

First [4 + 2] Cycloadditions Involving the Olefinic Bond of an ‘Aldoketeniminium Salt’ (= *N*-Alk-1-enylideneaminium Salt)

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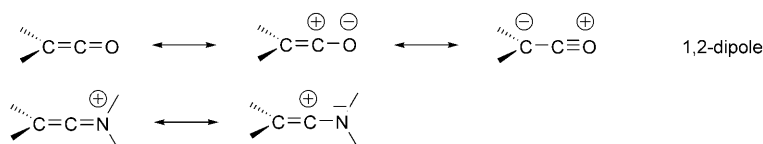
To Professor Rolf Huisgen, with admiration and respect

‘Keteniminium triflates’ (= *N*-alk-1-enylideneaminium trifluoromethanesulfonates; [MeN(Ts)CH=C=NR¹(R²)]⁺TrfO[−]) generated *in situ* from *N*^α-tosylsarcosinamides MeN(Ts)CH₂CONR¹(R²) unexpectedly react with cyclopenta-1,3-diene and cyclohexa-1,3-diene to give *Diels–Alder* reactions across the C=C bond of the cumulene. The use of *N*^α-tosylsarcosinamides derived from chiral pyrrolidines allows the direct preparation of trinorbornenone derivative **6** in high enantiomer purity.

Introduction. – The unique ability of ketenes to undergo [2 + 2] cycloadditions with electron-rich olefins was discovered as early as 1908 by *Chick* and *Wilsmore* [1a] and by *Staudinger* and *Klever* [1b]. Surprisingly little attention was paid to this reaction until the early sixties when its usefulness was demonstrated by several laboratories [2]. These studies brought about a remarkable resurgence of interest for this unusual cycloaddition reaction which is now a major component of the armory of the synthetic chemist [3]. Mechanistic studies among which one should especially mention the elegant and rigorous work of *Huisgen*’s group in Munich provided convincing arguments in favor of the formation of the two new σ bonds in a single elementary step [3]. Further experimental and theoretical studies provided further insight into this unique ability of ketene to undergo concerted [2 + 2] cycloadditions even with 1,3-dienes (*e.g.*, cyclopenta-1,3-diene) which are known to be highly reactive in *Diels–Alder* reactions [3]. In this context, it is interesting to mention that the reaction of bis(trifluoromethyl)ketene with olefins or conjugated dienes was shown to involve the reversible formation of a zwitterionic intermediate which cyclizes to give four-membered rings with olefins or six-membered rings with conjugated dienes [4]. A recent study claims that [2 + 2] cycloadducts of ketenes to olefins could be formed by a two-step sequence involving a [4 + 2] cycloaddition and a subsequent [3,3]-sigmatropic rearrangement [5].

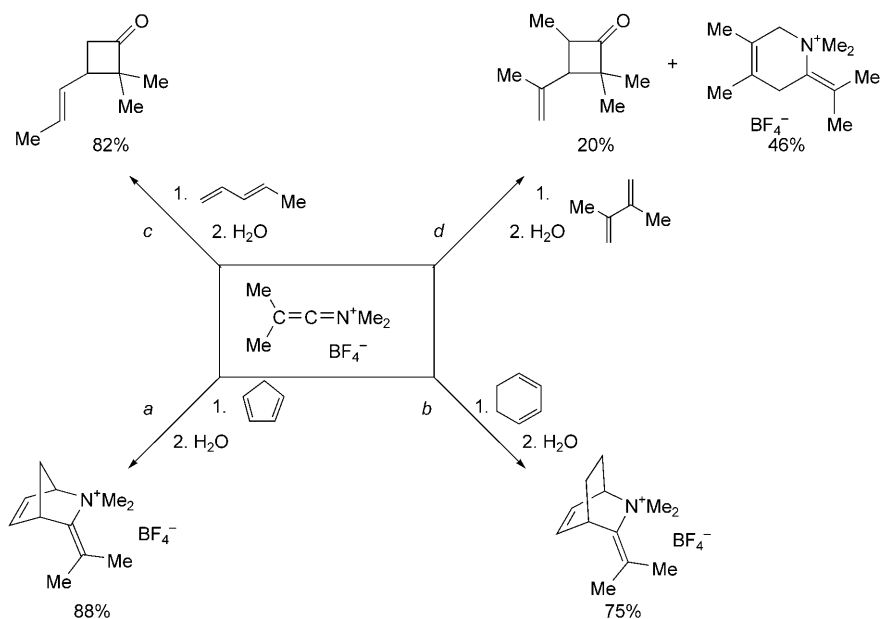
‘Keteniminium salts’ (= *N*-alk-1-enylideneaminium salts; R¹(R²)C=C=NR³(R⁴)⁺X[−]) are isoelectronic to allenes and lack the free electron-pair on the heteroatom which had been shown to give a 1,2-dipolar character to ketenes (*Scheme 1*) [6]. Still they also give [2 + 2] cycloadducts with olefins [3c] (for intermolecular cycloadditions, see [7]; for intramolecular cycloadditions, see [8]). However, their reactivity profile is somewhat different.

