174. Regioselective Electrophilic Additions of Bicyclo[2.2.*n*]alk-2-enes Controlled by Remote Epoxide Functions[1])

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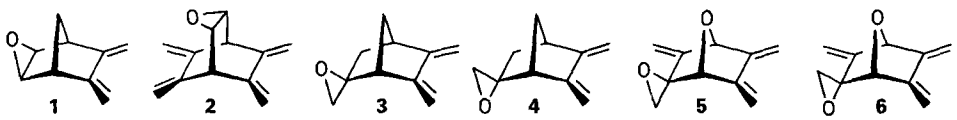
The electrophilic additions of 2-nitrobenzenesulfenyl chloride to (1*RS*,2*SR*,4*RS*)-spiro[bicyclo[2.2.1]hept-5-ene-2,2'-oxirane] (**12**) and (1*RS*,2*SR*,4*RS*)-spiro[bicyclo[2.2.2]oct-5-ene-2,2'-oxirane] (**14**) were not regioselective under conditions of kinetic control. However, good regioselectivity was observed for the addition of 2-nitro-benzenesulfenyl chloride to (1*RS*,2*RS*,4*RS*)-spiro[bicyclo[2.2.1]hept-5-ene-2,2'-oxirane] (**13**), giving (1*RS*,2*SR*,4*SR*,5*RS*,6*RS*)-6-*exo*-(2-nitrophenylthio)spiro[bicyclo[2.2.1]heptane-2,2'-oxirane]-5-*endo*-yl chloride (**24**), and for the *exo* addition to (1*RS*,2*RS*,4*RS*)-spiro[bicyclo[2.2.2]oct-5-ene-2,2'-oxirane] (**15**), giving preferentially (1*RS*,2*SR*,4*SR*,5*RS*,6*RS*)-6-*exo*-(2-nitrophenylthio)spiro[bicyclo[2.2.2]octane-2,2'-oxirane]-5-*endo*-yl chloride (**30**). The facial selectivity (electrophilic *exo vs. endo* attack on the bicyclic alkene) depended on the relative configuration of the spiroepoxide ring in the bicyclo[2.2.2]octenes **14** and **15**. The *exo*-epoxide **14** was attacked preferentially (6:1) on the *endo* face by sulfenyl whereas *exo* attack was preferred (7:2) in the case of the *endo*-epoxide **15**. No products resulting from transannular ring expansion of the spiro-epoxide moieties could be detected.

Introduction. – Epoxide moieties are able to affect the reactivity of homoconjugated π-functions. For instance, we have shown that 2-*exo*,3-*exo*-epoxy-5,6-dimethylidenebicyclo[2.2.1]heptane (**1**) is significantly less reactive than 2,3-dimethylidenebicyclo[2.2.1]heptane toward strong dienophiles [2], probably because of a LUMO(epoxide)-HOMO(diene) interaction in **1**. Similar interaction is believed to intervene between the epoxide and *anti*-diene moieties of epoxy-tetraene **2**, thus making the *syn*-diene unit the preferred site in *Diels-Alder* reactions[3]) [3]. We have reported also that epoxy-dienes **3** and **4** and epoxy-trienes **5** and **6** add to unsymmetrical dienophiles regioselectively, the regioselectivity depending on the relative configuration (*exo vs. endo*) of the oxiranes [4].



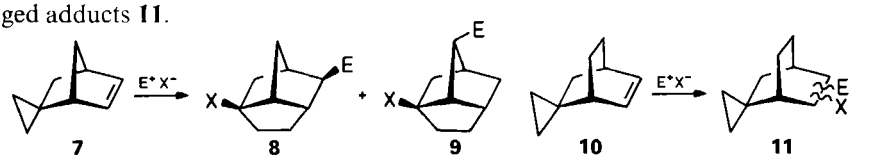
Recently, *Adam* and coworkers [5] have shown that on treatment with arenesulfenyl chloride (E^+X^-), spiro[bicyclo[2.2.1]hept-5-ene-2,1'-cyclopropane] (**7**) readily undergoes transannular ring expansion of the spirocyclopropane moiety to substituted brendanes **8**

[1]) Interactions between non-conjugated chromophores, Part 28. Part 27, see [1].

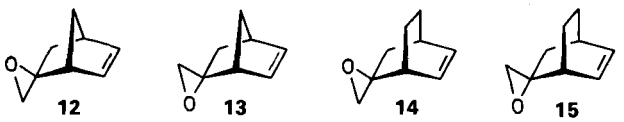
[2]) Part of the planned Ph. D. thesis of *F. Claret*, Ecole Polytechnique Fédérale de Lausanne.

[3]) The descriptors *syn* and *anti* refer to the positions of groups on the same and opposite side, respectively, with respect to the epoxy group.

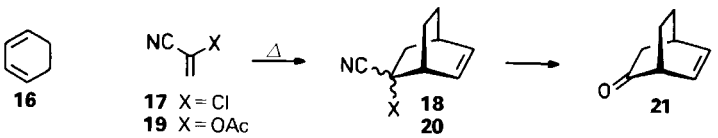
and **9**. In contrast, electrophilic addition of the homologue **10** gave mixtures of unrearranged adducts **11**.



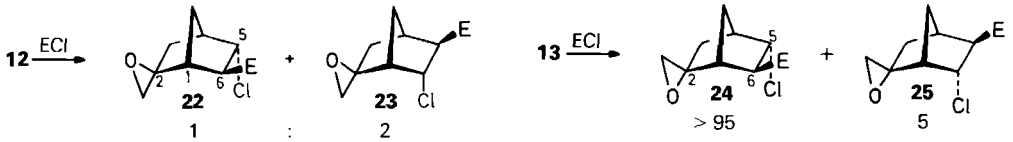
In the light of these results, we have studied the additions of 2-nitrobenzenesulfenyl chloride (NBSCl) to spiro[bicyclo[2.2.*n*]alk-5-ene-2,2'-oxiranes] **12**–**15**. We shall show that transannular ring expansion of the spirooxirane moieties does not occur, neither in the bicyclo[2.2.1]heptene nor in the bicyclo[2.2.2]octene series. Moreover, we have found that electrophilic addition is only regioselective for epoxy-alkenes **13** and **15** in which the O-atom of the oxirane moieties is in *endo* position[4]). Furthermore, we have found that the face selectivity of the additions of bicyclo[2.2.2]octene derivatives **14** and **15** depends on the relative configuration of the epoxide.



Results. – The known epoxides **12** and **13** were derived from bicyclo[2.2.1]hept-5-en-2-one [6] using known procedures [7] [8]. The same methods were applied in the preparation of the spiro[bicyclo[2.2.2]oct-5-ene-2,2'-oxiranes] **14** and **15**. Heating cyclohexa-1,3-diene (**16**) with 2-chloroacrylonitrile (**17**) gave a mixture of adducts **18** [9] (53%) which was transformed into bicyclo[2.2.2]oct-5-en-2-one (**21**; 63%) on treatment with KOH in DMSO. Alternatively, **21** was obtained in 45% yield on treating the mixture of acetates **20** in anh. MeOH containing MeONa and formaline [10]. Adducts **20** were made by cycloaddition of *16* to *1*-cyanovinyl acetate (*19*) in the presence of a catalytical amount of ZnI_2 at 20°.



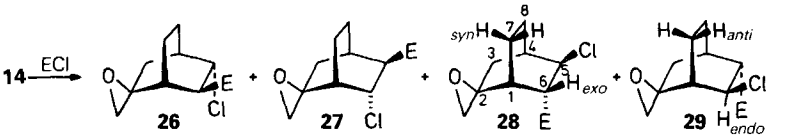
Treatment of **21** with dimethyloxosulfonium methide (Me_3SOI/DMSO + NaH [6]) gave a 92:8 mixture **14**/**15**. With dimethylsulfonium methide (Me_3SI/DMSO/THF + NaH [7]), **21** gave a 8:2 mixture **14**/**15** (74%) which was separated and purified by medium-pressure column chromatography on silical gel, affording **14** in 41% and **15** in 10% yield.



