Homotropylium-8-sulfinate Complexes by SbF_5-Promoted Ring Opening of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene and 9-Thiabarbaralane 9,9-Dioxides

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Abstract: The reaction of SbF_5 (2.5 mol equiv) with either 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (**6**) or 9-thiabarbaralane 9,9-dioxide (**7**) in liquid sulfur dioxide solution produces the identical *endo* homotropylium-8-sulfinate complex **10**. Upon warming to room temperature, stereochemical inversion of **10** to give the corresponding exo isomer takes place. Dideuteration of **6** at its exchangeable sites and treatment as above provide the *3,8-d*$_2$ homotropylium species. Starting with **7**-*1,5-d*$_2$, the symmetrical *4,8-d*$_2$ zwitterion was obtained. Thermal equilibrium in both instances leads to *exo*-8-sulfinate complexes without alteration in the original ring deuterium positions. These findings rule out the operation of a [1,6] suprafacial circumambulatory migration. Rather, conformational ring inversion likely proceeds by passage through a planar, classical cyclooctatrienyl cation, a conclusion further supported by the behavior of monomethyl ion **20**. The selectivity noted during ring opening of 1-methyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide is noteworthy. Zwitterion **23** which is formed by SbF_5-promoted ionization of **22** does not experience formal epimerization at C_8. This finding, together with the discovery that **29** has no homoaromatic character but is rather a classical bicyclic structure, points up the striking effect caused by a 4-methyl group.

Studies of protonation reactions of cyclooctatetraene (**1**) and a number of its derivatives have played an important role in the development of our understanding of homotropylium ions. The ^1H NMR spectrum of this $C_8H_9^+$ cation, which can be generated merely by dissolving **1** in concentrated sulfuric acid,[1] displays a series of signals in the ratio of 5:2:1:1, the chemical shifts of which are consistent with a delocalized structure enjoying considerable levels of 1,7-orbital interaction.[1,2] The attendant ring current in **2** appears chiefly responsible for the large difference in shielding observed for H_{8endo} and H_{8exo}. In an investigation aimed at elucidation of the rate of ring inversion in **2**, Winstein, Kreiter, and Brauman noted that treatment of **1** with D_2SO_4 at $-15°$ resulted in positioning of the incoming deuterium at H_{8endo} to a level of ca. 80%.[3] On the basis of more recent investigations, it now appears that electrophilic additions to cyclooctatetraene generally proceed with high stereoselectivity from inside the "tub" to initially form endo-8-substituted homotropylium ions. In those cases where biparticulate electrophiles[4] have been employed, subsequent reaction is seen to involve bonding of the counteranion at C_1 from that direction syn to the C_8 bridge (cf. **3**).[5] In contrast, uniparticulate electrophilic additions to **1** are observed to proceed by intramolecular charge annihilation utilizing C_3 bonding schemes as in **4**.[6]

Because alternative pathways for charge neutralization in **3** or **4** had not been observed, the tacit assumption which has prevailed is that these homotropylium intermediates are both more stable[3] and more reactive than their classical counterparts having a relatively fully formed cyclopropane ring as in **5**. Recent findings in this laboratory now show the earlier tests to be incomplete and point up the feasibility of kinetically controlled cyclizations involving **5**.[7] Thus, SbF_5-promoted reaction of cyclooctatetraene with liquid sulfur dioxide results not only in the formation of **6** but also in the production of 9-thiabarbaralane 9,9-dioxide (**7**).[8] This unprecedented 1,5-cycloaddition provides the most direct route to a 9-heterobarbaralane yet uncovered.[10]

In this paper, we describe a detailed ^1H NMR study of the reverse process, viz., the SbF_5-induced ring opening reactions of **6** and **7** in SO_2 solution. The existing capability for conversion of **6** and **7** to their mono- and dianions[11] has also permitted examination of suitable deuterium and methyl substituted derivatives of these sulfones. Evidence is presented that **6** and **7** do comprise suitable precursors to the same endo homotropylium-8-sulfinate cation complex at low temperatures, that 8-endo–8-exo interchange occurs upon warming, and that possible degenerate scrambling of these homotropylium ions is inoperative.[12] Perhaps most striking are the consequences of alkyl substitution in both **6** and **7** as it affects the attainment of homoaromatic character and the facility of bridge flipping.