Scheme 1



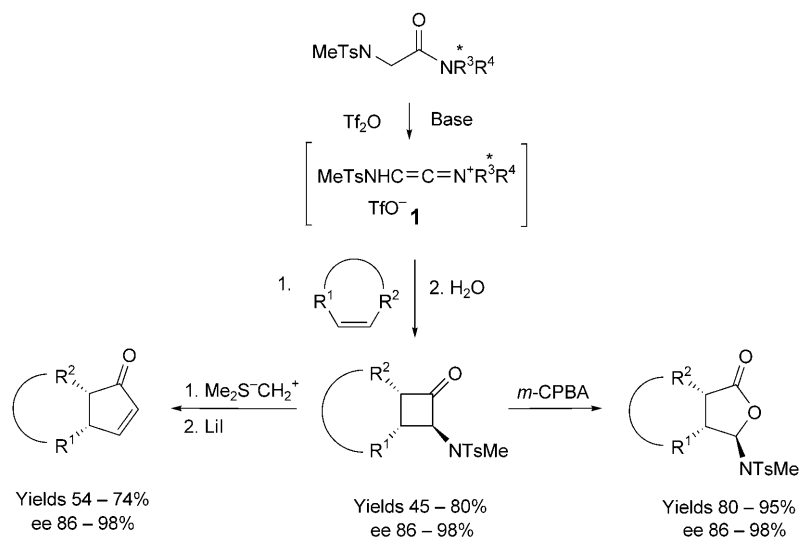
Thus, the reaction of ‘tetramethylketeniminium salts’ with *s-cis*-dienes exclusively yielded a [4 + 2] cycloadduct involving the C=N⁺ bond as dienophile component (Scheme 2, *a* and *b*) [8]. On the other hand, *s-trans* dienes such as buta-1,3-diene or (3*E*)-penta-1,3-diene only gave [2 + 2] cycloadducts (Scheme 2, *c*), while 2,3-dimethylbuta-1,3-diene gave a mixture of [2 + 2] and [2 + 4] adducts as a result of the lower energy barrier between the *s-cis* and *s-trans* conformations (Scheme 2, *d*) [9].

Scheme 2



Inter- and intramolecular cycloadditions of *in situ* generated ‘keteniminium salts’ derived from enantiomerically pure amides have been successfully used in asymmetric syntheses [10]. Thus, our group developed a short and practical enantioselective synthesis of prostanoid synthons involving an intramolecular [2 + 2] cycloaddition of a ‘keteniminium salt’ as key step [11]. More recently, we described an asymmetric [2 + 2 + 1] cyclopentannulation of olefins involving an enantioselective intermolecular [2 + 2] cycloaddition of ‘keteniminium salt’ **1** to olefins followed by the regioselective insertion of an O-atom or a CH₂ group into the strained four-membered ring adduct (Scheme 3) [12].

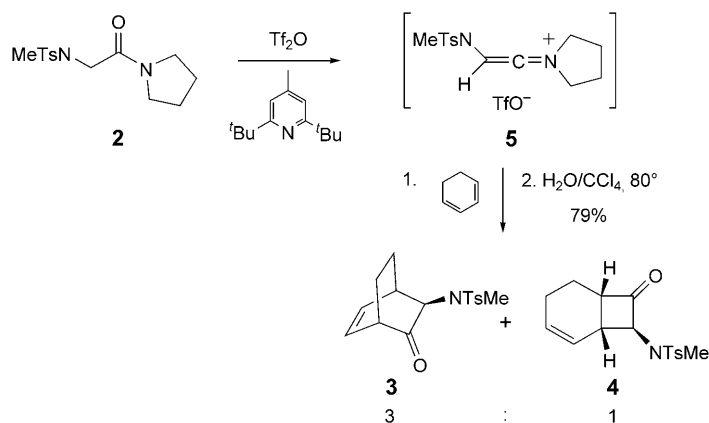
Scheme 3



In the course of these investigations, we encountered the first example of a *Diels–Alder* reaction involving the olefinic $\text{C}=\text{C}$ bond of a ‘keteniminium salt’. We describe here the details of these unexpected observations.

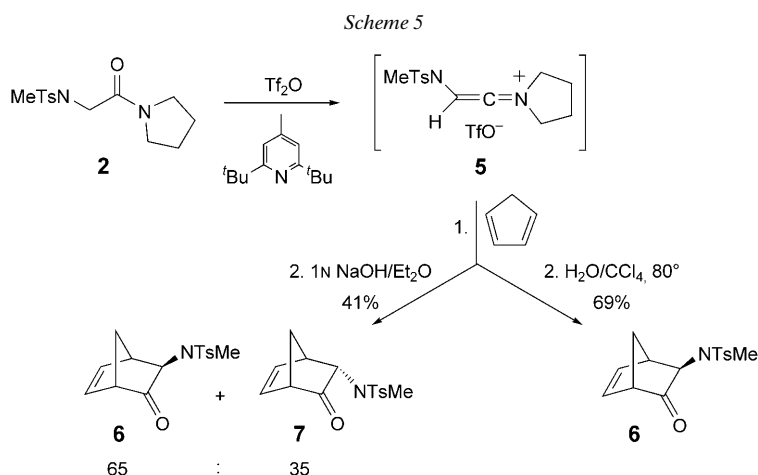
Results and Discussions. – *Racemic [4+2] Cycloadducts.* The slow addition of a diluted 1,2-dichloroethane solution of cyclohexa-1,3-diene into a mixture of N^α -tosyl-protected sarcosinamide **2**, triflic anhydride (=trifluoromethanesulfonic anhydride), and 2,6-di(*tert*-butyl)-4-methylpyridine in CH_2Cl_2 at room temperature followed by hydrolysis at 80° gave a 3:1 mixture (79% yield) of the N^α -tosyl-protected aminobicyclo[2.2.2]heptenone **3** and the expected hydrolyzed *exo*-[2+2] cycloadduct **4** (Scheme 4).