E = 2-nitrobenzenesulfenyl (NBS)

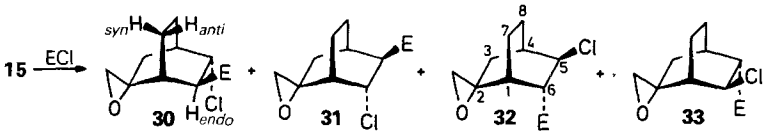
[4]) The descriptors *endo*/*exo* for bicyclo[2.2.2]alk-2-enes or -alkanes refer to orientations of groups with respect to the unsubstituted main bridge CH_2CH_2.

The *exo*-epoxide **12** added 1 equiv. of NBSCl in $CHCl_3$ at 20° and afforded a 1:2 mixture **22**/**23** (79% isolated). Under the same conditions, the *endo*-epoxide **13** gave a single product **24** (75% isolated), no trace of the isomeric adduct **25** could be detected by 360-MHz ^{1}H-NMR of the crude reaction mixture. As expected for bicyclo[2.2.1]hept-2-ene systems [11], the electrophile added preferably to the *exo* face of the olefinic moieties of **12** and **13**. The relatively high regioselectivity of the reaction **13** + NBSCl→**24** (the electrophile occupying the *exo* position at C(6), the nucleophile (Cl) the *endo* position at C(5)) is noteworthy and in contrast to the weak regioselectivity (1:2) observed for the addition **12** + NBSCl→**22** + **23**. Preliminary results of the electrophilic additions of benzeneselenyl chloride and 2,4-dinitrobenzenesulfenyl chloride to **12** and **13** (360-MHz ^{1}H-NMR analysis of crude reaction mixtures) suggested similar selectivities as those observed with the reactions of NBSCl. In the former cases, unfortunately, adducts could not be isolated and purified because of their instability.



E = 2-nitrobenzenesulfenyl (NBS)

On treating the *exo*-epoxide[4]) **14** with 1 equiv. of NBSCl in $CHCl_3$, a 1:1:6:6 mixture **26**/**27**/**28**/**29** (70%, isolated) was obtained after 15 h at 20°. The major products **28** and **29** were isolated and purified by HPLC. Under the same conditions, the *endo*-epoxide[4]) **15** afforded a 6:1:1:1 mixture **30**/**31**/**32**/**33** (80%) from which **30**, **32**, and **33** could be isolated and purified by HPLC. It is interesting that facial selectivity (*exo vs. endo* face[4])) of electrophilic addition is invested when going from **14** (*endo* preferred by 6:1) to **15** (*exo* face preferred by 7:2). For both modes of additions (*exo* and *endo* attack by E^+) on **14**, there is no regioselectivity. The same is also true for *endo* attack of **15** by the electrophilic S-atom of NBSCl. Nevertheless, a 6:1 regioselectivity for the *exo* addition of **15** is observed. The latter is of the same type as that of the addition **13** + NBSCl→**24**. All the adducts **22**–**33** were formed under conditions of kinetic control, *i.e.* they were not isomerized under the conditions of their formation ($CHCl_3$, 20°) or upon heating to 50° for several hours.



E = 2-nitrobenzenesulfenyl (NBS)

The structures of adducts **22**–**24**, **28**–**30**, **32**, and **33** followed from their spectral data and elemental analyses. The 360-MHz ^{1}H-NMR spectra of the crude reaction mixture confirmed the structures proposed for the minor compounds **26**, **27**, and **31** which could not be isolated. Signals in the 360-MHz ^{1}H-NMR spectra were assigned by double irradiation experiments and measurements of nuclear *Overhauser* effects (NOE; see *Exper. Part*). The

position of the *exo* and *endo* protons at C(3), C(5), and C(6) in the bicyclo[2.2.1]heptyl derivatives **22–24** was established by their vicinal coupling constants with the adjacent bridgehead protons H–C(1) and H–C(4) [12]. The signals of *H*–C–Cl and *H*–C–SAr were easily distinguished by their NOE's observed upon irradiating the aromatic-proton signals of the ArS substitutent. Significantly, larger NOE's were observed for *H*–C–SAr than for *H*–C–Cl signals. NOE measurements confirmed also the relative configurations (*exo. vs. endo*) of the protons at C(3), C(5), and C(6). The *trans* relationship between the Cl and ArS substituents was expected since arenesulfenyl chlorides have been shown to undergo *anti* addition to a large variety of olefins [13]. The relative configuration (*exo vs. endo*) of the methano moieties of the epoxide rings in **14** and **15** and in adducts **22–24**, **28–30**, **32**, and **33** was established by NOE measurements involving the proton pairs shown in *Fig. 1*. The same technique confirmed the structural assignment made earlier for **12** and **13** in an unambiguous fashion [6].

On treating adduct **29** with an excess of *t*-BuOK in THF (–70° to 20°), 1 equiv. of HCl was eliminated to give the unstable alkene **34**. The structure of **34** followed from its 360-MHz ^{1}H-NMR spectrum with the help of NOE and double-irradiation experiments, thus confirming the regioselectivity of reaction **14** + NBSCl→**29**.

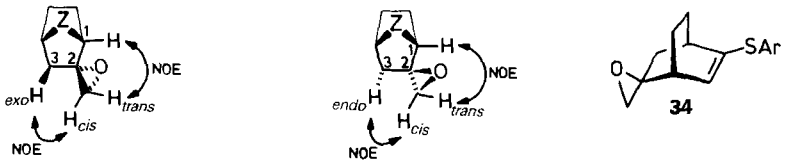
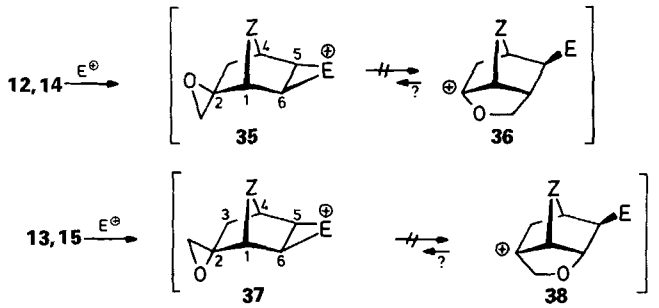


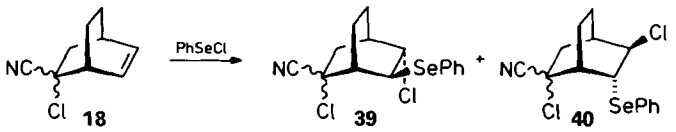
Fig. 1

Discussion. – In contrast to the reaction of the spirocyclopropane derivative **7** which gave brendane derivatives **8** and **9** on reaction with arenesulfenyl chloride [5], the *exo*-epoxide analog **12** (and also **14**) did not give any products arising from the hypothetical rearrangement **35**→**36** involving transannular migration (1,3-alkyl shift) of the *endo* C–C bond of the epoxide. This is possibly due to the inductive effect of the O-atom in **35** [14]. Neither did products result from the hypothetical rearrangement **37**→**38** involving migration of the alkoxy function in electrophilic additions of the *endo*-epoxide **13** (and **15**). This may be due to the relative instability of the *β*-alkoxy substituted carbenium ion intermediate **38** (inductive destabilization effect of the *β*-alkoxy substituent [15–17a]).



