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4-Azatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octanes: New Hetereocycles by Addition of Sulfonyl Azides to 7-Substituted Norbornadienes – Experimental Verification of σ* Interactions in the Norbornane Skeleton

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The reaction of six 7-substituted norbornadienes with seven sulfonyl azides has been investigated. The products consist of either the novel azatetracyclic system **1** or the stereoisomeric bicycles **2** or of a mixture of them. The chemical behaviour of **1** has been studied. Mechanistically the results may be rationalized within the frame of the Mazzocchi-Houk model. The theoretical predictions of this model, concerning the π* and σ* energies, were confirmed experimentally by using electron-transmission spectroscopy.

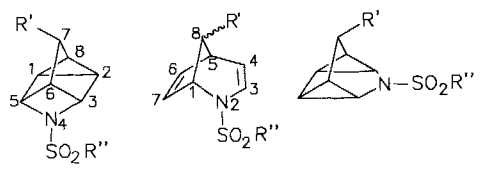
1,3-Dipolar cycloadditions to 7-substituted norbornadienes do not exclusively follow Alder's *exo* rule[2], but show a complex stereochemical behaviour with regard to their *exo/endo* and *syn/anti* stereoselectivity. Thus, for the addition of phenyl azide to 7-*tert*-butoxynorbornadiene Klumpp et al.[3] found 55% *syn-endo*, 30% *anti-exo*, and even 15% of the sterically demanding *syn-exo* adduct.

Contrary to this, Franck-Neumann[4], Wilt[5], and co-workers reported on a stereoselective *endo-anti* cycloaddition of diazoalkanes to 7-chloronorbornadiene. However, such a stereoselectivity was not found for 7-oxygenated norbornadienes.

Kinetic studies on cycloadditions of hexachlorocyclopentadiene[6,7] showed that the reactivity decreases with increasing electronegativity of the substituent in the 7-position and that the *exo-anti* attack is strongly inhibited. These findings were confirmed by recent investigations performed by De Micheli, Gandolfi, and Houk[8] concerning the addition of mesitylenecarbonitrile oxide to 7-substituted norbornadienes.

The addition of sulfonyl azides to norbornadienes is particularly interesting since the resulting unstable triazolines undergo remarkable rearrangement reactions. Thus, Franz and Osuch[9] found that the addition of phenylsulfonyl azide to 7-substituted norbornadienes afforded the azabicycles **2** in 68% yield besides an isomeric sideproduct which displayed only signals of aliphatic hydrogen atoms in its ^{1}H-NMR spectrum and for which one of the two tetracyclic structures **1** or **3** was assumed.

Scheme 1



1 2 3

NMR investigations performed by Oehlschlager and Zalkow[10] showed that in the course of reaction first an aziridine is formed which subsequently rearranges to the bicycle.

Additions of electron-deficient azides to 2,3-substituted norbornadienes for the first time led to stable *exo*-aziridines whose photolytic conversion into the tetracycle **3** was studied by Prinzbach and Klaus[11], whose thermal behaviour, however, was investigated by Umano et al.[12]. It could be shown that the *endo*-aziridincs are stable up to 250°C whereas the *exo*-aziridines rearrange to **2**.

Such an azabicycle was also found by Hedayatullah et al.[13]. For the addition of phenyl azidosulfate to norbornadicne they suggested a homo-1,4-Diels-Alder addition leading to an azetidine as unstable, undetectable intermediate on the way to the bicycle.

We have now studied the addition of sulfonyl azides to 7-substituted norbornadienes, and our results will prove that azetidines **1** are not unstable intermediates, but stable by-products of the well-known azabicycles **2**.

Results

Triazolines with strong electron acceptors at the terminal nitrogen atom are thermally unstable. Already at or even below room temperature they eliminate nitrogen spontaneously and form the corresponding aziridines, imines, or seldomly enamines[14,15]. *N*-Sulfonyl-[16–18], *N*-cyano-[19–21], and *N*-picryltriazolines[22–24] are characterized by an extremely remarkable lability.

For the reaction of sulfonyl azides with 7-substituted norbornadienes described in this paper a high percentage of decomposition and polymerization products was observed, which amounted to an average value of 80% and could not be decreased even by variation of the reaction conditions. Benzene and trichloromethane proved to be the most suitable solvents in which in an inert gas atmosphere and with

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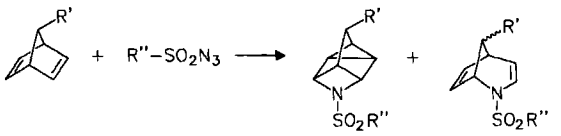
the exclusion of light the reaction takes place within 14–28 days at room temperature, depending on the electron-acceptor strength of the substituent. In some cases the separation of polymeric components was achieved by fractional crystallization or column chromatography.

In all addition reactions carried out by us only three different isolable products were found. The products in question were the azabicycle **2** on the one hand for which both *syn* and *anti* isomers were found and on the other hand the tetracyclic azetidine **1** postulated in the literature but so far never isolated.

In Table 1 all results are summarized.

Scheme 2



4 5 1 2

4a: R' = t-BuO
4b: = AcO
4c: = BzO
4d: = OH
4e: = Cl
4f: = SMe
4g: = H

5a: R" = CH_3-
5b: = $p-CH_3O-C_6H_4-$
5c: = $p-CH_3-C_6H_4-$
5d: = C_6H_5-
5e: = $p-Cl-C_6H_4-$
5f: = $o-NO_2-C_6H_4-$
5g: = $p-NO_2-C_6H_4-$

The addition of sulfonyl azides to 7-*tert*-butoxynorbornadiene (**4a**) resulted in relatively high yields after reaction times of ca. 14 days. Here, the azetidine was found almost exclusively; only in the reaction with *p*-toluenesulfonyl azide (**5c**) small amounts of *anti*-**2ac** could be isolated, whereas with *p*-nitrobenzenesulfonyl azide (**5g**) a 1:1 mixture of **1ag** and *syn*-**2ag** was formed.

The addition of sulfonyl azides to 7-acetoxynorbornadiene (**4b**) led to slightly lower yields with the same reaction time but provided a larger variety of products. Thus, in trichloromethane as solvent the azabicycles **2** could in all cases be identified NMR-spectroscopically in the crude product, but due to the low yields could only be isolated and identified as *syn* isomers in the cases of *p*-chloro- and *p*-nitrobenzenesulfonyl azide (**5e** and **5g**). For solvents which are more polar than trichloromethane or benzene, e. g. methanol, slightly larger proportions of *syn*-**2** were found.

As may furthermore be inferred from Table 1, electron-withdrawing substituents at the phenyl ring tend to influence the product ratio, favouring the bicycles **2**.

Compared with 7-acetoxynorbornadiene (**4b**) 7-benzoyloxynorbornadiene (**4c**) shows an even higher lability. For slightly longer reaction times lower yields are obtained. The trend towards the formation of *syn*-**2** is so distinct that in the reaction with *p*-nitrobenzenesulfonyl azide (**5g**) *syn*-**2cg** is formed exclusively, whereas the formation of the azetidine **1** cannot be observed in this case.

The addition of sulfonyl azides to 7-norbornadienol (**4d**) is susceptible to particular influences. Only two of five reactions were successful of which in particular the reaction with *p*-nitrobenzenesulfonyl azide, otherwise furnishing the highest yields, provided no results. The reaction with *p*-chlorobenzene- and *p*-toluenesulfonyl azide (**5e** and **5c**) led to overall yields of 3% after reaction times of roughly 21 days which can probably be explained by the oxidation sensitivity of secondary alcohols in the presence of sulfonyl azides[25]. Not only the fact that in those two experiments exclusively the azabicycle **2** was found is amazing but also that the product concerned is the *anti* isomer.

This is also true for 7-chloronorbornadiene (**4e**). In five cases the bicycle **2** could be isolated as the *anti* isomer. In

Table 1. Product ratios and total yields of **1**/**2** from **4** and **5**; the first letter in the product notation relates to the norbornadiene **4**, the second denotes the corresponding sulfonyl azide **5**

		5a	5b	5c	5d	5e	5f	5g
	Total yield	25.2		24.8	23.5	22.8		28.5
4a	Azetidine	**1aa** (100)		**1ac** (97)	**1ad** (100)	**1ae** (100)		**1ag** (50)
	Bicycle	**2aa** (---)		**2ac** (3[a])	**2ad** (---)	**2ae** (---)		**2ag** (50[s])
	Total yield	13.1		21.2	17.3	20.0		23.8
4b	Azetidine	**1ba** (100)		**1bc** (96)	**1bd** (100)	**1be** (50)		**1bg** (10)
	Bicycle	**2ba** (--[b])		**2bc** (4[s])	**2bd** (--[b])	**2be** (50[s])		**2bg** (90[s])
	Total yield	2.7		18.4	17.4	24.5		21.0
4c	Azetidine	**1ca** (100)		**1cc** (100)	**1cd** (100)	**1ce** (50)		**1cg** (---)
	Bicycle	**2ca** (---)		**2cc** (---)	**2cd** (---)	**2ce** (50[s])		**2cg** (100[s])
	Total yield	---[c]		3.9	---[c]	2.6		---[c]
4d	Azetidine			**1dc** (---)		**1de** (---)		
	Bicycle			**2dc** (100[a])		**2de** (100[a])		
	Total yield	---[c]	11.3	5.3	---[c]	11.6	9.7	31.0
4e	Azetidine		**1eb** (72)	**1ec** (---)		**1ee** (83)	**1ef** (---)	**1eg** (94)
	Bicycle		**2eb** (28[a])	**2ec** (100[a])		**2ee** (17[a])	**2ef** (100[a])	**2eg** (6[a])
	Total yield	17.7	39.5	38.4	16.8	38.0	26.6	63.1
4f	Azetidine	**1fa** (---)	**1fb** (---)	**1fc** (---)	**1fd** (---)	**1fe** (---)	**1ff** (---)	**1fg** (---)
	Bicycle	**2fa** (100[a])	**2fb** (100[a])	**2fc** (100[a])	**2fd** (100[a])	**2fe** (100[a])	**2ff** (100[a])	**2fg** (100[a])

[a] *anti* isomer of the azabicycle **2**. – [b] By using methanol as solvent the *syn* azabicycle could be identified by means of the ^{1}H-NMR spectrum of the crude product, but it could not be isolated because of the too low yield. – [c] The reaction leads to an unidentifiable product mixture. – [s] *syn* isomer of the azabicycle **2**.

the cases of *p*-methoxy-, *p*-chloro-, and *p*-nitrosulfonyl azide (**5b**, **5e**, and **5g**) the bicycle **2** is formed only as a byproduct of the azetidine **1**. A dependence of the product ratio on the electronic properties of the *para* substituent at the phenyl ring cannot be stated here. The exclusive formation of *anti*-**2ef** in the case of *o*-nitrobenzenesulfonyl azide (**5f**) seems to be sterically caused.

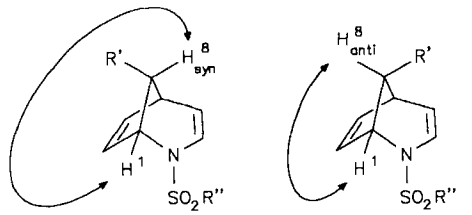
The addition of sulfonyl azides to 7-methylthionorbornadiene (**4f**) takes place much faster. After 10 days already **4f** can no longer be detected in the reaction mixture. In evidently higher yields of about 30% solely the *anti* bicycle **2** is formed.

NMR-Spectroscopic Data of the Bicyclic Systems

The ^{1}H-NMR spectrum of the azabicycle **2ac** shows four olefinic signals at δ = 5.10, 5.20, 6.08, and 6.28, a multiplet at δ = 4.35, and two "broad" singlets at δ = 3.78 and 2.43. This is characteristic of 2-azabicyclo[3.2.1]octa-3,6-dienes[26–29] which were described by Oehlschlager and Zalkow[30] for the first time.

The MNDO-optimized geometry for the parent compound unsubstituted in the 8-position specifies two dihedral angles which are important in this context. The dihedral angle of 1-H and 8-H_{syn} is calculated to an average value of 73° and is thus clearly larger than that of 1-H and 8-H_{anti} with 48°. According to Karplus this results in two different coupling constants which should amount to 1 Hz for the first case and 4 Hz for the second case. Thus, the coupling pattern of 8-H offers a safe criterion for the determination of the *syn*/*anti* configuration.

Scheme 3



anti-2 Θ = 73°

syn-2 Θ = 48°

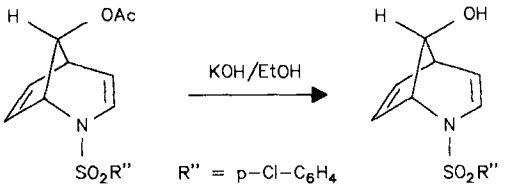
In the ^{1}H-NMR spectrum of the *syn* bicycle the signal of 8-H_{anti} appears as a triplet of doublets due to two ^3J couplings of 4 Hz with 1-H and 5-H and to a long-range coupling of 1.5 Hz with 4-H.

However, in the ^{1}H-NMR spectrum of the *anti* bicycle 8-H_{syn} displays a broad singlet with a quintuplet fine structure which is caused both by two ^3J couplings with 1-H and 5-H and two ^4J couplings with the olefinic protons 6-H and 7-H, which all amount to ca. 1 Hz.

In these bicyclic systems the chemical shift can be influenced significantly by the substituent R'. From *syn*-**2** it can be seen that due to its central position in relation to the *syn* substituent the proton 3-H is most strongly influenced by through-space effects. In contrast to this, conjugational effects through the *N*-sulfonyl group are weak, which is in good agreement with literature data[31–33].

The remarkable *anti* selectivity of norbornadienol **4d** induced us to synthesize the bicycle *syn*-**2de**, which is important as a spectroscopic reference compound, by saponification of *syn*-**2be**.

Scheme 4



syn-2be **syn-2de**

The direct spectroscopic comparison of *syn*- and *anti*-8-hydroxy-2-azabicyclo[3.2.1]octa-3,6-dienes confirms the predictions made above.