Scheme 4



Compound **3** obviously resulted from a $[4+2]$ cycloaddition of the diene to the olefinic bond of ‘keteniminium triflate’ **5** generated *in situ* [7c] followed by hydrolysis of the iminium function. The *exo*-configuration of the 3-[methyl(tosyl)amino] group was assigned on the basis of the value (1.6 H) of the $J(3,4)$ coupling constant.

With cyclopenta-1,3-diene (Scheme 5), the reaction was even more selective in favor of the *Diels–Alder* product. Under neutral hydrolysis, aminotrinorbornenone **6** was obtained in 69% yield, and less than 5% of the hydrolyzed $[2+2]$ cycloadduct was detected in the crude mixture. The *exo*-configuration of the 3-[methyl(tosyl)amino] substituent in **6** was again assigned on the basis of the value (1.5 H) of the $J(3,4)$ coupling constant.



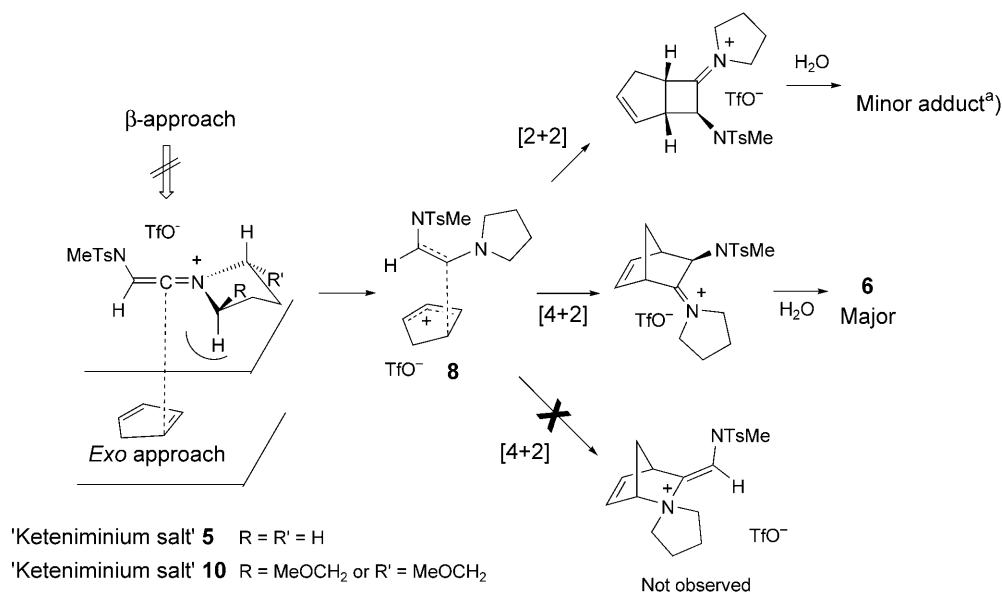
When the hydrolysis of the *Diels–Alder* adduct was performed under basic conditions, a 2 : 1 mixture of *exo*- and *endo* isomers **6** and **7**, respectively, was obtained in 41% yield (Scheme 5). This result was interesting as it indicated that the *exo*-adduct was the kinetic product which epimerized under the basic conditions of the hydrolysis.

This unique behavior of ‘keteniminium salt’ **5** can be most simply rationalized by the two-step cycloaddition mechanism proposed earlier (Scheme 6) [12a]. The first step of the reaction would lead to a homoallylic cation **8** originating from an *α-exo*-approach of the two reactants. As a result of the constrained *s-cis* conformation of the diene, the second C–C bond can be formed at each end of the allylic system. In the case of ‘keteniminium triflate’ **5**, the cyclization occurred at the less-substituted C-atom of the C=C bond rather than at the more-substituted N-atom.

To test this hypothesis, we attempted the reaction of cyclopenta-1,3-diene and cyclohexa-1,3-diene with other ‘aldoketeniminium salts’ but, in each case, we obtained intractable mixtures of products (Scheme 7).