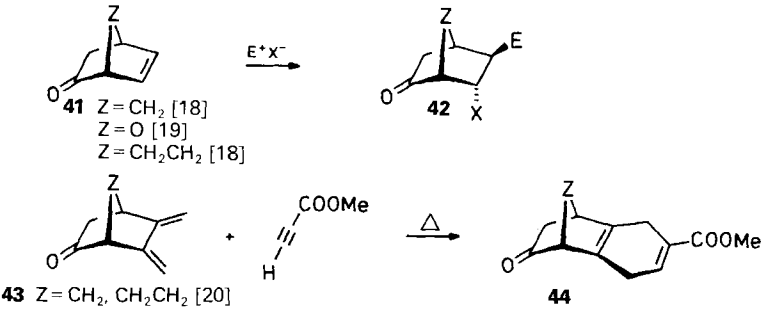
Although the hypothetical α-alkoxy-substituted carbenium ion **36** is expected to be a relatively stable intermediate, its formation does not compete with nucleophilic quenching (by Cl^-) of the bridged sulfonium ions **35**. The relatively high energy barrier to migration **35**→**36** might be interpreted in the following way. At the earlier stage of the hypothetical C–C bond cleavage of the epoxide moiety in **35**, little positive charge

appears at C(2). Because of that, the inductive (permanent dipole) destabilizing effect of the O-atom dominates as its stabilizing polarisability effect (n(O)↔pC(+) conjugation) cannot compete [17b].



In the case of the addition of benzeneselenyl chloride to the double bond of the bicyclo[2.2.2]oct-2-ene derivatives **18**, both *exo* and *endo* attack led exclusively to the formation of adducts **39** and **40** [18] in which the nucleophile (Cl^-) is attached to the C-atom most remote (C(5)) from the electron-withdrawing Cl and CN substituents at C(2). It is thus a surprise to find only weak or no regioselectivity in the electrophilic additions **12** + NBSCl→**22** + **23** and **14** + NBSCl→**26**–**29**. It could be argued that steric repulsions between the *endo* substituents at C(2) of **18** and the attacking Cl^- are responsible for the regioselectivity **18**→**39**. Nevertheless, this argument is not valid in the case of the reaction **18**→**40**. Therefore, the latter regioselectivity must be explained by an electronic factor. Inspection of molecular models suggests that the *endo*-methano group of the *exo*-epoxide functions in **12** and **14** is not bulking that the $CH_2(3)$ group and thus should not affect the regioselectivity of the additions of olefins **12** and **14** through a steric factor. The lack of regioselectivity of additions **12** + NBSCl→**22** + **23** and **14** + NBSCl→**26** + **27** + **28** + **29** agrees with that hypothesis. It further suggests that the dipole moment of the *exo*-epoxide functions has little or no influence on the regioselectivity of the quenching of cationic intermediates **35** by Cl^-.

The relatively high regioselectivity of reactions **13** + NBSCl→**24** and of the electrophilic *exo* addition **15** + NBSCl→**30** + **31** (6:1) is also surprising. We attribute it to the electrostatic effect of the *endo* O-atom in the *endo*-epoxides **13** and **15** which repels attack of chloride ion onto the *endo* face of the epi-sulfonium intermediate **37**, thus favouring attack at C(5) instead of C(6).



There is a correspondence between electrophilic additions to the endocyclic double bond in bicyclo[2.2.*n*]alk-5-en-2-ones **41** [18] [19], giving exclusively adducts **42** under conditions of kinetic control, and the *Diels-Alder* regioselectivity of the exocyclic dienes **43** toward an electron-poor dienophile such as methyl propynoate, which gave preferen-

tially cycloadducts **44** [20]. The regioselectivity of both types of reactions was attributed to the electron-donating ability of the homoconjugated carbonyl group because of a favourable hyperconjugative interaction of the type n(CO), σ[C(2),C(1)], π[C(6),C(5)] [21] [22]. On the other hand no parallelism exists between the regioselectivity of electrophilic additions to the bicyclo[2.2.*n*]alk-5-en-2-yl derivatives **12**–**15** and that of the *Diels-Alder* additions of epoxy-dienes **3** and **4** and epoxy-trienes **5** and **6** as it was found that the *exo*-epoxide moieties in **3** and **5**, apparently, were playing the role of electron-withdrawing substituents and the *endo*-epoxide moieties in **4** and **6** acted as remote electron-donating groups [4].

We are grateful to *Hoffmann-La Roche & Co. AG,* Basel, the *Fonds Herbette,* Lausanne, and the *Swiss National Science Foundation* for financial support. We thank Mr. *M. Rey* and Mr. *G. Jaccard* for help in the high-field ^{1}H-NMR measurements.

Experimental Part

1. *General.* See [19]. Prep. HPLC: *Dupont Instruments 830* liquid chromatograph. IR spectra: *Perkin-Elmer-1420* instrument. MS: *Nermag-R10-10C* or *Finningan-1020* spectrometer (GC/MS systems).

2. *2*-exo- *and 2*-endo-*Chlorobicyclo[2.2.2]oct-5-ene-2-carbonitriles* (**18**). A mixture of 1,3-cyclohexadiene (21 g, 0.20 mol), 2-chloroacrylonitrile (27.5 g, 0.31 mol, freshly distilled from KOH pellets) and hydroquinone (50 mg) was heated under reflux in the dark for 20 h. After cooling to 20°, CH_2Cl_2 (25 ml) was added and the soln. filtered through a short column of silica gel (300 g, CH_2Cl_2) and evaporated: 23.2 g (53.2%), brownish solid [9].

Bicyclo[2.2.2]oct-5-en-2-one (**21**). A soln. of KOH (30 g, 0.536 mol) in H_2O (50 ml) was added dropwise to a soln. of **18** (23.2 g, 0.139 mol) in DMSO (100 ml). After stirring at 20° for 15 h, H_2O (500 ml) was added and the mixture extracted with pentane (100 ml, 5 times). The combined org. extracts were washed with sat. aq. NaCl soln. (100 mol, 4 times), dried ($MgSO_4$), and evaporated: 10.7 g (63%), colourless solid [9].

*(1*RS,*2*SR,*4*RS*)-Spiro[bicyclo[2.2.2]oct-5-ene-2,2'-oxirane]* (**14**) *and (1*RS,*2*RS,*4*RS*)-Spiro[bicyclo-[2.2.2]oct-5-ene-2,2'-oxirane]* (**15**). A suspension of NaH (4 g, 0.13 mol) in anh. DMSO (50 ml) was heated to 70–75° for 45 min. After cooling to 20°, anh. THF (50 ml) was added. The soln. was cooled to −20°, and a soln. of trimethylsulfonium iodide (27 g, 0.13 mol, *Fluka*) in anh. DMSO (100–150 ml) was added under stirring with in *ca.* 3 min. Stirring was continued for *ca.* 10 min until the end of H_2 evolution. Then, **21** (11 g, 0.09 mol) was added and the mixture stirred at −20° for 7 min, then at 20° for 15 h. The mixture was poured into H_2O (400 ml) and extracted with pentane (100 ml, 5 times, then with 50 ml twice). The combined org. extracts were washed with a sat. aq. NaCl soln. (100 ml, twice), dried ($MgSO_4$), and evaporated: 11.72 g of colourless oil, 8:2 mixture **14**/**15** contaminated with **21**. Separation by CC on silica gel (*Lobar*, column *C*, Et_2O/petroleum ether 1:5, 8 ml/min) gave successively 5.05 g (41%) of **14**, 1.25 g (10%) of **15**, and 3.55 g (32%) of **21**.