NMR-Spectroscopic Data of the Tetracyclic Systems 1

The ^{1}H-NMR spectrum of azetidine **1aa** shows five groups of signals belonging to the tetracyclic system at δ = 2.15–2.38, 2.45–2.65, 4.00, 4.24, and 4.62. The integration shows that three protons are to be assigned to the most high-field-shifted signal and one proton each to the other signals.

The two low-field-shifted multiplets are assigned to the protons 3-H (δ = 4.24) and 5-H (δ = 4.62) assuming that the latter is shifted to lower field owing to the anisotropic effect of the *tert*-butoxy group.

Since a seven-spin system is present here all the signals appear as complex multiplets, whose interpretation was made possible by double-resonance experiments. Thus, the signal at δ = 4.00 could be assigned to 7-H, and the peak at δ = 2.62 originates from 1-H, all the more since, just as for 5-H, it is shifted to lower field than the other three-membered ring-proton signals because of its *syn* orientation towards the *tert*-butoxy group.

In order to investigate the anisotropic effect in the azetidinol, too, we saponified the acetoxy derivative **1bd** to obtain the corresponding azetidinol **1dd**.

The spectrum of the azetidinol **1dd** is comparable to that of the azetidine **1aa** discussed above. Here, too, the *syn* or *anti* assignment of the azetidine protons 3-H and 5-H cannot be carried out empirically. For that reason, the spectrum of the azetidinol was measured in the presence of the shift reagent Eu(FOD)$_3$.

In this way the ^3J couplings of the three-membered ring protons could be ascertained to amount to 4.9 and 6.8 Hz. However, it could not yet be decided which values are to be assignnet to the couplings $^3J_{(1,8)} \approx {}^3J_{(2,8)}$ and $^3J_{(1,2)}$. On the other hand, such an assignment should be made accessible by means of the coupling behaviour of symmetrical azetidines, as for example the azetidine without substituent in the 7-position or the corresponding azetidinone.

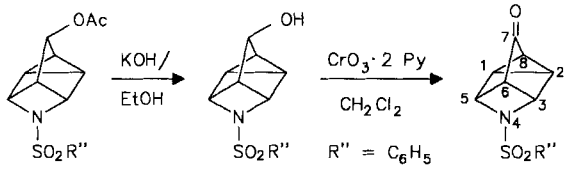
Synthesis of the Azetidinone 6

Due to its sensitivity to acids and bases the possible oxidation methods for the azetidinol are strongly limited. Reactions as e.g. the Etard[34] oxidation in whose course an unsoluble chromium complex must be hydrolyzed, reactions with extremely acidic reagents such as Jones reagent[35] or

the method according to Oppenauer and Oberrach[36,37] with di-*tert*-butyl chromate in tetrachloromethane or benzene with the addition of acetic anhydride and acetic acid led to ring-opened nortricyclanes. Oxidations of 7-substituted benzonorbornadienes according to Oppenauer[38] or the reaction of quadricyclanole with *tert*-butyl hypochlorite[39] resulted in comparatively low yields.

However, the use of a twentyfold excess of Collins reagent[40] in absolute dichloromethane gave the azetidinone **6** in 23% yield after a reaction time of 20 h.

Scheme 5



1bd **1dd** **6**

The ^{1}H-NMR spectrum of the ketone **6** shows only four groups of signals. Only the two low-field-shifted multiplets of 3/5-H and 1/2-H are of higher order in spite of the six-spin system. The signal of the three-membered ring proton 8-H lying in the symmetry plane displays a triplet of doublets from which the coupling constants $^3J_{(1,8)} = {}^3J_{(2,8)} = 4.7$ Hz and $^4J_{(6,8)} = 1.7$ Hz can be taken directly. Thus, the three-membered ring couplings $^3J_{(1,8)}$ and $^3J_{(2,8)}$ for 7-substituted azetidines can be ascertained to a value of 4.7 Hz and analogously the $^3J_{(1,2)}$ coupling to a value of 6.8 Hz.

Further resonance experiments allowed the determination of all coupling constants except those of the four long-range couplings $^4J_{(1,3)}$, $^4J_{(2,5)}$, $^4J_{(3,8)}$ and $^4J_{(5,8)}$. Though from the signal widths one can deduce that the couplings in question must be very small W couplings, their real values and the influence on the multiplet patterns can only be estimated by means of a simulation. The data from 300-MHz spectra show that significant influences on the multiplet structure can be observed for W couplings >0.1 Hz.

Table 2. Coupling constants [Hz] of the tetracyclic system **1**

J/Hz	2-H	3-H	5-H	6-H	7-H	8-H
1-H	6.8	<0.1	1.8[a] 2.2[b] 2.2[c]	0.5	<1.0	4.9[a] 4.7[b] 4.5[c]
2-H		2.2	<0.1	0.5	<1.0	4.9[a] 4.7[b] 4.5[c]
3-H			5.7	3.0[a] 3.2[b] 3.0[c]	<1.0	<0.1
5-H				2.9[a] 3.2[b] 3.0[c]	<1.0	<0.1
6-H					1.3	1.5[a] 1.7[b] 1.5[c]
7-H						1.5[a] 1.3[b] 1.3[cb]

[a] Coupling constants of the alcohol **1dc**. — [b] Coupling constants of the ketone **6**. — [c] Coupling constants of the azetidine **1gd**.

Table 2 shows all determined coupling constants of the azatetracyclic system **1**, whose values vary by less than 0.2 Hz for all synthesized derivatives.

Unsubstituted Norbornadiene

In the reaction of norbornadiene (**4g**) with benzenesulfonyl azide (**5d**) Franz and Osuch[9] found besides 68% of bicycle **2gd** also a sideproduct in 3% yield which did not show any olefinic signals in its spectrum and for which they suggested the structures **1** or **3** without coming to a decision on the real structure. The repetition of this experiment showed that in addition to **2gd** the azetidine **1gd** is formed as a stable byproduct.

Thus, it has been shown that azetidines are no unstable intermediates en route to azabicyclic systems[13], but that they are stable byproducts of bicycles and other imaginable products.

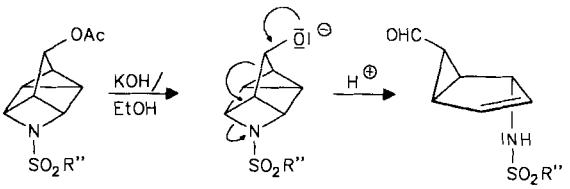
Chemical Properties of Azetidines

The solid azetidines are stable at room temperature and form colourless crystals which can be recrystallized from diethyl ether. Whereas they are quite stable in slightly alkaline media, they are highly sensitive to traces of acid.

a) *Reactions with Strong Bases:* In the saponification of the azetidine **1bc** an excess of base should be avoided in any case, since otherwise fragmentation takes place[41].

Structure **7** of the fragmentation product can be deduced from literature data since there are reference values for similar systems[42]. Owing to the small ^3J coupling of the three-membered ring α-proton amounting to 4.2 Hz one can conclude that it is the *exo* isomer. Besides, the spectrum of the crude product shows that small quanitities of the corresponding *endo*-aldehyde are present.

Scheme 6



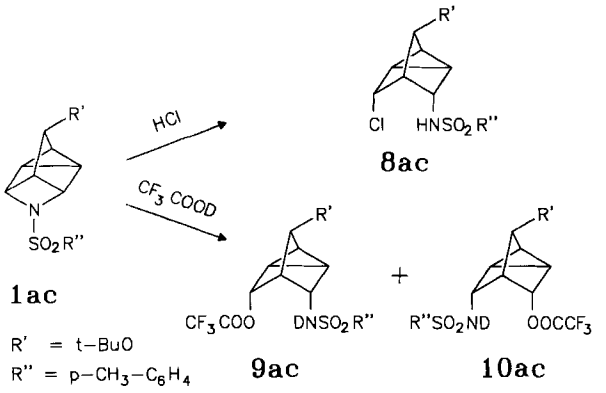
1bc R" = p-CH_3-C_6H_4- **exo-7**

b) *Reactions with Acids:* Preliminary experiments with the azetidine **1ac** in the presence of diluted hydrochloric acid showed that sidereactions such as ether cleavage, addition of water (appearence of strong OH and NH bands in the IR spectrum) or opening of the three-membered ring structure after longer reaction times led to a complex reaction mixture. Therefore, the attempted ring-opening reaction of the azetidine **1ac** was carried out with concd. hydrochloric acid in $CDCl_3$, so that the ^{1}H-NMR spectrum of the reaction

mixture could be measured directly and unwanted consecutive products formed by possible workup procedures could be avoided.

Ring opening takes place spontaneously and is strongly exothermic. Within one minute the azetidine signal is no longer detected. On the other hand, the spectrum shows signals characteristic of a nortricyclane, which was identified as *endo,endo* isomer **8ac** by adaptation of the empirical method developed by Chizov et al.[43]. Reactions with deuterated trifluoroacetic acid showed, that besides **9ac** two other isomers are formed in a ratio of 4:1:1. Structure **10ac** could be assigned to one of them. Both **9ac** and **10ac** turned out to be too labile to be isolated from the product mixture.

Scheme 7



Analogous reactions with the 7-hydroxyazetidines **1d** led to similar results. A dependence of the product ratio on the sulfonamide substituent could not be detected. The reaction of 7-acyloxy derivatives **1b**, however, yielded additional hydrolysis products whose NMR signals prevent an assignment to components.

Discussion

a) *exo/endo* Selectivity

The results of Table 1 show that slight electronic changes in the azide molecule (variation of the *para* substituent at the benzenesulfonyl group) lead to drastic variations of the product ratio of **1** to **2**. Proceeding from the assumption, that the bicycles **2** are formed from an *exo*-aziridine via an intermediate heteroanalogous divinylcyclopropane by a following aza-Cope rearrangement, and suggesting an *endo* attack for the formation of the azetidines **1**, the change of the *para* substituent in the azide molecule should be responsible for the inverted *exo/endo* stereoselectivity in the example mentioned above.

However, the following two arguments contradict such a hypothesis:

1) The differences in charge density in the azide sequence (calculated by MNDO) seem to be too small, so that electrostatic interactions should not lead to such differences in the *exo/endo* attack. Neither do sterical effects serve as an explanation, since the molecular structure of the *para*-substituded azides remains largely unchanged.

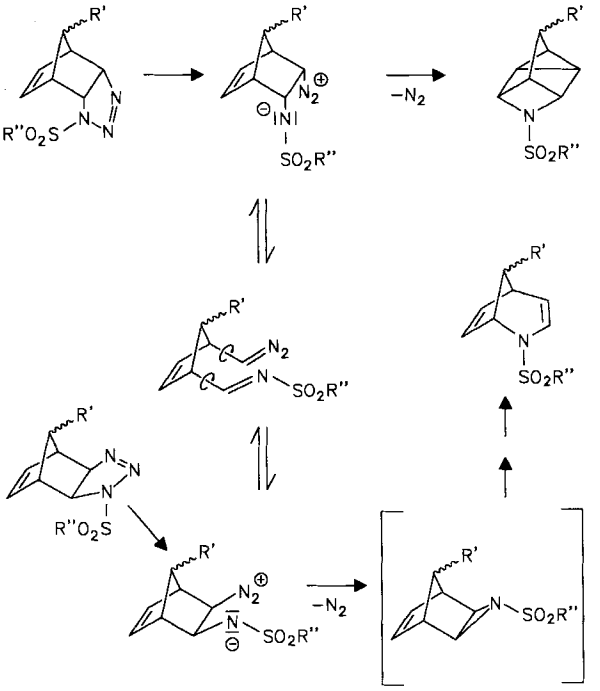
2) Since for 7-oxygenated norbornadienes almost exclusively *syn* bicycles **2** are found, an *exo-syn* attack should be responsible for that fact according to the hypothesis discussed above. However, of all four possible kinds of attack this one seemed to be the sterically least favourable.

Nevertheless, there are some examples for such an *exo-syn* attack in the literature[3,8,26].

In another, possibly realistic hypothesis the relative stability of intermediately generated betaines is a primary consideration. Those zwitterionic intermediates could positively profit from the given *para* substitution, above all they are attractive intermediates for an *exo/endo* isomerization already discussed in the literature.

There are numerous examples for complex successive reactions of arylsulfonyltriazolines[17,29,30,44–46], of which ring opening with the formation of diazonium compounds represents a variant. The issue of a possible *exo/endo* isomerization by a dipolar cycloreversion has been sufficiently dealt with in the literature[15,47–49].

Scheme 8



b) *syn/anti* Selectivity

Whereas no statement can be made concerning *syn/anti* selectivity in the formation of azetidines **1** due to their symmetry the bicycles **2** show a distinct dependence of the *syn/anti* attack on the substituent in 7-position.

The results of this work reveal an obvious *syn* selectivity with the 7-oxygenated norbornadienes whereas only *anti* bicycles are formed in the reactions with 7-norbornadienol (**4d**), 7-chloronorbornadiene (**4e**), and 7-methylthionorbornadiene (**4f**). Figure 1 shows the dependence of the direction of the attack of the 1,3-dipole on the 7-substituent.

Different hypotheses have been developed to account for similar selectivities: Thus, Alston and Ottenbrite[50] explain

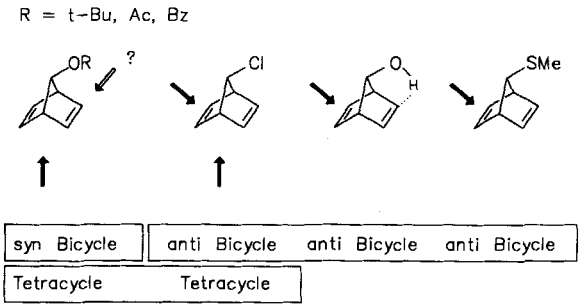


Figure 1. Dependence of the direction of attack of sulfonyl azide on the 7-substituent of norbornadiene

this *syn/anti* orientation to be due to a through-space interaction of the nonbonding donor orbitals of the 7-substituent with the frontier orbitals of the *syn* double bond, which should lead to its energetic destabilization. This was supported by CNDO/2 calculations. In fact, they succeeded in explaining the course of several cycloadditions by this approximation[4,6,51-53].

