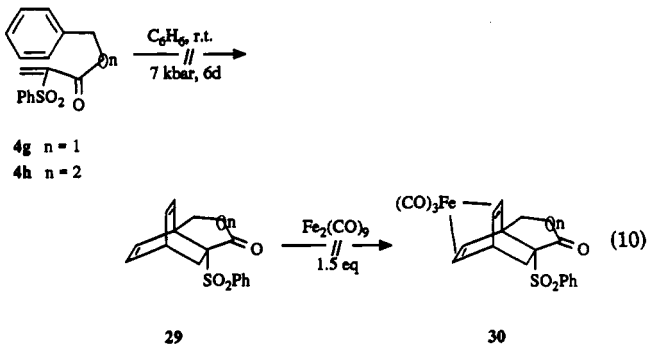
As a further test of the dienophilic reactivity of **4a**, we thought it of interest to investigate the extreme case of an intramolecular cycloaddition to benzene. Since the cycloreversion of cycloadduct **29** from **4g** and **4h** should be facile, one can speculate that complexation of desired adduct **29** with a metal carbonyl fragment might drive the intramolecular cyclization (iron tricarbonyl complexes of 1,4-dihydro-1,4-bridged benzenes have been prepared[37,38]). However, no evidence for tricyclization was obtained (eq 10).

3-(Benzenesulfonyl)-3-butene-2-one (**4a**) is an excellent partner for hetero-Diels–Alder reactions with inverse electron demand[39] (Table VI). Electron-rich 2π compounds react well, including sterically hindered 2-isopropylidene-1,3-dithiane (entry 1). While the dihydrofuran adduct could be isolated without difficulty at room temperature (entry 4), the reaction with 2,3-dihydro-4*H*-pyran had to be conducted at 0 °C (entry 7). Apparently, de-

(37) Landesberg, J. M.; Sieczkowski, J. *J. Am. Chem. Soc.* **1971**, *93*, 972.

(38) (Bicyclo[3.2.2]nona-6,8-dien-3-one)(tricarbonyl)iron: Hill, A. E.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1974**, *96*, 4597.

(39) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987. Tietze, L. F. *J. Heterocycl. Chem.* **1990**, *27*, 47.



(10)

parture of the vinylogous benzenesulfonyloxy leaving group (vinylogous benzenesulfonate) in **37** is easier compared with the more rigid **34**, behaving as formulated for the combination with enamines (Scheme II, **17** → **16**). With acetylenic dienophiles, only 2:1 adduct **41** was isolated (entry 12). As an orthoester it was found to be quite unstable.

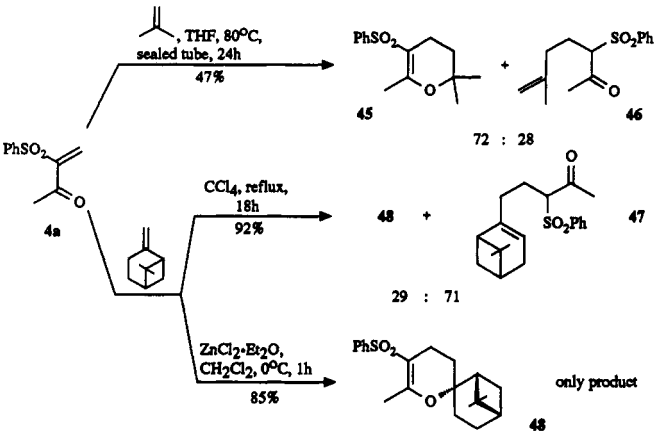
The reaction with heteroaromatic benzofuran (Scheme III) is of interest because adduct **43** was not observed, although HMO calculations[39] had predicted the lowest transition-state energy for its formation. Instead, "wrongly oriented" regioisomer **42** was isolated after comparatively forcing conditions (thermodynamic control). Because of the combined effect of heteroaromaticity and benzenesulfonate vinylogy, hypothetical adduct **43** is probably too fragile. The formation of **44** mirrors the electrophilic substitution of parent furan with **4a** (formation of **21**, eq 6).

The conditions for the reaction of **4a** with isobutene (Scheme IV) were identical with those of the Diels–Alder reaction of **4a** with 2,3-dimethylbutadiene (Table V, entry 1). Aside from major product **45**, i.e., cycloadduct formed via inverse electron demand, the ene product **46** was formed also. Ene products were not detected in the normal Diels–Alder reaction of 2,3-dimethylbutadiene and **4a**.

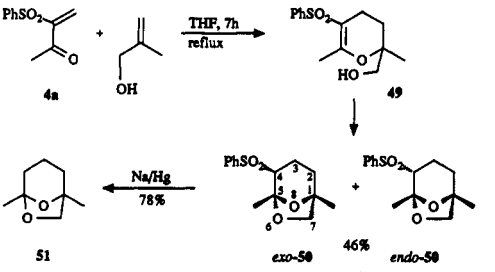
Being a 1,1-dialkylated ethylene, (−)-β-pinene is a reactive and common ene component. With **4a** as an *enophile*,[40] the ene product **47** indeed predominated over cycloadduct **48** under normal conditions of thermal activation. To our surprise, in the presence of activated zinc chloride[41] the ene product was not formed. Instead, cycloadduct **48** arose as only product[42,43] in high yield. Tricycle **48** contains part of the skeleton of robustadial A and B,[44] which are used as antimalaria agents and isolated from the leaves of *Eucalyptus robusta* Smith (Myrtaceae).

Another application of **4a** natural product chemistry concerns the synthesis of pheromones (Scheme V).[45] Sulfonylated frontalin precursor **50** was obtained on reaction with methallyl alcohol in one pot. While intermediate **49** could be isolated as colorless oil, it was unstable and suffered easy 5-*exo-trig* cyclization to crystalline di-

Scheme IV. Isobutene and β-Pinene in Reactions with 4a

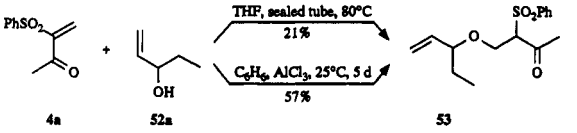


Scheme V. One-Pot Route to Sulfonylated Frontalin



oxabicycle **50**. Reductive desulfonylation afforded racemic frontalin **51**.[46]

In contrast, allyl alcohol **52** reacted with **4a** to Michael adduct **53** under two sets of conditions (comparison with eq 3 suggests that secondary alcohol **52** should react *less* readily than primary methallyl alcohol (cf. also Scheme V) in the Michael addition to **4a**). Apparently, on changing from methallyl alcohol to **42**, the *1-oxadienophilicity* of the olefinic double bond is reduced decisively. Attempted reaction of the corresponding *tert*-butyldimethylsilyl ether gave no cycloadduct either (eq 11). After activation of



(11)

the double bond of an allyl alcohol by incorporation of enol ether oxygen (cf. **54**, **57**), cycloaddition to form dihydropyrans **55** and **58** occurred (Scheme 6). These cyclized to tricycles **56** and **59**, but more slowly than the less rigid monocyclic alcohol **49** (Scheme 5).

Tricycles **56** and **59** were formed as diastereomeric mixtures, both with endo and exo benzenesulfonyl groups. The major (endo) epimer of **59** was obtained by fractional crystallization from ether and its structure was determined by X-ray diffraction analysis (unpublished results). Ring fusion at C(1)–C(6) is cis, consistent with a concerted hetero Diels–Alder addition in the first reaction step. Eventually, the endo and exo series were distinguished by the ^3J coupling pattern of the proton α to the sulfonyl group (cf. Scheme VI). In the case of the two epimeric compounds **56**, the oxacyclohexane chair is flattened by

(40) Nomenclature, definition, and reactivity of ene reactions: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

(41) Mayr, H.; Striepe, W. *J. Org. Chem.* **1985**, *50*, 2995. Cf. also Mucha, B.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1989**, *30*, 4489. Kolb, H. C.; Hoffmann, H. M. R. *Tetrahedron* **1990**, *46*, 5127.

(42) β-Pinene and simple methyl vinyl ketone have been reported to react, in the presence of $ZnBr_2$, to give only ene product (62%): Snider, B. B. *J. Org. Chem.* **1974**, *39*, 255.

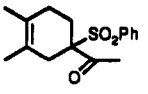
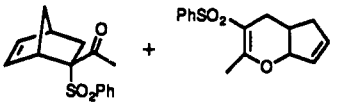
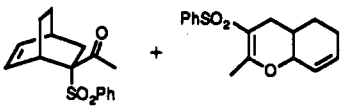
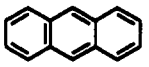
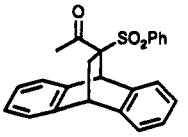
(43) There was no evidence for the formation of a second diastereomer. We assume that **4a** attacks β-pinene from the sterically more accessible direction in diastereofacial manner, as usual.

(44) (a) Cheng, Q.; Snyder, J. K. *J. Org. Chem.* **1988**, *53*, 4562. (b) Salomon, R. G.; Lal, K.; Mazza, S. M.; Zarate, E. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 5213. Krause, M.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1990**, *31*, 6629.

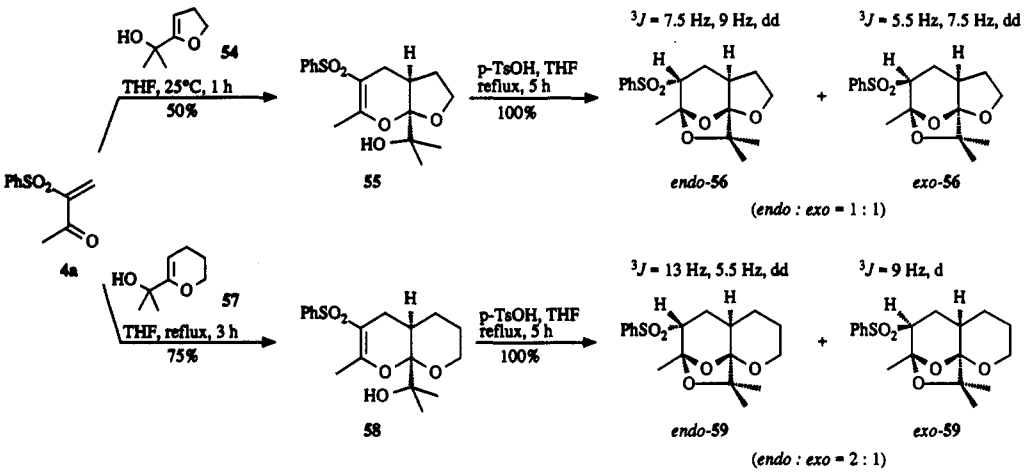
(45) Mori, K. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981, Vol. 4, p 1.

(46) Previously, rac-**51** was obtained from acetone (6 equiv), methallyl alcohol (1 equiv) and aqueous polyformaldehyde (1 equiv) in 12% overall yield: D'Silva, T. D. J.; Peck, D. W. *J. Org. Chem.* **1972**, *37*, 1828. We believe this approach is mechanistically related to ours. Cf. also Mundy, B. P.; Otzenberger, R. D.; DeBernadis, A. R. *J. Org. Chem.* **1971**, *36*, 2390.

Table V. Activated Olefin 4a as a Dienophile

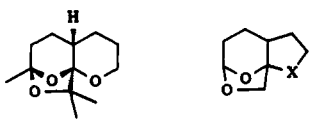
diene	reaction conditions	cycloadduct(s)	isolated yield (%)
	THF, 80 °C, 24 h, sealed tube	 **25**	72
	neat	 **26a** + **26b** 5:1	76
	toluene, rt, 19 h	 **27a** + **27b** 3:2	72
	benzene, 80 °C, 3 h	 **28**	76

Scheme VI. Tandem Route to Novel Trioxatricycles



the C(1)–C(6) fusion with the five-membered ring, and the ^3J coupling contants approach each other, more so than in *endo*-**59**. In *exo*-**59**, the signal of the equatorial proton adjacent to the axial benzenesulfonyl group appears as a simple doublet. In fact, the ^{1}H NMR pattern of trioxatricycle *exo*- and *endo*-**59** is analogous to that of the sulfonylated frontalins *exo*-**50** ($^3J_{3,4}$ = 7 Hz, b d) and *endo*-**50** ($^3J_{3,4}$ = 12, 5 Hz, dd). Electron-attracting, axial benzenesulfonyl reduces $^3J_{3,4}$ of the trans diaxial proton. Reductive removal of the benzenesulfonyl group of **59** gave **60** in 83% yield.

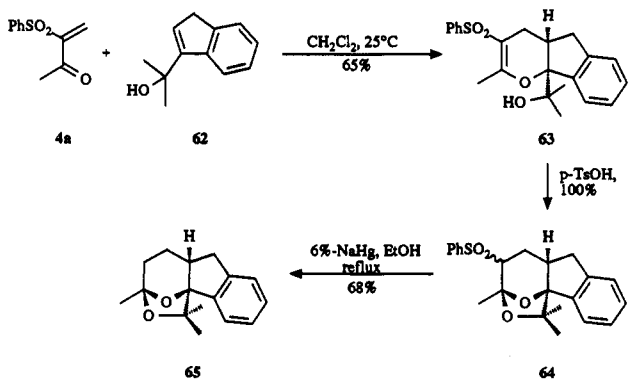
Previously, neither trioxatricycle **61a** nor any derivatives appears to have been described (CAS online). Surpris-



60 (12) **61a**: X = O; **61b**: X = CH_2

ingly, even dioxatricyclic skeleton **61b** was unknown (cf. **65**). Following the approach to frontalin **51**, benzotricycle **65** was easily prepared (Scheme VII) and had a weak citrus odor.

Scheme VII. Synthesis of Benzotricycle 65

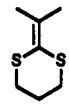
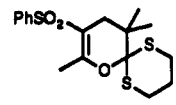
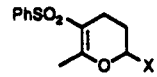
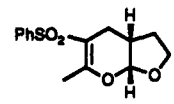
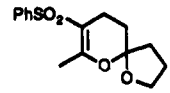
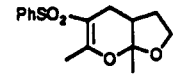
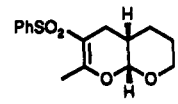
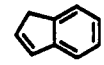
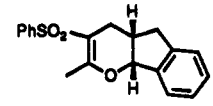
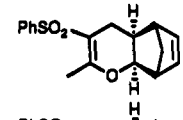
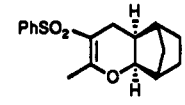
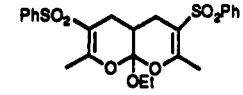
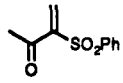


Conclusions

While a number of α-alkylidene-β-keto sulfones had been known before,[47] the parent α-methylene-β-keto sulfones **4** are accessible for the first time. As a class of compounds, these sulfones are highly reactive and unlike methyl vinyl ketone (MVK), they do not dimerize. Their

(47) Steroidal ring-D building block: Posner, G. H.; Switzer, C. *J. Am. Chem. Soc.* **1986**, *108*, 1239.

Table VI. Hetero-Diels–Alder Reactions of 4a

entry	olefin	reactn cond solvent, temp, time	product(s) structure	no.	isolated yield (%)
1		CCl_4, 25 °C, 5 h		31	91
2	 X = SPh	THF, 0 °C, 0.5 h		32	66
3	X = OEt	CCl_4, 0 °C, 0.5 h		33	93
4	 X = H	THF, 25 °C, 2.5 h		34	86
5	X = CN	THF, 25 °C, 30 h	none		
				35	
6		THF, 25 °C, 6 h	+1:1		57
				36	
7		THF, 0 °C, 1 h		37	36
8		nat, 25 °C, 3 h		38	58
9		THF, reflux, 5 h		39	42
10		THF, 25 °C, 36 h		40	42
11	 X = NEt_2	THF, 0 → 25 °C, 2–5 h	none		
12	ethoxyacetylene	THF, 25 °C, 22 h		41	43
12	X = $SiMe_3$	THF, reflux, 19 h	none		
14		toluene, 160 °C, 48 h, sealed tube	none		

kinetic stability is attributed to the bulk[48-50] of the benzenesulfonyl group. The title compounds enter into a variety of selective condensation and cyclization reactions that cannot be realized with methyl vinyl ketone and its analogues.