14: Colourless liquid, B.p. 75°/15 Torr. UV (CH_3CN): 206 (400). IR (film): 3025, 2925, 2850, 1600, 1475, 1455, 1435, 1380, 1355, 1230, 1210, 1180, 1160, 1120, 1100, 1070, 1040, 1010, 985, 955, 905, 885, 835, 805, 780, 710, 680. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.34 (*m*, ^3J = 8); 6.23 (*m*, ^3J = 8, H–C(5), H–C(6)); 2.69 (*d*, ^2J = 4.5, H of epoxide *trans* to C(2),C(3)); 2.64 (*m*, H–C(4)); 2.60 (*d*, ^2J = 4.5, H of epoxide *cis* to C(2),C(3)); 1.99 (*m*, H–C(1), H_{exo}–C(3)); 1.70, 1.30 (2*m*, CH_2(7), CH_2(8)); 1.50 (*dd*, ^2J = 14, ^3J = 2, H_{endo}–C(3)); NOE effects between H of epoxide *trans* to C(2),C(3) (2.69 ppm)/H–C(1) (1.99 ppm), H of epoxide *cis* to C(2),C(3) (2.60 ppm)/H_{endo}–C(3) (1.50 ppm). ^{13}C-NMR (90.55 MHz, $CDCl_3$; in brackets relative induced shift due to added $Yb(thd)_3$): 136.0 (*d*, ^1J(C,H) = 165, C(5), [15.5]); 131.5 (*d*, ^1J(C,H) = 166, C(6), [19.0]); 61.8 (*s*, C(2), [92.4]); 55.9 (*t*, ^1J(C,H) = 172, CH_2–C(2), [100]); 38.1 (*d*, ^1J(C,H) = 140, C(1), [42.1]); 34.5 (*t*, ^1J(C,H) = 130, C(3), [38.6]); 30.6 (*d*, ^1J(C,H) = 140, C(4), [18.0]); 24.4 (*t*, ^1J(C,H) = 130, C(8), [12.9]); 21.4 (*t*, ^1J(C,H) = 134, C(7), [21.6]). MS (70 eV): 136 (9, $M^{+\cdot}$), 106 (22), 91 (46), 80 (45), 79 (71), 78 (100), 77 (32), 66 (81), 65 (8), 59 (8), 54 (6), 53 (7), 52 (11), 41 (23).

15: Colourless liquid. B.p. 75°/15 Torr. UV (CH_3CN): 205 (400). IR (film): 3025, 2925, 2850, 1710, 1605, 1470, 1455, 1435, 1380, 1360, 1330, 1310, 1280, 1260, 1210, 1160, 1120, 1090, 1070, 1040, 1005, 970, 950, 925, 905, 875, 845, 800, 790, 710, 680. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.40 (*ddd*, ^3J(H–C(5),H–C(6)) = 8.5, ^3J(H–C(4),H–C(5)) = 6.5, ^4J(H–C(1),H–C(5)) = 1.5, H–C(5)); 6.30 (*ddd*, ^3J(H–C(5),H–C(6)) = 8.5, ^3J(H–C(1),H–C(6)) = 6.5, ^4J(H–C(4),H–C(6)) = 1.5, H–C(6)); 2.77 (*d*, ^2J = 5, H of epoxide *cis* to C(2),C(3));

2.73 (*dd*, ^2J = 5, ^4J(H epoxide, H–C(1)) = 1, H of epoxide *trans* to C(2),C(3)): 2.69 (*m*, H–C(4)); 2.05 (*m*, H–C(1)); 1.84 (*dd*, ^2J = 13.5, ^3J = 2.2, H_{endo}–C(3)); 1.73, 1.53, 1.39, 1.28 (**4***m*, CH_2(7), CH_2(8)); 1.53 (*m*, H_{exo}–C(3)); NOE between H of epoxide *cis* to C(2),C(3) (2.77 ppm)/H_{exo}–C(3) (1.53 ppm), H of epoxide *trans* to C(2),C(3) (2.73 ppm)/H–C(1) (2.05 ppm). ^{13}C-NMR (90.55 MHz, $CDCl_3$; in brackets relative induced shift due to Yb(thd)$_3$): 134.9 (*d*, ^1J(C,H) = 166, C(5), [12.6]); 131.7 (*d*, ^1J(C,H) = 168, C(6), [19.8]); 61.9 (*s*, C(2), [94.0]); 52.9 (*t*, ^1J(C,H) = 172, CH_2–C(3), [100]); 37.9 (*d*, ^1J(C,H) = 136, C(1), [42.2]); 35.7 (*t*, ^1J(C,H) = 132, C(3), [39.9]); 30.5 (*d*, ^1J(C,H) = 138, C(4), [18.4]); 24.0 (*t*, ^1J(C,H) = 132, C(8), [14.9]); 22.5 (*t*, ^1J(C,H) = 130, C(7), [19.8]); the absolute Yb(thd)$_3$-induced shifts were *ca.* 30% larger for **15** than for **14** (more favourable complexation of the *endo*-epoxide moiety in **15** than the *exo*-epoxide moiety in **14** due to differential steric effect between the etheno and ethano bridges). MS (70 eV): 136 (7, $M^{+\cdot}$), 106 (26), 91 (49), 80 (49), 79 (69), 78 (100), 77 (30), 66 (7), 65 (9), 59 (7), 54 (7), 53 (7), 52 (11), 41 (24).

3. *Addition of NBSCl to (1*RS,*2*SR,*4*RS*)-Spiro[bicyclo[2.2.1]hept-5-ene-2,2'-oxirane]* (**12**). A mixture of **12** (170 mg, 1.4 mmol), NBSCl (262 mg, 1.4 mmol), and $CHCl_3$ (5 ml) was allowed to stand at 20° for 2 h (control of the complete disappearance of **12** by TLC on silical gel, Et_2O/petroleum ether 1:1). Column chromatography on silica (CH_2Cl_2/petroleum ether 1:1) gave a 1:2 mixture **22**/**23** (341 mg, 79%) which was separated by HPLC (silica gel, CH_2Cl_2), giving first 105 mg (24%) of **22** and then 208 mg (48%) of **23**, after recrystallization from CH_2Cl_2/hexane.

*(1*RS,*2*RS,*4*SR,*5*RS,*6*RS*)-6-*exo-*(*2-Nitrophenylthio*)spiro[bicyclo[2.2.1]heptane-2,2'-oxirane]-5-*endo-*yl Chloride* (**22**). Yellow crystals. M.p. 121–123°. UV (CH_3CN): 245 (13900), 272 (sh, 4500), 369 (3300). IR (KBr): 2970, 1585, 1560, 1505, 1480, 1450, 1430, 1390, 1340, 1295, 1250, 1105, 1055, 1040, 1015, 990, 920, 900, 890, 865, 840. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.20 (*dd*, ^3J = 8.5, ^4J = 1.5), 7.58 (*ddd*, ^3J = 8.5, 7, ^4J = 1.5), 7.51 (*dd*, ^3J = 8.5, ^4J = 1.5), 7.32 (*ddd*, ^3J = 8.5, 7, ^4J = 1.5, 4 arom. H); 4.16 (*ddd*, ^3J(H_{exo}–C(5),H_{endo}–C(6)) = 4, ^3J(H–C(4),H_{exo}–C(5)) = 4, ^4J(H_{exo}–C(5),H_{exo}–C(3)) = 2, H–C(5)); 3.44 (*dd*, ^3J(H_{exo}–C(5),H_{endo}–C(6)) = 4, ^4J(H_{syn}–C(7),H_{endo}–C(6)) = 2, H–C(6)); 3.06 (*d*, ^2J = 4.5, H of epoxide *cis* to C(2),C(3)); 2.98 (*d*, ^2J = 4.5, H of epoxide *trans* to C(2),C(3)); 2.77 (*m*, H–C(4)); 2.45 (*dd*, ^2J = 14.5, ^4J(H_{endo}–C(3),H_{anti}–C(7) = 2.5, H_{endo}–C(3)); 2.06–1.93 (*m*, CH_2(7), H–C(1)); 1.80 (*ddd*, ^2J = 14.5, ^3J(H_{exo}–C(3),H–C(4)) = 5, ^4J(H_{exo}–C(3),H_{exo}–C(5)) = 2, H_{exo}–C(3)); NOE between arom. H (7.51 ppm)/H–C(6) (3.44 ppm), arom. H/H–C(1) (1.93 ppm), arom. H/H of epoxide *trans* to C(2),C(3) (2.98 ppm), H–C(6)/H–C(5) (4.16 ppm), H–C(6)/H–C(1) (1.93 ppm), H–C(6)/H of epoxide *trans* to C(2),C(3) (2.98 ppm), H–C(6)/H_{endo}–C(3) (2.45 ppm), H–C(5)/H–C(4) (2.77 ppm), H–C(5)/H_{anti}–C(7) (2.06 ppm). CI-MS (NH_3): 331 (7, $M^{+\cdot}$ + 18(^{37}Cl)), 329 (16, $M^{+\cdot}$ + 18(^{35}Cl)), 284 (30), 283 (20), 282 (87), 281 (16), 246 (12), 157 (34), 138 (50), 126 (74), 125 (96), 93 (53), 80 (100). Anal. calc. for $C_{14}H_{14}ClNO_3S$ (311.79): C 53.93, H 4.53, N 4.49; found: C 54.25, H 4.56, N 4.64.