However, Mazzocchi and Houk et al.[7] showed by means of experimental ionization energies, that the π levels undergo a stabilization by the 7-substituent. They rather attribute the polarization of the *syn* double bond to an electrostatic effect. Additionally, these authors postulate that the closed-shell repulsive interaction is affected by the 7-substituent[54].

Otherwise, Franck-Neumann and Sedrati attribute the *anti-endo* attack at 7-halonorbornadienes to a participation of the σ^* orbitals of the C-7–halogen bond[4].

In our opinion, at present the Mazzocchi-Houk model[7] provides a useful but not yet satisfactory answer.

It is based on experimental measurements of reaction rates (for the addition of hexachlorocyclopentadiene) and STO-3G ab initio calculations for the corresponding 7-substituted norbornadienes.

The kinetic experiments show a large decrease of the reaction rate of the *exo-anti* attack, depending on the group electronegativity (according to Huheey[55]) of the 7-substituent. For the corresponding *endo-syn* or *endo-anti* attack this dependence is only slightly distinctive. Figure 2 shows this fact applied to the present results.

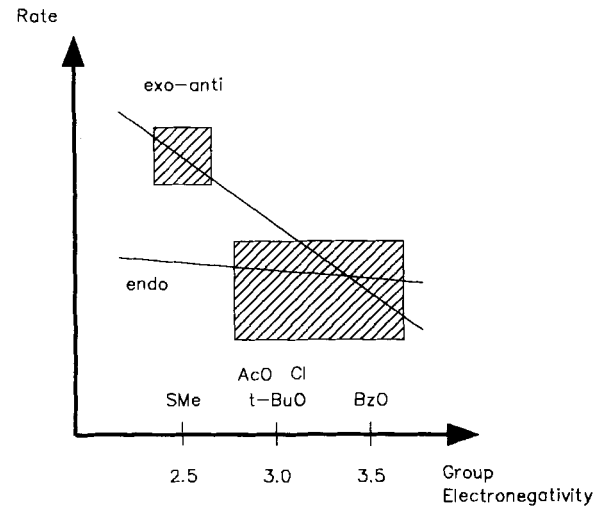


Figure 2. Dependence of *exo-anti* and *endo* attack on the group electroncgativity[7]

STO-3G ab initio calculations provide a possible explanation for this remarkable addition behaviour[7]. As shown in Figure 3, a partial negative charge in the 7-position leads to a polarization of the HOMO on the *syn* side whereas a partial positive charge shows the opposite effect. Presumably, these polarizations are caused by a field effect and not by orbital interactions.

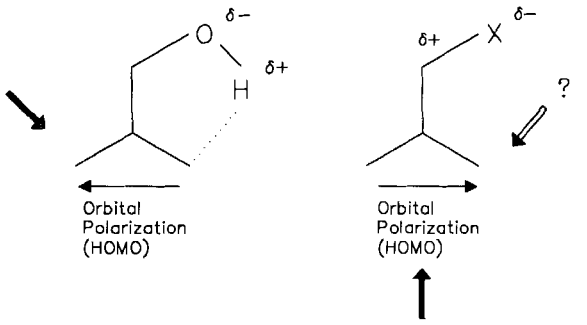


Figure 3. Field effect and orbital polarization[7]

The MNDO-calculated negative charges on the hetero atoms of the 7-substituent are in agreement with the predictions made by this model:
O: $\delta^- = 0.33$ (**4a**); Cl: $\delta^- = 0.19$ (**4e**); S: $\delta^- = 0.12$ (**4f**).

The exclusive formation of *anti* bicycles from the alcohol **4d** which has been observed in this work contrasts with the product mixture obtained by the reaction of **4d** with hexachlorocyclopentadiene at 120°C[54a]. However, it is possible, that the established hydrogen bond[56-58] depicted in Figure 3 plays no role anymore under such drastic reaction conditions whereas it may be significant in azide additions at room temperature described in this paper.

Since the Mazzocchi-Houk model supplies the most useful predictions at present, it seemed reasonable to us to check and complete two aspects of this model *experimentally*. These two aspects are the following:

1) Whereas the calculated orbital energies of the occupied orbitals are in good agreement with the measured ionization energies (PES), there are no experimental references for the calculated, relevant unoccupied levels.

2) On quoting earlier interpretations the authors point out that according to their own calculations the formerly postulated σ^*_{C-Cl}/π^* interaction in 7-chloronorbornadiene (**4e**) cannot be perceived: *"Franck-Neumann and Sedrati suggested that the highly preferred anti-endo attack of diazoalkanes on 7-halonorbornadienes arises from the interaction of the anti-π bond with the σ^*_{C-X} bond, which lowers the LUMO of the anti orbital. While our calculations do indicate polarizations of the LUMO ..., the mixing of σ^*_{C-Cl} into the norbornadiene LUMO is not evident in the STO-3G calculations."* (quoted from ref.[7]).

Therefore, an experimental investigation must clarify in which norbornadiene derivatives σ* levels play a role and which symmetry restrictions they are subject to.

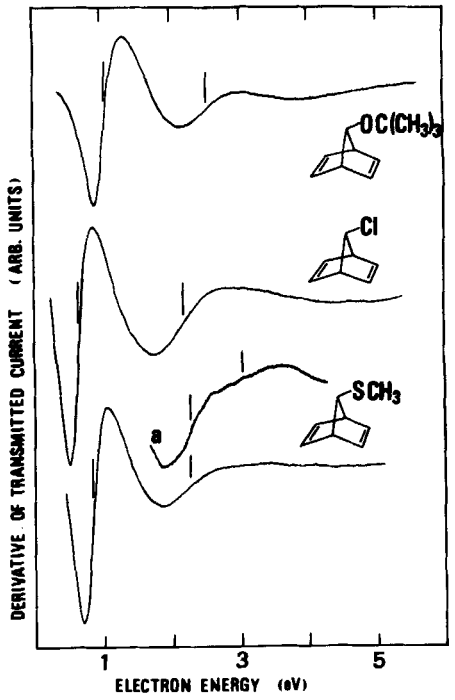


Figure 4. ET spectra; derivative of the electron current transmitted through **4a**, **4e**, and **4f** as a function of the incident electron energy; vertical bars locate the most probable attachment energies (AE); a) signal related to the back-scattering differential cross section

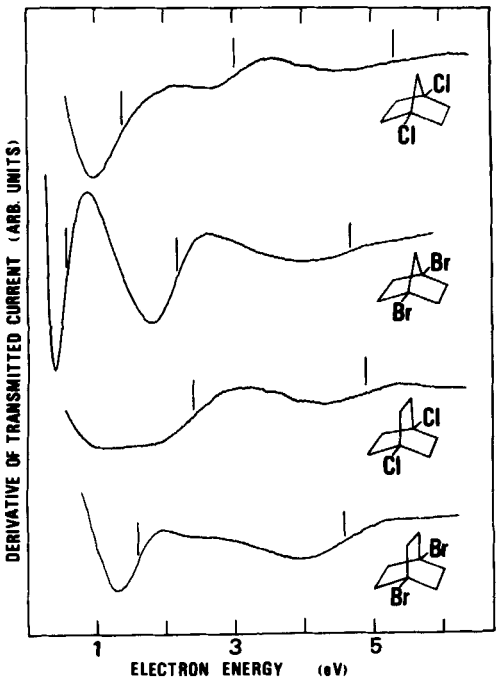


Figure 5. ET spectra; derivative of the electron current transmitted through **11**, **12**, **13**, and **14** as a function of the incident electron energy; vertical bars locate the most probable attachment energies (AE)

Electron-Transmission Spectroscopy, σ* Interactions, and Their Symmetry Restrictions

Electron-transmission spectroscopy (ETS) takes advantage of the sharp variations in the total electron-molecule scattering cross section caused by resonance processes, that is, the formation of temporary anion states. The energies (AEs) at which electron attachment occurs are the negative vertical electron affinities.

In Figures 4 and 5 the ET spectra of **4a**, **4e**, **4f**, **11**–**14** are shown. The corresponding attachment energies (negative electron affinities) are given in Table 3.

Scheme 9

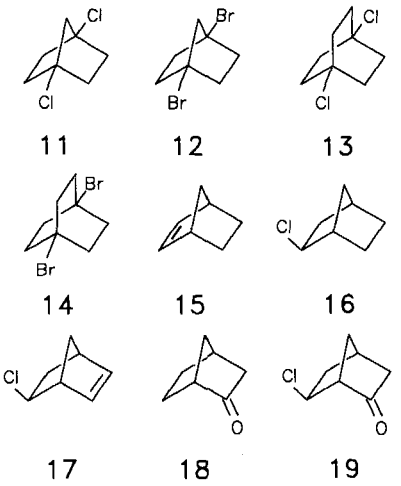


Table 3. Attachment energies (negative vertical electron affinities) of **4a**, **4e**, **4f**, **11**–**13**, and **14**

Compound	AE_1	AE_2	AE_3
11	1.42	3.00	5.3
12	0.55	2.18	4.7
13	2.4	4.9	
14	1.60	4.63	
4a	1.06	2.52	
4e	0.65	2.18	
4f	0.85	2.22	3.0

It is obvious from the experimental data that σ* interactions can be seen in some cases, whereas in others they are absent.

7-tert-Butoxynorbornadiene (**4a**): Compared with the π* energies of norbornadiene[59] those of **4a** are essentially not changed. This is remarkable since the group electronegativity of the *tert*-butoxy substituent is given as 3.02[7,55c] and, therefore, a stabilization of all levels could have been expected. But it has been stated that there is no good correlation between the electronegativity of the 7-substituent and ionization energies[7]. We may conclude that the same holds for unoccupied levels. Moreover, this nonresponse of the norbornadiene π* levels to the *tert*-butoxy substituent is excellently reproduced by ab initio STO-3G calculations[7] (Figure 6).

These findings correspond precisely to the behaviour of the *tert*-butoxy group in aromatic compounds: Compared with the energy levels in benzene [$\pi(a_2)$: −9.24 eV; $\pi^*(a_2)$:

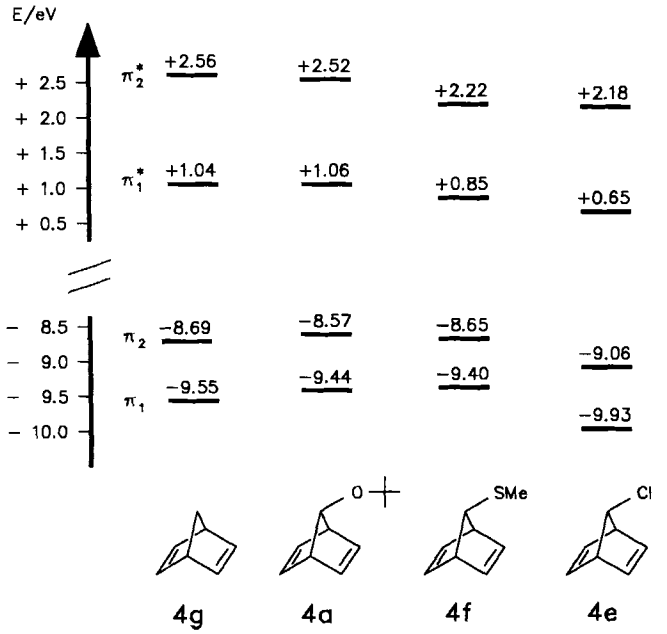


Figure 6. Correlation diagram of experimental π-ionization energies and π*-electron affinities of the norbornadienes **4a**, **4e**–**4g**

1.12 eV[60]], the ionization and attachment energies in *tert*-butoxybenzene are not significantly changed: −9.33 eV[61] and 1.08 eV[62], respectively.

7-Chloronorbornadiene (**4e**): Having a similar electronegativity (3.11[7,55c]) as the *tert*-butoxy substituent, chlorine nevertheless affects the orbital energies of **4g** in quite a different manner. Both π and π* levels are considerably stabilized. The increase in the ionization energies (0.37 eV) coincides with the decrease of the attachment energies (0.38 eV). Such a behaviour is indicative of an almost *pure inductive* or *electrostatic* substituent effect. If any orbital interaction involving σ^*_{C-Cl} occurred, a clear difference between occupied and unoccupied levels would have to be seen since the symmetry and basis energy of the interacting orbitals are completely different. The *a'* symmetry of σ^*_{C-Cl} does not match the π* orbital which transforms as *a''*. These findings are in agreement with the aforementioned calculations of Mazzocchi et al. who could not observe any mixing of σ^*_{C-Cl} into the norbornadiene LUMO[7] (Figure 6).

Again, the influence of the 7-chloro substituent is not much different from that in benzene: the π- and π*-a_2 levels are both stabilized in chlorobenzene, −9.68 eV[63] and 0.75 eV[64]. At first sight, it might seem surprising that the *tert*-butoxy group and the chloro substituent, although having nearly the same (group) electronegativity, affect the π and π* levels in quite a different way. According to recent ET-spectroscopic results the main reason for this diverging behaviour is the existence of low-lying unoccupied σ^*_{C-Cl} and $3d_{Cl}$ levels in the chloro derivative but not in the oxygen compounds[62] (cf. discussion of **4f**).

7-Methylthionorbornadiene (**4f**): The methylthio group exerts an influence that is negligible for the occupied levels but is of similar importance for unoccupied π* orbitals as is observed with the chloro substituent. Despite its lower electronegativity value (2.5[55a]) the methylthio group is accordingly capable of stabilizing especially anion states where the extra electron enters orbitals which are unoccupied in the ground state of the neutral species. This effect is doubtlessly due to the existence of low-lying σ^*_{C-S} and $3d_S$ levels[62,65,66]. Since the calculated geometry of **4f** indicates strong twisting of the substituent (MNDO: 143°; AM1: 159°) there is no longer any symmetry restriction to the mixing of $\sigma^*_{C-S}/3d_S$ and π* levels (Figure 6).