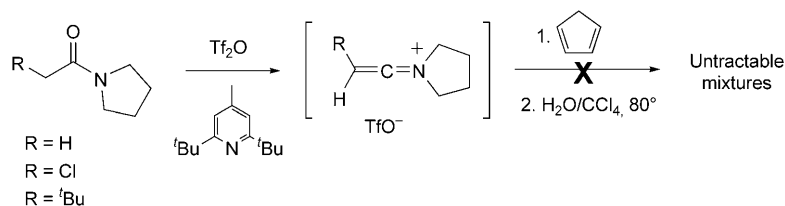
Scheme 6 shows that the configuration of the adducts is the result of the mode of approach of the two reacting partners in the first step of the reaction. Since we had observed that ‘*N*-methyl-*N*-tosylketeniminium salts’ derived from enantiomerically pure prolinol methyl ether or 2,5-dimethylpyrrolidine gave $[2+2]$ cycloadducts with

Scheme 6



^{a)} Less than 5% of the [2+2] adduct corresponding to **4** in the case of addition to cyclohexadiene (see Scheme 4).

Scheme 7



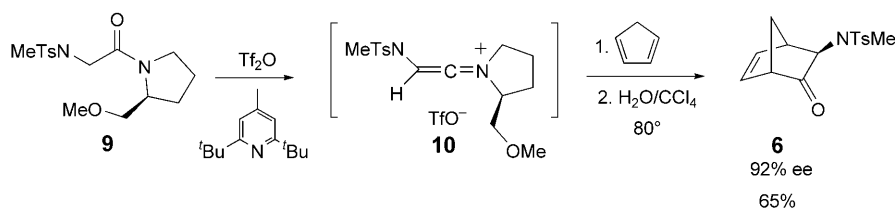
olefins with high facial selectivities, we anticipated that they should also yield [4+2] cycloadducts of high enantiomer purities.

Asymmetric [4+2] Cycloadditions. We then studied the behavior of 'keteniminium salt' **10** derived from C₁-symmetric amide **9** (Scheme 8). The reaction gave a 65% yield of *exo*-3-aminotrinorbornenone **6**. No [2+2] cycloadduct was detected.

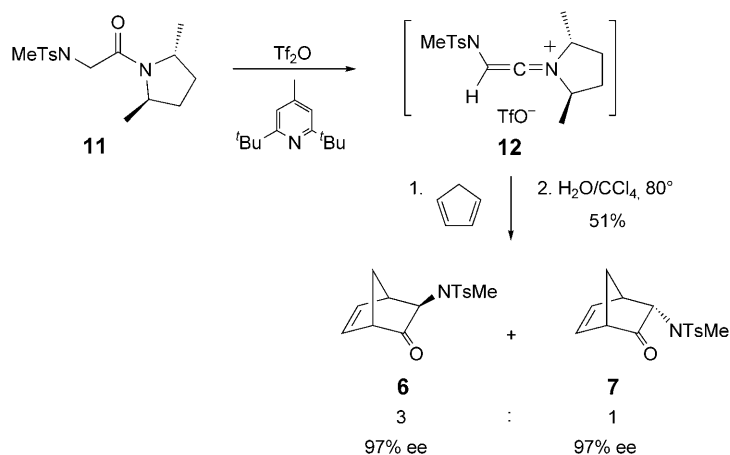
On the other hand, 'keteniminium salt' **12** derived from C₂-symmetric amide **11** yielded a 3:1 mixture of *exo*- and *endo*-3-aminotrinorbornenones **6** and **7** (Scheme 9). The formation of the *endo*-isomer **7** probably resulted from partial epimerization of the *exo*-adduct during the hydrolysis of the iminium function. This step was quite slow as a result of steric hindrance around the C=N⁺ bond.

Both amides **9** and **11** gave good yields of aminotrinorbornenones. They were formed in high enantiomer purities (92% ee and 97% ee). Enantiomer excesses were determined by chiral HPLC (AD column).

Scheme 8



Scheme 9

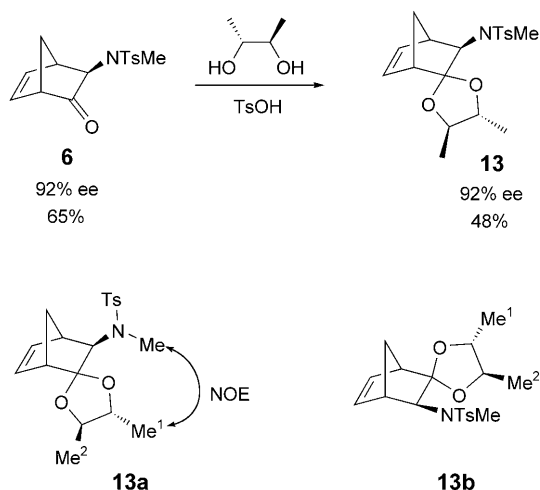


To determine the absolute configurations, ketal **13** was prepared starting from a chiral diol. Compound **13** could be either diastereoisomer **13a** or **13b** (Scheme 10). A nuclear *Overhauser* effect (NOE) was observed between the Me group of the methyl(phenylthio)amino group and Me¹ of **13**. Only **13a** could lead to such an NOE effect.