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR*)-5-*exo-*(*2-Nitrophenylthio*)spiro[bicyclo[2.2.1]heptane-2,2'-oxirane]-6-*endo-*yl Chloride* (**23**). Yellow crystals. M.p. 72–74°. UV (CH_3CN): 245 (15000), 272 (sh, 4600), 370 (3500): IR (KBr): 2960, 2920, 1590, 1560, 1505, 1485, 1450, 1430, 1410, 1385, 1360, 1330, 1305, 1290, 1270, 1260, 1245, 1215, 1165, 1150, 1135, 1100, 1075, 1055, 1040, 1020, 960, 940, 915, 890. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.22 (*dd*, ^3J = 8, ^4J = 1.5), 7.60 (*ddd*, ^3J = 8, 8, ^4J = 1.5), 7.54 (*dd*, ^3J = 8, ^4J = 1.5), 7.33 (*ddd*, ^3J = 8, 8, ^4J = 1.5, 4 arom. H); 4.19 (*dd*, ^3J(H_{endo}–C(5),H_{exo}–C(6)) = 3.5, ^3J(H–C(1),H_{exo}–C(6)) = 4.5, H_{exo}–C(6)); 3.38 (*dd*, ^3J(H–C(5),H–C(6)) = 3.5, ^4J(H_{endo}–C(5),H_{syn}–C(7)) = 1, H_{endo}–C(5)); 3.17 (*d*, ^2J = 4.5, H of epoxide *cis* to C(2),C(3)); 3.10 (*d*, ^2J = 4.5, H of epoxide *trans* to C(2),C(3)); 2.61 (*m*, H–C(4)); 2.22 (*m*, H–C(1)); 2.0 (*m*, CH_2(7), CH_2(3)); NOE between arom. H (7.54 ppm)/H–C(5) (3.38 ppm), arom. H/H–C(4) (2.61 ppm), H_{endo}–C(5)/H–C(4) (2.61 ppm), H_{endo}–C(5)/H_{endo}–C(3) (2.0 ppm), H_{exo}–C(6) (4.19 ppm)/H–C(1) (2.22 ppm), H_{exo}–C(6)/H_{anti}–C(7) (2.0 ppm), H–C(1)/H of epoxide *trans* to C(2),C(3) (3.10 ppm). CI-MS (NH_3): 330 (12), 329 (55), 328 (17), 327 (74), 313 (4, $M^{+\cdot}$ (^{37}Cl)), 312 (6), 311 (19, $M^{+\cdot}$ (^{35}Cl)), 310 (13), 309 (31), 295 (23), 280 (13), 279 (19), 278 (36), 277 (87), 276 (16), 271 (17), 174 (26), 157 (50), 140 (60), 138 (82), 125 (60), 123 (65), 108 (40), 94 (81), 93 (76), 91 (100). Anal. calc. for $C_{14}H_{14}ClNO_3S$ (311.79): C 53.93, H 4.53, N 4.49; found: C 54.13, H 4.50, N 4.61.

4. *Addition of NBSCl to (1*RS,*2*RS,*4*RS*)-Spiro[bicyclo[2.2.1]hept-5-ene-2,2'-oxirane]* (**13**). A mixture of **13** (200 mg, 1.6 mmol), NBSCl (310 mg, 1.6 mmol), and $CHCl_3$ (5 ml) was allowed to stand at 20° for 2 h. The crude mixture was purified by flash chromatography on silica gel (Et_2O/petroleum ether 1:1), yielding 374 mg (75%) of pure **24**, after recrystallization from CH_2Cl_2/hexane.

*(1*RS,*2*SR,*4*SR,*5*RS,*6*RS*)-6-*exo-*(*2-Nitrophenylthio*)spiro[bicyclo[2.2.1]heptane-2,2'-oxirane]-5-*endo-*yl Chloride* (**24**). Yellow crystals. M.p. 134–137°. UV (CH_3CN): 244 (14000), 272 (sh, 4100), 371 (3300). IR (KBr): 2980, 2950, 2930, 1585, 1555, 1505, 1450, 1430, 1395, 1365, 1330, 1305, 1290, 1250, 1205, 1170, 1155, 1145, 1125, 1100, 1055, 1040, 1010, 990, 945, 930, 910, 890, 850, 810. ^{1}H-NMR (360 MHz, C_6D_6): 8.03 (*dd*, ^3J = 8, ^4J = 1.5), 7.53 (*dd*, ^3J = 8, ^4J = 1.5), 7.08, 6.72 (2 *ddd*, ^3J = 8, 7, ^4J = 1.5, 4 arom. H); 4.12 (*dd*, ^3J(H_{exo}–C(5),H_{endo}–C(6)) = 4.5, ^4J(H_{endo}–C(6),H_{syn}–C(7)) = 2.5, H_{endo}–C(6)); 4.03 (*ddd*,

$^3J(H_{exo}–C(5),H_{endo}–C(6)) = 4.5$, $^3J(H–C(4),H_{exo}–C(5)) = 4.5$, $^4J(H_{exo}–C(3),H_{exo}–C(5)) = 1.5$, $H_{exo}–C(5)$); 2.64, 2.53 (*2m*, $CH_2–C(2)$); 2.31 (*dd*, $^2J = 14$, $^4J(H_{endo}–C(3),H_{anti}–C(7)) = 3.5$, $H_{endo}–C(3)$); 2.27 (*m*, H–C(4)); 1.73 (*m*, H–C(1)); 1.68–1.58 (*m*, $CH_2(7)$); 1.40 (*m*, $H_{exo}–C(3)$); NOE between arom. H (7.53 ppm)/H–C(6) (4.12 ppm), H–C(6)/H–C(1) (1.73 ppm), H–C(5) (4.03 ppm)/H–C(4) (2.27 ppm), H–C(5)/H_{anti}–C(7) (1.60 ppm). CI-MS (NH_3): 331 (6, $M^{+\cdot}$ + 18 (^{37}Cl)), 329 (17, $M^{+\cdot}$ + 18 (^{35}Cl)), 284 (29), 283 (18), 282 (80), 281 (11), 157 (18), 149 (27), 141 (31), 140 (29), 139 (13), 138 (38), 137 (12), 136 (32), 127 (14), 126 (100). Anal. calc. for $C_{14}H_{14}ClNO_3S$ (311.79): C 53.93, H 4.53, N 4.49; found: C 53.95, H 4.53, N 4.49.

5. *Addition of NBSCl to* **14**. A mixture of **14** (0.5 g, 3.7 mmol), NBSCl (0.7 g, 3.7 mmol), and $CHCl_3$ (5 ml) was allowed to stay at 20° for 15 h (^{1}H-NMR: 1:1:6:6 mixture of **26**/**27**/**28**/**29**). Chromatography on silica gel (*Lobar*, column *C*, CH_2Cl_2) gave 840 mg (70%) of a mixture which was separated by HPLC (silica gel, CH_2Cl_2) yielding first 340 mg (28%) of **29** and then 335 mg (28%) of **28**, after recrystallization from CH_2Cl_2/hexane.