The methylthio group in **4f** behaves as in methylthiobenzene: there is no effect on occupied levels [π(a_2): −9.28 eV[67]] but a moderate stabilization of the unoccupied π*(a_2) orbital (0.9 eV[62]).

1,4-Dichloronorbornadiene (**11**) *and Related Compounds* **12**–**14**: Strong mixing, on the other hand, is observed in those cases in which symmetry as well as overlap allows the interaction of the participating orbitals. Typical norbornane derivatives are **11** and **12**. The two lowest resonances of **11** and **12** are indeed split by 1.58 eV and 1.63 eV, respectively. Since these two levels of **11** are grouped almost symmetrically around the mean value 2.21 eV for a noninteracting σ^*_{C-Cl} level (which corresponds with the observed σ^*_{C-Cl} energy of **16**: 2.30 eV[68]), it is concluded that in **11** and **12** a strong through-space interaction between the localized σ^*_{C-Cl} bond orbitals leads to the experimentally observed pattern. It is interesting to note that this effect is not displayed by the bicyclooctanes **13** and **14**, possibly because of the extended bridgehead – bridgehead distance: MNDO calculations give 225 pm for **11**, but 258 pm for **13**.

A similar strong interaction has been discerned in the olefin **17** and the ketone **19**. Although nondegenerate levels are mixed in these cases, a considerable splitting is observed with respect to the basis attachment energies of the isolated chromophores[68]: **15**: 1.70 eV; **16**: 2.30 eV; **17**: 1.10, 2.78 eV; **18**: 1.14 eV; **19**: 0.53, 2.25 eV.

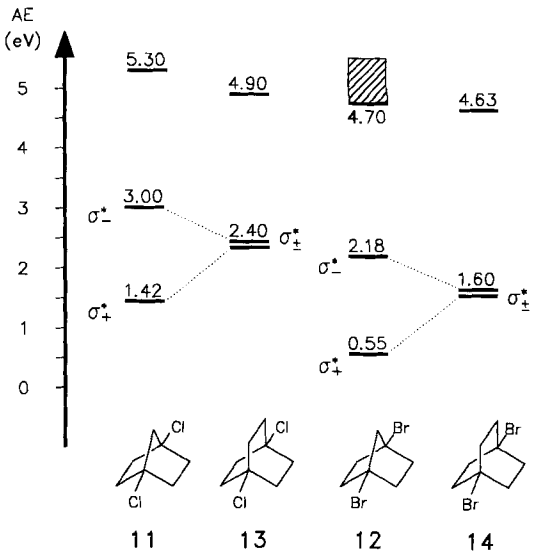


Figure 7. Correlation diagram of experimental σ*-electron affinities of the bicycles **11**–**14**

STO-3G calculations are useful in interpreting the recorded attachment energies of all these molecules[7,68]. For **11** and **13** the calculated splittings compare favourably with the measured ones: 1.33 eV (**11**) and 0.07 (**13**).

Conclusion

Although strong σ^*_{C-Hal} interactions, either with a second σ^*_{C-Hal} bond orbital or with another π^* orbital, can be observed in suitable norbornane skeletons, where symmetry restrictions are absent, e.g. **11**, **17**, and **19**, no such mixing can be inferred from the ET spectra of 7-chloronorbornadiene (**4e**) or 7-*tert*-butoxynorbornadiene (**4a**). The pronounced substituent effect that is observed in **4e** can solely be explained by an inductive or electrostatic perturbation without having to resort to orbital-interaction effects. This result is remarkable in that it lends strong support to the hypothesis put forward by Mazzocchi and Houk et al.[7]. Thus, a through-space electrostatic or field effect of the substituent in the 7-position of norbornadiene influences the shapes and, in some cases, the energy of the π orbirtals as well as the propensity to distort the olefinic hydrogen atoms in the *exo* or *endo* direction[7].

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Experimental

Melting points: Büchi 510 melting-point apparatus (uncorrected): – ^{1}H NMR: Bruker WP 80 (80 MHz), Varian VXR 300 (300 MHz). – ^{13}C NMR: Varian LX 100 (25.2 MHz), Varian VXR 300 (75.4 MHz). – UV: Zeiss DMR 21 114 Q III. – IR: Perkin-Elmer Spectrometer 297, Perkin-Elmer Spectrometer 710 B. – PE: Leybold-Heraeus Spectrometer UPG 200. – MS: Varian MAT CH-5. – TLC: Polygram SIL G/UV$_{254}$ (Macherey-Nagel). – Column chromatography: Silica gel 60, 230–400 mesh ASTM (Macherey-Nagel). – Elemental analyses: Institute of Pharmaceutical Chemistry, University of Düsseldorf. – The electron-transmission apparatus is in the format divised by Sanche and Schulz[69] and has been previously described[60]. The present spectra have been obtained by using the apparatus in the "high-rejection" mode[70] (unless otherwise specified), and are therefore related to the nearly total scattering cross section. The electron-beam resolution is ca. 50 meV (fwhm). The energy scales are calibrated with reference to the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is $\pm$0.05 or $\pm$0.1 eV, depending on the number of decimal digits reported.

The sulfonyl azides **5a**–**5g** required for the cycloaddition reactions have been prepared by treatment of the corresponding sulfonyl chlorides with sodium azide in acetone/water[71].

7-tert-Butoxynorbornadiene (**4a**) and *7-acetoxynorbornadiene* (**4b**) have been synthesized according to Story[72], *7-benzoyloxynorbornadiene* (**4c**) and *7-norbornadienol* (**4d**) according to Tanida[73]. *7-Chloronorbornadiene* (**4e**) can be obtained by passing a stream of hydrogen chloride gas through an ethereal solution of **4a**[74].

7-Methylthionorbornadiene (**4f**): To a solution of 49.3 g (0.3 mol) of **4a** in 400 ml of dry THF is added 43.2 g (0.3 mol) of 70% perchloric acid. The reaction mixture is cooled to –60 °C, and 16.8 g (0.35 mol) of methanthiol is condensed into the flask. After standing for ca. 12 h and warming up to room temperature, a black solution is obtained which is neutralized with aqueous $NaHCO_3$ solution and extracted twice with ether. The combined ethereal extracts are dried with $MgSO_4$, and after evaporation of the solvent the residue is destilled through a 20-cm Vigreux column; yield 30.4 g (73%), b.p. 78 °C/18 Torr. – IR (Film): $\tilde{\nu}$ = 3100 cm^{-1} (CH), 2940 (CH, CH_3), 1540 (C=C), 1430 (CH). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3H, SCH_3), 3.41 ("t", 1H, 7-H), 3.66 (m, 2H, 1-, 4-H), 6.67 ("dt", 2H, 2-, 3-H), 6.80 ("t", 2H, 5-, 6-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.42 (q, SCH_3), 55.27 (d"sext", C-1, -4), 90.19 (dm, C-7), 140.36 (d"q", C-2, -3), 142.96 (d"t", C-5, -6). – MS (70 eV): *m/z* (%) = 138 (5) [M^+], 123 (21) [$M^+ - CH_3$], 91 (100) [$M^+ - SCH_3$].

A. *Cycloadditions to 7-tert-Butoxynorbornadiene* (**4a**): 20 mmol of **4a** and 22 mmol of the respective azide are dissolved in 50 ml of trichloromethane (or benzene) and are allowed to stand at room temperature under nitrogen and with the exclusion of light. While liberating nitrogen the reaction mixture slowly turns dark. The course of the reaction is controlled by TLC. As soon as **4a** cannot be detected any more, the black reaction mixture of polymers is added dropwise to ca. 1000 ml of boiling dry *n*-hexane. The precipitating polymeric components are removed by filtration at 50 °C. At 6 °C the cycloadducts crystallize from the filtrate in analytically pure form.

From the addition of *p*-nitrobenzene sulfonyl azide (**5g**) results a crystalline product mixture consisting of **1ag** and **2ag** in a ratio of 1:1 which can be separated by column chromatography [eluent: *n*-hexane/ethyl acetate (65:35)]; R_f(**1ag**) = 0.24; R_f(**2ag**) = 0.35.

B. *Cycloadditions to 7-Acetoxynorbornadiene* (**4b**): **4b** can be brought to react with the respective azides as described under method A. After analogous workup, the reactions with **5a** and **5d** lead to colourless crystals of the tetracycles.

In the reaction of toluenesulfonyl azide (**5c**) a crystalline product mixture is obtained whose ^{1}H-NMR spectrum shows the presence of tetracycle **1bc** together with low amounts of an impurity consisting of **2bc.**

The reaction with p-chlorobenezesulfonyl azide (**5e**) yields a 1:1 mixture of **1be** and **2be** which is separated by column chromatography (eluent: *n*-hexane/ethyl acetate/acetic acid (85:20:2)]; R_f(**1be**) = 0.32; R_f(**2be**) = 0.44.

From the reaction with *p*-nitrobenzenesulfonyl azide (**5g**) results a crystalline product mixture of **1bg** and **2bg** (ratio 1:9), which is separated by column chromatography [eluent: *n*-hexane/ethyl acetate (70:30)]; R_f(**1bg**) = 0.20; R_f(**2bg**) = 0.30.

C. *Cycloadditions to 7-Benzoyloxynorbornadiene* (**4c**): **4c** reacts with the respective azides as described under A. After analogous workup, the corresponding cycloadducts are obtained as analytically pure crystals. Only in the reaction with *p*-chlorobenzenesulfonyl azide (**5e**) a crystalline mixture of the products **1ce** and **2ce** in a ratio of 1:1 is obtained, which is separated by column chromatography [eluent: *n*-hexane/ethyl acetate/acetic acid (70:30:2)]; R_f(**1ce**) = 0.40; R_f(**2ce**) = 0.55.

D. *Cycloadditions to 7-Norbornadienol* (**4d**): **4d** reacts with the corresponding azides as described under A. Here, complex reaction mixtures consisting chiefly of polymeric components are formed. Only in two cases it is possible to isolate the azabicycle as byproduct in yields of ca. 3%. An addition of radical inhibitors does not result in higher yields.

E. *Cycloadditions to 7-Chloronorbornadiene* (**4e**): 15.8 mmol of **4e** is treated with 60 mmol of the respective azide in 40 ml of dry trichloromethane as described under A. Besides excess azide and polymeric components the reaction mixture contains the corre-

sponding cycloadducts which could be isolated by column chromatography (eluent: toluene); R_f(**1eb**) = 0.22; R_f(**2eb**) = 0.68; R_f(**2ec**) = 0.36; R_f(**1ee**) = 0.18; R_f(**2ee**) = 0.53; R_f(**2ef**) = 0.44; R_f(**1eg**) = 0.44; R_f(**2eg**) = 0.15.

F. *Cycloadditions to 7-Methylthionorbornadiene* (**4f**): As described under A, 6.1 mmol of **4f** is treated with 9.3 mmol of the corresponding azide in 10 ml of dry trichloromethane. Besides excess azide and polymeric byproducts the reaction mixture formed contains the respective azabicycles which are isolated by column chromatography (eluent: toluene); R_f(**2fa**) = 0.18; R_f(**2fb**) = 0.16; R_f(**2fc**) = 0.35; R_f(**2fd**) = 0.27; R_f(**2fe**) = 0.40; R_f(**2ff**) = 0.34; R_f(**2fg**) = 0.33.

Cycloaddition of Benzenesulfonyl Azide (**5d**) *to Norbornadiene* (**4g**): Under nitrogen 35.0 g (0.19 mol) of **5d** in 30 ml of absolute benzene is added to 40.0 g (0.43 mol) of freshly distilled **4g**. After a few minutes, a vigorous liberation of nitrogen sets in which subsides after 2 h. After 8 h, the solvent as well as excess **4g** are removed from the yellowish solution by distillation under slightly reduced pressure. The highly viscous distillation residue is diluted with trichloromethane and the obtained mixture added dropwise to 2 ml of boiling hexane. Precipitating polymeric components are filtered off at 50–55°C; 25.5 g (39%) of the already known 2-phenylsulfonyl-2-azabicyclo[3.2.1]octa-3,6-diene[9,10] (**2gd**) crystallizes from the filtrate at room temperature. The NMR spectrum of the re-

Table 4. Reaction times, melting points, and elemental analyses of cycloaddition products