The formation of enantiomer **6** from **9** can be readily explained by the mechanism shown in Scheme 6 ($\text{R} = \text{MeOCH}_2$ or $\text{R}' = \text{MeOCH}_2$) [12a]. The preferred approach of the two reactants (Scheme 6) avoids steric interactions with two axial H-atoms of the ring.

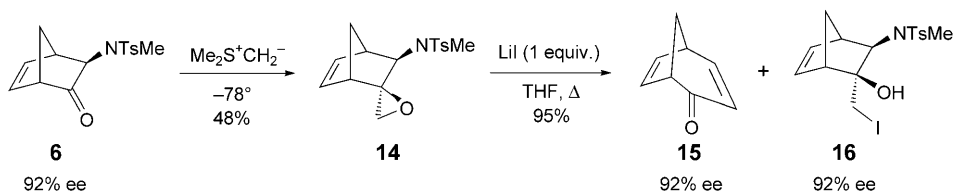
Conclusions. – In summary, we reported here the first examples of *Diels–Alder* reactions involving the C=C bond of a ‘keteniminium salt’ (= *N*-alk-1-enylideneaminium salt). This further emphasizes the difference of behavior of ketenes and ‘keteniminium salts’ as a result of the lack of a free electron pair at the heteroatom responsible for the 1,2 dipolar character of ketenes (Scheme 1) and their unique ability to give [2 + 2] cycloadditions with conjugated dienes even when they are constrained in a *s-cis* conformation favorable to a *Diels–Alder* reaction. At this point, however, the scope of our observations appear to be limited to ‘keteniminium salts’ derived from *N*^α-tosylsarcosinamides $\text{MeN}(\text{Ts})\text{CH}_2\text{CONR}^1(\text{R}^2)$.

Scheme 10



Remarkably, the *Diels–Alder* reactions of *N*^α-tosylsarcosinamide **9** derived from enantiomerically pure prolinol methyl ether are highly enantioselective giving a trinorbornenone derivative of high enantiomer purity. A direct access to trinorbornenones or bicyclo[2.2.2]octenones of high enantiomer purities should be of synthetic interest. Until now, *Diels–Alder* routes to these bicyclic enones used ketene synthetic equivalents as dienophiles which required several additional steps to regenerate the carbonyl group [13]. Also trinorbornenone derivatives **6** should be easily converted into a variety of other enantiomerically pure bicyclic systems as illustrated by a preliminary study shown in Scheme 11 [12b] ($\rightarrow$ **11–16**).

Scheme 11



This work was generously supported by the *Ministère de l'Éducation et de la Recherche, Communauté française de Belgique* (action concertée, conventions 96/01-197) and the University of Louvain.

Experimental Part

General. All solvents were distilled before use. All reagents were reagent grade. TLC: silica gel 60F₂₅₄. Column chromatography (CC): silica gel 40 (230–440 μm, Merck). HPLC: Millipore-Waters-600 controller, UV-Millipore-Waters-486 detector; anal. Diacel Chiralpack-AD column for the determination of ee; *t*_R in min. M.p.: uncorrected. [*α*]_D: Perkin-Elmer 241-MC polarimeter. IR Spectra: BioRad TFS-135-FT-IR spectrometer; $\tilde{\nu}$ in cm^{−1}. NMR Spectra: CDCl₃ solns.; Varian Gemini-200 or -300 spectrometers at 200 or 300 MHz (¹H) and

Bruker ARX-400 at 400 MHz (^1H) and 50 or 75 MHz (^{13}C) at r.t.; chemical shifts δ in ppm rel. to Me_4Si ($=0$ ppm, ^1H) or CDCl_3 ($=77.0$ ppm, ^{13}C); J in Hz. Mass Spectra: *Finnigan MAT-TSQ-700* spectrometer; in m/z (rel. %).

[4 + 2] *Cycloaddition–Hydrolysis Sequence: General Procedure (G.P.)*. Triflic anhydride (1.2 equiv.) was added to 0.1M sarcosinamide (1 equiv.) in 1,2-dichloroethane at 0° . After 5 min, the mixture was treated over 1 h with a 0.15M 2,6-di(*tert*-butyl)-4-methylpyridine (1.1 equiv.) and diene (4 equiv.) in 1,2-dichloroethane at 0° . After 3 h at r.t., the solvent was evaporated and the solid residue was taken up in a biphasic mixture of H_2O and CCl_4 . After 12 h at 80° , the aq. layer was extracted with CCl_4 ($3 \times$). The combined org. phase was dried (MgSO_4) and evaporated and the product purified by FC (silica gel, AcOEt/cyclohexane 2:8).

Cycloaddition of 5 with Cyclohexa-1,3-diene. According to the *G.P.*, with 1-[2-[methyl[(4-methylphenyl)sulfonyl]amino]acetyl]pyrrolidine (**2**; 500 mg, 1.7 mmol), triflic anhydride (340 μl , 2.0 mmol), 2,6-di(*tert*-butyl)-4-methylpyridine (380 mg, 1.9 mmol), and cyclohexa-1,3-diene (630 μl , 6.7 mmol): **3/4** 3:1 (408 mg, 79%).