Experimental Section

General Comments. Solvents were distilled and dried before use. Anhydrous conditions were achieved by flame-drying flask and equipment under N_2. Merck silica gel (0.02–0.063 mm) was used for flash chromatography. Reactions were monitored by TLC. Yields were not optimized except for the preparation of 3-(benzenesulfonyl)-3-buten-2-one (**4a**).

Preparation of Allylic Alcohols (3α–3h). 2-(Benzenesulfonyl)-2-propen-1-ol (3α). Sulfone 1 (840 mg, 5 mmol), paraformaldehyde (450 mg, 5 mmol), and DABCO (60 mg, 0.5 mmol) were dissolved in dry THF (4 mL) and refluxed for 48 h, while a further 2 equiv of paraformaldehyde were added. After the mixture was cooled to room temperature and concentration in vacuo, flash chromatography (Et_2O/PE, (3:1)) gave 0.33 g (33%) of oily **3α**: IR ($CHCl_3$) 1315, 1310, 1140, 1080 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.92–7.46 (m, 5 H, arom H), 6.40 (d, ^2J = 0.75 Hz, 1 H, olef H), 6.08 (m, 1 H, olef H), 4.27 (m, 2 H, CH_2), 2.59 (b s, 1 H, OH); 50-MHz ^{13}C NMR ($CDCl_3$) δ 149.82 (s, CH_2CCHOH), 139.04 (s, arom C), 133.90, 129.32, 128.06 (d, arom C), 125.00 (t, $=CH_2$), 60.04 (t, CH_2); MS (70 eV, rt) *m/z* (relative intensity) 198 (3, M^+), 168 (14), 142 (14), 125 (100), 97 (17), 78 (34), 77 (89); MS exact mass calcd for $C_9H_{10}O_3S$ 198.0350, found 198.0351.

General Procedure for the Preparation of Alcohols 3a–h. DABCO (0.1 equiv) was added to a mixture of sulfone 1 (1 equiv) and aldehyde (1–5 equiv) and left at room temperature for the

(48) α-Trialkylsilyl vinyl ketones as annulating agents: Stork, G.; Singh, J. *J. Am. Chem. Soc.* **1974**, *96*, 6181. Stork, G.; Ganem, B. *Ibid.* **1973**, *95*, 6152.
(49) Jung, M. E. *Tetrahedron* **1976**, *32*, 3.
(50) Boeckman, R. K., Jr. *Tetrahedron* **1983**, *39*, 925.
(51) Jones, B. in Chinn, L. J. *Selection of Oxidants in Synthesis*; Marcel Dekker: New York, 1971.

indicated reaction time. Excess volatile aldehyde was removed in vacuo, and the oily residue was purified as described in the following text.

3-(Benzenesulfonyl)-3-buten-2-ol (3a). Sulfone 1 (20.16 g, 120 mmol), 33 mL of freshly distilled acetaldehyde, DABCO (1.5 g, 12 mmol); reaction time 10 days; the product was distilled in a Kugelrohr apparatus (130 °C oven temperature (0.05 Torr)) to give 20.61 g (81%) of a colorless oil, which crystallized at −20 °C, mp 34–36 °C. For spectroscopic data, see ref 19.

2-(Benzenesulfonyl)-1-penten-3-ol (3b). (a) General procedure: sulfone 1 (1.68 g, 10 mmol), propanal (2.9 g, 50 mmol), DABCO (0.12 g, 50 mmol); reaction time 11 days; conversion 50%. The product was purified by flash chromatography (Et_2O/PE, gradient 1:2–1:1) to yield 0.75 g (66%, based on recovered 1) of a colorless oil. (b) The same quantities of reactants were left in an autoclave (200 bar, room temperature) for 8 days, and the resulting oil was easily purified by column filtration (Et_2O/PE, 2:1). Yield (0.75 g) as for a: IR ($CHCl_3$) 1450, 1305, 1170, 1040, 1080, 590 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.95–7.48 (m, 5 H, arom H), 6.42 (d, ^2J = 0.75 Hz, 1 H, olef H), 6.09 (m, 1 H, olef H), 4.29 (m,1 H, C*H*OH), 2.87 (b s, 1 H, OH), 1.61 (m, 2 H, CH_2CH_3), 0.81 (t, ^3J = 7 Hz, 3 H, CH_2CH_3); 50-MHz ^{13}C NMR ($CDCl_3$) δ 153.26 (s, CH_2CCHOH), 139.39 (s, arom C), 133.70, 129.30, 128.16 (d, arom C), 124.98 (t, $=CH_2$), 69.97 (d, *C*HOH), 29.01 (t, CH_2CH_3), 9.57 (q, CH_2CH_3); MS (70 eV, rt) *m/z* (relative intensity) 226 (2, M^+), 197 (100), 125 (21), 77 (53); MS exact mass calcd for $C_{11}H_{14}O_3S$ 226.0663, found 226.0663.

2-(Benzenesulfonyl)-1-hexen-3-ol (3c) was prepared from butanal (4 w, 60%), **2-(benzenesulfonyl)-5-methyl-1-hexen-3-ol (3d)** from isovaleraldehyde (11 w, 65%), and **2-(benzenesulfonyl)-3-phenyl-1-propen-3-ol (3e)** from benzaldehyde (3 w, 44%). Spectroscopic data, see ref 19.

2-(Benzenesulfonyl)-1-pyridyl-2-propen-1-ol (3f). Sulfone 1 (840 mg, 5 mmol), nicotinic aldehyde (1.6 g, 15 mmol), DABCO (60 mg, 0.5 mmol); reaction time 24 h; purification by flash chromatography (ethyl acetate/Et_2O (1:1)) afforded an oil, which solidified at −20 °C. Crystallization from Et_2O gave **3f** (630 mg, 46%), needles: mp 121 °C; IR ($CHCl_3$) 1320, 1310, 1165, 1145, 690 cm^{-1}; 200-MHz ^1H NMR (DMSO-d_6) δ 8.53–8.32 (m, 2 H, C*H*=NCH=), 7.74–7.40 (m, 6 H, arom H), 7.18 (m, 1 H, C=CHC*H*=CH), 6.59 (s, 1 H, olef H), 6.42 (s, 1 H, olef H), 6.36 (b s, 1 H, OH), 5.50 (b s, 1 H, C*H*OH); 50-MHz ^{13}C NMR (DMSO-d_6) δ 152.82 (s, CH_2CCHOH), 139.40 (s, arom C), 136.41 (s, CCHOH*C*), 148.68, 148.59, 134.48, 133.45, 129.15, 127.56, 123.11 (d, arom C), 126.45 (t, $=CH_2$), 66.11 (d, CHOH); MS (70 eV, 130 °C) *m/z* (relative intensity) 275 (1, M^+), 133 (100), 105 (25), 77 (31); MS exact mass calcd for $C_{14}H_{13}NO_3S$ 275.0616, found 275.0614.

2-(Benzenesulfonyl)-5-phenyl-1-penten-3-ol (3g). Sulfone 1 (1.68 g, 10 mmol), 3-phenyl-1-propanal (6.70 g, 50 mmol), DABCO (120 mg, 1 mmol); reaction time 21 days; conversion 78%. Purification by flash chromatography (Et_2O/PE (1:1)) yielded 1.09 g (46%) of a colorless oil: IR ($CHCl_3$) 1450, 1310, 1140, 1080, 700, 690 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.91–7.37 (m, 5 H, arom H), 7.31–6.97 (m, 5 H, arom H), 6.40 (d, ^2J = 0.75 Hz, 1 H, olef H), 6.08 (b s, 1 H, olef H), 4.31 (t, ^3J = 7 Hz, 1 H, C*H*OH), 3.03 (b s, 1 H, OH), 2.54 (m, 2 H, $CH_2C_6H_5$), 1.85 (m, 2 H, $CH_2CH_2C_6H_5$); 50-MHz ^{13}C NMR ($CDCl_3$) δ 153.53 (s, CH_2CCHOH), 140.97, 139.11 (s, arom C), 133.62, 129.26, 128.40, 128.35, 128.11, 125.91 (d, arom C), 124.75 (t, $=CH_2$), 67.70 (d, CHOH), 37.61 (t, $CH_2CH_2C_6H_5$), 31.49 (t, $CH_2CH_2C_6H_5$); MS (70 eV, rt) *m/z* (relative intensity) 302 (1, M^+), 143 (24), 142 (100), 141 (40), 105 (15), 91 (42), 77 (37); MS exact mass calcd for $C_{17}H_{18}O_3S$ 302.0976, found 302.0975.

2-(Benzenesulfonyl)-6-phenyl-1-hexen-3-ol (3h). Sulfone 1 (2.52 g, 15 mmol), 4-phenyl-1-butanal (6.66 g, 45 mmol), DABCO (170 mg, 1.5 mmol); reaction time 15 days. The oily product (3.0 g, 67%) was obtained after flash chromatography (Et_2O/PE (2:1)): IR ($CHCl_3$) 1315, 1305, 1150 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.91–7.40 (m, 5 H, arom H), 7.28–6.98 (m, 5 H, arom H), 6.36 (d, ^2J = 0.75 Hz, 1 H, olef H), 6.03 (s, 1 H, olef H), 4.37 (m, 1 H, C*H*OH), 2.93 (b s, 1 H, OH), 2.46 (m, 2 H), 1.57 (m, 4 H); 50-MHz ^{13}C NMR ($CDCl_3$) δ 153.45 (s, CH_2CCHOH), 141.86, 139.33 (s, arom C), 133.63, 129.33, 128.30, 128.25, 128.06, 125.74 (d, arom C), 124.87 (t, $=CH_2$), 68.45 (d, CHOH), 35.57, 35.28 (t, $CH_2CH_2CH_2$), 26.91 (t, $CH_2CH_2CH_2$); MS (70 eV, 200 °C) *m/z* (relative intensity) 316 (0, M^+), 168 (30), 125 (100), 104 (46), 77 (72); MS exact mass calcd for $C_{18}H_{17}O_2S$ 297.0949, found 297.0948.

General Procedure for the Oxidation of Allylic Alcohols (3a–h) with Jones Reagent. Jones reagent was prepared by dissolving CrO_3 (26.7 g) in concd H_2SO_4 (23 mL) and diluting to 100 mL total volume with distilled H_2O. The alcohol was dissolved in acetone (13 mL/mmol of **3**), and Jones reagent (0.25 mL/mmol of **3**) was added at once under vigorous stirring at −78 °C. After 1 h at −78 °C, the solution was allowed to warm, within 2 h, to 0 °C. The Cr(III) salts were separated by decantation and washed with acetone. The extracts and the mother liquor were combined and freed from acetone on a rotary evaporator in the cold to afford a heterogeneous mixture that was easily freed from inorganic material by extraction with several portions of ether. The combined ether extract was concentrated in vacuo (0 °C) to give the product as nearly colorless oil, which was purified as described in the following text.

3-(Benzenesulfonyl)-3-buten-2-one (4a). Optimized Procedure. Allyl alcohol **3a** (2.12 g, 10 mmol) was allowed to react with 2.5 mL of oxidation reagent. The colorless oil obtained after concentration of the mother liquor was dissolved in Et_2O (16 mL, cloudy solution) and left overnight at −20 °C. The given amount of ether effected rapid crystallization. Decantation and cautious drying of the product (0 °C, vacuum oil pump) afforded 1.23 g (59%) of **4a**, needles, mp 47 °C. The *well-dried* product could be stored for a longer period at −20 °C without change: UV (MeOH) λ_{max} 220 nm; IR (KBr) 1695, 1445, 1385, 1365, 1300, 1265, 1150, 1075, 1015, 755, 745, 690 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 8.05–7.48 (m, 5 H, arom H), 7.18 (d, ^2J = 1.5 Hz, 1 H, olef H), 6.82 (d, ^2J = 1.5 Hz, 1 H, olef H), 2.36 (s, 3 H, CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 191.79 (s, C=O), 150.08 (s, *C*C=O), 139.49 (s, arom C), 135.32 (t, $=CH_2$), 133.80, 129.27, 128.99 (d, arom C), 27.89 (q, CH_3); MS (70 eV, 40 °C) *m/z* (relative intensity) 210 (10, M^+), 195 (10), 168 (6), 146 (51), 131 (51), 125 (38), 103 (82), 77 (100), 52 (33), 44 (89); MS exact mass calcd for $C_{10}H_{10}O_3S$ 210.0350, found 210.0350. Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79. Found: C, 57.14; H, 4.86.

2-(Benzenesulfonyl)-1-penten-3-one (4b). Reaction of alcohol **3b** (0.23 g, 1 mmol) and oxidation reagent (0.25 mL) gave an oil that could neither be purified by crystallization nor by distillation. Rapid chromatography on a short silica column with ether afforded 0.11 g (49%) of oily **4b**, contaminated by decomposition products: IR (CCl_4) 1700, 1445, 1325, 1310, 1150, 1080, 690 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 8.01–7.45 (m, 5 H, arom H), 7.17 (d, ^2J = 1.5 Hz, 1 H, olef H), 6.86 (d, ^2J = 1.5 Hz, 1 H, olef H), 2.75 (q, ^3J = 7 Hz, 2 H, CH_2CH_3), 1.20 (t, ^3J = 7 Hz, 3 H, CH_2CH_3); 50-MHz ^{13}C NMR (CD_2Cl_2, APT) δ 195.57 (s, C=O), 149.42 (s, *C*C=O), 140.14 (s, arom C), 135.68 (t, $=CH_2$), 134.04, 129.26, 128.95 (d, arom C), 33.46 (t, CH_2CH_3), 7.48 (q, CH_2CH_3); MS (70 eV, rt) *m/z* (relative intensity) 224 (M^+, 1), 168 (30), 125 (100), 77 (87), 103 (25).

2-(Benzenesulfonyl)-1-hexen-3-one (4c). Oxidation of **3c** (0.24 g, 1 mmol) and purification were carried out as described for **4b**, yielding 90 mg (38%) of oily **4c**: IR (CCl_4) 1700, 1325, 1150 cm^{-1}; 200-MHz ^1H NMR (CD_2Cl_2) δ 7.99–7.45 (m, 5 H, arom H), 7.16 (d, ^2J = 1.5 Hz, 1 H, olef H), 6.82 (d, ^2J = 1.5 Hz, 1 H, olef H), 2.65 (t, ^3J = 6.5 Hz, 2 H, $CH_2CH_2CH_3$), 1.53 (m, 2 H, $CH_2CH_2CH_3$), 0.84 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_3$); 50-MHz ^{13}C NMR (CD_2Cl_2, APT) δ 195.23 (s, C=O), 149.87 (s, *C*C=O), 140.17 (s, arom C), 135.25 (t, $=CH_2$), 134.05, 129.28, 128.99 (d, arom C), 42.07 (t, $CH_2CH_2CH_3$), 17.32 (t, $CH_2CH_2CH_3$), 13.50 (q, $CH_2CH_2CH_3$); MS (70 eV, 90 °C) *m/z* (relative intensity) 238 (M^+, 2), 168 (29), 125 (98), 97 (18), 77 (100).