No.	Name	React. time	M.p. (Solvent)	Empirical formula (Molar mass)		Analysis C	H	N
1aa	7-*t*-Butoxy-4-methylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	28 d	126 (Hexane)	$C_{12}H_{19}NO_3S$ (257.3)	Calcd.	56.03	7.39	5.45
					Found	56.03	7.36	5.51
1ac	7-*t*-Butoxy-4-(4'-methylphenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	28 d	123 (Hexane)	$C_{18}H_{23}NO_3S$ (333.4)	Calcd.	64.86	6.91	4.20
					Found	65.12	7.05	4.15
2ac	*anti*-8-*t*-Butoxy-2-(4'-methylphenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	28 d	140 (Ethanol)	$C_{18}H_{23}NO_3S$ (333.4)	Calcd.	64.86	6.91	4.20
					Found	65.05	7.06	4.12
1ad	7-*t*-Butoxy-4-phenylsulfonyl 4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	60 d	101 (Hexane)	$C_{17}H_{21}NO_3S$ (319.4)	Calcd.	63.95	6.58	4.39
					Found	64.18	6.73	4.43
1ae	7-*t*-Butoxy-4-(4'-chlorophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	28 d	153 (Hexane)	$C_{17}H_{20}ClNO_3S$ (354.8)	Calcd.	57.71	5.66	3.96
					Found	57.88	5.72	3.89
1ag	7-*t*-Butoxy-4-(4'-nitrophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	14 d	158 (Hexane)	$C_{17}H_{20}N_2O_5S$ (364.4)	Calcd.	56.04	5.49	7.89
					Found	56.25	5.51	7.52
2ag	*syn*-8-*t*-Butoxy-2-(4'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	28 d	150 (Hexane)	$C_{17}H_{20}N_2O_5S$ (364.4)	Calcd.	56.04	5.49	7.69
					Found	55.71	5.53	7.59
1ba	7-Acetoxy-4-methylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	210 d	122 (Hexane)	$C_{10}H_{13}NO_4S$ (243.3)	Calcd.	50.44	5.35	5.76
					Found	50.36	5.45	5.89
1bc	7-Acetoxy-4-(4'-methylphenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	18 d	144 (Hexane)	$C_{16}H_{17}NO_4S$ (319.4)	Calcd.	60.15	5.33	4.39
					Found	60.13	5.28	4.38
1bd	7-Acetoxy-4-phenylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	210 d	102 (Hexane)	$C_{15}H_{15}NO_4S$ (305.3)	Calcd.	59.02	4.92	4.59
					Found	58.97	4.98	4.60
1be	7-Acetoxy-4-(4'-chlorophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	28 d	148 (Hexane)	$C_{15}H_{14}ClNO_4S$ (339.8)	Calcd.	53.02	4.15	4.12
					Found	52.77	4.18	4.05
2be	*syn*-8-Acetoxy-2-(4'-chlorophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	28 d	122 (Hexane)	$C_{15}H_{14}ClNO_4S$ (339.8)	Calcd.	53.02	4.15	4.12
					Found	53.19	4.17	4.03
1bg	7-Acetoxy-4-(4'-nitrophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	14 d	164 (Hexane)	$C_{15}H_{14}N_2O_6S$ (350.4)	Calcd.	51.43	4.00	7.99
					Found	51.64	4.06	7.82
2bg	*syn*-8-Acetoxy-2-(4'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	14 d	158 (Hexane)	$C_{15}H_{14}N_2O_6S$ (350.4)	Calcd.	51.43	4.00	7.99
					Found	51.40	4.04	7.73
1ca	7-Benzoyloxy-4-methylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	180 d	127 (Hexane)	$C_{15}H_{15}NO_4S$ (305.4)	Calcd.	58.99	4.95	4.59
					Found	59.09	4.92	4.50
1cc	7-Benzoyloxy-4-(4'-methylphenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	24 d	154 (Hexane)	$C_{21}H_{19}NO_4S$ (381.5)	Calcd.	65.14	5.02	3.67
					Found	64.92	5.00	3.62
1cd	7-Benzoyloxy-4-phenylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	60 d	132 (Hexane)	$C_{20}H_{17}NO_4S$ (367.4)	Calcd.	65.38	4.66	3.81
					Found	64.95	4.61	3.74
1ce	7-Benzoyloxy-4-(4'-chlorophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	28 d	148 (Hexane)	$C_{20}H_{16}ClNO_4S$ (402.8)	Calcd.	59.70	4.00	3.48
					Found	59.99	3.98	3.43
2ce	*syn*-8-Benzoyloxy-2-(4'-chlorophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	28 d	145 (Hexane)	$C_{20}H_{16}ClNO_4S$ (402.8)	Calcd.	59.70	4.00	3.48
					Found	59.90	4.03	3.47

maining mother liquor shows signals of the tetracyclic skeleton. The separation by column chromatography [eluent: *n*-hexane/ethyl acetate/acetic acid (80:19:1)] leads to colourless crystals of 4-phenylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane(**1gd**);R_f(**2gd**) = 0.55; R_f(**1gd**) = 0.40; yield 0.5 g (0.8%). – IR (KBr): $\tilde{\nu}$ = 1310, 1145 cm^{-1} (SO_2–N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 ("t", 2H, 7a,b-H), 2.06 (dm, 2H, 1-, 2-H), 2.29 (tq, 1H, 8H), 2.50 (tq, 1H, 6-H), 4.30 (m, 2H, 3-, 5-H), 7.45–7.92 (m, 5H, C_6H_5). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1 (dm, C-1, -2), 29.2 (tm, C-7), 35.8 (ddt, C-8), 43.9 (dm, C-6), 72.1 (dm, C-3, -5), 127.5 (dt, C-2′), 128.8 (dd, C-3′), 132.6 (dt, C-4′), 140.7 ("t", C-1′). – MS (70 eV): *m/z* (%) = 247 (1) [M$^+$], 220 (2) [M$^+$ – C_2H_3], 141 (17) [$PhSO_2^+$], 106 (99) [M$^+$ – $PhSO_2$].

$C_{13}H_{13}NO_2S$ (247.3) Calcd. C 63.13 H 5.30 N 5.66
Found C 62.99 H 5.22 N 5.59

Saponification of **1bc** *to N-(exo-6-Formylbicyclo[3.1.0]hex-3-en-exo-2-yl)-p-toluenesulfonamide* (**7**): 30 ml of a 0.1 N ethanolic KOH solution is added to 880 mg (2.76 mmol) of **1bc**. After stirring for 2.5 h, the reddish solution is diluted with 90 ml of water, and the pH of the solution is adjusted to 5–6 with 3 N H_2SO_4. At the same time a cream-coloured precipitate separates which is extracted with

Table 4 *(Continued)*

No.	Name	React. time	M.p. (Solvent)	Empirical formula (Molar mass)		Analysis C	H	N
2cg	*syn*-8-Benzoyloxy-2-(4'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	14 d	167 (Hexane)	$C_{20}H_{16}N_2O_4S$ (412.4)	Calcd. Found	58.26 58.23	3.91 3.94	6.80 6.81
1dc	7-Hydroxy-4-(4'-methylphenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane		136 (Ether)	$C_{14}H_{15}NO_3S$ (277.3)	Calcd. Found	60.65 60.64	5.42 5.46	5.05 4.93
2dc	*anti*-8-Hydroxy-2-(4'-methylphenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	20 d	111 (Hexane)	$C_{14}H_{15}NO_3S$ (277.3)	Calcd. Found	60.65 60.50	5.42 5.48	5.05 5.00
1dd	7-Hydroxy-4-phenylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane		110 (Ether)	$C_{13}H_{13}NO_3S$ (263.3)	Calcd. Found	59.32 59.55	4.94 4.96	5.32 5.23
2de	*anti*-8-Hydroxy-2-(4'-chlorophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	20 d	126 (Hexane)	$C_{13}H_{12}ClNO_3S$ (297.8)	Calcd. Found	52.44 52.37	4.06 4.13	4.70 4.61
1eb	7-Chloro-4-(4'-methoxyphenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	21 d	101 (Hexane)	$C_{14}H_{14}ClNO_3S$ (311.8)	Calcd. Found	53.93 53.88	4.53 4.32	4.49 4.41
2eb	*anti*-8-Chloro-2-(4'-methoxyphenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	21 d		$C_{14}H_{14}ClNO_3S$ (311.8)	Calcd.	59.70	4.00	3.48
2ec	*anti*-8-Chloro-2-(4'-methylphenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	21 d	128 (Ether)	$C_{14}H_{14}ClNO_2S$ (295.8)	Calcd. Found	56.85 56.72	4.77 4.72	4.74 4.60
1ee	7-Chloro-4-(4'-chlorophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	21 d	102 (Hexane)	$C_{13}H_{11}Cl_2NO_2S$ (316.2)	Calcd. Found	49.38 49.57	3.51 3.53	4.43 4.38
2ee	*anti*-8-Chloro-2-(4'-chlorophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	21 d		$C_{13}H_{11}Cl_2NO_2S$ (316.2)	Calcd.	49.38	3.51	4.43
2ef	*anti*-8-Chloro-2-(2'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	21 d	102 (Ether)	$C_{13}H_{11}ClN_2O_4S$ (326.8)	Calcd. Found	47.79 47.46	3.39 3.22	8.57 8.73
1eg	7-Chloro-4-(4'-nitrophenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}0^{3,6}]octane	21 d	179 (Ether)	$C_{13}H_{11}ClN_2O_4S$ (326.8)	Calcd. Found	47.79 47.42	3.39 3.41	8.57 8.48
2eg	*anti*-8-Chloro-2-(4'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	21 d	133 (Ether)	$C_{13}H_{11}ClN_2O_4S$ (326.8)	Calcd.	47.79	3.39	8.57
2fa	*anti*-8-Methylthio-2-methylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d		$C_9H_{13}NO_2S_2$ (231.3)	Calcd. Found	46.73 46.48	5.66 5.72	6.05 6.02
2fb	*anti*-8-Methylthio-2-(4'-methoxyphenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d		$C_{15}H_{17}NO_3S_2$ (323.4)	Calcd. Found	55.70 55.63	5.30 5.32	4.33 4.19
2fc	*anti*-8-Methylthio-2-(4'-methylphenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d		$C_{15}H_{17}NO_2S_2$ (307.4)	Calcd. Found	58.60 58.74	5.57 5.64	4.56 4.55
2fd	*anti*-8-Methylthio-2-phenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d		$C_{14}H_{15}NO_2S_2$ (293.4)	Calcd. Found	57.31 57.17	5.15 5.24	4.77 4.61
2fe	*anti*-8-Methylthio-2-(4'-chlorophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d	123 (Ether)	$C_{14}H_{14}ClNO_2S_2$ (327.9)	Calcd. Found	51.29 51.16	4.30 4.25	4.27 4.21
2ff	*anti*-8-Methylthio-2-(2'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d	108 (Ether)	$C_{14}H_{14}N_2O_4S_2$ (338.4)	Calcd. Found	49.69 49.66	4.17 4.19	8.28 8.24
2fg	*anti*-8-Methylthio-2-(4'-nitrophenylsulfonyl)-2-azabicyclo[3.2.1]octa-3,6-diene	7 d	152 (Ether)	$C_{14}H_{14}N_2O_4S_2$ (338.4)	Calcd. Found	49.69 49.70	4.17 4.12	8.28 8.18