Data of (1R,3SR,4SR)-3-[Methyl(tosyl)amino]bicyclo[2.2.2]oct-5-en-2-one (=N,4-Dimethyl-N-[(1R,2RS,4SR)-3-oxobicyclo[2.2.2]oct-5-en-2-yl]benzenesulfonamide; 3): IR (neat): 2950, 2880, 1739, 1338, 1166. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.71 (*d*, $J=8.4$, 2 H); 7.33 (*d*, $J=8.4$, 2 H); 6.45 (*ddd*, $J=7.9$, 6.3, 1.2, 1 H); 6.10 (*ddd*, $J=7.9$, 6.8, 1.9, 1 H); 4.28 (*d*, $J=1.6$, 1 H); 3.25–3.20 (*m*, 1 H); 2.95–2.80 (*m*, 1 H); 2.55 (*s*, 3 H); 2.42 (*s*, 3 H); 2.05–1.80 (*m*, 2 H); 1.40–1.15 (*m*, 2 H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 205.6; 143.0; 136.3; 136.1; 129.2 (2C); 127.1 (2C); 126.0; 61.1; 48.0; 38.5; 31.0; 24.5; 21.5; 19.6. EI-MS: 305 (20), 277 (100), 155 (8), 91 (24). HR-MS: 305.1083 ($\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}^+$; calc. 305.1086).

Data of (1R,6SR,8SR)-8-[Methyl(tosyl)amino]bicyclo[4.2.0]oct-2-en-7-one (=N,4-Dimethyl-N-[(1R,6SR,7RS)-8-oxobicyclo[4.2.0]oct-4-en-7-yl]benzenesulfonamide; 4): IR (neat): 2926, 1781, 1340, 1166. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.71 (*d*, $J=8.4$, 2 H); 7.33 (*d*, $J=8.4$, 2 H); 6.05–5.95 (*m*, 1 H); 5.90–5.85 (*m*, 1 H); 4.95 (*dd*, $J=7.5$, 2.9, 1 H); 3.15 (*tdd*, $J=9.9$, 7.5, 2.9, 1 H); 2.95–2.80 (*m*, 1 H); 2.79 (*s*, 3 H); 2.43 (*s*, 3 H); 2.05–1.80 (*m*, 2 H); 1.40–1.15 (*m*, 2 H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 206.1; 143.7; 135.7; 129.7 (2C); 129.5; 127.4 (2C); 126.2; 76.8; 52.0; 31.7; 29.4; 21.8; 21.5; 20.6. EI-MS: 305 (4), 277 (44), 225 (12), 185 (12), 160 (100), 91 (52). HR-MS: 305.1091 ($\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}^+$; calc. 305.1086).

Cycloaddition of 5 with Cyclopenta-1,3-diene. According to the *G.P.*, with **2** (500 mg, 1.7 mmol), triflic anhydride (340 μl , 2.0 mmol), 2,6-di(*tert*-butyl)-4-methylpyridine (520 mg, 2.5 mmol), and cyclopenta-1,3-diene (550 μl , 6.7 mmol): **6** (340 mg, 69%).

After application of the *G.P.* as described above, basic hydrolysis was performed in a biphasic mixture of Et_2O and 1N aq. NaOH at r.t. during 12 h: **6/7** 2:1 (200 mg, 41%).

Data of (1R,3SR,4SR)-3-[Methyl(tosyl)amino]bicyclo[2.2.1]hept-5-en-2-one (=N,4-Dimethyl-N-[(1R,2RS,4SR)-3-oxobicyclo[2.2.1]hept-5-en-2-yl]benzenesulfonamide; 6): IR (neat): 2963, 2917, 2853, 1753, 1340, 1160. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.70 (*d*, $J=8.3$, 2 H); 7.30 (*d*, $J=8.3$, 2 H); 6.61 (*dd*, $J=5.6$, 2.8, 1 H); 6.21 (*ddt*, $J=5.6$, 3.2, 0.8, 1 H); 3.93 (*d*, $J=3.5$, 1 H); 3.25–3.20 (*m*, 1 H); 2.95 (*dt*, $J=3.2$, 1.7, 1 H); 2.78 (*s*, 3 H); 2.42 (*s*, 3 H); 2.32 (*dt*, $J=10.2$, 1.7, 0.8, 1 H); 2.24 (*dddd*, $J=10.2$, 3.5, 1.7, 1.5, 1 H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 209.0; 143.6; 135.6; 133.6; 129.7 (2C); 127.4 (2C); 58.4; 53.6; 46.8; 46.7; 33.2; 21.5. CI-MS (pos.): 292 (12); HR-CI-MS (pos.): 292.1011 ($\text{C}_{15}\text{H}_{17}\text{NO}_3\text{S}^+$; calc. 292.1007).