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR*)-6*-endo-*(2-Nitrophenylthio)spiro[bicyclo[2.2.2]octane-2,2'-oxirane]-5*-exo-*yl Chloride* (**28**). Yellow crystals. M.p. 139–140°. UV (CH_3CN): 245 (13900), 272 (sh, 4600), 370 (3100). IR (KBr): 3080, 3030, 2980, 2930, 2910, 2860, 1590, 1560, 1510, 1465, 1450, 1400, 1365, 1325, 1300, 1260, 1245, 1185, 1170, 1145, 1130, 1100, 1085, 1055, 1040, 1025, 980, 970, 955, 925, 890, 850. ^{1}H-NMR (360 MHz, C_6D_6): 7.65 (*dd*, $^3J = 8$, $^4J = 1.5$), 7.19 (*dd*, $^3J = 8$, $^4J = 1.5$), 6.83 (*ddd*, $^3J = 8$, 7.5, $^4J = 1.5$), 6.49 (*ddd*, $^3J = 8$, $^3J = 7.5$, $^4J = 1.5$, 4 arom. H); 3.70 (*ddd*, $^3J(H_{endo}–C(5),H_{exo}–C(6)) = 4$, $^3J(H–C(4),H_{endo}–C(5)) = 4$, $^4J(H_{endo}–C(5),H_{syn}–C(8)) = 1.5$, $H_{endo}–C(5)$); 3.46 (*dd*, $^3J(H–C(5),H–C(6)) = 4$, $^3J(H–C(1),H_{exo}–C(6)) = 3$, $H_{exo}–C(6)$); 2.52 (*d*, $^2J = 5$, H of epoxide *trans* to C(2),C(3)); 2.36 (*d*, $^2J = 5$, H of epoxide *cis* to (C(2),C(3)); 2.01–1.88 (*m*, $H_{exo}–C(3)$, H–C(7)); 1.63 (*m*, H–C(4)); 1.55 (*ddd*, $^2J = 15$, $^3J(H_{endo}–C(3),H–C(4)) = 2.5$, $^4J(H_{endo}–C(3),H_{anti}–C(8)) = 2.5$, $H_{endo}–C(3)$); 1.45–1.25 (*m*, H–C(7), $CH_2(8)$); 1.23 (*m*, H–C(1)); NOE between arom. H (7.19 ppm)/H–C(6) (3.46 ppm), arom. H/H–C(1) (1.23 ppm), $H_{endo}–C(3)$ (1.55 ppm)/$H_{endo}–C(5)$ (3.70 ppm), $H_{exo}–C(6)/H_{anti}–C(7$ or 8), H–C(1)/H of epoxide *trans* to C(2),C(3) (2.52 ppm), $H_{endo}–C(3)$/H of epoxide *cis* to C(2),C(3) (2.36 ppm). MS (70 eV): 327 (1.1, $M^{+\cdot}$ (^{37}Cl)), 325 (3.3, $M^{+\cdot}$ (^{35}Cl)), 173 (10), 171 (32), 139 (19), 138 (49), 107 (14), 105 (21), 93 (25), 91 (44), 80 (14), 79 (100). Anal. calc. for $C_{15}H_{16}ClNO_3S$ (325.81): C 55.30, H 4.95, N 4.30; found: C 55.41, H 4.96, N 4.45.

*(1*RS,*2*RS,*4*SR,*5*RS,*6*RS*)-5*-endo-*(2-Nitrophenylthio)spiro[bicyclo[2.2.2]octane-2,2'-oxirane]-6*-exo-*yl Chloride* (**29**). Yellow crystals. M.p. 118–120°. UV (CH_3CN): 245 (13500), 272 (sh, 4400), 370 (3000). IR (KBr): 3080, 3030, 2930, 2910, 2870, 1980, 1585, 1560, 1505, 1475, 1450, 1430, 1395, 1330, 1300, 1290, 1270, 1245, 1210, 1195, 1180, 1170, 1145, 1125, 1100, 1070, 1055, 1045, 970, 960, 940, 920, 895, 850, 830, 800. ^{1}H-NMR (360 MHz, C_6D_6): 7.63 (*dd*, $^3J = 8$, $^4J = 1.5$), 7.07 (*dd*, $^3J = 7.5$, $^4J = 1$), 6.79 (*ddd*, $^3J = 8$, 7.5, $^4J = 1.5$), 6.48 (*ddd*, $^3J = 8$, 7.5, $^4J = 1.5$, 4 arom. H); 3.85 (*ddd*, $^3J(H_{exo}–C(5),H_{endo}–C(6)) = 5$, $^3J(H–C(1),H_{endo}–C(6)) = 3$, $^4J(H_{endo}–C(6),H_{syn}–C(7)) = 1.5$, $H_{endo}–C(6)$); 3.35 (*ddd*, $^3J(H–C(5),H–C(6)) = 5$, $^3J(H–C(4),H_{exo}–C(5)) = 2$, $^4J(H_{exo}–C(3),H_{exo}–C(5)) = 2$, $H_{exo}–C(5)$); 2.14 (*d*, $^2J = 5$, H of epoxide *trans* to C(2),C(3)); 2.06 (*d*, $^2J = 5$, H of epoxide *cis* to C(2),C(3)); 1.94 (*ddd*, $^2J = 15$, $^3J(H_{endo}–C(3),H–C(4)) = 3$, $^4J(H_{endo}–C(3),H_{anti}–C(8)) = 3$, $H_{endo}–C(3)$); 1.89 (*m*, $H_{anti}–C(7)$); 1.76 (*m*, $H_{syn}–C(7)$); 1.54 (*m*, H–C(4)); 1.37 (*m*, $H_{syn}–C(8)$); 1.28 (*m*, $H_{anti}–C(8)$); 1.26 (*m*, H–C(1)); 1.20 (*ddd*, $^2J = 15$, $^3J(H–C(3),H–C(4)) = 2$, $^4J(H_{exo}–C(3),H_{exo}–C(5)) = 2$, $H_{exo}–C(3)$); relatively important NOE between arom. H (7.07 ppm)/H–C(5) (3.35 ppm), H–C(6) (3.85 ppm)/H of epoxide *trans* to C(2),C(3) (2.14 ppm); the DQF-COSY (H/H correlated spectrum) of **29** (see *Fig. 2*) allowed to attribute all the H-signals and their coupling constants. MS (70 eV): 327 (0.9, $M^{+\cdot}$ (^{37}Cl)), 325 (3.4, $M^{+\cdot}$ (^{35}Cl)), 171 (9), 155 (17), 139 (13), 138 (37), 108 (10), 107 (16), 106 (11), 105 (21), 96 (11), 93 (16), 92 (11), 91 (57), 79 (100). Anal. calc. for $C_{15}H_{16}ClNO_3S$ (325.81): C 55.30, H 4.95, N 4.30; found: C 55.30, H 4.83, N 4.36.

6. *Addition of NBSCl to* **15**. A soln. of NBSCl (47 mg, 0.25 mmol) in CH_2Cl_2 (3 ml) was added to a soln. of **15** (32.5 mg, 0.24 mmol) in CH_2Cl_2 (3 ml). After 2 days at 20°, NBSCl (23 mg, 0.12 mmol) was added and the mixture allowed to stand at 20° for 1 day (360-MHz ^{1}H-NMR: 6:1:1:1 mixture **30**/**31**/**32**/**33**). Flash chromatography on silica gel (Et_2O/petroleum ether 2:1) gave 64 mg (80%) of the adduct mixture which was then separated by HPLC (silica gel, CH_2Cl_2) giving successively **30** (39 mg, 49%), **33** (6 mg, 8%), **32** (6 mg, 8%), and impure **31** (1 mg), after recrystallization from CH_2Cl_2/hexane.