2-(Benzenesulfonyl)-5-methyl-1-hexen-3-one (4d) and 2-(Benzenesulfonyl)-5-methyl-2-hexen-1-al (5). Alcohol **3d** (0.51 g, 2 mmol) was allowed to react with 0.5 mL of oxidation reagent following the standard procedure. Flash chromatography (Et_2O/PE (2:1)) on silica gel gave 180 mg (36%) of oily **4d**: IR (CCl_4) 1330, 1155 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 8.01–7.48 (m, 5 H, arom H), 7.17 (d, ^2J = 2 Hz, 1 H, olef H), 6.79 (d, ^2J = 2 Hz, 1 H, olef H), 2.55 (d, ^3J = 7 Hz, 2 H, CH_2CH), 2.07 (m, 1 H, $CH(CH_3)_2$), 084 (d, ^3J = 7 Hz, 6 H, CH_3); 50-MHz ^{13}C NMR ($CDCl_3$) δ 194.66 (s, C=O), 150.24 (s, *C*C=O), 139.58 (s, arom C), 132.47 (t, $=CH_2$), 133.71, 129.05, 128.72 (d, arom C), 48.82 (t, CH_2CH), 24.73 (d, $CH(CH_3)_2$), 22.30 (q, CH_3); MS (70 eV, rt) *m/z* (relative intensity) 252 (7, M^+), 168 (30), 125 (100), 85 (24), 77 (78). Oily **5** (60 mg, 12%): IR ($CHCl_3$) 1320, 1150 cm^{-1}; 90-MHz

^{1}H NMR ($CDCl_3$) δ 9.92 (d, ^4J = 1 Hz, 1 H, CHO), 8.01–7.50 (m, 5 H, arom H), 7.85 (dt, ^4J = 1 Hz, ^3J = 8 Hz, 1 H, =CH), 2.67 (dd, ^3J = 7, 8 Hz, 2 H, CH_2CH), 1.96 (m, 1 H, $CH(CH_3)_2$), 0.99 (d, ^3J = 7 Hz, 6 H, CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 184.43 (d, C=O), 159.01 (d, =$CHCH_2$), 140.91, 104.01 (s, O=CC, arom C), 133.74, 129.23, 128.26 (d, arom C), 37.10 (t, CH_2CH), 28.65 (d, $CH(CH_3)_2$), 22.34 (q, CH_3); MS (70 eV, rt) *m/z* (relative intensity) 252 (0, M^+), 166 (65), 165 (66), 157 (57), 142 (75), 141 (100).

2-(Benzenesulfonyl)-1-phenyl-2-propen-1-one (4e).[52] Alcohol **3e** (100 mg, 0.37 mmol) and Jones reagent (0.1 mL) gave crude oily **4e**. Crystallization at −20 °C (Et_2O/PE) furnished 70 mg (71%) of **4e**, needles: mp 98 °C; IR (KBr) 1660, 1320 cm^{-1}; 300-MHz ^{1}H NMR ($CDCl_3$) δ 8.05–7.40 (m, 10 H, arom H), 7.14 (b s, 1 H, olef H), 6.33 (b s, 1 H, olef H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 189.87 (s, C=O), 149.45 (s, CC=O), 132.47 (t, =CH_2), 139.61, 135.90 (s, arom C), 134.11, 133.86, 129.80, 129.03, 128.81, 128.71 (d, arom C); MS (70 eV, 80 °C) *m/z* (relative intensity) 272 (0, M^+), 208 (51), 105 (100); MS exact mass calcd for $C_{15}H_{12}O$ 208.0881, found 208.0889. Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 66.22; H, 4.49.

2-(Benzenesulfonyl)-5-phenyl-1-penten-3-one (4g). Alcohol **3g** (300 mg, 1 mmol) was oxidized with Jones reagent (0.25 mL) to give oily product, which was crystallized from ether to furnish **4g** (170 mg, 56%): needles; mp 89 °C; IR (KBr) 1695, 1305, 1155, 745 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 8.03–7.48 (m, 5 H, arom H), 7.31–7.04 (m, 5 H, arom H), 7.12 (d, ^2J = 1.5 Hz, 1 H, olef H), 6.72 (d, ^2J = 1.5 Hz, 1 H, olef H), 3.02, 2.85 (m, 2 H, 2 H, AA'BB', CH_2CH_2); 75-MHz ^{13}C NMR ($CDCl_3$) δ 194.22 (s, C=O), 150.14 (s, CC=O), 140.80, 140.21 (s, arom C), 134.15, 129.39, 129.08, 128.90, 128.67, 126.65 (d, arom C), 135.20 (t, =CH_2), 42.07 (t, $CH_2CH_2C_6H_5$), 29.78 (t, $CH_2C_6H_5$); MS (70 eV, 80 °C) *m/z* (relative intensity) 300 (0, M^+), 298 (26), 157 (100), 128 (34), 105 (27), 91 (58), 77 (26); MS exact mass calcd for $C_{17}H_{14}O_3S$ 298.0664, found 298.0663. Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.25; H, 5.21.

2-(Benzenesulfonyl)-6-phenyl-1-hexen-3-one (4h). Alcohol **3h** (1.58 g, 5 mmol) was oxidized by Jones reagent (1.25 mL) to **4h**, which crystallized from Et_2O, needles (800 mg, 51%): mp 63 °C; IR (KBr) 1695, 1305, 1145, 750 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 8.00–7.43 (m, 5 H, arom H), 7.32–7.03 (m, 6 H, arom H, olef H), 6.68 (s, 1 H, olef H), 2.65 (t, ^3J = 7.5 Hz, 2 H, $CH_2C_6H_5$), 2.55 (t, ^3J = 7.5 Hz, 2 H, $CH_2CH_2CH_2C_6H_5$), 1.86 (quint, ^3J = 7.5 Hz, 2 H, $CH_2CH_2CH_2C_6H_5$); 50-MHz ^{13}C NMR ($CDCl_3$) δ 194.39 (s, C=O), 149.66 (s, CC=O), 141.01, 139.48 (s, arom C), 134.54 (t, =CH_2), 133.75, 128.96, 128.72, 128.39, 126.05 (d, arom C), 38.98 (t, $CH_2(CH_2)_2C_6H_5$), 34.50 (t, $CH_2CH_2CH_2C_6H_5$), 24.72 (t, $CH_2CH_2C_6H_5$); MS (70 eV, 90 °C) *m/z* (relative intensity) 314 (0, M^+), 172 (19), 104 (100), 91 (42), 77 (34); MS exact mass calcd for $C_{18}H_{17}O_3S$ 313.0898, found 313.0898. Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found: C, 68.55; H, 5.75.

Michael-Type Reactions. General Procedure for the Addition of Alcohols to 4a. Reactions were carried out by mixing Michael acceptor **4a** with various alcohols (neat) at room temperature. After the indicated reaction time, excess alcohol was removed at reduced pressure. Flash chromatography (Et_2O/PE (2:1)) of the crude products yielded compounds **6a–e** as oils.

3-(Benzenesulfonyl)-4-methoxy-2-butanone (6a). With MeOH, **4a** reacted quantitatively within 1 h to give **6a**, pure by ^{1}H NMR, *without* further purification: IR ($CHCl_3$) 1325, 1150 cm^{-1}; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.90–7.50 (m, 5 H, arom H), 4.39 (m, X-part of ABX, 1 H, $CHSO_2C_6H_5$), 3.82 (m, AB-part of ABX, diastereotopic, 2 H, OCH_2), 3.24 (s, 3 H, OCH_3), 2.41 (s, 3 H, CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 198.33 (C=O), 134.49 (s, arom C), 129.26, 128.99, 128.96 (d, arom C), 74.67 (d, $CHSO_2C_6H_5$), 68.32 (t, OCH_2), 59.18 (q, OCH_3), 31.58 (q, CH_3); MS (70 eV, 140 °C) *m/z* (relative intensity) 242 (0, M^+), 168 (20), 167 (26), 125 (75), 101 (100), 77 (53).

3-(Benzenesulfonyl)-4-ethoxy-2-butanone (6b). Reaction of **4a** (50 mg, 0.24 mmol) with dry ethanol (2 mL) for 1 h afforded 55 mg (90%) of **6b** after purification: IR ($CHCl_3$) 1720, 1320, 1150, 1110, 1085, 910 cm^{-1}; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.88–7.53 (m, 5 H, arom H), 4.39 (m, X-part of ABX, 1 H, $CHSO_2C_6H_5$), 3.88 (m, AB-part of ABX, diastereotopic, 2 H, OCH_2CH), 3.39, 3.38 (q, ^3J = 6.5 Hz, diastereotopic, 2 H, CH_2CH_3), 2.41 (s, 3 H, $COCH_3$), 1.08 (t, ^3J = 6.5 Hz, 3 H, CH_2CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 198.27 (s, C=O), 138.02 (s, arom C), 134.43, 129.38, 129.28 (d, arom C), 74.88 (d, $CHSO_2C_6H_5$), 67.11 (t, OCH_2CH), 66.31 (t, OCH_2CH_3), 31.56 (q, $COCH_3$), 14.78 (q, CH_2CH_3); MS (70 eV, 140 °C) *m/z* (relative intensity) 256 (0, M^+), 168 (34), 125 (91), 115 (100), 77 (98).

3-(Benzenesulfonyl)-4-(1,1-dimethylethoxy)-2-butanone (6c). Stirring **4a** (60 mg, 0.29 mmol) in dry *t*-BuOH (5 mL) for 24 h gave **6c** (70 mg, 86% after flash chromatography): IR ($CHCl_3$) 1725, 1320, 1310, 1190, 1150, 1080 cm^{-1}; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.89–7.52 (m, 5 H, arom H), 4.32 (m, X-part of ABX, 1 H, $CHSO_2C_6H_5$), 3.84 (m, AB-part of ABX, diastereotopic, 2 H, OCH_2), 2.37 (s, 3 H, $COCH_3$), 1.08 (s, 9 H, $C(CH_3)_3$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 198.54 (s, C=O), 138.82 (s, arom C), 134.27, 129.15, 128.89 (d, arom C), 75.44 (d, $CHSO_2C_6H_5$), 74.24 (s, $C(CH_3)_3$), 58.55 (t, OCH_2), 31.53 (q, $COCH_3$), 27.13 (q, $C(CH_3)_3$); MS (70 eV, rt) *m/z* (relative intensity) 284 (0, M^+), 269 (20), 210 (47), 141 (55), 125 (35), 87 (100), 77 (38); MS exact mass calcd for $C_{13}H_{17}O_4S$ 269.0848, found 269.0847.

3-(Benzenesulfonyl)-4-(1',1',2'-trimethylpropoxy)-2-butanone (6d). Enone **4a** (50 mg, 0.24 mmol) and 1,1,2-trimethylpropanol (1 mL) yielded 60 mg (81%) of **6d** after purification: IR ($CHCl_3$) 1720, 1320, 1310, 1150, 1080 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.98–7.52 (m, 5 H, arom H), 4.32 (m, X-part of ABX, 1 H, $CHSO_2C_6H_5$), 3.84 (m, AB-part of ABX, diastereotopic, 2 H, OCH_2), 2.36 (s, 3 H, $COCH_3$), 1.63 (m, 1 H, $CH(CH_3)_2$), 1.00, 0.98 (s, diastereotopic, 6 H, $C(CH_3)_2$), 0.77 (d, ^3J = 7 Hz, 6 H, $CH(CH_3)_2$); 50-MHz ^{13}C NMR ($CDCl_3$) δ 198.85 (s, C=O), 138.15 (s, arom C), 134.31, 129.21, 128.93 (d, arom C), 78.75 (s, $C(CH_3)_2$), 75.48 (d, $CHSO_2C_6H_5$), 58.11 (t, OCH_2), 36.19 (d, $CH(CH_3)_2$), 31.53 (q, $COCH_3$), 21.68, 21.42 (q, $C(CH_3)_2$, diastereotopic), 17.39, 17.28 (q, $CH(CH_3)_2$,m diastereotopic); MS (70 eV, rt) *m/z* (relative intensity) 312 (0, M^+), 268 (35), 250 (40), 210 (64), 141 (100), 77 (95); MS exact mass calcd for $C_{14}H_{20}O_3S$ 268.1132, found 268.1133.

3-(Benzenesulfonyl)-4-hydroxy-2-butanone (6e). Departing from the standard procedure, **4a** (600 mg, 2.88 mmol) was allowed to react in acetone (12 mL) and water (6 mL) for 3 days, giving unstable **6e** (360 mg, 51%) after rapid column filtration (silica gel, Et_2O/PE (2:1)): 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.90–7.51 (m, 5 H, arom H), 4.38 (t, ^3J = 6 Hz, 1 H, $CHSO_2C_6H_5$), 4.05 (d, ^3J = 6 Hz, 2 H, CH_2), 2.46 (s, 3 H, CH_3).

2-(Benzenesulfonyl)ethyl Propanoate (9). On attempted crystallization of the crude oxidation product from alcohol **3b** (300 mg, 1.33 mmol) and Jones reagent (0.35 mL), the resulting *moist* Et_2O mother liquor was allowed to stand at −20 °C for several days. When PE was added, ester **9** (70 mg, 22%) crystallized, needles: mp 61–63 °C; IR ($CHCl_3$) 1745, 1330, 1220, 1150, 1090, 690 cm^{-1}; 200-MHz ^{1}H NMR (CD_2Cl_2) δ 7.98–7.53 (m, 5 H, arom H), 4.39 (t, ^3J = 5.5 Hz, 2 H, OCH_2), 3.46 (t, ^3J = 5.5 Hz, 2 H, OCH_2CH_2), 2.04 (q, ^3J = 8 Hz, 2 H, CH_2CH_3), 0.97 (t, ^3J = 8 Hz, 3 H, CH_3); 50-MHz ^{13}C NMR (CD_2Cl_2) δ 173.94 (s, C=O), 140.22 (s, arom C), 143.31, 129.76, 128.51 (d, arom C), 57.90 (t, OCH_2), 55.62 (t, OCH_2CH_2), 27.40 (t, CH_2CH_3), 8.94 (q, CH_3); MS (70 eV, rt) *m/z* (relative intensity) 242 (2, M^+), 101 (98), 77 (45), 57 (100); MS exact mass calcd for $C_{11}H_{14}O_4S$ 242.0628, found 242.0612. Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.57; H, 5.84.

2-[2'-(Benzenesulfonyl)-3'-oxobutyl]-2-(ethoxycarbonyl)cyclopentanone (11). A solution of **4a** (100 mg, 0.48 mmol) in dry MeCN (2 mL) was added to a solution of ester **10** (80 mg, 0.48 mmol) in dry MeCN (2 mL) by syringe under N_2 at room temperature. The solution was stirred for 2 h and concentrated at reduced pressure. Flash chromatography (Et_2O/PE (2:1)) of the residue gave **11** (120 mg, 69%), colorless oil, diastereomeric ratio 3:2: IR ($CHCl_3$) 1740, 1720, 1320, 1310, 1265, 1200, 1150 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ (major isomer/minor isomer) 7.98–7.49 (m, 5 H, arom H), 4.62 (dd, ^3J = 9.5/2 Hz)/4.71 (dd, ^3J = 7.5/3 Hz, 1 H, $CHSO_2C_6H_5$), 4.09 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 2.46/2.42 (s, 3 H, $COCH_3$), 2.46–1.64 (m, 8 H, $CH_2CHSO_2C_6H_5$, $CH_2CH_2CH_2$), 1.19 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3); 50-MHz ^{13}C NMR ($CDCl_3$) δ 214.97/213.06 (s, CH_2C=O), 199.05/199.12 (s, CHC=O), 170.28/170.44 (s, CC=O), 136.94 (s, arom C), 134.21, 129.15 (d, arom C), 71.99/70.76 (d, $CHSO_2C_6H_5$), 61.71/61.61 (t, OCH_2), 57.96/57.88 (s, CC=O), 35.26/34.39 (t,

(52) Bazavova, I. M.; Neplyuev, V. M. *Zh. Org. Chim.* **1983**, *19*, 1237; *J. Org. Chem.* USSR (*Engl. Trans.*) **1983**, *19*, 1105.

$CH_2CHSO_2C_6H_5$), 32.16/32.01 (q, $COCH_3$), 30.12/29.86 (t, CCH_2CH_2), 19.27/19.21 (t, $CH_2CH_2CH_2$), 13.73 (q, CH_2CH_3); MS (70 eV, 140 °C) m/z (relative intensity) 366 (25, M^+), 244 (32), 196 (54), 178 (50), 155 (100), 150 (50), 125 (50), 115 (67), 77 (87); MS exact mass calcd for $C_{18}H_{22}O_6S$ 366.1137, found 366.1142.