Data of (1R,3RS,4SR)-3-[Methyl(tosyl)amino]bicyclo[2.2.1]hept-5-en-2-one (=N,4-Dimethyl-N-[(1R,2SR,3SR)-3-oxobicyclo[2.2.1]hept-5-en-2-yl]benzenesulfonamide; 7): IR (neat): 2963, 2917, 2853, 1753, 1340, 1160. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.73 (*d*, $J=8.3$, 2 H); 7.28 (*d*, $J=8.3$, 2 H); 6.52 (*dd*, $J=5.5$, 2.7, 1 H); 6.10 (*dd*, $J=5.5$, 4.4, 1 H); 4.36 (*d*, $J=3.0$, 1 H); 3.25–3.20 (*m*, 1 H); 3.09 (*m*, 1 H); 2.63 (*s*, 3 H); 2.42 (*s*, 3 H); 2.30–2.20 (*m*, 1 H); 2.01 (*br. d*, $J=9.7$, 1 H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 207.8; 143.3; 140.9; 135.9; 133.5; 129.8 (2C); 127.1 (2C); 61.4; 55.0; 47.2; 45.5; 31.9; 21.5. CI-MS (pos.): 292 (12). HR-CI-MS (pos.): ($\text{C}_{15}\text{H}_{17}\text{NO}_3\text{S}^+$; calc. 292.1007).

Cycloaddition of 10 with Cyclopenta-1,3-diene. According to the *G.P.*, with (2*S*)-2-(methoxymethyl)-1-[2-[methyl[(4-methylphenyl)sulfonyl]amino]acetyl]pyrrolidine (**9**; 500 mg, 1.4 mmol), triflic anhydride (300 μl , 1.7 mmol), 2,6-di(*tert*-butyl)-4-methylpyridine (330 mg, 1.5 mmol), and cyclopenta-1,3-diene (490 μl , 5.6 mmol): **6** (280 mg, 65%; 92% ee). HPLC (*AD*, EtOH , flow 0.3 ml min^{-1} , λ 254 nm): t_R 19.5 ((1*S*,3*R*,4*R*), 30.7 (1*R*,3*S*,4*S*)). $[\alpha]_D = -124.3$ ($c=0.59$, CH_2Cl_2).

Cycloaddition of 12 with Cyclopenta-1,3-diene. According to the *G.P.*, with (2*R*,5*R*)-2,5-dimethyl-1-[2-[methyl[(4-methylphenyl)sulfonyl]amino]acetyl]pyrrolidine (**11**; 500 mg, 1.5 mmol), triflic anhydride (310 μl , 1.8 mmol), 2,6-di(*tert*-butyl)-4-methylpyridine (350 mg, 1.7 mmol), and cyclopenta-1,3-diene (510 μl , 6.0 mmol): **6** (97% ee) and **7** (97% ee) (230 mg, 51%) in the ratio 3:1. HPLC (*AD*, EtOH , flow 0.3 ml min^{-1} , λ 254 nm): t_R 19.5 (**6** (1*S*,3*R*,4*R*)), 22.8 (**7** (1*S*,3*S*,4*R*)), 30.7 (**6** (1*R*,3*S*,4*S*)), and 44.5 (**7** (1*R*,3*R*,4*S*)).

(1*S*,3*R*,4*R*)-3-[Methyl(tosyl)amino]bicyclo[2.2.1]hept-5-en-2-one (1*R*,2*R*)-1,2-Dimethylethane-1,2-diyl Acetal (=N,4-Dimethyl-N-[(1*S*,3*R*,4*R*,4'*R*,5'*R*)-4',5'-dimethylspiro[bicyclo[2.2.1]hept-5-ene-2,2'-[1,3]dioxolan]-3-yl]benzenesulfonamide; **13**). A mixture of 0.02M **6** (100 mg, 0.3 mmol) in toluene, (2*R*,3*R*)-butane-2,3-diol, and a catalytic amount of TsOH was refluxed overnight in a Dean–Stark apparatus. The mixture was cooled to r.t. and washed twice with 5% aq. NaHCO₃ soln. The combined org. layer was dried (MgSO₄) and evaporated and the product purified by FC silica gel, AcOEt/cyclohexane 2:8; **13** (60 mg, 48%). [α]_D = +45.1 (*c* = 0.75, CH₂Cl₂). IR (neat): 2979, 1340, 1151. ¹H-NMR (200 MHz, CDCl₃): 7.65 (*d*, *J* = 8.3, 2 H); 7.31 (*d*, *J* = 8.3, 2 H); 6.22 (*dd*, *J* = 5.7, 3.0, 1 H); 6.16 (*dd*, *J* = 5.7, 3.0, 1 H); 3.98 (*dq*, *J* = 8.4, 6.0, 1 H); 3.88 (*d*, *J* = 2.7, 1 H); 3.64 (*dq*, *J* = 8.4, 6.0, 1 H); 2.89 (*s*, 3 H); 2.50–2.40 (*m*, 1 H); 2.44 (*s*, 3 H); 2.01 (*br. s*, 1 H); 1.96 (*d*, *J* = 9.3, 1 H); 1.63 (*br. d*, *J* = 9.3, 1 H); 1.33 (*d*, *J* = 6.0, 3 H); 1.23 (*d*, *J* = 6.0, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 143.0; 138.8; 136.4; 135.6; 129.6 (2C); 126.9 (2C); 113.6; 79.9; 78.4; 64.5; 49.5; 46.5; 42.4; 31.0; 21.5; 16.5; 16.4.