*(1*RS,*2*SR,*4*SR,*5*RS,*6*RS*)-6*-exo-*(2-Nitrophenylthio)spiro[bicyclo[2.2.2]octane-2,2'-oxirane]-5*-endo-*yl Chloride* (**30**). Yellow crystals. M.p. 94–97°. UV (CH_3CN): 245 (13600), 272 (sh, 4200), 370 (3100). IR (KBr): 2940, 2860, 1590, 1560, 1515, 1450, 1430, 1395, 1335, 1305, 1285, 1250, 1235, 1170, 1145, 1100, 1055, 1040, 970, 955, 915, 890, 875, 850, 805, 775. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.17 (*dd*, $^3J = 8$, $^4J = 1.5$), 7.58 (*m*, 2 H); 7.28 (*m*, 4 arom. H); 4.10 (*ddd*, $^3J(H_{exo}–C(5),H_{endo}–C(6)) = 5.5$, $^3J(H–C(1),H_{endo}–C(6)) = 2$, $^4J(H_{endo}–C(6),H_{syn}–C(7)) = 2$, $H_{endo}–C(6)$); 4.06 (*ddd*, $^3J(H–C(5),H–C(6)) = 5.5$, $^3J(H–C(4),H_{exo}–C(5)) = 2.5$, $^4J(H_{exo}–C(5),$

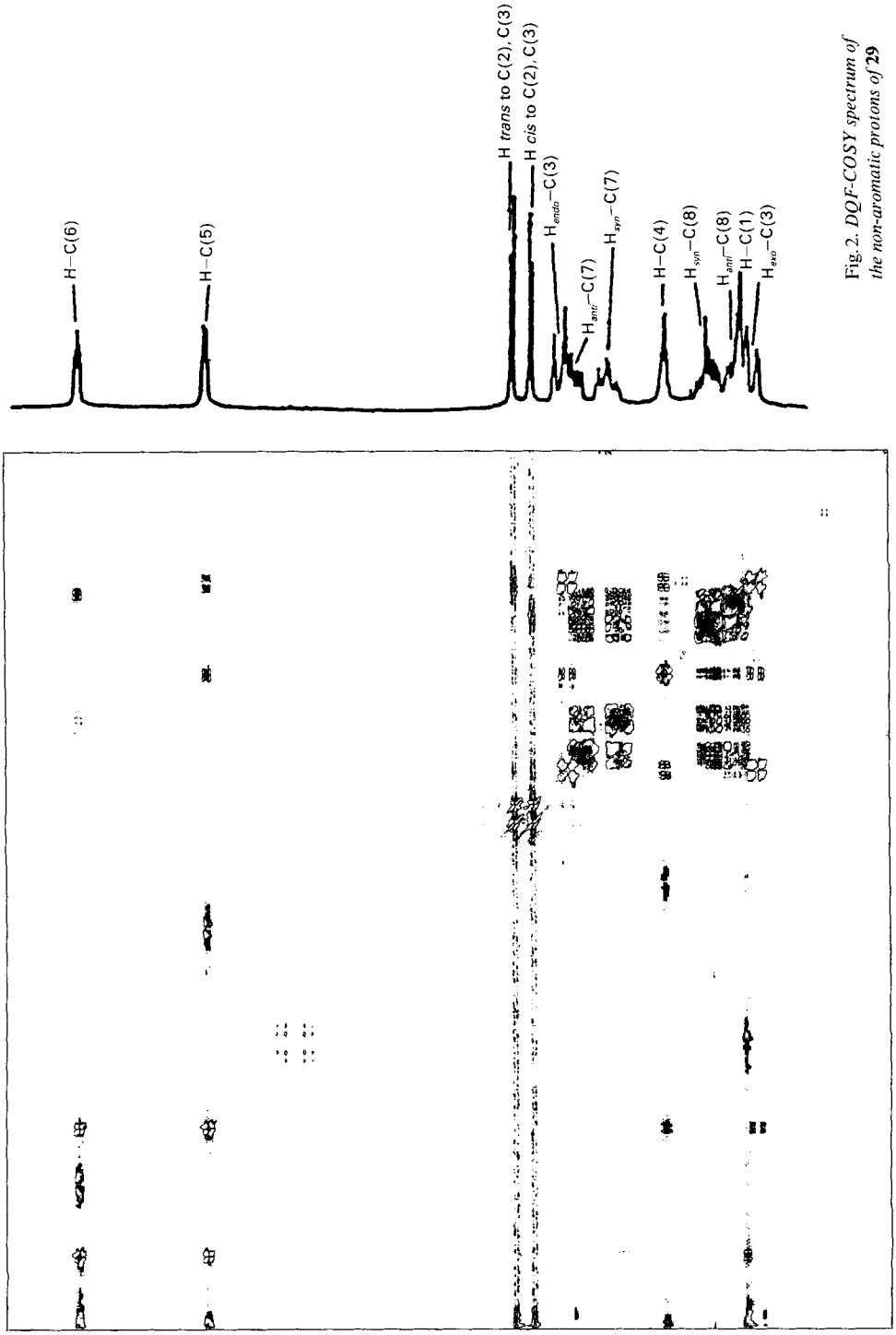


Fig. 2. *DQF-COSY spectrum of the non-aromatic protons of* **29**

H_{exo}–C(3)) = 1.5, H_{exo}–C(5)); 2.85 (*d*, ^2J = 4.8, H of epoxide *cis* to C(2),C(3)); 2.78 (*d*, ^2J = 4.8, H of epoxide *trans* to C(2),C(3)); 2.37 (*ddd*, ^2J = 15, ^3J(H_{endo}–C(3),H–C(4)) = 2.5, ^4J(H_{endo}–C(3),H_{anti}–C(8)) = 2.5, H_{endo}–C(3)); 2.25 (*m*, H–C(4)); 2.07 (*m*, H_{anti}–C(7)); 1.89 (*ddd*, ^2J = 15, ^3J(H–C(3),H–C(4)) = 3, ^4J(H_{exo}–C(3),H_{exo}–C(5)) = 1.5, H_{exo}–C(3)); 1.75 (*m*, CH_2(8)); 1.61 (*m*, H_{syn}–C(7)); 1.46 (*td*, ^3J(H–C(1),CH_2(7)) = 2.5, ^3J(H–C(1),H–C(6)) = 2, H–C(1)); NOE between arom. H (7.58 ppm)/H–C(6) (4.10 ppm; strong effect), arom. H/H–C(1) (1.46 ppm) and arom. H/H–C(5) (4.06 ppm, smaller effects), H_{endo}–C(6)/H_{endo}–C(3) (2.37 ppm), H_{exo}–C(5)/H_{anti}–C(8) (1.75 ppm), H of epoxide *cis* to C(2),C(3) (2.85 ppm)/H_{exo}–C(3) (1.89 ppm), H of epoxide *trans* to C(2),C(3) (2.78 ppm)/H–C(1). MS (70 eV): 327 (0.3, $M^{+\cdot}$ (^{37}Cl)), 325 (0.6, $M^{+\cdot}$ (^{35}Cl)), 324 (1.3), 171 (4), 155 (10), 138 (14), 117 (9), 108 (9), 107 (15), 106 (12), 105 (18), 96 (11), 93 (32), 91 (59), 86 (13), 84 (21), 80 (18), 79 (100). Anal. calc. for $C_{15}H_{16}ClNO_3S$ (325.81): C 55.30, H 4.95, N 4.30; found: C 55.43, H 5.00, N 4.39.