2-[2′-(Benzenesulfonyl)-3′-oxobutyl]cyclopentanone (14) and 3β-(Benzenesulfonyl)-2β-hydroxy-2α-methylbicyclo-[3.2.1]octan-8-one (20). Michael acceptor **4a** (1 equiv) in dry THF was cooled to 0 °C, and enamine (4 equiv) was added. After the indicated reaction time at 0 °C (Scheme VI), the solvent was removed in vacuo and the crude product was purified on silica gel to give solid cyclopentanone derivative **14**, mp 86–88 °C (Et_2O), mixture of diastereomers. (a) 100 mg (0.48 mmol) of **4a** in THF (2 mL), 300 mg (1.90 mmol) of morpholinocyclopentene **12a**; reaction time 2 h, flash chromatography (Et_2O/PE (3:1)), yield 70 mg (50%), diastereomeric ratio 37:63. (b) 300 mg (1.43 mmol) of **4a** in THF (4 mL), 690 mg (5.71 mmol) of (dimethylamino)-cyclopentene **12b**; reaction time 1.5 h, flash chromatography (Et_2O/PE (9:1)), yield 180 mg (43%), diastereomeric ratio 33:67. (c) 200 mg (0.95 mmol) **4a** in THF (4 mL), 520 mg (3.8 mmol) of pyrrolidinocyclopentene **12c**; reaction time 1 h, flash chromatography (Et_2O/PE (2:1)), yield 110 mg (38%), diastereomeric ratio 19:81: IR ($CHCl_3$) 1730, 1320, 1310, 1150, 1080 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ (minor isomer/major isomer) 7.85–7.51 (m, 5 H, arom H), 4.90 (dd, ^3J = 8/7 Hz)/4.40 (dd, ^3J = 9/3 Hz, 1 H, $CHSO_2C_6H_5$), 2.46 (s, 3 H, CH_3), 2.34–1.31 (m, 9 H, $CH_2CHSO_2C_6H_5$, cyclopentanone H); 50-MHz ^{13}C NMR ($CDCl_3$) δ 219.58/218.92 (s, CH_2C=O), 200.61/199.44 (s, CH_3C=O), 136.59 (s, arom C), 134.42, 129.22 (d, arom C), 73.98/72.65 (d, $CHSO_2C_6H_5$), 45.14/46.21 (d, $CH(CH_2)_3$), 38.00/37.60 (t, CH_2C=O), 32.31/31.42 (q, CH_3), 30.44/29.76 (t, $CH_2CHSO_2C_6H_5$), 27.28/26.96 (t, $CHCH_2(CH_2)_2$), 20.55/20.35 (t, CH_2CH_2C=O); MS (70 eV, 120 °C) m/z (relative intensity) 294 (2, M^+), 168 (26), 152 (64), 151 (100), 109 (25), 84 (56); MS exact mass calcd for $C_{15}H_{18}O_4S$ 294.0926, found 294.0926. Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.21; H, 6.16. Found: C, 61.29; H, 6.18. In run a, more polar bicycle **20** was detected by TLC and isolated. Crystallization from ether afforded 10 mg (7%), needles: mp 156–158 °C; IR ($CHCl_3$) 1760, 1140 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.95–7.53 (m, 5 H, arom H), 3.75 (s, 1 H, OH), 3.46 (dd, ^3J = 12/6 Hz, 1 H, $CHSO_2C_6H_5$), 2.39–2.14 (m, 2 H, $CHCOCH$), 1.98–1.83 (m, 2 H, $CH_2CHSO_2C_6H_5$), 1.70 (s, 3 H, CH_3), 1.69–1.45 (m, 4 H, CH_2CH_2); 75-MHz ^{13}C NMR ($CDCl_3$) δ 212.31 (s, C=O), 139.22 (s, arom C), 134.24, 129.46, 128.60 (d, arom C), 77.24 (s, CCH_3), 63.86 (d, $CHSO_2C_6H_5$), 56.62 (d, CHCOH), 42.22 (d, $CHCH_2CH$), 33.42 (t, $CHCH_2CH$), 27.63 (q, CH_3), 21.28, 19.49 (t, CH_2CH_2); MS (70 eV, 130 °C) m/z (relative intensity) 294 (6, M^+), 152 (19), 96 (100), 77 (23); MS exact mass calcd for $C_{15}H_{18}O_4S$: 294.0926, found 294.0926. Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.21; H, 6.16. Found: C, 61.27; H, 6.19.

2-[2′-(Benzenesulfonyl)-3′-oxobutyl]cyclohexanone (15). A 100-mg (0.48-mmol) portion of **4a** in THF (2 mL), 400 mg (2.4 mmol) of morpholinocyclohexene **13**; reaction time 2 h. Flash chromatography (Et_2O/PE (2:1)) yielded 110 mg (75%) of white solid, mp 67–69 °C, diastereomeric ratio 2:1: IR ($CHCl_3$) 1710, 1320, 1310, 1145, 1130 cm^{-1}; 200-MHz ^1H NMR (CD_2Cl_2) δ 7.91–7.52 (m, 5 H, arom H), 4.53 (dd, ^3J = 11/3.5 Hz)/4.22 (dd, ^3J = 7.5/5 Hz, 1 H, $CHSO_2C_6H_5$) 2.35 (s, 3 H, CH_3), 2.32–1.20 (m, 11 H, $CHCH_2CH$, cyclohexanone H); 50-MHz ^{13}C NMR (CD_2Cl_2, APT) δ 212.14/211.96 (s, CH_2C=O), 200.43/200.32 (s, CH_3C=O), 137.53/137.30 (s, C_{arom}), 134.71/134.64, 129.56/129.47 (d, C_{arom}), 74.24/73.45 (d, $CHSO_2C_6H_5$), 48.75/47.62 (d, $CH(CH_2)_4$), 42.37/42.21 (t, CH_2C=O), 35.31/34.56 (t, $CHCH_2(CH_2)_3$), 32.47/31.60 (q, CH_3), 28.16, 28.10, 27.82, 27.54 (t, $CH_2(CH_2)_2CH_2$), 25.27 (t, $CH_2CHSO_2C_6H_5$); MS (70 eV, 90 °C) m/z (relative intensity) 308 (M^+, 1), 196 (11), 167 (35), 84 (81), 44 (100); MS exact mass calcd for $C_{10}H_{15}O_2$ 167.1072, found 167.1071.

2-[2′-(Benzenesulfonyl)-3′-oxobutyl]furan (21). Freshly distilled furan (2 mL) was added to **4a** (50 mg, 0.24 mmol) with stirring at 0 °C. After 4 h at 0 °C, excess furan was removed at reduced pressure and the residue purified by flash chromatography (Et_2O/PE (2:1)), giving **21** (30 mg, 45%), colorless oil: IR ($CHCl_3$) 1320, 1150, 1085 cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 7.91–7.41 (m, 5 H, arom H), 7.23 (dd, ^3J = 2 Hz, ^4J = 1 Hz, 1 H, OCH), 6.22 (dd, ^3J = 3, 2 Hz, 1 H, $OCHCH$), 5.97 (dd, ^3J = 3 Hz, ^4J = 1 Hz, 1 H, $OCCH$), 4.50 (t, ^3J = 7.5 Hz, 1 H, $CHSO_2C_6H_5$), 3.25 (d, ^3J = 7.5 Hz, 2 H, $CH_2CHSO_2C_6H_5$), 2.33 (s, 3 H, CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 199.03 (s, C=O), 149.23 (s, CO), 142.13 (d, OCH), 136.58 (s, arom C), 134.53, 129.34 (d, arom C), 110.59, 107.60 (d, $CCHCH$), 73.65 (d, $CHSO_2C_6H_5$), 31.68 (q, CH_3), 25.94 (t, CCH_2); MS (70 eV, 130 °C) m/z (relative intensity) 278 (1, M^+), 137 (100), 121 (32), 94 (29), 77 (23); MS exact mass calcd for $C_{14}H_{14}O_4S$ 278.0613, found 278.0620.

***p*- and *o*-[2′-(Benzenesulfonyl)-3′-oxobutyl]anisole (22A,B).** Crystalline **4a** (100 mg, 0.48 mmol) was added to freshly distilled anisole (2 mL). The mixture was heated at 120 °C (oil bath) for 3 h, affording colorless needles (120 mg, 79%), mp 105–107 °C, as a mixture of regioisomers (p:o = 88:12) after flash chromatography (Et_2O/PE (2:1)): IR (KBr) 1730, 1515, 1310, 1260, 1140 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ (para/ortho) 7.91–7.52 (m, 5 H, arom H), 6.86 (m, 4 H, arom H), 4.40/4.58 (dd, ^3J = 11.5/4 Hz, 1 H, $CHSO_2C_6H_5$), 3.73/3.69 (s, 3 H, OCH_3), 3.13 (m, 2 H, CH_2), 2.16/2.23 (s, 3 H, CH_3); MS (70 eV, 150 °C) m/z (relative intensity) 318 (0, M^+), 268 (44), 266 (33), 177 (100), 160 (49), 105 (49), 77 (49). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.10; H, 5.86.

3-(Benzenesulfonyl)-4-(2′-tetrahydrofuryl)-2-butanone (23). By use of a flame-dried flask fitted with a reflux condenser, **4a** (100 mg, 0.48 mmol) was dissolved in dry THF (1 mL) and dry benzene (1 mL). After a catalytic amount of AIBN was added, the mixture was refluxed for 2 h. The solvents were removed, and the crude oil was purified by flash chromatography (Et_2O/PE (2:1)) to yield 70 mg (52%) of oily **23** consisting of two diastereomers (1:1): IR ($CHCl_3$) 1720, 1320, 1310, 1150, 1080, 910 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.96–7.50 (m, 5 H, arom H), 4.49/4.25 (dd, ^3J = 10/4 Hz, 1 H, $CHSO_2C_6H_5$), 4.05–3.55 (m, 3 H, CH_2OCH), 2.43/2.35 (s, 3 H, CH_3), 2.23–1.39 (m, 6 H, $CH_2CH_2CHCH_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 200.14/199.94 (s, C=O), 136.80 (s, arom C), 134.23, 129.46, 129.09 (d, arom C), 77.25/76.62, 73.99/77.43 (d, OCH, $CHSO_2C_6H_5$), 67.88/67.38 (t, OCH_2), 33.70/32.70, 32.26/31.58 (t, $CH_2(CH_2)_2$), 31.41/31.37 (q, CH_3), 25.55/25.41 (t, $CH_2CHSO_2C_6H_5$); MS (70 eV, 120 °C) m/z (relative intensity) 282 (2, M^+), 168 (28), 141 (66), 71 (100); MS exact mass calcd for $C_{14}H_{18}O_4S$ 282.0925, found 282.0925.

3-(Benzenesulfonyl)-4-[2′-(1′,3′-dioxolanyl)]-2-butanone (24). With 1,3-dioxolane (instead of THF), **24** was obtained, 52% yield, colorless oil after column filtration (Et_2O): IR (CCl_4) 1725, 1325, 1150, 1130, 1085 cm^{-1}; 200-MHz ^1H NMR (CD_2Cl_2) δ 7.87–7.52 (m, 5 H, arom H), 4.87 (t, ^3J = 3.75 Hz, 1 H, OCH), 4.32 (dd, ^3J = 11/3 Hz, 1 H, $CHSO_2C_6H_5$), 3.93–3.68 (m, 4 H, OCH_2CH_2), 2.43–2.26 (m, 2 H, $CHCH_2$), 2.32 (s, 3 H, CH_3); 50-MHz ^{13}C NMR (CD_2Cl_2) δ 199.42 (s, C=O), 137.13 (s, arom C), 134.76, 129.61, 129.57 (d, arom C), 101.27 (d, OCH), 70.41 (d, $CHSO_2C_6H_5$), 65.63, 65.37 (t, $O(CH_2)_2$), 31.52 (q, CH_3), 31.29 (t, $CHCH_2$); MS (70 eV, 110 °C) m/z (relative intensity) 284 (0, M^+), 73 (100); MS exact mass calcd for $C_{10}H_{11}O_3S$ 211.0428, found 211.0425.

Pericyclic Reactions. 4-Acetyl-4-(benzenesulfonyl)-1,2-dimethyl-1-cyclohexene (25). Sulfonyl enone **4a** (0.2 g, 0.95 mmol) in dry THF (4 mL) was allowed to react with 2,3-dimethyl-1,3-butadiene (0.39 g, 4.76 mmol) in a sealed tube for 24 h at 80 °C. After concentration of the reaction solution, the colorless crude oil was purified by flash chromatography (Et_2O/PE (2:1)), giving oily **25** (200 mg, 72%), as the only product: IR ($CHCl_3$) δ 1310, 1145 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.80–7.48 (m, 5 H, arom H), 2.72 (b s, 2 H, CH_3CCH_2C), 2.46–2.23 (m, 2 H, $CH_2CH_2CCH_2$), 2.39 (s, 3 H, $COCH_3$), 1.97–1.88 (m, 2 H, $CH_3CCH_2CH_2$), 1.67, 1.52 (b s, 6 H, H_3CC=CCH_3); 50-MHz ^{13}C NMR ($CDCl_3$) δ 202.22 (s, C=O), 135.16 (s, arom C), 134.14, 130.14, 128.79 (d, arom C), 126.09, 122.11 (s, C=C), 75.85 (s, CC=O), 32.64 (t, CH_3CCH_2C), 28.79 (t, $CH_3CCH_2CH_2$), 27.74 (q, $COCH_3$), 25.49 (t, $CH_3CCH_2CH_2$), 19.33, 18.44 (q, H_3CC=CCH_3); MS (70 eV, rt) m/z (relative intensity) 292 (0, M^+), 151 (30), 150 (18), 135 (22), 88 (32), 86 (99), 84 (100); MS exact mass calcd for $C_{10}H_{15}O$ 151.1122, found 151.1122.

***exo*-4-Acetyl-4-(benzenesulfonyl)bicyclo[2.2.1]hept-1-ene (26a).** Freshly distilled cyclopentadiene (2 mL) was added to crystalline **4a** (100 mg, 0.48 mmol) at 0 °C with stirring. After 2 h, excess cyclopentadiene was removed in vacuo. Flash chromatography (Et_2O/PE 2:1) gave a 5:1 mixture (^1H NMR) of **26a** and **26b** (100 mg, 76%) as an oil. Further separation of the isomers by column chromatography failed. The oil was heated in toluene

at reflux, but could not be converted into **26b**, the isomer ratio remaining constant: IR ($CHCl_3$, inter alia) 1305, 1145 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.78–7.47 (m, 5 H, arom H), 6.32 (dd, ^3J = 5.5 Hz/^3J = 3 Hz, 1 H, CCHC*H*), 5.98 (dd, ^3J = 5.5 Hz/^3J = 3 Hz, 1 H, CH_2CHCH), 3.67 (m, 1 H, CCH), 3.02 (m, 1 H, CCH_2CH), 2.56–2.28 (m, 2 H, CCH_2), 2.33 (s, 3 H, CH_3), 2.03 (sym m, 1 H, $CCHCH_2$), 1.53 (sym m, 1 H, $CCHCH_2$); 50-MHz ^{13}C NMR ($CDCl_3$) δ 202.02 (s, C=O), 142.55 (d, CCHCH), 137.48 (s, arom C), 134.25 (d, CCHCHCH), 133.99, 129.48, 128.83 (d, arom C), 84.89 (s, CCO), 49.14 (d, CCH), 47.72 (t, CCH_2), 42.36 (d, CCH_2CH), 33.05 (t, $CCHCH_2$), 29.83 (q, CH_3); MS (70 eV, 50 °C) *m/z* (relative intensity) 276 (28, M^+), 210 (27), 150 (26), 135 (99), 117 (23), 92 (30), 77 (25), 43 (100); MS, exact mass calcd for $C_{15}H_{16}O_3S$ 276.0820, found 276.0820.