(1*S*,2*S*,3*R*,4*R*)-3-[Methyl(tosyl)amino]spiro[bicyclo[2.2.1]hept-5-ene-2,2'-oxirane] (=N,4-Dimethyl-N-[(1*S*,2*S*,3*R*,4*R*)-spiro[bicyclo[2.2.1]hept-5-ene-2,2'-oxiran]-3-yl]benzenesulfonamide; **14**). At –15°, 2.5M BuLi in hexanes (410 μ l) was added to 0.05M trimethylsulfonium tetrafluoroborate (135 mg, 0.8 mmol) in THF. After 15 min, the mixture was cooled to –78° and treated with a soln. of **6** (200 mg, 0.7 mmol). After 15 h at r.t., the mixture was diluted with Et₂O washed twice with H₂O, the org. layer dried (MgSO₄), and evaporated, and the residue purified by FC (silica gel, AcOEt/cyclohexane 2:8); **11** (60 mg, 48%). [α]_D = –2.4 (*c* = 0.42, CH₂Cl₂). IR (neat): 2984, 1340, 1171. ¹H-NMR (300 MHz, CDCl₃): 7.66 (*d*, *J* = 8.4, 2 H); 7.32 (*d*, *J* = 8.4, 2 H); 6.26 (*dd*, *J* = 5.6, 3.2, 1 H); 6.16 (*dd*, *J* = 5.6, 2.8, 1 H); 4.07 (*d*, *J* = 1.6, 1 H); 2.93 (*s*, 3 H); 2.76 (*d*, *J* = 4.9, 1 H); 2.74 (*d*, *J* = 4.9, 1 H); 2.44 (*s*, 3 H); 2.36 (*m*, 1 H); 2.30 (*s*, 1 H); 2.12 (*d*, *J* = 9.2, 1 H); 1.75 (*dd*, *J* = 9.2, 1.6, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 143.2; 139.9; 136.5; 135.4; 129.6 (2C); 126.9 (2C); 62.4; 56.9; 48.2; 47.0; 46.8; 43.5; 31.4; 21.4. EI-MS: 351 (84), 239 (100), 155 (44), 150 (36), 91 (52), 42 (40). HR-EI-MS: 305.1095 (C₁₆H₁₉NO₃S⁺; calc. 305.1086).

Rearrangement of Spirooxirane **14**. LiI (36 mg, 0.27 mmol) was added to a soln. of **14** (83 mg, 0.27 mmol) in THF (3 ml). The mixture was heated for 2 h at 65°, then cooled to r.t. and evaporated. The crude was purified by FC (AcOEt/cyclohexane 2:8); **15** (15 mg, 45%) and **16** (60 mg, 50%).

Data of (1*S*,5*R*)-Bicyclo[3.2.1]oct-3,6-dien-2-one (**15**): This compound has already been described as a racemic mixture (CA Registry Number 1122-53-8). [α]_D = –5.8 (*c* = 0.12, CH₂Cl₂). ¹H-NMR (200 MHz, CDCl₃): 7.34 (*dd*, *J* = 9.7, 6.4, 1 H); 6.68 (*dd*, *J* = 5.3, 2.9, 1 H); 6.18 (*dd*, *J* = 5.3, 3.3, 1 H); 5.44 (*ddd*, *J* = 9.7, 1.9, 0.8, 1 H); 3.30 (*m*, 1 H); 3.21 (*m*, 1 H); 2.54 (*m*, 1 H).

Data of (1*S*,2*S*,3*R*,4*R*)-2-(Iodomethyl)-3-[methyl(tosyl)amino]bicyclo[2.2.1]hept-5-en-2-ol (=N-[(1*R*,2*R*,3*S*,4*S*)-3-Hydroxy-3-(iodomethyl)bicyclo[2.2.1]hept-5-en-2-yl]-N,4-dimethylbenzenesulfonamide; **16**): [α]_D = +59.2 (*c* = 0.52, CH₂Cl₂). IR (neat): 3523, 2986, 1340, 1171. ¹H-NMR (200 MHz, CDCl₃): 7.66 (*d*, *J* = 8.3, 2 H); 7.35 (*d*, *J* = 8.3, 2 H); 6.23 (*dd*, *J* = 5.6, 2.9, 1 H); 6.14 (*dd*, *J* = 5.6, 3.0, 1 H); 3.68 (*d*, *J* = 10.8, 1 H); 3.59 (*d*, *J* = 1.6, 1 H); 3.18 (*d*, *J* = 10.8, 1 H); 3.00–2.90 (*m*, 1 H); 2.93 (*s*, 3 H); 2.59 (*br. s*, 1 H); 2.45 (*s*, 3 H); 2.14 (*d*, *J* = 9.4, 1 H); 1.63 (*d*, *J* = 9.4, 1 H). ¹³C-NMR (50 MHz, CDCl₃): 143.9; 138.3; 136.2; 136.2; 134.0; 129.9 (2C); 127.3 (2C); 78.3; 64.1; 51.2; 46.2; 45.4; 31.7; 21.5; 19.6. EI-MS: 434 (20), 306 (20), 292 (100).

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Received April 4, 2005