*(1RS,2SR,4SR,5SR,6SR)-6-*endo*-(2-Nitrophenylthio)spiro[bicyclo[2.2.2]octane-2,2'-oxirane]-5-*exo*-yl Chloride* (**32**). Yellow crystals. M.p. 129–130°. UV (CH_3CN): 247 (12500), 272 (sh, 4400), 373 (2800). IR (KBr): 3080, 3030, 2940, 2920, 2860, 1585, 1560, 1450, 1430, 1360, 1330, 1275, 1265, 1245, 1210, 1200, 1180, 1170, 1145, 1135, 1100, 1090, 1055, 1040, 1020, 980, 960, 920, 890. ^{1}H-NMR (360 MHz, C_6D_6): 8.1 (*dd*, ^3J = 8.5, ^4J = 1.5), 7.69 (*dd*, ^3J = 8, ^4J = 1.5), 7.57 (*ddd*, ^3J = 8, 7, ^4J = 1.5), 7.32 (*ddd*, ^3J = 8.5, 7, ^4J = 1.5, 4 arom. H); 4.35 (*ddd*, ^3J(H_{endo}–C(5),H_{exo}–C(6)) = 4.5, ^3J(H–C(4),H–C(5)) = 3, ^4J(H_{endo}–C(5),H_{syn}–C(8)) = 2, H_{endo}–C(5)); 3.73 (*dd*, ^3J(H–C(5),H–C(6)) = 4.5, ^3J(H–C(1),H_{exo}–C(6)) = 2.5, H_{exo}–C(6)); 2.66 (*d*, ^2J = 4.9, H of epoxide *cis* to C(2),C(3)); 2.63 (*d*, ^2J = 4.9, H of epoxide *trans* to C(2),C(3)); 2.23 (*m*, H–C(4)); 2.15 (*m*, H_{anti}–C(8)); 2.10 (*dd*, ^2J = 14.5, ^3J(H_{exo}–C(3),H–C(4)) = 3.5, H_{exo}–C(3)); 1.99 (*ddd*, ^3J = 14.5, ^3J(H_{endo}–C(3),H–C(4)) = 2.5, ^4J(H_{endo}–C(3),H_{anti}–C(8)) = 2.5, H_{endo}–C(3)); 1.92 (*m*, CH_2(7)); 1.65 (*m*, H–C(1)); 1.55 (*m*, H_{syn}–C(8)); NOE between arom. H (7.69 ppm)/H–C(6) (3.73 ppm, strong effect), arom. H (7.69 ppm)/H–C(1) (1.65 ppm), H–C(5) (4.35 ppm)/H–C(4) (2.23 ppm), H–C(5)/H_{endo}–C(3) (1.94 ppm), H–C(6) (3.73 ppm)/H–C(1) (1.65 ppm), H–C(6)/H–C(7) (1.92 ppm), H–C(1) (1.65 ppm)/H of epoxide *trans* to C(2),C(3) (2.63 ppm). MS (70 eV): 327 (0.3, $M^{+\cdot}$ (^{37}Cl)), 326 (0.7), 325 (0.8, $M^{+\cdot}$ (^{35}Cl)), 324 (1.6), 171 (14), 155 (5), 138 (22), 108 (10), 107 (19), 106 (13), 105 (23), 93 (24), 91 (59), 79 (100). Anal. calc. for $C_{15}H_{16}NO_3S$ (325.81): C 55.30, H 4.95, N 4.30; found: C 55.30, H 4.96, N 4.54.

*(1RS,2SR,4SR,5RS,6RS)-5-*endo*-(2-Nitrophenylthio)spiro[bicyclo[2.2.2]octane-2,2'-oxirane]-6-*exo*-yl Chloride* (**33**). Yellow crystals. M.p. 114–116°. UV (CH_3CN): 245 (13400), 272 (sh, 4500), 370 (3000). IR (KBr): 2940, 2870, 1590, 1560, 1510, 1450, 1440, 1395, 1330, 1300, 1250, 1215, 1165, 1150, 1100, 1060, 1040, 980, 960, 950, 920, 890, 880, 850, 835. ^{1}H-NMR (360 MHz, C_6D_6): 7.59 (*dd*, ^3J = 8.5, ^4J = 1.5), 7.18 (*dd*, ^3J = 8.5, ^4J = 1.5), 6.8, 6.51 (2*ddd*, ^3J = 8.5, 6.5, ^4J = 1.5, 4 arom. H); 4.50 (*ddd*, ^3J(H_{exo}–C(5),H_{endo}–C(6)) = 5, ^3J(H–C(1),H_{endo}–C(6)) = 3, ^4J(H_{endo}–C(6),H_{syn}–C(7)) = 1, H_{endo}–C(6)); 3.44 (*ddd*, ^3J(H–C(5),H–C(6)) = 5, ^3J(H–C(4),H–C(5)) = 3, ^4J(H_{exo}–C(3),H_{exo}–C(5)) = 2, H_{exo}–C(5)); 2.14 (*d*, ^2J = 5, H of epoxide *cis* to C(2),C(3)); 2.10 (*d*, ^2J = 5, H of epoxide *trans* to C(2),C(3)); 2.01 (*ddd*, ^2J = 15, ^3J(H_{endo}–C(3),H–C(4)) = 3, ^4J(H_{endo}–C(3),H_{anti}–C(8)) = 2.5, H_{endo}–C(3)); 1.93 (*m*, H_{anti}–C(7)); 1.64 (*m*, H–C(4)); 1.28 (*m*, H_{anti}–C(8)); 1.26 (*m*, H–C(1)); 1.15 (*ddd*, ^2J = 15, ^3J(H_{exo}–C(3),H–C(4)) = 3, ^4J(H_{exo}–C(3),H_{exo}–C(5)) = 2, H_{exo}–C(3)); 1.10 (*m*, H_{syn}–C(7),H_{syn}–C(8)); NOE between arom. H (7.18 ppm)/H–C(5) (3.44 ppm, strong effect), arom. H (7.18 ppm)/H–C(4) (1.64 ppm, weak effect), H–C(6) (4.50 ppm)/H–C(1) (1.26 ppm), H–C(5) (3.44 ppm)/H–C(4) (1.64 ppm), H–C(5)/H_{anti}–C(8) (1.28 ppm), H of epoxide *cis* to C(2),C(3) (2.14 ppm)/H_{exo}–C(3) (1.15 ppm), H of epoxide *trans* to C(1),C(3) (2.10 ppm)/H–C(1) (1.26 ppm). MS (70 eV): 327 (0.1, $M^{+\cdot}$ (^{37}Cl)), 326 (0.4), 325 (0.4, $M^{+\cdot}$ (^{35}Cl)), 324 (0.7), 171 (5), 155 (12), 138 (16), 108 (10), 107 (18), 106 (12), 105 (20), 93 (20), 91 (56), 79 (100). Anal. calc. for $C_{15}H_{16}ClNO_3S$ (325.81): C 55.30, H 4.95, N 4.30; found: C 55.45, H 4.97, N 4.46.

7. *(1RS,2RS,4SR)-5-(2-Nitrophenylthio)spiro[bicyclo[2.2.2]oct-5-ene-2,2'-oxirane]* (**34**). Freshly sublimed *t*-BuOK (35 mg, 0.31 mmol) was added to a stirred mixture of **29** (30 mg, 0.09 mmol) in anh. THF (5 ml) cooled to –78°. After stirring at –78° for 1 h, the temp. was allowed to reach 20° in *ca.* 4 h. H_2O (20 ml) was added and the mixture extracted with CH_2Cl_2. The org. extract was dried ($MgSO_4$) and filtered through silica gel. After solvent evaporation, **34** was obtained as a yellow, unstable oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.72, 7.06 (2*dd*, ^3J = 8, ^4J = 1), 6.78, 6.54 (2*ddd*, ^3J = 8, 8, ^4J = 1, 4 arom. H); 6.36 (*dd*, ^3J(H–C(1),H–C(6)) = 7, ^4J(H–C(6),H_{syn}–C(7)) = 1.5, H–C(6)); 2.34, 2.28 (2*d*, ^2J = 5, CH_2 of epoxide); 2.05 (*m*, CH_2(7)); 1.75 (*m*, H–C(1)); 1.56 (*dm*, ^2J = 14, H–C(3)); 1.45–1.28 (*m*, H–C(3), H–C(8)); 1.22–1.07 (*m*, H–C(8), H–C(4)); NOE between H–C(6) (6.36 ppm)/H–C(1) (1.75 ppm), H–C(1)/H of epoxide *trans* to C(2),C(3) (2.34 ppm).

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