Table 5. Spectral data of cycloaddition products

Comp.	IR (cm^{-1})	UV ($CHCl_3$) λ_{max} (nm)	lg ε	^1H NMR ($CDCl_3$) (ppm)	^{13}C NMR ($CDCl_3$) (ppm)	MS m/z (rel. Int.)	
1aa	1310 1130 1080	238	2.09	80 MHz: 1.18 (s, 9H, C_4H_9), 2.15-2.38 (m, 3H), 2.45-2.65 (m, 1H, 1-H), 2.93 (s, 3H, CH_3-SO_2R), 4.00 ("t", 1H, 7-H), 4.24 (m, 1H, 3-H), 4.62 (m, 1H, 5-H).	25.2 MHz: 24.8 (dm, C-2), 25.6 (dm, C-1), 28.3 (q"sept", -$C(CH_3)_3$), 40.5 (dd, C-8), 42.0 (q, SO_2CH_3), 46.0 (dm, C-6), 69.1 (d"d", C-3), 72.8 (d, C-7), 72.9 (d"t", C-5), 73.5 (m, C-Me_3).	201 (11) 57 (100)	[M^+-C_4H_9] [$C_4H_9^+$]
1ac	1320 1140 1080	273 263 241 238	2.54 2.77 3.56 3.55	80 MHz: 1.12 (s, 9H, C_4H_9), 2.05-2.45 (m, 4H), 2.45 (s, 3H, Ph-CH_3), 3.90 ("t", 1H, 7-H), 4.23 (m, 1H, 3-H), 4.62 (m, 1H, 5-H), 7.17-7.93 (m, 4H, C_6H_4).	25.2 MHz: 21.4 (qt, Ph-CH_3), 24.5 (dm, C-2), 25.3 (dm, C-1), 28.3 (q"sept", C-$(CH_3)_3$), 40.4 (dd, C-8), 47.3 (dm, C-6), 69.3 (d"d", C-3), 72.5 (d, C-7), 72.9 (dm, C-5), 73.4 (m, C-Me_3), 127.3 (dd, C-2', C-6'), 129.2 (d"qint", C-3', C-5'), 137.6 ("t", C-1'), 143.1 ("sx", C-4').	333 (5) 276 (45)	[M^+] [M^+-C_4H_9]
2ac	1590 1320 1160 1080	266 234	3.84 4.16	80 MHz: 1.00 (s, 9H, C_4H_9), 2.38 (s, 3H, Ph-CH_3), 2.43 (m, 1H, 5-H), 3.78 ("br s", 1H, 8-H), 4.35 (m, 1H, 1-H), 5.10 (dd, 1H, 7-H), 5.20 (dd, 1H, 4-H), 6.08 (dd, 1H, 6-H), 6.28 dd, 1H, 3-H), 7.18-7.80 (m,4H,C_6H_4).		333 (2) 276 (13) 57 (100)	[M^+] [M^+-C_4H_9] [$C_4H_9^+$]
1ad	1330 1150 1080	272 265 258 241 238	2.87 2.97 2.93 3.25 3.26	80 MHz: 1.12 (s, 9H, C_4H_9), 2.12-2.48 (m, 4H), 3.95 ("t", 1H, 7-H), 4.29 (m, 1H, 3-H), 4.66 (m, 1H, 5-H), 7.45-8.10 (m, 5H, C_6H_5).	25.2 MHz: 24.6 (dm, C-2), 25.4 (dm, C-1), 28.3 (q"sept", C-$(CH_3)_3$), 40.5 (dd, C-8), 47.2 (dm, C-6), 69.4 (d"d", C-3), 72.5 (ds, C-7), 73.1 (dm, C-5), 73.5 (m, C-$(CH_3)_3$), 127.2 (d"t", C-2', C-6'), 128.6 (d"d", C-3', C-5'), 132.4 (dt, C-4'), 140.7 ("t", C-1').	263 (17) 57 (100)	[M^+-C_4H_9] [$C_4H_9^+$]
1ae	1335 1150 1080	265 235	2.87 4.03	80 MHz: 1.17 (s, 9H, C_4H_9), 2.12-2.52 (m, 4H), 3.92 ("t", 1H, 7-H), 4.20 (m, 1H, 3-H), 4.59 (m, 1H, 5-H), 7.35-7.75 (m, 4H, C_6H_4).	25.2 MHz: 24.7 (dm, C-2), 25.5 (dm, C-1), 28.3 (q"sept", C-$(CH_3)_3$), 40.6 (dd, C-8), 47.0 (dm, C-6), 69.6 (d"d", C-3), 72.6 (ds, C-7), 73.3 (dm, C-5), 73.6 (m, C-$(CH_3)_3$), 128.7 (dd, C-2', C-6'), 128.9 (dd, C-3', C-5'), 138.8 ("tt", C-4'), 139.3 ("t", C-1').	355 (1) 298 (12) 57 (100)	[M^+] [M^+-C_4H_9] [$C_4H_9^+$]
1ag	1520 1360 1325 1140 1070	265	4.01	80 MHz: 1.18 (s, 9H, C_4H_9), 2.25-2.33 (m, 3H), 2.47-2.52 ("ddd", 1H, 1-H), 3.98 ("t", 1H, 7-H), 4.29 (m, 1H, 3-H), 4.67 (m, 1H, 5-H), 8.06-8.34 (m, 4H, C_6H_4).	25.2 MHz (^1H decoupled): 25.1 (C-2), 25.9 (C-1), 28.3 (C-$(CH_3)_3$), 40.9 (C-8), 46.8 (C-6), 70.3 (C-3), 72.8 (C-7), 73.8 (C-5), 74.1 (C-$(CH_3)_3$), 124.1 (C-3', C-5'), 128.5 (C-2', C-6'), 146.8 (C-1'), 150.0 (C-4').	307 (10) 57 (100)	[M^+-C_4H_9] [$C_4H_9^+$]
2ag	1610 1515 1340 1330 1160 1070	336 252	3.52 4.18	80 MHz: 0.98 (s, 9H, C_4H_9), 2.47 (m, 1H, 5-H), 3.94 ("dt", 1H, 8-H), 4.30 (m, 1H, 1-H), 5.15 (ddd, 1H, 4-H), 5.50 (dd, 1H, 7-H), 6.23 (dd, 1H, 6-H), 6.58 (dd, 1H, 3-H), 8.00-8.55 (m, 4H, C_6H_4).	25.2 MHz: 28.1 (q"sept", C-$(CH_3)_3$), 39.5 (dm, C-5), 61.3 (dm, C-1), 67.2 (dm, C-8), 73.9 (m, C-$(CH_3)_3$), 106.1 (dm, C-4), 121.4 (d"d", C-7), 122.6 (ds, C-3), 123.9 (dd, C-3', C-5'), 128.1 (dd, C-2', C-6'), 138.9 (d"br.d", C-6), 146.6 ("t", C-1'), 149.7 ("t", C-4').	364 (2) 307 (13) 57 (100)	[M^+] [M^+-C_4H_9] [$C_4H_9^+$]
1ba	1730 1320 1130	238	2.04	80 MHz: 2.05 (s, 3H, CH_3CO), 2.38-2.65 (m, 4H), 2.93 (s, 3H, SO_2-CH_3), 4.32 (m, 1H, 3-H), 4.60 (m, 1H, 5-H), 4.93 ("t", 1H, 7-H).	25.2 MHz: 20.9 (q, OOC-CH_3), 25.5 (dm, C-2), 25.5 (dm, C-1), 38.1 (dd, C-8), 42.1 (q, SO_2-CH_3), 43.3 (dm, C-6), 69.3 (d"d", C-3), 72.4 (dm, C-5), 75.1 (ds, C-7), 170.5 (q, OOC-CH_3).	243 (1) 200 (5) 184 (3) 43 (100)	[M^+] [M^+-CH_3CO] [M^+-CH_3CO_2] [CH_3CO^+]
1bc	1730 1330 1145	273 262 241 238	2.57 2.77 3.49 3.49	80 MHz: 2.02 (s, 3H, CH_3CO), 2.30-2.65 (m, 4H), 2.45 (s, 3H, Ph-CH_3), 4.37 (m, 1H, 3-H), 4.65 (m, 1H, 5-H), 4.93 ("t", 1H, 7-H), 7.33-7.97 (m, 4H, C_6H_4).	25.2 MHz: 20.9 (q, OOC-CH_3), 21.5 (qt, PhCH_3), 25.2 (dm, C-2), 25.3 (dm, C-1), 38.1 (dd, C-8), 44.5 (dm, C-6), 69.3 (d"d", C-3), 72.5 (d"br.t", (C-5), 74.9 (d, C-7), 127.3 (dd, C-2', C-6'), 129.3 (d"quint", C-3', C-5'), 137.3 ("t", C-1'), 143.5 ("sext", C-4'), 170.5 (q, OOC-CH_3).	318 (6) 275 (21) 164 (9) 155 (31) 43 (65)	[M^+-H] [M^+-CH_3CO] [M^+-Tos] [Tos$^+$] [CH_3CO^+]
1bd	1725 1320 1215 1150	272 265 258 240	3.45 3.51 3.47 3.60	80 MHz: 2.02 (s, 3H, CH_3CO), 2.34-2.61 (m, 4H), 4.35 (m, 1H, 3-H), 4.62 (m, 1H, 5-H), 4.87 ("t", 1H, 7-H), 7.43 (m, 5H, C_6H_5).	25.2 MHz: 20.8 (q, OOC-CH_3), 25.3 (dm, C-2), 25.3 (dm, C-1), 38.1 (dd, C-8), 44.5 (dm, C-6), 69.5 (d"d", C-3), 72.6 (dm, C-5), 74.8 (d, C-7), 127.2 (ddd, C-2', C-6'), 128.7 (dd, C-3', C-5'), 132.6 (dt, C-4'), 140.3 ("t", C-1'), 170.4 (q, OOC-CH_3).	305 (14) 262 (10) 164 (14) 141 (21) 43 (100)	[M^+] [M^+-CH_3CO] [M^+-$PhSO_2$] [$PhSO_2^+$] [CH_3CO^+]
1be	1720 1320 1140	234	4.16	80 MHz: 2.02 (s, 3H, CH_3CO), 2.32-2.65 (m, 4H), 4.35 (m, 1H, 3-H), 4.63 (m, 1H, 5-H), 4.90 ("t", 1H, 7-H), 7.40-7.95 (m, 4H, C_6H_4).	25.2 MHz: 20.9 (q, OOC-CH_3), 25.4 (dm, C-2), 25.4 (dm, C-1), 38.2 (dd, C-8), 44.3 (dm, C-6), 69.6 (d"d", C-3), 72.8 (dm, C-5), 74.9 (d, C-7), 128.7 (dd, C-2', C-6'), 129.0 (dd, C-3', C-5'), 139.0 ("tt", C-4'), 139.0 ("t", C-1'), 170.4 (q, OOC-CH_3).	339 (2) 296 (6) 175 (31) 164 (11) 122 (100) 43 (95)	[M^+] [M^+-CH_3CO] [RSO_2^+] [M^+-RSO_2] [$C_7H_8NO^+$] [CH_3CO^+]

Table 5 *(Continued)*

Comp.	IR (cm^{-1})	UV ($CHCl_3$) λ_{max} (nm)	lg ε	^1H NMR ($CDCl_3$) (ppm)	^{13}C NMR ($CDCl_3$) (ppm)	MS m/z (rel. Int.)
2be	1725 1330 1160	268 228	3.80 4.13	80 MHz: 1.63 (s, 3H, CH_3CO), 2.75 (m, 1H, 5-H), 4.58 (m, 1H, 1-H), 4.83 ("dt", 1H, 8-H), 5.03 (ddd, 1H, 4-H), 5.36 (dd, 1H, 7-H), 6.14 (dd, 1H, 6-H), 6.53 (dd, 1H, 3-H), 7.38-7.90 (m, 4H, C_6H_4).	25.2 MHz: 20.4 (q, OOC-CH_3), 37.2 (dm, C-5), 58.3 (dm, C-1), 67.2 (dm, C-8), 104.3 (dm, C-4), 120.6 (d"dt", C-7), 122.9 (s, C-3), 128.2 (dd, C-2', C-6'), 129.2 (dd, C-3', C-5'), 137.7 (d"br.d", C-6), 138.9 ("t", C-1'), 139.1 ("t", C-4'), 169.9 (q, OOC-CH_3).	339 (14) [M^+] 296 (6) [M^+-CH_3CO] 175 (25) [RSO_2^+] 164 (11) [M^+-RSO_2] 122 (88) [$C_7H_8NO^+$] 43 (100) [CH_3CO^+]
1bg	1725 1520 1340 1315 1140	265	3.96	80 MHz: 2.03 (s, 3H, CH_3CO), 2.45-2.75 (m, 4H), 4.41 (m, 1H, 3-H), 4.71 (m, 1H, 5-H), 4.96 ("t", 1H, 7-H), 8.05-8.58 (m, 4H, C_6H_4).		348 (4) [M^+-2] 307 (5) [M^+-CH_3CO] 291 (5) [M^+-CH_3COO] 186 (7) [RSO_2^+] 164 (5) [M^+-RSO_2] 43 (100) [CH_3CO^+]
2bg	1725 1520 1335 1150	326 247	3.54 4.11	80 MHz: 1.63 (s, 3H, CH_3CO), 2.81 (m, 1H, 5-H), 4.69 (m, 1H, 1-H), 4.91 ("dt", 1H, 8-H), 5.15 (ddd, 1H, 4-H), 5.43 (dd, 1H, 7-H), 6.25 (dd, 1H, 6-H), 6.60 (dd, 1H, 3-H), 8.02-8.54 (m, 4H, C_6H_4).		350 (6) [M^+] 307 (5) [M^+-CH_3CO] 291 (4) [M^+-CH_3COO] 186 (4) [RSO_2^+] 164 (9) [M^+-RSO_2] 43 (100) [CH_3CO^+]
1ca	1700 1300 1120	282 273 240 237	2.68 2.81 3.48 3.54	80 MHz: 2.43-2.75 (m, 4H), 2.93 (s, 3H, CH_3SO_2R), 4.40 (m, 1H, 3-H), 4.69 (m, 1H, 5-H), 5.18 ("t", 1H, 7-H), 7.30-8.10 (m, 5H, C_6H_5).	25.2 MHz: 25.6 (dm, C-2), 25.7 (dm, C-1), 38.3 (dd, C-8), 42.1 (q, SO_2-CH_3), 43.5 (dm, C-6), 69.4 (d"br.d", C-3), 72.4 (dm, C-5), 75.7 (d, C-7), 128.2 (dd, C-3', C-5'), 129.4 (dt, C-2', C-6'), 129.6 ("t", C-1'), 133.0 (d"t", C-4'), 165.9 (q, OOC-Ph).	305 (2) [M^+] 226 (4) [M^+-RSO_2] 200 (15) [M^+-PhCO] 183 (49) [RSO_2^+] 105 (100) [$PhCO^+$] 77 (100)
1cc	1710 1290 1140	272 228	3.26 4.42	80 MHz: 2.35-2.75 (m, 4H), 2.45 (s, 3H, CH_3Ph), 4.41 (m, 1H, 3-H), 4.73 (m, 1H, 5-H), 5.15 ("t", 1H, 7-H), 7.25-8.18 (m, 9H, C_6H_4, C_6H_5).	25.2 MHz: 21.5 (qt, Ph-CH_3), 25.3 (dm, C-2), 25.4 (dm, C-1), 38.3 (dd, C-8), 44.7 (dm, C-6), 69.5 (d"br.d", C-3), 72.6 (dm, C-5), 75.4 (d, C-7), 127.2 (dd, C-2', C-6'), 128.2 (dd, C-3", C-5"), 129.3 (dd, C-3', C-5'), 129.3 (dd, C-2", C-6"), 129.6 ("t", C-1"), 133.0 (d"t", C-4"), 137.4 ("t", C-1'), 143.4 ("sext", C-4'), 165.9 (q, OOC-Ph).	381 (6) [M^+] 276 (24) [M^+-PhCO] 260 (9) [M^+-PhCOO] 155 (32) [Tos^+] 105 (100) [$PhCO^+$]
1cd	1705 1320 1140	273 228 266	3.22 5.13 3.23	80 MHz: 2.32-2.77 (m, 4H), 4.35 (m, 1H, 3-H), 4.74 (m, 1H, 5-H), 5.17 ("t", 1H, 7-H), 7.33-8.20 (m, 10H, C_6H_5).	25.2 MHz: 25.4 (dm, C-2), 25.5 (dm, C-1), 38.3 (dd, C-8), 44.6 (dm, C-6), 69.6 (d"br.d", C-3), 72.7 (dm, C-5), 75.4 (d, C-7), 127.2 (dt, C-7), 127.2 (dt, C-2', C-6'), 128.2 (dd, C-3", C-5"), 128.7 (dd, C-3', C-5'), 129.4 (dt, C-2", C-6"), 129.5 ("t", C-1"), 132.6 ("dt", C-4'), 133.0 (d"t", C-4'), 140.3 ("t", C-1'), 165.9 (q, OOC-Ph).	367 (1) [M^+] 262 (9) [M^+-PhCO] 246 (4) [M^+-PhCOO] 226 (6) [M^+-$PhSO_2$] 141 (14) [$PhSO_2^+$] 105 (100) [$PhCO^+$]
1ce	1705 1320 1140	232 265	4.48 3.27	80 MHz: 2.43-2.79 (m, 4H), 4.47 (m, 1H, 3-H), 4.75 (m, 1H, 5-H), 5.21 ("t", 1H, 7-H), 7.54-8.22 (m, 9H, C_6H_4, C_6H_5).	25.2 MHz: 25.5 (dm, C-2), 25.6 (dm, C-1), 38.4 (dd, C-8), 44.5 (dm, C-6), 69.8 (d"br.d", C-3), 72.9 (dm, C-5), 75.4 (d, C-7), 128.2 (dd, C-3",C-5"), 128.6 (dd, C-2', C-6'), 129.0 (dd, C-3',C-5'), 129.4 (dd, C-2", C-6"), 129.5 ("t", C-1"), 133.0 (d"t", C-4"), 139.0 ("t", C-4'), 139.1 ("t", C-1'), 165.9 (q, OOC-Ph).	403 (1) [M^+] 298 (3) [M^+-PhCO] 226 (6) [M^+-RSO_2] 175 (16) [RSO_2^+] 105 (100) [$PhCO^+$]
2ce	1705 1330 1160	266 228	3.84 4.00	80 MHz: 2.87 (m, 1H, 5-H), 4.83 (m, 1H, 1-H), 5.18 ("t", 1H, 8-H), 5.18 ("dd", 1H, 4-H), 5.59 (dd, 1H, 7-H), 6.25 (dd, 1H, 6-H), 6.70 (dd, 1H, 3-H), 7.40-7.95 (m, 9H, C_6H_4, C_6H_5).	25.2 MHz: 37.5 (dm, C-5), 58.3 (dm, C-1), 67.4 (dm, C-8), 103.8 (dm, C-4), 121.1 (d"dt", C-7), 122.9 (d"dt", C-3), 127.8 (dd, C-2', C-6'), 128.1 (dd, C-3", C-5"), 128.9 ("t", C-1"), 129.1 (dd, C-3', C-5'), 129.2 (dd, C-2", C-6"), 133.1 (d"t", C-4"), 137.1 (d"d", C-6), 138.6 ("t", C-4'), 138.9 ("t", C-1'), 165.4 (q, OOC-Ph).	403 (9) [M^+] 401 (23) [M^+] 298 (9) [M^+-PhCO] 296 (24) [M^+-PhCO] 226 (21) [M^+-RSO_2] 175 (19) [RSO_2^+] 105 (100) [$PhCO^+$]
2cg	1710 1525 1340 1330 1240 1160	272 228	3.54 4.35	80 MHz: 2.81 (m, 1H, 5-H), 4.85 (m, 1H, 1-H), 5.15 ("t", 1H, 8-H), 5.25 ("dd", 1H, 4-H), 5.65 (dd, 1H, 7-H), 6.28 (dd, 1H, 6-H), 6.68 (dd, 1H, 3-H), 7.18-8.00 (m, 9H, C_6H_4).		412 (15) [M^+] 307 (6) [M^+-PhCO] 291 (9) [M^+-PhCOO] 105 (100) [$PhCO^+$]
1dc	3400 1325 1140	263 229	2.78 4.01	80 MHz: 2.11-2.35 (m, 4H), 2.45 (s, 3H, CH_3), 2.64 (br.s, 1H, OH), 4.02 (br.s, 1H, 7-H), 4.23 (m, 1H, 3-H), 4.66 (m, 1H, 5-H), 7.27-7.97 (m, 4H, C_6H_4).	25.2 MHz: 21.5 (qt, CH_3), 24.8 (dm, C-1), 25.6 (dm, C-2), 41.0 (dd, C-8), 47.6 (dm, C-6), 69.9 (dd, C-3), 72.5 (dm, C-5), 72.5 (d, C-7), 127.3 (dd, C-2', C-6'), 129.4 ("q", C-3',C-5'), 137.2 ("t", C-1'), 143.5 (m, C-4').	277 (3) [M^+] 260 (32 [M^+-OH] 155 (19) [Tos^+] 122 (85) [M^+-Tos]