***exo*-5-Acetyl-5-(benzenesulfonyl)bicyclo[2.2.2]oct-2-ene (27a) and 4-(Benzenesulfonyl)-3-methyl-2-oxabicyclo-[4.4.0]deca-3,9-diene (27b).** Enone **4a** (100 mg, 0.48 mmol) was allowed to react with 1,3-cyclohexadiene (80 mg, 0.95 mmol) in dry CCl_4 (3 mL) for 19 h at room temperature. After evaporation, flash chromatography (Et_2O/PE (2:1)) afforded **27a** (60 mg, 43%) and **27b** (40 mg, 29%) as a colorless oil. Compound **27a** did not rearrange to **27b** when heated in toluene at reflux. **27a**: IR ($CHCl_3$) 1305, 1145 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.76–7.45 (m, 5 H, arom H), 6.29 (dd, ^3J = 9/7 Hz, 1 H, CCHC*H*), 6.13 (dd, ^3J = 9/7 Hz, 1 H, CCHCHC*H*), 3.59 (m, 1 H, CCH), 2.76 (m, 1 H, CCH_2CH), 2.34 (s, 3 H, CH_3), 2.65–2.55, 2.34–2.31, 2.18–1.27 (m, 6 H, CCH_2, $(CH_2)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 202.10 (s, C=O), 137.62 (s, arom C), 137.59, 133.97, 131.50, 129.27, 129.01 (d, arom C, HC=CH), 81.42 (s, CCH_2), 34.12 (d, CCH), 30.63 (t, CCH_2), 30.04 (d, CCH_2CH), 28.62 (q, CH_3), 24.55, 20.74 (t, $(CH_2)_2$); MS (70 eV, rt) *m/z* (relative intensity) 290 (3, M^+), 149 (63), 72 (54), 44 (100); MS exact mass calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0978. **27b**: IR ($CHCl_3$) 1625, 1240, 1150, 910 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.94–7.47 (m, 5 H, arom H), 5.94 (dt, ^3J = 10 Hz/^3J = 3.5 Hz, 1 H, OCHC*H*), 5.78 (sym m, 1 H, OCHCHC*H*), 4.35 (dd, ^3J = 3.5 Hz/^3J = 4 Hz, 1 H, OCH), 2.28 (t, ^5J = 1.5 Hz, 3 H, $OCCH_3$), 2.16–1.27 (m, 7 H, $CH_2CH(CH_2)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 160.91 (s), 142.92 (s, arom C), 132.98, 129.93, 129.67 (d, arom C), 126.63 (d, OCHCH), 125.05 (d, OCHCHCH), 108.55 (s), 71.48 (d, OCH), 29.92 (d, CCH_2CH), 26.56, 24.58, 22.66 (t, $CCH_2CH(CH_2)_2$), 19.18 (q, CH_3); MS (70 eV, rt) *m/z* (relative intensity) 290 (3, M^+), 168 (27), 149 (21), 125 (100), 77 (77); MS exact mass calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0978.

11-Acetyl-11-(benzenesulfonyl)dibenzobicyclo[2.2.2]octadiene (28). A mixture of enone **4a** (50 mg, 0.24 mmol) and anthracene (90 mg, 0.48 mmol) in dry benzene (5 mL) was refluxed for 3 h. Removal of the solvent gave a crystalline residue, which was separated by flash chromatography (Et_2O/PE (1:2)), affording **28** (70 mg, 76%), colorless needles, mp 175 °C dec: IR ($CHCl_3$) 1305, 1140, 1080, 910 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.87–7.07 (m, 13 H, arom H), 5.22 (s, 1 H, $H_5C_6O_2SCCH$), 4.26 (t, ^3J = 3Hz, 1 H, $H_5C_6O_2SCCH_2CH$), 2.68 (AB-quartet, ^2J = 13.5 Hz/^3J = 3 Hz, 2 H, CH_2), 2.39 (s, 3 H, CH_3); 50-MHz ^{13}C NMR ($CDCl_3$) δ 199.59 (s, C=O), 144.07, 138.46, 137.94, 137.45 (s, arom C), 133.91, 129.51, 128.63, 127.01, 126.92, 126.39, 126.09, 125.01, 123.90, 123.09 (d, arom C), 83.39 (s, $H_5C_6O_2SC$), 48.42 (d, $H_5C_6O_2SCCH$), 43.86 (d, $H_5C_6O_2SCCH_2CH$), 33.12 (t, $H_5C_6O_2SCCH_2$), 28.45 (q, CH_3); MS (70 eV, 160 °C) *m/z* (relative intensity) 388 (8, M^+), 247 (44), 203 (25), 178 (100); MS exact mass calcd for $C_{24}H_{20}O_3S$ 388.1133, found 388.1133. Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19. Found: C, 73.98; H, 5.29.

General Procedure for the Preparation of Hetero-Diels–Alder Adducts (31–41). A solution of oxabutadiene **4a** in dry THF (1 mL/0.24 mmol) was added to the neat dienophile at 0 °C. Stirring was continued at the given temperature and reaction time. The solvent was removed (occasionally together with volatile dienophile) at reduced pressure. Flash chromatography (Et_2O/PE (2:1), unless stated otherwise) yielded the adducts.

3-(Benzenesulfonyl)-7,11-dithia-1-oxa-2,5,5-trimethylspiro[5.5]undec-2-ene (31). Enone **4a** (50 mg, 0.24 mmol) in dry CCl_4 (4 mL) (instead of THF) reacted with 2-isopropylidene-1,3-dithiane[53] (80 mg, 0.48 mmol) in CCl_4 (1 mL) for 5 h at room temperature. Flash chromatography (Et_2O/PE (1:1)) gave 80 mg (91%) of colorless needles, mp 98–100 °C (Et_2O): IR ($CHCl_3$) 1635, 1300, 1150, 1000, 910 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.85–7.50 (m, 5 H, arom H), 3.25, 2.75 (m, 4 H, $SCH_2CH_2CH_2$), 2.30 (d, ^5J = 1.5 Hz, 2 H, CCH_2), 2.25 (t, ^5J = 1.5 Hz, 3 H, $OCCH_3$), 2.01 (m, 2 H, SCH_2CH_2), 1.06 (s, 6 H, $C(CH_3)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 158.07 (s), 142.15 (s, arom C), 132.67, 128.91, 126.60 (d, arom C), 112.69 (s), 96.27, (s, OCS), 37.87 (s, $C(CH_3)_2$), 35.37 (t, $SCH_2CH_2CH_2$), 26.54 (t, CCH_2), 24.36 (t, SCH_2CH_2), 24.08, 18.23 (q, $C(CH_3)_2$); MS (70 eV, 90 °C) *m/z* (relative intensity) 370 (1, M^+), 159 (100), 144 (11), 86 (8), 77 (8); MS exact mass calcd for $C_{17}H_{22}O_3S_3$ 370.0731, found 370.0729. Anal. Calcd for $C_{17}H_{22}O_3S_3$: C, 55.11; H, 5.98. Found: C, 55.17; H, 5.98.

5-(Benzenesulfonyl)-3,4-dihydro-6-methyl-2-(phenylthio)-2*H*-pyran (32). Sulfonyl enone **4a** (100 mg, 0.48 mmol) was combined with phenyl vinyl sulfide (330 mg, 2.4 mmol) at 0 °C. After 0.5 h **32** was isolated (110 mg, 66%), colorless needles: mp 112–114 °C (ether); IR ($CHCl_3$) 1630, 1305, 1200, 1150, 1070 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.85–7.52 (m, 5 H, arom H), 7.42–7.28 (m, 5 H, arom H), 5.44 (dd, ^3J = 6.5/4 Hz, 1 H, OCH), 2.46 (m, 2 H, $=CCH_2$), 2.26 (t, ^5J = 1 Hz, 3 H, CH_3), 2.09 (m, 2 H, $=CCH_2CH_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 160.05 (s, $CSO_2C_6H_5$), 142.43 (s, arom C), 132.81 (s, arom C), 132.79, 132.41, 129.08, 128.09, 126.76 (d, arom C), 111.95 (s, CCH_3), 83.61 (d, OCH), 27.10 (t, $=CCH_2$), 20.41 (t, $=CCH_2CH_2$), 19.08 (q, CH_3); MS (70 eV, 70 °C) *m/z* (relative intensity) 346 (13, M^+), 236 (20), 205 (19), 136 (100), 109 (19), 77 (30); MS exact mass calcd for $C_{18}H_{18}O_3S_2$ 346.0697, found 346.0698. Anal. Calcd for $C_{18}H_{18}O_3S_2$: 62.40; H, 5.24. Found: C, 62.45; H, 5.32.

5-(Benzenesulfonyl)-3,4-dihydro-2-ethoxy-6-methyl-2*H*-pyran (33). A solution of ethyl vinyl ether (2 mL) in CCl_4 (4 mL) was added to **4a** (100 mg, 0.48 mmol) in CCl_4 (4 mL). After the solution was stirred for 0.5 h at 0 °C, attempted purification of the crude oil by chromatography on silica gel failed due to decomposition. However, crystallization from PE (−20 °C) afforded 130 mg (93%) of **33**, colorless needles: mp 69–70 °C; IR (KBr) 1630, 1300, 1250, 1160, 1060 cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 7.94–7.46 (m, 5 H, arom H), 5.04 (dd, ^3J = 3.5/3 Hz, 1 H, OCH), 3.80, 3.58 (dq, ^3J = 9.5/7.5 Hz, diastereotopic, 2 H, OCH_2), 2.27 (t, ^5J = 1.5 Hz, 3 H, $OCCH_3$), 2.0–1.68 (m, 4 H, CH_2CH_2), 1.15 (t, ^3J = 7 Hz, 3 H, CH_2CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 159.98 (s, $CSO_2C_6H_5$), 143.15 (s, arom C), 132.55, 129.24, 126.60 (d, arom C), 111.95 (s, OC=C), 97.64 (d, OCH), 64.29 (t, OCH_2), 26.28 (t, $=CCH_2$), 18.86 (t, $=CCH_2CH_2$), 18.54 (q, $OCCH_3$), 15.09 (q, CH_2CH_3); MS (70 eV, 60 °C) *m/z* (relative intensity) 282 (27, M^+), 141 (56), 140 (58), 125 (20), 111 (84), 77 (44), 72 (100); MS exact mass calcd for $C_{14}H_{18}O_4S$ 282.0926, found 282.0926. Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43. Found: C, 59.64; H, 6.49.

5-(Benzenesulfonyl)-3,4-dihydro-6-methyl-2*H*-tetrahydrofuro[2,3-*b*]pyran (34). Oxabutadiene **4a** (50 mg, 0.24 mmol) was allowed to react with dihydrofuran (1 mL) for 2 h at room temperature. After chromatography (ether), 60 mg (86%) of **34** was obtained as a colorless oil: IR ($CHCl_3$) 1630, 1305, 1155, 1070 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.91–7.48 (m, 5 H, arom H), 5.37 (d, ^3J = 3.5 Hz, 1 H, OCH), 4.17–3.87 (m, 2 H, OCH_2), 2.57 (b s, 2 H, $=CCH_2$), 2.31 (t, ^5J = 1 Hz, 3 H, CH_3), 1.97 (b m, 3 H, OCH_2CH_2CH); 50-MHz ^{13}C NMR ($CDCl_3$) δ 160.34 (s, $CSO_2C_6H_5$), 142.49 (s, arom C), 132.73, 129.09, 126.76 (d, arom C), 108.16 (s, OC=C), 100.93 (d, OCH), 68.51 (t, OCH_2), 36.66 (d, $=CCH_2CH$), 26.97 (t, $=CCH_2$), 22.33 (t, OCH_2CH_2), 19.08 (q, CH_3); MS (70 eV, 150 °C) *m/z* (relative intensity) 280 (20, M^+), 137 (53), 77 (27), 70 (100). MS exact mass calcd for $C_{14}H_{16}O_4S$ 280.0769, found 280.0769.

8-(Benzenesulfonyl)-7-methyl-1,6-dioxaspiro[4.5]dec-7-ene (35) and 5-(Benzenesulfonyl)-3,4-dihydro-2,6-dimethyltetrahydrofuro[2,3-*b*]pyran (36). Oxabutadiene **4a** (100 mg, 0.48 mmol) was allowed to react with 2-methylenetetrahydrofuran[54] (200 mg, 2.4 mmol) for 7.5 h at room temperature in the presence of K_2CO_3 (100 mg). Column filtration (Et_2O/PE (1:1)) afforded a 1:1 mixture (80 mg, 57%) of isomers **35** and **36**, separated by preparative TLC, giving colorless oils. **35**: IR (CCl_4) 1630, 1315, 1305, 1160, 1145, 720 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.90–7.46 (m, 5 H, arom H), 4.00 (m, 2 H, OCH_2), 2.47 (m, 2 H,

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=CCH_2), 2.24 (t, ^5J = 1 Hz, 3 H, CH_3), 2.20–1.67 (m, 6 H, =CCH_2CH_2, $OCH_2(CH_2)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 160.66 (s, $CSO_2C_6H_5$), 142.82 (s, arom C), 132.49, 129.21, 126.65 (d, arom C), 110.55, 107.70 (s, =COC), 68.72 (t, OCH_2), 36.49, 29.46, 23.77, 20.56 (t, $OCH_2(CH_2)_2$, =$C(CH_2)_2$), 19.22 (q, CH_3); MS (70 eV, 130 °C) *m/z* (relative intensity) 294 (9, M^+), 153 (10), 124 (13), 85 (100), 77 (13); MS exact mass calcd for $C_{15}H_{18}O_4S$ 294.0925, found 294.0926. **36**: IR (CCl_4) 1625, 1320, 1310, 720 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.91–7.48 (m, 5 H, arom H), 3.93 (m, 2 H, OCH_2), 2.57 (m, 2 H, =CCH_2), 2.29 (t, ^5J = 1 Hz, 3 H, =CCH_3), 1.94 (m, 2 H, OCH_2CH_2), 1.60 (m, 1 H, OCCH), 1.43 (s, 3 H, –CCH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 160.88 (s, $CSO_2C_6H_5$), 142.61 (s, arom C), 132.66, 129.07, 126.63 (d, arom C), 107.72, 106.94 (s, =COC), 66.96 (t, OCH_2), 39.89 (d, =CCH_2CH), 27.69 (t, =CCH_2), 23.29 (t, OCH_2CH_2), 22.11 (q, –CCH_3), 19.24 (q, =CCH_3); MS (70 eV, 140 °C) *m/z* (relative intensity) 294 (10, M^+), 85 (100). MS exact mass calcd for $C_{15}H_{18}O_4S$ 294.0925, found 294.0926.

5-(Benzenesulfonyl)-3,4-dihydro-6-methyl-2*H*-tetrahydropyrano[2,3-*b*]pyran (37). Enone **4a** (100 mg, 0.48 mmol) and freshly distilled 2,3-dihydro-4*H*-pyran (2 mL) were allowed to react for 1 h at 0 °C, giving 50 mg (36%) of a colorless oil, slightly contaminated by decomposition products: IR (CCl_4) 1630, 1310, 1155, 1080, 720 cm^{-1}; 200-MHz ^1H NMR (CD_2Cl_2) δ 7.88–7.48 (m, 5 H, arom H), 5.14 (t, ^3J = 3 Hz, 1 H, OCH), 3.84–3.57 (m, 2 H, OCH_2), 2.55–1.50 (m, 7 H, $OCH_2CH_2CH_2CHCH_2$), 2.30 (t, ^5J = 1.5 Hz, 3 H, CH_3); 50-MHz ^{13}C NMR ($CDCl_3$, APT) δ 160.90 (s, $CSO_2C_6H_5$), 142.91 (s, arom C), 133.06, 129.45, 127.03 (d, arom C), 109.32 (s, OCC=), 97.28 (d, OCH), 62.31 (t, OCH_2), 31.39 (d, =CCH_2CH), 27.39 (t, =CCH_2), 24.12, 23.26 (t, $OCH_2(CH_2)_2$), 18.80 (q, CH_3); MS (70 eV, 80 °C) *m/z* (relative intensity) 294 (17, M^+), 152 (69), 125 (63), 84 (100), 77 (85), 44 (100); MS exact mass calcd for $C_{15}H_{18}O_4S$ 294.0926, found 294.0926.