Table 5 *(Continued)*

Comp.	IR (cm^{-1})	UV ($CHCl_3$) λ_{max} (nm)	lg ε	^1H NMR ($CDCl_3$) (ppm)	^{13}C NMR ($CDCl_3$) (ppm)	MS m/z (rel. Int.)
2dc	3500 1600 1580 1320 1150	263 228	3.76 3.93	80 MHz: 1.86 ("br.s", 1H, O*H*), 2.45 (s, 3H, C*H*$_3$-Ph), 2.50 (m, 1H, 5-H), 3.90 ("br.s", 1H, 8-H), 4.55 (m, 1H, 1-H), 5.20 (dd, 1H, 4-H), 5.25 (dd, 1H, 7-H), 6.21 (dd, 1H, 6-H), 6.33 (dd, 1H, 3-H), 7.27-7.88 (m, 4H, C$_6$*H*$_4$).		277 (29) [M$^+$] 260 (5) [M$^+$-OH] 234 (17) [M$^+$-C$_2$H$_3$O] 155 (27) [Tos$^+$] 122 (100) [M$^+$-Tos]
1dd	3450 1315 1140	273 265 258 234	2.82 2.93 2.85 2.37	300 MHz: 2.16-2.38 (m, 4H), 2.62 (br.s, 1H, O*H*), 4.06 (br.s, 1H, 7-H), 4.25 (m, 1H, 3-H), 4.62 (m, 1H, 5-H), 7.27-7.97 (m, 5H, C$_6$*H*$_5$).	25.2 MHz: 24.9 (dm, C-1), 25.6 (dm, C-2), 41.0 (dd, C-8), 47.6 (dm, C-6), 70.0 (dd, C-3), 72.5 (dm, C-5), 72.7 (d, C-7), 127.2 (ddd, C-2', C-6'), 128.7 (dd, C-3',C-5'), 132.7 (dd, C-4'), 140.2 ("t", C-1').	263 (2) [M$^+$] 246 (3) [M$^+$-OH] 141 (18) [PhSO$_2^+$] 122 (100) [M$^+$-RSO$_2$]
2de	3450 1610 1575 1330 1150	268 227	3.78 4.12	80 MHz: 2.05 ("br.s", 1H, O*H*), 2.56 (dm, 1H, 5-H), 3.94 ("br.s", 1H, 8-H), 4.54 (m, 1H, 1-H), 5.17 (dd, 1H, 7-H), 5.23 (dd, 1H, 4-H), 6.19 (dd, 1H, 6-H), 6.34 (dd, 1H, 3-H), 7.43-7.90 (m, 4H, C$_6$*H*$_4$).	25.2 MHz: 43.7 (dm, C-5), 64.0 (dm, C-1), 74.7 (dm, C-8), 110.0 (dm, C-4), 119.1 (d"dt", C-7), 122.5 (d, C-3), 128.0 (dd, C-2', C-6'), 129.5 (dd, C-3', C-5'), 137.7 (dm, C-6), 139.4 ("t", C-4'), 139.6 ("t", C-1').	299 (20) [M$^+$] 297 (49) [M$^+$] 282 (3) [M$^+$-OH] 280 (9) [M$^+$-OH] 177 (19) [M$^+$-RSO$_2$] 175 (50) [M$^+$-RSO$_2$] 122 (100) [RSO$_2^+$]
1eb	2870 1580 1320 1140	232	4.51	300 MHz: 2.30-2.50 (m, 2H, 1-H, 2-H), 2.58 (m, 2H, 6-H, 8-H), 3.87 (s, 3H, C*H*$_3$O), 4.03 (t, 1H, 7-H), 4.30 (m, 1H, 3-H), 4.57 (m, 1H, 5-H), 6.9-7.8 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 25.51 (C-2), 27.94 (C-1), 42.68 (C-8), 48.66 (C-6), 55.63 (OC*H*$_3$), 58.44 (C-7), 69.72 (C-3), 72.36 (C-5), 114.12 (C-3',C-5'), 129.68 (C-2', C-6'), 131.52 (C-1'), 163.16 (C-4').	
2eb				300 MHz: 2.77 (dm, 1H, 5-H), 3.88 (s, 3H, C*H*$_3$O), 3.89 (m, 1H, 8-H), 4.71 (m, 1H, 1-H), 5.20 (ddd, 1H, 7-H), 5.23 (dd, 1H, 4-H), 6.16 (ddd, 1H, 6-H), 6.28 (br.dd, 1H, 3-H), 7.0-7.8 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 45.07 (C-5), 55.69 (*C*H$_3$O), 62.53 (C-8), 65.02 (C-1), 109.40 (C-4), 114.58 (C-3', C-5'), 118.69 (C-7), 122.70 (C-3), 128.88 (C-2', C-6'), 130.80 (C-1'), 137.07 (C-6), 163.37 (C-4').	
2ec	1600 1350 1160	260 228	3.88 3.97	300 MHz: 2.45 (s, 3H, PhC*H*$_3$), 2.77 (dm, 1H, 5-H), 3.88 (br.t, 1H, 8-H), 4.73 (m, 1H, 1-H), 5.21 (ddd, 1H, 7-H), 5.24 (dd, 1H, 4-H), 6.16 (ddd, 1H, 6-H), 6.28 (ddd, 1H, 3-H), 7.3-7.7 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 21.62 (C-7'), 45.06 (C-5), 62.45 (C-8), 65.08 (C-1), 109.50 (C-4), 118.69 (C-7), 122.64 (C-3), 126.73 (C-2', C-6'), 130.05 (C-3', C-5'), 136.29 (C-1'), 137.08 (C-6), 144.31 (C-4').	295 (44) [M$^+$] 260 (48) [M$^+$-Cl] 155 (92) [Tos$^+$] 140 (90) [M$^+$-Tos] 91 (100) [C$_7$H$_7^+$]
1ee	1580 1340 1150	232	4.18	300 MHz: 2.45-2.65 (m, 4H), 4.07 (t, 1H, 7-H), 4.34 (ddd, 1H, 3-H), 4.61 (ddd, 1H, 5-H), 7.5-7.8 (m, 4H, C$_6$*H*$_4$).		315 (3) [M$^+$] 280 (48) [M$^+$-Cl] 175 (100) [RSO$_2^+$] 140 (75) [M$^+$-RSO$_2^+$]
2ee				300 MHz: 2.80 (dm, 1H, 5-H), 3.94 (br.t, 1H, 8-H), 4.74 (m, 1H, 1-H), 5.22 (ddd, 1H, 7-H), 5.29 (dd, 1H, 4-H), 6.19 (ddd, 1H, 6-H), 6.27 (ddd, 1H, 3-H), 7.5-7.8 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 45.03 (C-5), 62.42 (C-8), 65.26 (C-1), 110.11 (C-4), 118.70 (C-7), 122.37 (C-3), 128.13 (C-2', C-6'), 129.78 (C-3', C-5'), 137.42 (C-6), 137.87 (C-1'), 139.94 (C-4').	
2ef	1590 1540 1360 1165	231	3.86	300 MHz: 2.89 (dm, 1H, 5-H), 4.28 (br.t, 1H, 8-H), 4.84 (m, 1H, 1-H), 5.33 (dd, 1H, 4-H), 5.38 (ddd, 1H, 7-H), 6.25 (m, 1H, 6-H), 6.28 (m, 1H, 3-H), 7.6-8.2 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 45.04 (C-5), 62.95 (C-8), 65.83 (C-1), 109.16 (C-4), 118.99 (C-7), 122.23 (C-3), 124.57 (C-3'), 130.63 (C-6'), 132.20 (C-5'), 132.40 (C-1'), 134.49 (C-4'), 137.58 (C-6), 147.82 (C-2').	326 (10) [M$^+$] 291 (12) [M$^+$-Cl] 186 (84) [RSO$_2^+$] 140 (48) [M$^+$-RSO$_2$]
1eg	1600 1525 1350 1340 1160	263	4.01	300 MHz: 2.5-2.7 (m, 4H), 4.11 (t, 1H, 7-H), 4.41 (ddd, 1H, 3-H), 4.67 (ddd, 1H, 5-H), 8.0-8.4 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 26.24 (C-2), 28.60 (C-1), 43.01 (C-8), 48.03 (C-6), 58.52 (C-7), 70.69 (C-3), 73.37 (C-5), 124.21 (C-3',C-5'), 128.49 (C-2', C-6'), 146.30 (C-1'), 163.16 (C-4').	326 (12) [M$^+$] 291 (12) [M$^+$-Cl] 186 (84) [RSO$_2^+$] 140 (75) [M$^+$-RSO$_2$]
2eg	1520 1340 1150	249	4.03	300 MHz: 2.84 (dm, 1H, 5-H), 3.97 (br.t, 1H, 8-H), 4.80 (m, 1H, 1-H), 5.22 (ddd, 1H, 7-H), 5.36 (dd, 1H, 4-H), 6.21 (br."ddd", 1H, 6-H), 6.30 (ddd, 1H, 3-H), 8.0-8.5 (m, 4H, C$_6$*H*$_4$).	75 MHz (^1H decoupled): 44.99 (C-5), 62.41 (C-8), 65.56 (C-1), 111.00 (C-4), 118.69 (C-7), 122.03 (C-3), 124.73 (C-3', C-5'), 127.97 (C-2', C-6'), 137.87 (C-6), 145.10 (C-1'), 150.37 (C-4').	326 (22) [M$^+$] 291 (50) [M$^+$-Cl] 186 (52) [RSO$_2^+$] 140 (90) [M$^+$-RSO$_2$]