4-(Benzenesulfonyl)-3-methyl-2-oxabenzobicyclo[4.3.0]-nona-3,8-diene (38). Departing from the standard method, crystalline **4a** (100 mg, 0.48 mmol) and neat indene (1 mL) were allowed to react for 3 h at room temperature. After removal of excess indene, the crude oil was purified on silica (Et_2O/PE (1:2)), furnishing an oil, which crystallized on standing at –20 °C. Recrystallization from ether gave 90 mg (58%) of **38** as colorless needles: mp 108–109 °C; IR ($CHCl_3$) 1630, 1300, 1240, 1160 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.93–7.43 (m, 5 H, arom H), 7.43–7.16 (m, 4 H, arom H), 5.29 (d, ^3J = 5.5 Hz, 1 H, OCH), 2.95 (dd, ^2J = 14 Hz/^3J = 5.5 Hz, 1 H, =$CCH_2CHCH_{2(\alpha)}$), 2.85–2.56 (m, 3 H, =$CCH_{2(\beta)}$, =CCH_2CH, =$CCH_2CHCH_{2(\beta)}$), 2.31 (t, ^5J = 1.5 Hz, 3 H, CH_3), 2.20 (m, 1 H, =$CCH_{2(\alpha)}$); 50-MHz ^{13}C NMR ($CDCl_3$) δ 163.13 (s, $CSO_2C_6H_5$), 142.73, 142.10, 141.69 (s, arom C), 132.50, 128.99, 126.66, 129.35, 126.98, 125.47, 124.83 (d, arom C), 108.98 (s, OC=C), 81.23 (d, OCH), 36.73 (d, =CCH_2CH), 36.12 (t, =CCH_2CHCH_2), 23.78 (t, =CCH_2), 19.37 (q, CH_3); MS (70 eV, 70 °C) *m/z* (relative intensity) 326 (0, M^+), 183 (13), 106 (100), 105 (29), 89 (11); MS exact mass calcd for $C_{19}H_{17}O_3S$ 325.0898, found 325.0898.

5-(Benzenesulfonyl)-4-methyl-3-oxatricyclo[6.2.1.0^{2,7}]-undeca-4,9-diene (39). Oxabutadiene **4a** (50 mg, 0.24 mmol) and 2,5-norbornadiene (80 mg, 0.87 mmol) were refluxed for 5 h in dry THF, yielding 30 mg (42%) of **39** as an unstable oil: IR (CCl_4) 1635, 1300, 1155, 1070, 720 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 7.92–7.45 (m, 5 H, arom H), 6.09 (AM-quartet, *J* = 6.5/3 Hz, 2 H, HC=CH), 3.85 (b d, ^3J = 6.5 Hz, 1 H, OCH), 3.00–1.52 (m, 7 H), 2.31 (d, ^5J = 2 Hz, 3 H, CH_3); MS (70 eV, 190 °C) *m/z* (relative intensity) 302 (6, M^+), 234 (67), 161 (20), 95 (100), 77 (20); MS exact mass calcd for $C_{17}H_{18}O_3S$ 302.0977, found 302.0977.

5-(Benzenesulfonyl)-4-methyl-3-oxatricyclo[6.2.1.0^{2,7}]undec-4-ene (40). 2-Norbornene (110 mg, 1.2 mmol) and **4a** (50 mg, 0.24 mmol) were allowed to react for 36 h, giving **40** (30 mg, 42%), colorless oil: IR ($CHCl_3$) 1630, 1300, 1150, 1070 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.88–7.48 (m, 5 H, arom H), 3.76 (d, ^3J = 6.5 Hz, 1 H, OCH), 2.67 (dd, *J* = 13/8 Hz), 2.39 (d, *J* = 5 Hz, 2 H, =CCH_2), 2.28 (d, ^5J = 1 Hz, 3 H, CH_3), 1.97, 1.77–1.40, 1.18–1.00 (m, 9 H); 50-MHz ^{13}C NMR ($CDCl_3$) δ 165.02 (s, $CSO_2C_6H_5$), 142.68 (s, arom C), 132.55, 129.03, 126.77 (d, arom C), 115.47 (s, OC=C), 83.86 (d, OCH), 45.97, 42.94, 42.56 (d, $OCHCH(CH_2)_2$, =$CCH_2CHCH(CH_2)_2$), 32.99, 28.53, 24.46, 24.19 (t, =CCH_2, $(CH_2)_2$, $CHCH_2CH$), 19.02 (q, CH_3); MS (70 eV, 150 °C) *m/z* (relative intensity) 304 (26, M^+), 210 (19), 163 (45), 133 (47), 118 (25), 91 (39), 79 (30), 66 (100); MS exact mass calcd for $C_{17}H_{20}O_3S$ 304.1133, found 304.1145.

4,8-Bis(benzenesulfonyl)-1-ethoxy-3,9-dimethyl-2,10-dioxabicyclo[4.4.0]deca-3,8-diene (41). After 22 h at room temperature, **4a** (100 mg, 0.48 mmol) and ethoxyacetylene (160 mg, 2.38 mmol, 40% solution in hexane) gave 50 mg (43%) of unstable **41**, pale yellow oil: IR ($CHCl_3$) 1150 cm^{-1}; 300-MHz ^1H NMR (C_6D_6) δ 7.71 (m, 4 H, arom H, ortho to SO_2), 6.91 (m, 6 H, arom H), 3.53 (q, ^3J = 7 Hz, 2 H, OCH_2), 2.14 (t, ^5J = 1.5 Hz, 6 H, =CCH_3), 2.49–1.97 (m, 5 H, CH_2CHCH_2), 0.99 (t, ^3J = 7 Hz, 3 H, CH_2CH_3); 75-MHz ^{13}C NMR (C_6D_6) δ 167.89 (s, OCO), 157.44 (s, $CSO_2C_6H_5$), 142.85 (s, arom C), 132.71, 129.18, 126.95 (d, arom C), 112.85 (s, OC=C), 58.37 (t, OCH_2), 30.90 (d, CH_2CHCH_2), 26.01 (t, CH_2CHCH_2), 17.92 (q, =CCH_3), 15.04 (q, CH_2CH_3); MS (70 eV, rt) *m/z* (relative intensity) 490 (0, M^+), 280 (72), 235 (17), 125 (85), 77 (45), 44 (100).

4-(Benzenesulfonyl)-2,7-dioxa-3-methylbenzobicyclo-[4.3.0]nona-3,8-diene (42). A solution of **4a** (50 mg, 0.24 mmol) and benzo[*b*]furan (140 mg, 1.2 mmol) in THF (1 mL) was heated at 80 °C for 24 h in a sealed tube. Standard workup yielded 30 mg (39%) of tricycle **42** as a colorless oil: IR ($CHCl_3$) 1630, 1320, 1310, 1150 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 7.83–7.52 (m, 5 H, arom H), 7.39 (dd, ^3J = 7.5 Hz/^4J = 1 Hz, 1 H, OCHCCH), 7.23 (dt, ^4J = 1 Hz/^3J = 8.5 Hz, 1 H, OCCHCH), 6.91 (dt, ^4J = 1 Hz/^3J = 7.5 Hz, 1 H, OCHCCHCH), 6.62 (b d, ^3J = 8.5 Hz, 1 H, OCCH), 5.51 (d, ^3J = 6.5 Hz, 1 H, OCHCHO), 5.11 (ddd, ^3J = 6.5/4.5/3 Hz, 1 H, $OCHCH_2$), 3.01 (dd, ^2J = 17 Hz/^3J = 3 Hz, 1 H, $OCHCH_{2(\alpha)}$), 2.72 (dm, ^2J = 17 Hz, 1 H, $OCHCH_{2(\beta)}$), 2.16 (m, 3 H, CH_3); 75-MHz ^{13}C NMR ($CDCl_3$) δ 164.56 (s, $CSO_2C_6H_5$), 160.38 (s, OCCH), 142.16 (s, arom C), 132.66, 131.50, 129.02, 126.97, 126.06 (d, arom C), 125.79 (s, OCHCCH), 121.27 (d, OCHCCHCH), 111.73 (s, OC=C), 110.41 (d, OCCH), 81.05 (d, OCHC), 78.37 (d, $OCHCH_2$), 24.91 (t, CH_2), 19.53 (q, CH_3); MS (70 eV, 90 °C) *m/z* (relative intensity) 328 (17, M^+), 186 (24), 167 (37), 140 (33), 125 (99), 118 (62), 77 (100); MS exact mass calcd for $C_{18}H_{16}O_4S$ 328.0769, found 328.0778.

2-[3′-(Benzenesulfonyl)-2′-oxobutyl]-2,3-benzo[*b*]furan (44). Oxabutadiene **4a** (200 mg, 0.95 mmol) and neat benzo-[*b*]furan (2 mL) were allowed to react for 4 h at room temperature, affording 100 mg (32%) of **44**, colorless needles (mp 90–92 °C, ether), besides **42** (20 mg, 7%). Separation of the reaction mixture was accomplished by flash chromatography (Et_2O/PE (1:1)) on silica gel: IR ($CHCl_3$) 1720, 1450, 1440, 1320, 1310, 1150, 1080 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 7.94–7.11 (m, 9 H, arom H), 6.38 (d, ^5J = 1 Hz, 1 H, OC=CH), 4.67 (t, ^3J = 7.5 Hz, 1 H, $C_6H_5SO_2CH$), 3.39 (d, ^3J = 7.5 Hz, 2 H, CH_2), 2.37 (s, 3 H, CH_3); 50-MHz ^{13}C NMR (CD_2Cl_2) δ 199.03 (s, C=O), 155.14 (s, $OC(CH)_4$), 152.85 (s, OC=CH), 136.95 (s, arom C), 134.98, 129.72, 129.60 (d, arom C), 128.67 (s, $OC(CH)_4C$), 124.43 (d, OCCHCH), 123.29 (d, $OC(CH)_2CH$), 121.09 (d, $OC(CH)_3CH$), 111.15 (d, $OCCH(CH)_3$), 104.92 (d, OCCHC), 73.37 (d, $CSO_2C_6H_5$), 32.17 (q, CH_3), 26.67 (t, CH_2); MS (70 eV, 130 °C) *m/z* (relative intensity) 328 (M^+, 5), 187 (87), 186 (79), 171 (100), 115 (44); MS exact mass calcd for $C_{18}H_{16}O_4S$ 328.0769, found 328.0769.

5-(Benzenesulfonyl)-3,4-dihydro-2,2,6-trimethyl-2*H*-pyran (45) and 3-(Benzenesulfonyl)-6-methylhept-6-en-2-one (46). Enone **4a** (50 mg, 0.24 mmol) and isobutene (70 mg, 1.2 mmol) in dry THF (1 mL) were allowed to react as described for adduct **25**, giving 30 mg (47%) of an oil consisting of pyran **45** and ketone **46** (72:28): IR (mixture) ($CHCl_3$) 1615, 1300, 1275, 1150, 1025, 1090 cm^{-1}; MS (70 eV, 50 °C) *m/z* (relative intensity) (mixture) 266 (100, M^+), 210 (76), 125 (73), 109 (60), 81 (62), 77 (53); MS exact mass calcd for $C_{14}H_{18}O_3S$ 266.0976, found 266.0976 (supplementary material, no. **45/46**).

2-[3′-(Benzenesulfonyl)-4′-oxopentyl]-6,6-dimethylbicyclo[3.1.1]hept-2-ene (47). A solution of **4a** (63 mg, 0.3 mmol) and (–)-β-pinene (82 mg, 0.6 mmol) in dry CCl_4 (2 mL) was refluxed for 18 h and concentrated in vacuo. The crude oil was purified by flash chromatography (Et_2O/PE (1:1)) to yield a colorless oil (95 mg, 92%) consisting of major ene adduct **47** (2 diastereomers, 1:1) and minor cycloadduct **48** (71:29): IR ($CHCl_3$) (inter al.) 1720, 1320, 1310, 1150 cm^{-1}. **47**: 200-MHz ^1H NMR ($CDCl_3$) δ (inter al.) 7.89–7.48 (m, 5 H, arom H), 5.16 (m, 1 H, =CH), 4.14 (m, 1 H, $C_6H_5SO_2CH$), 2.42/2.40 (s, 3 H, $COCH_3$), 2.32 (m, 1 H, $CHCH_{2(exo)}CH$), 2.22–1.52 (m, 8 H), 1.23 (s, 3 H, CH_3), 1.05/1.01 (d, *J* = 8 Hz, 1 H, $CHCH_{2(endo)}CH$), 0.79/0.77 (s, 3 H, CH_3); 50-MHz ^{13}C NMR ($CDCl_3$) δ (inter alia) 200.06/199.97 (s,

C=O), 145.85/145.76 (s, *C*=CH), 136.69/136.65 (s, arom C), 134.26, 129.27, 129.23, 129.11, 128.93, 128.76 (d, arom C), 116.41/116.22 (d, C=*C*H), 75.23/74.97 (d, *C*HSO$_2$C$_6$H$_5$), 45.59/45.21 (d, HC=CH), 40.71/40.65 (d, =CHCH$_2$*C*H), 38.04/37.91 (s, *C*(CH$_3$)$_2$), 33.63/33.53 (t, =CCH$_2$*C*H$_2$), 31.75/31.69, 31.58/31.28 (t, C=CH*C*H$_2$, =CCH*C*H$_2$), 27.70/27.54 (q, CO*C*H$_3$), 26.23/26.17 (t, CH=*C*CH$_2$), 24.67/24.58, 21.23/21.04 (q, C(*C*H$_3$)$_2$); MS (70 eV, 120 °C) *m/z* (relative intensity) 346 (13, M$^+$), 205 (56), 186 (81), 163 (17), 161 (33), 148 (100), 142 (76), 105 (43), 93 (58), 91 (57), 77 (41); MS exact mass calcd for C$_{20}$H$_{26}$O$_3$S 346.1603, found 346.1603.

7,7-Dimethylbicyclo[3.1.1]heptane-2-spiro-6′-(3′-(benzenesulfonyl)-2′-methyl-1′-oxahex-2′-ene) (48). Zinc dichloride monoetherate (2.2 M solution in CH$_2$Cl$_2$, 0.01 mL, ca. 0.024 mmol) was added to a stirred solution of **4a** (50 mg, 0.24 mmol) and (−)-β-pinene (30 mg, 0.24 mmol) in dry CH$_2$Cl$_2$ (2 mL) at 0 °C. The solution turned cloudy, while stirring was continued for 1 h at 0 °C. After being diluted with CH$_2$Cl$_2$, the reaction mixture was washed with aqueous saturated NaHCO$_3$ and the organic layer was dried (MgSO$_4$). Flash chromatography (Et$_2$O/PE (1:1)) gave **48** (70 mg, 85%), colorless oil, as only product: IR (CHCl$_3$) 1620, 1300, 1150, 1065, 725 cm^{-1}; 300-MHz ^{1}H NMR (CDCl$_3$) δ 7.85–7.48 (m, 5 H, arom H), 2.23 (t, ^5J = 1.5 Hz, 3 H, OCCH$_3$), 2.0–1.5 (m, 12 H), 1.27, 0.92 (s, 6 H, C(CH$_3$)$_2$); 75-MHz ^{13}C NMR (CDCl$_3$) δ 162.13 (s, *C*SO$_2$C$_6$H$_5$), 143.75 (s, arom C), 132.71, 129.36, 126.83 (d, arom C), 109.61 (s, OC=C), 83.79 (s, OCCH$_2$), 50.06 (d, OCCH), 41.17 (d, OCCHCH$_2$*C*H), 38.44 (s, *C*(CH$_3$)$_2$), 32.84, 28.81, 26.71, 25.07, 20.23 (t, 5x CH$_2$), 27.68, 23.27 (q, C(*C*H$_3$)$_2$), 19.81 (q, =CCH$_3$); MS (70 eV, 80 °C) *m/z* (relative intensity) 346 (5, M$^+$), 204 (19), 115 (100), 107 (29), 93 (34), 91 (30); MS exact mass calcd for C$_{20}$H$_{26}$O$_3$S 346.1603, found 346.1604.