Table 5 *(Continued)*

Comp.	IR (cm^{-1})	UV ($CHCl_3$) λ_{max} (nm)	UV ($CHCl_3$) lg ε	^1H NMR ($CDCl_3$) (ppm)	^{13}C NMR ($CDCl_3$) (ppm)	MS m/z (rel. Int.)
2fa	1620 1340 1160			300 MHz: 2.17 (s, 3H, S-C*H*$_3$), 2.81 (dm, 1H, 5-H), 2.96 (s, 3H, SO_2-CH_3) 3.16 (br."t", 1H, 8-H), 4.78 (m, 1H, 1-H), 5.40 (dd, 1H, 4-H), 5.50 (dd, 1H, 7-H), 6.14 (ddd, 1H, 3-H), 6.27 (dd, 1H, 6-H).		231 (22) [M^+] 216 (22) [M^+-CH_3] 184 (33) [M^+-CH_3S] 152 (83) [M^+-CH_3SO_2] 104 (100) [$C_7H_6N^+$] 79 (47) [$CH_3SO_2^+$]
2fb	2860 1600 1500 1340 1160	235 265	4.17 4.00	80 MHz: 1.95 (s, 3H, S-C*H*$_3$), 2.60 (br.s, 1H, 8-H), 2.67 (dm, 1H, 5-H), 3.88 (s, 3H, OC*H*$_3$), 4.65 (m, 1H, 1-H), 5.18 (dd, 1H, 7-H), 5.28 (dd, 1H, 4-H), 6.10 (dd, 1H, 6-H), 6.30 (dd, 1H, 3-H), 6.8-7.9 (m, 4H, C_6H_4).		323 (26) [M^+] 307 (18) [M^+-CH_4] 276 (29) [M^+-CH_3S] 171 (71) [RSO_2^+] 152 (100) [M^+-RSO_2^+] 104 (40) [$C_7H_6N^+$]
2fc	1600 1500 1350 1170	233 264	3.55 3.56	80 MHz: 1.94 (s, 3H, S-C*H*$_3$), 2.44 (s, 3H, Ph-C*H*$_3$), 2.59 (br.s, 1H, 8-H), 2.66 (dm, 1H, 5-H), 4.68 (m, 1H, 1-H), 5.19 (dd, 1H, 7-H), 5.28 (dd, 1H, 4-H), 6.11 (dd, 1H, 6-H), 6.30 (dd, 1H, 3-H), 7.20-7.86 (m, 4H, C_6H_4).		307 (21) [M^+] 292 (20) [M^+-CH_3] 260 (32) [M^+-CH_3S] 155 (43) [Tos^+] 152 (100) [M^+-Tos] 104 (45) [$C_7H_6N^+$]
2fd	1620 1450 1350 1170			300 MHz: 1.91 (s, 3H, S-C*H*$_3$), 2.55 (br.s, 1H, 8-H), 2.68 (dm, 1H, 5-H), 4.69 (m, 1H, 1-H), 5.21 (ddd, 1H, 7-H), 5.32 (dd, 1H, 4-H), 6.15 (dd, 1H, 6-H), 6.31 (dd, 1H, 3-H), 7.43-8.00 (m, 5H, C_6H_5).	75 MHz (^1H decoupled): 15.63 (CH_3S), 42.67 (C-5), 53.16 (C-8), 63.52 (C-1), 111.54 (C-4), 119.75 (C-7), 122.13 (C-3), 126.75 (C-2', C-6'), 129.32 (C-3', C-5'), 133.13 (C-4'), 138.32 (C-6), 139.33 (C-1').	293 (28) [M^+] 278 (20) [M^+-CH_3] 246 (34) [M^+-CH_3S] 152 (100) [M^+-$PhSO_2$] 141 (32) [$PhSO_2^+$] 104 (53) [$C_7H_6N^+$]
2fe	1620 1580 1480 1350 1170	229 272	4.13 3.75	80 MHz: 1.97 (s, 3H, S-C*H*$_3$), 2.65 (br.s, 1H, 8-H), 2.73 (dm, 1H, 5-H), 4.69 (m, 1H, 1-H), 5.19 (dd, 1H, 7-H), 5.30 (dd, 1H, 4-H), 6.14 (dd, 1H, 6-H), 6.29 (dd, 1H, 3-H), 7.44-7.84 (m, 4H, C_6H_4).		329 (6) [M^+] 327 (11) [M^+] 311 (10) [M^+-CH_4] 279 (18) [M^+-CH_4S] 175 (26) [RSO_2^+] 152 (100) [M^+-RSO_2]
2ff	1620 1540 1370 1360 1170	236	3.80	80 MHz: 2.06 (s, 3H, S-C*H*$_3$), 2.78 (dm, 1H, 5-H), 3.00 (br.s, 1H, 8-H), 4.80 (m, 1H, 1-H), 5.33 (dd, 1H, 7-H), 5.44 (dd, 1H, 4-H), 6.23 (dd, 1H, 6-H), 6.30 (dd, 1H, 3-H), 7.65-8.15 (m, 4H, C_6H_4).		338 (21) [M^+] 323 (3) [M^+-CH_3] 290 (9) [M^+-CH_3S] 186 (38) [RSO_2^+] 152 (100) [M^+-RSO_2] 104 (52) [$C_7H_6N^+$]
2fg	1610 1530 1360 1170	252	4.30	80 MHz: 2.03 (s, 3H, S-C*H*$_3$), 2.75 (br.s, 1H, 8-H), 2.75 (dm, 1H, 5-H), 4.84 (m, 1H, 1-H), 5.25 (ddd, 1H, 7-H), 5.48 (dd, 1H, 4-H), 6.23 (dd, 1H, 6-H), 6.38 (dd, 1H, 3-H), 8.06-8.55 (m, 4H, C_6H_4).		338 (14) [M^+] 323 (8) [M^+-CH_3] 290 (22) [M^+-CH_4S] 186 (14) [RSO_2^+] 152 (100) [M^+-RSO_2] 104 (48) [$C_7H_6N^+$]

150 ml of ether. The obtained aldehyde **7** is extremely sensitive to oxidation; yield 320 mg (36%); m.p. 125°C. – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1} (N–H), 1680 (C=O), 1320, 1150 (SO_2). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.38 ("dt", 1H, 6-H), 2.28 ("dd", 1H, three-membered ring proton), 2.44 (s, 3H, CH_3), 2.55 ("dq", 1H, three-membered ring proton), 4.30 ("dq", 1H, 4-H), 4.74 (br. d, 1H, NH), 5.32 ("dt", 1H, =CH), 6.10 ("dt", 1H, =CH), 7.32–7.94 (m, 4H, C_6H_4), 9.19 (d, 1H, CH=O). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (qt, CH_3), 32.4 (d"t", C-5), 32.9 (dm, C-1), 42.8 (ddq, C-6), 59.9 (dm, C-4), 129.9 (dm, C-2), 129.9 (dm, C-3'), 136.0 (dm, C-3), 137.9 ("t", C-1'), 143.9 (m, C-4'), 197.2 (dt, C-7). – MS (70 eV): *m/z* (%) = 277 (15) [M^+], 249 (3) [M^+ – CO], 155 (24) [Tos^+], 122 (100) [M^+ – Tos].

$C_{14}H_{15}NO_3S$ (277.3) Calcd. C 60.63 H 5.45 N 5.05
Found C 60.51 H 5.41 N 5.06

Saponification of **1bc** *to 7-Hydroxy-4-(4'-methylphenylsulfonyl)-4-azatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane* (**1dc**): 1.2 g (3.76 mmol) of **1bc** is dissolved in 20 ml of absolute ethanol, and at ca. 0°C this solution is added dropwise over a period of 30 min to 3.7 ml of a 0.1 N ethanolic KOH solution. Subsequently, 50 ml of trichloromethane is added, and the mixture is washed three times with water. The organic layer is separated and dried with Na_2SO_4. After evaporation of the solvent, the remaining solid is recrystallized from ether. Thus, 900 mg (88%) of **1dc** is obtained as a white powder. For physical data see Tables 4 and 5.

Saponification of **1bd** *to 7-Hydroxy-4-phenylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane* (**1dd**): As has been described for the synthesis of **1cd**, 1.0 g (3.28 mmol) of **1bd** is dissolved in 20 ml of absolute ethanol and dropwise saponified with 3.1 ml of a 0.1 N ethanolic KOH solution. After analogous workup and recrystallization from ether, 735 mg (85%) of the azetidinol **1d** is obtained. For physical data see Tables 4 and 5.

Oxidation of **1dd** *to 4-Phenylsulfonyl-4-azatetracyclo[3.3.0.0^{2,8}.0^{3,6}]-octan-7-one* (**6**): To an ice-cooled, vigorously stirred solution of 3.50 g

(40 mmol) of dry pyridine in 40 ml of absolute dichloromethane is added 2.0 g (20 mmol) of chromium trioxide under nitrogen. The cooling bath is removed, and after 30 min, a solution of 250 mg (1.0 mmol) of **1dd** in 10 ml of dichloromethane is added dropwise. Subsequently, a spatula tip full of $MgSO_4$ is added, and the mixture is stirred at room temperature for 20 h. The reaction mixture is decanted from a tarry precipitate, the precipitate is washed with 100 ml of ether, and the combined solutions are filtered through a column filled 5 cm high with silica gel. Evaporation of the solvent yields 160 mg of a colourless, oily residue which is purified by a further column chromatography (eluent: ethyl acetate); R_f(**6**) = 0.80; yield 60 mg (23%), m.p. 113°C. – IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O), 1310, 1150 (SO_2), 1010 (C=O). – UV ($CHCl_3$): λ_{max} (lg ε) = 272 nm (2.83), 265 (2.92), 258 (2.82), 252 (2.71), 234 (2.96). – ^1H NMR (300 MHz, $CDCl_3$): δ = 2.22 (m, 1H, 6-H), 2.37 (dt, 1H, 8-H), 3.20 (dm, 2H, 1-, 2-H), 4.66 (m, 2H, 3-, 5-H), 7.49–7.92 (m, 5H, C_6H_5). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3 (dm, C-1, -2), 38.1 (dd, C-8), 41.2 (dm, C-6), 69.8 (ddq, C-3, -5), 127.1 (dt, C-2′), 129.1 (dd, C-3′), 133.1 (dt, C-4′), 140.3 ("t", C-1′), 205.9 ("s", C-7). – MS (70 eV): *m/z* (%) = 261 (1) [M^+], 233 (1) [M^+ – CO], 141 (8) [$PhSO_2^+$], 120 (6) [M^+ – $PhSO_2$], 92 (100) [$C_6H_6N^+$].

$C_{13}H_{11}NO_3S$ (261.3) Calcd. C 59.76 H 4.24 N 5.36
Found C 59.84 H 4.28 N 5.37

Hydrolysis of **1ac** *to N-(syn-7-tert-Butoxy-endo-5-chlorotricyclo-[2.2.1.0^{2,6}]heptan-endo-3-yl)-p-toluenesulfonamide* (**8**): 1.0 g (3.0 mmol) of **1ac** is dissolved in 15 ml of dry trichloromethane. At 0°C seven drops of concentrated HCl are added with vigorous stirring. The heterogeneous mixture is neutralized with an aqueous 10% $NaHCO_3$ solution, washed with water, and afterwards dried with Na_2SO_4. After evaporation of the solvent, a colourless oil is obtained in quantitative yield. After purification by chromatography [eluent: *n*-hexane/ethyl acetate/acetic acid (80:20:1)], **8** can be isolated as colourless crystals; yield 1.0 g (90%), m.p. 116°C. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (N–H), 1590 (C=C), 1320, 1150 (SO_2). – UV ($CHCl_3$): λ_{max} (lg ε) = 262 nm (2.70), 228 (4.10). – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.09 (s, 9H, C_4H_9), 1.21–1.90 (m, 4H), 2.45 (s, 3H, CH_3), 3.62 ("t", 1H, 7-H), 4.05 (m, 1H, 5-H), 4.31 (br. d, 1H, 3-H), 5.75 (br. d, 1H, NH), 7.20–7.95 (m, 4H, C_6H_4). – ^{13}C NMR (25.2 MHz, $CDCl_3$): δ = 17.7 (dm, C-2), 20.3 (dd, C-1), 21.4 (dm, Ph-CH_3), 22.5 (dt, C-6), 28.2 (d"sept", C_4H_9), 44.7 (d, C-4), 57.7 (dm, C-3), 61.4 (d"d", C-5), 72.0 (d, C-7), 74.0 [m, $OC(CH_3)_3$], 127.1 (dd, C-2′), 129.4 (d"quint", C-3′), 137.8 ("t", C-1′), 143.0 ("sext", C-4′), 170.5 ["q", $OC(CH_3)_3$]. – MS (70 eV): *m/z* (%) = 371 (1) [M^+], 369 (1) [M^+], 333 (3) [M^+ – HCl], 160 (35) [M^+ – $PhSO_2$], 141 (9) [$PhSO_2^+$], 91 (100) [$C_6H_5N^+$].

$C_{18}H_{24}ClNO_3S$ (369.9) Calcd. C 58.45 H 6.54 N 3.79
Found C 58.73 H 6.56 N 3.72

CAS Registry Numbers

1aa: 136708-45-7 / **1ac**: 136708-46-8 / **1ad**: 136708-48-0 / **1ae**: 136708-49-1 / **1ag**: 136708-50-4 / **1ba**: 136708-52-6 / **1bc**: 136708-53-7 / **1bd**: 136708-55-9 / **1be**: 136708-56-0 / **1bg**: 136708-58-2 / **1ca**: 136708-60-6 / **1cc**: 136708-61-7 / **1cd**: 136736-73-7 / **1ce**: 136708-62-8 / **1dc**: 136708-83-3 / **1dd**: 136708-84-4 / **1eb**: 136708-67-3 / **1ee**: 136708-70-8 / **1eg**: 136708-73-1 / **2ac** (*anti*): 136708-47-9 / **2ag**: (*syn*): 136708-51-5 / **2bc** (*syn*): 136708-54-8 / **2be**: (*syn*): 136708-57-1 / **2bg**: (*syn*): 136708-59-3 / **2ce**: (*syn*): 136708-63-9 / **2cg** (*syn*): 136708-64-0 / **2dc** (*anti*): 136708-65-1 / **2de** (*anti*): 136708-66-2 / **2eb** (*anti*): 136708-68-4 / **2ec** (*anti*): 136708-69-5 / **2ee** (*anti*): 136708-71-9 / **2ef** (*anti*): 136708-72-0 / **2eg** (*anti*): 136708-74-2 / **2fa** (*anti*): 136708-75-3 / **2fb** (*anti*): 136708-76-4 / **2fc** (*anti*): 136708-77-5 / **2fd** (*anti*): 136708-78-6 / **2fe** (*anti*): 136708-79-7 / **2ff** (*anti*): 136708-80-0 / **2fg** (*anti*): 136708-81-1 / **4a**: 877-06-5 / **4b**: 13426-49-8 / **4c**: 4796-68-3 / **4d**: 822-80-0 / **4e**: 1609-39-8 / **4f**: 136708-44-6 / **5a**: 1516-70-7 / **5b**: 4547-64-2 / **5c**: 941-55-9 / **5d**: 938-10-3 / **5e**: 4547-68-6 / **5f**: 6655-31-8 / **5g**: 4547-62-0 / **6**: 136708-85-5 / **7**: 136708-82-2 / **8**: 136708-86-6

[1] Dedicated to Professor *Leonhard Birkofer* on the occasion of his 80th birthday. – Part 78: B. Albert, D. Elsässer, H.-D. Martin, B. Mayer, T. J. Chow, A. P. Marchand, C.-T. Ren, M. N. Paddon-Row, *Chem. Ber.* **124** (1991) 2871, preceding paper.
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