4-(Benzenesulfonyl)-1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane (50). A solution of **4a** (840 mg, 4 mmol) and 3-hydroxy-2-methylpropene (1.44 g, 20 mmol) in dry THF (17 mL) was refluxed for 7 h under anhydrous conditions. After removal of the solvent, the crude brown oil was chromatographed (Et$_2$O/PE (2:1)), yielding 520 mg (46%) of frontalin precursor **50** as a white solid. Recrystallization from ether gave a 1:1 epimeric mixture, mp 119–121 °C. A second, oily fraction (100 mg, 9%) was obtained and assigned structure **49**, which was unstable on removing the solvent. *exo*-**50** (which is formed selectively at 0 °C in benzene in the presence of catalytic AlCl$_3$): IR (CHCl$_3$) 1320, 1310, 1150, 1080 cm^{-1}; 200-MHz ^{1}H NMR (CDCl$_3$) δ 7.96–7.48 (m, 5 H, arom H), 3.80 (d, ^2J = 7 Hz, 1 H, OCH$_{2(endo)}$), 3.44 (dd, ^2J = 7 Hz/^4J = 2 Hz, 1 H, OCH$_{2(exo)}$), 3.18 (b d, ^3J = 7 Hz, 1 H, C$_6$H$_5$SO$_2$C*H*$_{(endo)}$), 2.60–1.20 (m, 4 H, (CH$_2$)$_2$), 1.84 (s, 3 H, CHCC*H*$_3$), 1.26 (s, 3 H, CH$_2$CC*H*$_3$); 75-MHz ^{13}C NMR (CDCl$_3$) δ 139.97 (s, arom C), 133.58, 129.07, 128.99 (d, arom C), 106.79 (s, CH*C*), 81.49 (s, CH$_2$*C*), 75.00 (t, OCH$_2$), 65.08 (d, HCSO$_2$C$_6$H$_5$), 29.82 (t, CHCH$_2$), 25.18 (q, CHCCH$_3$), 22.25 (q, CH$_2$CCH$_3$), 20.23 (t, CHCH$_2$CH$_2$). *endo*-**50**: IR (CHCl$_3$) 1450, 1320, 1310, 1150, 1085, 1025 cm^{-1}; 200-MHz ^{1}H NMR (CDCl$_3$) δ (subtractive) 7.98–7.50 (m, 5 H, arom H), 3.83 (d, ^2J = 7 Hz, 1 H, OCH$_{2(endo)}$), 3.49 (d, ^2J = 7 Hz, 1 H, OCH$_{2(exo)}$), 3.32 (dd, ^3J = 12/5 Hz, 1 H, C$_6$H$_5$SO$_2$C*H*$_{(exo)}$), 2.44–1.89, 1.71–1.60 (m, 4 H, (CH$_2$)$_2$), 1.81 (s, 3 H, CHCC*H*$_3$), 1.31 (s, 3 H, CH$_2$CC*H*$_3$); 75-MHz ^{13}C NMR (CDCl$_3$) δ (subtrative) 139.78 (s, arom C), 133.56, 129.09, 129.05 (d, arom C), 106.46 (s, CH*C*), 79.80 (s, CH$_2$*C*), 73.21 (t, OCH$_2$), 68.21 (d, HCSO$_2$C$_6$H$_5$), 34.16 (t, CHCH$_2$), 24.60 (q, CHCCH$_3$), 22.05 (q, CH$_2$CCH$_3$), 21.10 (t, CHCH$_2$CH$_2$); MS (70 eV, 70 °C) *m/z* (relative intensity) 282 (6, M$^+$), 240 (100), 226 (22), 169 (48), 82 (54); MS exact mass calcd for C$_{14}$H$_{18}$O$_4$S 282.0926, found 282.0933. Anal. Calcd for C$_{14}$H$_{18}$O$_4$S: C, 59.55; H, 6.43. Found: C, 59.20; H, 6.34.

1,5-Dimethyl-6,8-dioxabicyclo[3.2.1]octane (51) ((±)-Frontalin). A mixture of bicycle **50** (100 mg, 0.36 mmol) and 6% NaHg (1.4 g, 3.6 mmol) in dry EtOH (2 mL) was refluxed for 17 h. After dilution with water, the mixture was extracted with ether. The ether extracts were dried (MgSO$_4$), the filtrate concentrated at 10 °C, and the crude oil purified by flash chromatography (Et$_2$O/PE (1:1)) to yield 40 mg (78%) of pure frontalin: 300-MHz ^{1}H NMR (CDCl$_3$) δ 3.93 (d, ^2J = 7 Hz, 1 H, OCH$_{2(endo)}$), 3.46 (dd, ^2J = 7 Hz/^4J = 1.5 Hz, 1 H, OCH$_{2(exo)}$), 1.95–1.47 (m, 6 H, (CH$_2$)$_3$), 1.44 (s, 3 H, CH$_2$OCC*H*$_3$), 1.33 (s, 3 H, OCH$_2$CC*H*$_3$); 75-MHz ^{13}C NMR (CDCl$_3$) δ 108.14 (s, CH$_2$O*C*), 80.06 (s, OCH$_2$*C*), 74.28 (t, OCH$_2$), 34.63, 34.01 (t, *C*H$_2$CH$_2$*C*H$_2$), 24.75 (q, CH$_2$OCCH$_3$), 23.08 (q, OCH$_2$C*C*H$_3$), 18.10 (t, CH$_2$*C*H$_2$CH$_2$).

3-[3′-(Benzenesulfonyl)-4′-oxobutoxy]-1-pentene (53). (a) In a sealed tube, **4a** (50 mg, 0.24 mmol) and 1-penten-3-ol (60 mg, 0.7 mmol) in dry THF (1 mL) were heated at 80 °C for 24 h. Flash chromatography (Et$_2$O/PE (2:1)) of the crude oil yielded 15 mg (21%) of Michael adduct **53** as a colorless oil. (b) Same amounts of reactants in dry benzene (1 mL) were used in the reaction catalyzed by AlCl$_3$ (8 mg, 0.06 mmol). After being stirred for 5 days at room temperature, the mixture was diluted with CH$_2$Cl$_2$ and washed with water. Extraction with CH$_2$Cl$_2$ and flash chromatography of the evaporated extracts afforded 40 mg (57%) of **53** (diastereomeric mixture): IR (CHCl$_3$) 1725, 1320, 1310, 1150, 1080 cm^{-1}; 90-MHz ^{1}H NMR (CDCl$_3$) δ 7.94–7.50 (m, 5 H, arom H), 5.79–4.96 (m, 3 H, H$_2$C=CH), 4.38 (m, 1 H, C*H*SO$_2$C$_6$H$_5$), 4.04–3.60 (m, 2 H, OCH$_2$), 3.47/3.44 (dt, ^3J = 6.5/6.5 Hz, 1 H, OCH), 2.40/2.38 (s, 3 H, COCH$_3$), 1.30 (m, 2 H, C*H*$_2$CH$_3$), 0.79/0.76 (t, ^3J = 7 Hz, 3 H, CH$_2$C*H*$_3$); 75-MHz ^{13}C NMR (CDCl$_3$) δ 198.61/198.60 (s, C=O), 137.88/137.86 (s, arom C), 137.78/137.52 (d, =CH), 134.36, 129.36/129.35, 129.20/128.97 (d, arom C), 118.09/117.85 (t, =CH$_2$), 84.23/83.56 (d, OCH), 75.07/74.96 (d, HCSO$_2$C$_6$H$_5$), 64.60/64.07 (t, OCH$_2$), 31.61/31.15 (q, CO*C*H$_3$), 28.04/27.94 (t, *C*H$_2$CH$_3$), 9.43/9.42 (q, CH$_2$*C*H$_3$); MS (70 eV, 120 °C) *m/z* (relative intensity) 296 (1, M$^+$), 267 (57), 211 (62), 169 (28), 141 (85), 125 (42), 87 (48), 77 (100); MS exact mass calcd for C$_{15}$H$_{20}$O$_4$S 296.1082, found 296.1082.

5-(1-Hydroxy-1,1-dimethylmeth-1-yl)-2,3-dihydrofuran (54). Acetone (1.70 g, 25.3 mmol) and 2,3-dihydrofuran (1.83 g, 26.07 mmol) were allowed to react by the literature method,[55] giving **54** (2.42 g, 75%), oil: IR (CHCl$_3$) 3440, 2980, 1360, 1180, 1140, 1100, 940 cm^{-1}; 200-MHz ^{1}H NMR (CDCl$_3$) δ 4.79 (t, ^3J = 2 Hz, 1 H, =CH), 4.38 (t, ^3J = 9.5 Hz, 2 H, OCH$_2$), 2.64 (dt, ^3J = 2/9.5 Hz, 2 H, OCH$_2$C*H*$_2$), 2.24 (b s, 1 H, OH), 1.39 (s, 6 H, CH$_3$).

4-(Benzenesulfonyl)-1-(hydroxy-1,1-dimethylmeth-1-yl)-3-methyl-2,9-dioxabicyclo[4.3.0]non-3-ene (55). Oxabutadiene **4a** (100 mg, 0.48 mmol) and alcohol **54** (120 mg, 0.96 mmol) in dry THF (2 mL) were allowed to react for 1 h at room temperature. Removal of the solvent and flash chromatography (Et$_2$O/PE (4:1)) gave **55** (80 mg, 50%), colorless oil: IR (CHCl$_3$) 1635, 1305, 1245, 1155, 1080, 980, 715 cm^{-1}; MS (70 eV, 60 °C) *m/z* (relative intensity) 338 (4, M$^+$), 110 (17), 72 (84), 71 (74); MS exact mass calcd for C$_{17}$H$_{22}$O$_6$S 338.1188, found 338.1188.

7-(Benzenesulfonyl)-8,10,10-trimethyl-2,9,11-trioxatricyclo[6.2.1.0^{1,5}]undecane (56). Alcohol **55** (60 mg, 0.18 mmol) was refluxed for 5 h in dry THF (2 mL) in the presence of *p*-TsOH (12 mg, 0.07 mmol). After cooling and removal of the solvent, column filtration (Et$_2$O/PE (2:1)) gave **56**, oily mixture of epimers (endo:exo = 1:1), in quantitative yield: IR (CHCl$_3$) 1320, 1310, 1180, 1150, 1105, 1085, 1040 cm^{-1}; 300-MHz ^{1}H NMR (CDCl$_3$) δ (mixture of epimers) 7.92–7.52 (m, 5 H, arom H), 4.12 (m, 1 H, OC*H*H), 3.92/3.86 (d, ^3J = 8 Hz, 1 H, OCH*H*), 3.34 (dd, ^3J = 7.5/9 Hz, 1 H, C$_6$H$_5$SO$_2$C*H*)/3.29 (dd, ^3J = 5.5/7.5 Hz, 1 H, C$_6$H$_5$SO$_2$C*H*), 2.49–1.78 (m, 5 H, CH$_2$CHCH$_2$), 1.72/1.74 (s, 3 H, CHCC*H*$_3$), 1.29/1.32, 1.12/1.24 (s, 6 H, C(CH$_3$)$_2$); 75-MHz ^{13}C NMR (CDCl$_3$) δ (mixture of epimers) 138.59/139.88 (s, arom C), 133.54/129.31, 129.21/128.81, 128.80/128.43 (d, arom C), 111.44/112.25, 102.62/102.77 (s, *C*OCOCH$_2$), 76.88/78.05 (s, *C*(CH$_3$)$_2$), 68.53/68.71 (t, OCH$_2$), 65.78/65.25 (d, HCSO$_2$C$_6$H$_5$), 36.12/34.82 (d, C$_6$H$_5$SO$_2$CHCH$_2$*C*H), 29.10/29.41 (t, C$_6$H$_5$SO$_2$CHCH$_2$), 26.61/25.86 (q, CHCCH$_3$), 24.36/24.22, 20.76/21.88 (q, C(*C*H$_3$)$_2$), 23.46 (t, OCH$_2$CH$_2$); MS (70 eV, rt) *m/z* (relative intensity) 338 (0, M$^+$), 96 (95), 94 (100); MS exact mass calcd for C$_{11}$H$_{17}$O$_5$S 261.0796, found 261.0796.

4-(Benzenesulfonyl)-1-(1-hydroxy-1,1-dimethylmeth-1-yl)-3-methyl-2,10-dioxabicyclo[4.4.0]dec-3-ene (58). Carbinol **57** (300 mg, 2.11 mmol)[56] and **4a** (230 mg, 1.06 mmol) in dry THF (4 mL) were refluxed for 6 h. After concentration of the reaction mixture, the crude orange oil was purified by flash chromatography (Et$_2$O/PE (2:1)) to give a colorless oil, which crystallized on standing at −20 °C. Recrystallization from the same solvent mixture afforded **58** (280 mg, 75%), white solid: mp 121–123 °C; IR (KBr) 3520, 1630, 1300, 1240, 1160, 1105, 1085, 985, 720 cm^{-1};

(55) Hedtmann, U.; Welzel, P. *Tetrahedron Lett.* **1985**, *26*, 2773.
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200-MHz ^{1}H NMR ($CDCl_3$) δ 7.88–7.44 (m, 5 H, arom H), 3.77–3.49 (m, 2 H, OCH_2), 2.84 (sym m, 1 H, $=CCH_2CH$), 2.36 (b s, 3 H, $=CCH_3$), 2.31–2.09 (m, 2 H, $=CCH_2$), 1.91 (b s, 1 H, OH), 1.71–1.42 (m, 4 H, $OCH_2(CH_2)_2$), 1.20, 1.14 (s, 6 H, $HOC(CH_3)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 161.38 (s, $CSO_2C_6H_5$), 142.57 (s, arom C), 132.56, 128.93, 126.66 (d, arom C), 109.86 (s, $=CCH_3$), 103.27 (s, OCO), 76.86 (s, $HOC(CH_3)_2$), 62.04 (t, OCH_2), 29.78 (t, OCH_2CH_2), 29.18 (d, $=CCH_2CH$), 26.56 (t, $=CCH_2$), 25.30 (q and t, $=CCH_3$ and $O(CH_2)_2CH_2$), 24.40, 18.08 (q, $HOC(CH_3)_2$); MS (70 eV, 90 °C) *m/z* (relative intensity) 352 (9, M^+), 293 (33), 192 (39), 142 (89), 127 (100), 77 (15); MS exact mass calcd for $C_{18}H_{24}O_5S$ 352.1344, found 352.1349. Anal. Calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86. Found: C, 61.44; H, 6.94.

8-(Benzenesulfonyl)-9,11,11-trimethyl-2,10,12-trioxatricyclo[7.2.1.0^{1,6}]dodecane (59). (a) The conditions for the preparation of tricyclic **56** were also employed to cyclize alcohol **58** (30 mg, 0.085 mmol) by *p*-TsOH (6 mg, 0.034 mmol) in dry THF (1 mL). Workup gave an epimeric mixture (endo:exo = 2:1) as an oil in quantitative yield. Fractional crystallization (Et_2O, −20 °C) yielded the endo epimer, mp 134–135 °C. (b) One-pot preparation of **59**: Oxabutadiene **4a** (790 mg, 3.76 mmol) and alcohol **57** (1.6 g, 11.23 mmol) in dry THF (16 mL) were refluxed for 4 h (TLC), then *p*-TsOH (65 mg, 0.38 mmol) was added and the reaction mixture heated overnight. Workup as described above gave 790 mg (60%) as an oil. *endo*-**59**: IR ($CHCl_3$) 1380, 1320, 1310, 1150, 1100, 1080, 910 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.91–7.49 (m, 5 H, arom H), 3.78 (m, 2 H, OCH_2), 3.33 (dd, ^3J = 13/5.5 Hz, 1 H, $C_6H_5SO_2CH_{exo}$), 2.30 (ddd, ^3J = 6 Hz/^2J = 13 Hz/^3J = 13 Hz, 1 H, $C_6H_5SO_2CHCH_{2(endo)}$), 1.95–1.52 (m, 5 H, $OCH_2(CH_2)_2CH$), 1.78 (s, 3 H, $CHCCH_3$), 1.46 (dd, ^2J = 13 Hz/^3J = 5.5 Hz, 1 H, $C_6H_5SO_2CHCH_{2(exo)}$), 1.12, 1.10 (s, 6 H, $C(CH_3)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 138.44 (s, arom C), 133.56, 129.31, 128.79 (d, arom C), 105.09, 104.34 (s, $COCOCH_2$), 82.91 (s, $C(CH_3)_2$), 65.58 (d, $HCSO_2C_6H_5$), 64.43 (t, OCH_2), 33.20 (d, CH_2CH), 28.20, 26.00, 25.08 (t, $CH_2CH(CH_2)_2$), 26.00 (overlapped), 25.00, 20.06 (q, CH_3); MS (70 eV, 100 °C) *m/z* (relative intensity) 352 (6, M^+), 211 (26), 184 (65), 153 (34), 124 (100); MS exact mass calcd for $C_{18}H_{24}O_5S$ 352.1344, found 352.1344. Anal. Calcd for $C_{18}H_{24}O_5S$: C 61.34; H, 6.86. Found: C, 61.31; H, 6.77. *exo*-**59**: 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.93–7.51 (m, 5 H, arom H), 3.88 (m, 2 H, OCH_2), 3.28 (d, ^3J = 9 Hz, 1 H, $C_6H_5SO_2CH_{endo}$), 2.45 (m, 1 H, $C_6H_5SO_2CHCH_{2(endo)}$), 1.87–1.47 (m, 6 H, $(CH_2)_2CH$, $C_6H_5SO_2CHCH_{2(exo)}$), 1.63 (s, 3 H, $CHCCH_3$), 1.26, 1.17 (6 H, $C(CH_3)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 140.73 (s, arom C), 133.44, 129.21, 128.34 (d, arom C), 105.47, 104.78 (s, $COCOCH_2$), 81.47 (s, $C(CH_3)_2$), 64.83 (t, OCH_2), 64.22 (d, $HCSO_2C_6H_5$), 31.33 (d, CH_2CH), 26.48, 25.17 (t, $CH_2CH(CH_2)_2$), 26.31 (q, $CHCCH_3$), 25.17 (q, H_3CCCH_3), 20.96 (q, H_3CCCH_3); MS (70 eV, 60 °C) *m/z* (relative intensity) 352 (1, M^+), 158 (22), 156 (62), 141 (45), 139 (35), 86 (66), 84 (100).

9,11,11-Trimethyl-2,10,12-trioxatricyclo[7.2.1.0^{1,6}]dodecane (60). NaHg (6%; 1.09 g, 2.8 mmol) was added to tricycle **59** (100 mg, 0.284 mmol) in dry EtOH (3 mL). After being refluxed for 6 h, the reaction mixture was poured into water, decanted from mercury, and extracted with CH_2Cl_2. After being dried ($MgSO_4$), the combined evaporated extracts were flash chromatographed (Et_2O/PE (1:2)), affording **60** (50 mg, 83%) as an oil with a pleasant odor: IR ($CHCl_3$) 2940, 1195, 1130, 1100 cm^{-1}; 300-MHz ^{1}H NMR ($CDCl_3$) δ 3.86–3.79 (m, 2 H, OCH_2), 2.19 (sym m, 1 H, CH), 1.94–1.22 (m, 8 H, 4x CH_2), 1.45 (s, 3 H, CH_2CCH_3), 1.32, 1.17 (s, 6 H, $C(CH_3)_2$); 75-MHz ^{13}C NMR ($CDCl_3$) δ 106.65, 104.36 (s, $COCOCH_2$), 81.74 (s, $C(CH_3)_2$), 64.39 (t, OCH_2), 32.75 (d, CH), 31.07 (t, CH_3CCH_2), 25.95, 25.50 (t and q, 3x CH_2, CH_2CCH_3), 25.10, 20.56 (q, $C(CH_3)_2$); MS (70 eV, rt) *m/z* (relative intensity) 212 (24, M^+), 184 (43), 154 (74), 124 (100), 97 (23), 69 (36); MS exact mass calcd for $C_{12}H_{20}O_3$ 212.1412, found 212.1413.

4-(Benzenesulfonyl)-1-(1-hydroxy-1,1-dimethylmeth-1-yl)-3-methyl-2-oxabenzobicyclo[4.3.0]nona-3,8-diene (63). Oxabutadiene **4a** (170 mg, 0.8 mmol) and carbinol **62** (140 mg, 0.8 mmol)[57] were dissolved in dry CH_2Cl_2 (2 mL), combining within 1 h at room temperature. After removal of the solvent, the crude product was purified by flash chromatography (Et_2O/PE (2:1)) to give 200 mg (65%) of **63** as a yellowish oil: IR (CCl_4) 1630, 1320, 1240, 1155, 1075, 720 cm^{-1}; MS (70 eV, 180 °C) *m/z* (relative intensity) 384 (0, M^+), 325 (40), 185 (100), 155 (84), 116 (77), 77 (80); MS exact mass calcd for $C_{19}H_{17}O_3S$ 325.0898, found 325.0899.

7-(Benzenesulfonyl)-9,11-dioxa-8,10,10-trimethylbenzotricyclo[6.2.1.0^{1,5}]undec-2-ene (64). Alcohol **63** (190 mg, 0.5 mmol) in CH_2Cl_2 (1 mL) cyclized in the presence of *p*-TsOH (9 mg, 0.05 mmol) within 1 h at room temperature. Evaporation and subsequent filtration through a short silica column (Et_2O/PE (2:1)) gave oily **64** (mixture of epimers, endo:exo = 3:1) in quantitative yield. Adding ether and storing the solution at −20 °C led to fractional crystallization of the endo epimer: mp 152–154 °C; IR (KBr) 1310, 1145 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.95–7.27 (m, 9 H, arom H), 3.32 (dd, ^3J = 10 Hz/7 Hz, 1 H, $C_6H_5SO_2CH_{exo}$), 3.14 (dd, ^2J = 16 Hz/^3J = 9 Hz, 1 H, $=CCH_{exo}$), 2.81 (dd, ^2J = 16 Hz/^3J = 5.5 Hz, 1 H, $=CCH_{endo}$), 2.65 (dddd, ^3J = 5.5/7/9/10 Hz, 1 H, $C_6H_5SO_2CHCH_2CH$), 1.93 (s, 3 H, $CHCCH_3$), 1.89 (ddd, ^2J = 14 Hz/^3J = 10/10 Hz, 1 H, $C_6H_5SO_2CHCH_{endo}$), 1.71 (ddd, ^2J = 14 Hz/^3J = 7/7 Hz, 1 H, $C_6H_5SO_2CHCH_{exo}$), 1.61 (s, 3 H, H_3CCCH_3), 1.20 (s, 3 H, H_3CCCH_3); 50-MHz ^{13}C NMR ($CDCl_3$, APT) δ 145.41, 139.73, 136.54 (s, arom C), 133.52, 129.79, 129.54, 128.41, 126.69, 126.48, 125.12 (d, arom C), 103.70 (s, OCO), 93.99 (s, $CC(CH_3)_2$), 81.67 (s, $C(CH_3)_2$), 67.19 (d, $HCSO_2C_6H_5$), 36.80 (t, $C_6H_5SO_2CHCH_2CHCH_2$), 35.25 (q, H_3CCCH_3), 26.62 (t, $C_6H_5SO_2CHCH_2$), 26.10 (d, CH_2CH), 25.16 (q, $CHCCH_3$), 22.33 (q, H_3CCCH_3); MS (70 eV, rt) *m/z* (relative intensity) 384 (0, M^+), 185 (100), 166 (18), 156 (95), 130 (30), 115 (23). Anal. Calcd for $C_{22}H_{24}O_4S$: C, 68.73; H, 6.29. Found: C, 68.50; H, 6.24.

9,11-Dioxa-8,10,10-trimethylbenzotricyclo[6.2.1.0^{1,5}]undec-2-ene (65). Reductive desulfonylation was carried out as described for **51** and **60**. Using **64** (70 mg, 0.18 mmol) and 6% NaHg (700 mg, 1.8 mmol) in dry ethanol (2 mL, reflux 1 h) gave, after aqueous workup and rapid column filtration (Et_2O/PE (1:1)) tetracycle **65** (30 mg, 68%), colorless oil, with a weak citrus odor: IR (CCl_4) 2940, 1380, 1220, 1205, 1145, 1000, 915 cm^{-1}; 300-MHz ^{1}H NMR (CD_2Cl_2) δ 7.56–7.13 (m, 4 H, arom H), 2.84 (dd, ^3J = 2/9 Hz, 2 H, $CHCH_2C$), 2.43 (m, 1 H, $C(CH_2)_2CH$), 2.06 (m, 1 H, CCH_2CH_{endo}), 1.79–1.51 (m, 3 H, CCH_2CH_{exo}, CCH_2CH_2), 1.63 (s, 3 H, CH_2CCH_3), 1.39 (s, 3 H, H_3CCCH_3), 1.31 (s, 3 H, H_3CCCH_3); 75-MHz ^{13}C NMR (CD_2Cl_2) δ 147.62, 140.17 (s, arom C), 129.16, 126.57, 125.54, 125.40 (d, arom C), 104.63 (s, CH_2CCH_3), 93.14 (s, $OCC(CH_3)_2$), 81.50 (s, $C(CH_3)_2$), 39.09 (d, CH_2CH), 35.59 (t, $(CH_2)_2CHCH_2$), 31.78 (t, CCH_2CH_2), 27.73, 26.32 (q, CH_2CCH_3, H_3CCCH_3), 22.61 (q, H_3CCCH_3), 21.73 (t, CCH_2CH_2). MS (70 eV, rt) *m/z* (relative intensity) 244 (0, M^+), 229 (23), 186 (13), 128 (18), 115 (31), 69 (25), 44 (100); MS exact mass calcd for $C_{16}H_{20}O_2$ 229.1229, found 229.1229.

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Registry No. 1, 5535-48-8; **2α**, 30525-89-4; **2a**, 75-07-0; **2b**, 123-38-6; **2c**, 123-72-8; **2d**, 590-86-3; **2e**, 100-52-7; **2f**, 500-22-1; **2g**, 104-53-0; **2h**, 18328-11-5; **3a**, 63068-00-8; (±)-**3a**, 133834-04-5; (±)-**3b**, 133834-04-5; (±)-**3c**, 133834-55-6; (±)-**3d**, 138834-56-7; (±)-**3e**, 133834-57-8; (±)-**3f**, 133834-58-9; (±)-**3g**, 133834-59-0; (±)-**3h**, 133834-60-3; **4a**, 133834-05-6; **4b**, 133834-06-7; **4c**, 133834-64-7; **4d**, 133834-65-8; **4e**, 87537-08-4; **4g**, 133834-74-9; **4h**, 133834-68-1; (*E*)-**5**, 133834-09-0; (*Z*)-**5**, 133834-08-9; (±)-**6a**, 133834-07-8; (±)-**6b**, 133834-24-9; (±)-**6c**, 133834-37-4; (±)-**6d**, 133834-61-4; (±)-**6e**, 133834-71-6; **9**, 91971-62-9; (±)-**10**, 53229-92-8; (±)-**11** (isomer 1), 133834-10-3; (±)-**11** (isomer 2), 133834-66-9; **12a**, 936-52-7; **12b**, 4840-12-4; **12c**, 7148-07-4; **13**, 670-80-4; (±)-**14** (isomer 1), 133834-11-4; (±)-**14** (isomer 2), 133834-12-5; (±)-**15** (isomer 1), 133834-13-6; (±)-**15** (isomer 2), 133834-14-7; (±)-**20**, 133834-15-8; (±)-**21**, 133834-16-9; (±)-**22A**, 133834-17-0; (±)-**22B**, 133834-67-0; (±)-**23** (isomer 1), 133834-18-1; (±)-**23** (isomer 2), 133834-72-7; (±)-**24**, 133834-19-2; (±)-**25**, 133834-19-2; (±)-**26a**, 133834-21-6; (±)-**26b**, 133834-62-5; (±)-**27a**, 133834-22-7; (±)-**27b**, 133834-63-6; (±)-**28**, 133834-23-8; (±)-**29**, 133850-31-4; **31**, 133834-25-0; (±)-**32**, 133834-26-1; (±)-**33**, 133834-27-2; (±)-**34**, 133834-28-3; (±)-**35**, 133834-29-4; (±)-**36**, 133834-30-7; (±)-**37**,

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Supplementary Material Available: ^1H spectra for **3a, 3f, 3g, 3h, 6a, 6c, 9, 11, 24, 26a, 27a/27b, 34, 35, 36, 40, 42, 44, 45/46, 47, 48, 55,** *endo*-**56**/*exo*-**56, 60, 63, 65.** ^{13}C NMR spectra for **34-36, 40** (29 pages). Ordering information is given on any current masthead page.

A Facile Synthesis of Bicyclo[*m*.*n*.1]alkan-1-ols. Evidence for Organosamarium Intermediates in the Samarium(II) Iodide Promoted Intramolecular Barbier-Type Reaction

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Samarium(II) iodide (SmI_2) has been successfully employed as a reductive coupling agent for the intramolecular Barbier-type synthesis of bicyclo[*m*.*n*.1]alkan-1-ols. Thus, a variety of 3-(ω-iodoalkyl)cycloalkanones, upon treatment with SmI_2 and a catalytic quantity of iron complex in tetrahydrofuran (THF), provide the title compounds in excellent yields. The reaction is quite general for the construction of diverse bicyclic ring systems, including the highly strained bicyclo[2.1.1]hexan-1-ol. In addition to exploring the synthetic utility of this reaction, studies have been performed which provide insight on the mechanistic details of the SmI_2-promoted intramolecular Barbier-type synthesis. Compelling evidence for the intermediacy of organosamarium species has thus been gathered.

Bridgehead bicyclic alcohols and their derivatives have played an integral role in the development of organic chemistry. Such compounds have been instrumental tools for the elucidation of fundamental reaction mechanisms,[2] and the rigid carbon skeletons which characterize these molecules have also provided ideal templates on which to examine the structural requirements and thermodynamic features of reactive intermediates (carbocations, radicals, and carbanions).[3] Synthetic chemists have also taken advantage of the inherent features of bridgehead-functionalized bicyclic systems for the construction of complex natural products and theoretically interesting molecules.[4]

Conventional syntheses of even the simplest bridgehead bicyclic alcohols are often long, involved sequences that lead to mixtures of products.[5] In fact, no unified, efficient strategy for the synthesis of bridgehead bicyclic alcohols exists. An intramolecular Barbier-type synthesis, utilizing appropriately substituted halo ketone precursors, would provide one such approach to this important class of compounds. The SmI_2-promoted version of the intramolecular Barbier reaction has already proven to be a convenient method for the synthesis of monocyclic[6] and fused bicyclic or polycyclic alcohols,[7] comprising an impressive range of substitution patterns. A single example of bridged

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