Results

The Parent Sulfones. Addition of >2 equiv of SbF_5[13] to a cold ($-50°$) SO_2 solution of **6** gave an NMR spectrum (Figure 1) comprising two sets of multiplets at δ 7.95–9.0 (5 H) and 6.10–6.75 (3 H) which bear great similarity to those seen in the downfield sector of **2** [δ 8.47 (5 H), 6.42 (2 H), 5.10 (1 H), and -0.67 (1 H)].[2a] These features, taken together with the apparent downfield shifting of H_{8exo} and the absence of a signal due to a highly shielded bridge proton, correspond with those expected of homotropylium ion **10**. Comparable treatment of **7** afforded the identical spectrum. When such solutions were neutralized without giving careful attention to those conditions needed to isolate **7**,[7] the bicyclic sulfone was readily isolated and only trace

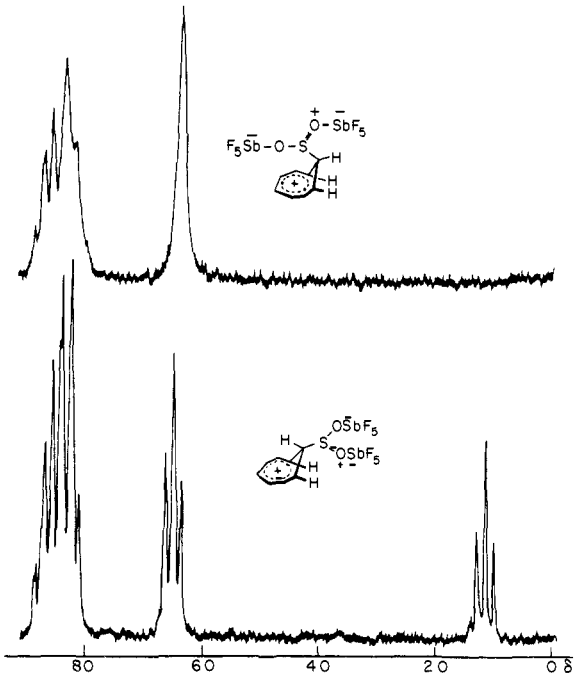


Figure 1. ^{1}H NMR spectra (60 MHz) of: (top) the *endo*-8-homotropyliumsulfinate complex **10** in SO_2 at −50°; (bottom) the epimeric exo complex **11** recorded under identical conditions.

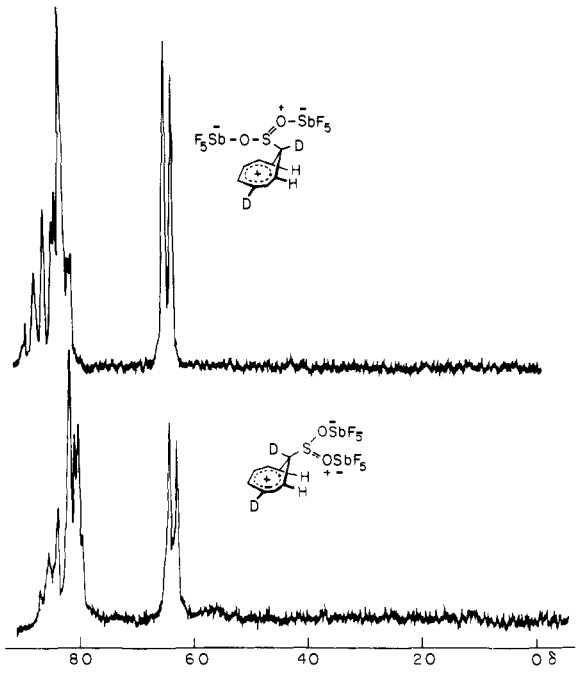
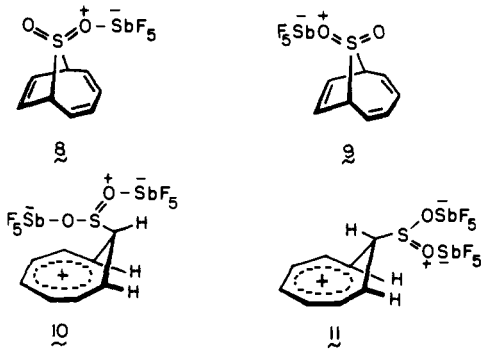


Figure 2. ^{1}H NMR spectra (60 MHz) of: (top) the *endo*-8-homotropylium-*3,8-d*$_2$-sulfinate complex **14** in SO_2 at −53°; (bottom) the epimeric exo complex **16** recorded under identical conditions.



amounts of the thiabarbaralane dioxide were found. Evidently, the formation of **6** is thermodynamically favored.

After either of these SO_2 solutions was allowed to remain at room temperature for 1 hr and the proton NMR redetermined at −50°, comparable spectral alteration was evidenced. As illustrated in Figure 1, a diminution in intensity of the δ 6.47 signal (2 H) is accompanied by the appearance of an upfield triplet (J = 8.8 Hz) of area 1 at 1.12. The latter peak can be ascribed to H_{8endo} in **11**, the Δδ in the **10**–**11** pair amounting to approximately 5.3 ppm in agreement with the value of 5.7 found for the 8-chlorohomotropylium ion epimers.[14] The H_1–H_7 absorption regions conform in their shifts to values expected for maintenance of a homoaromatic ring current in **11**. Although these findings reveal that C_8 can experience stereochemical inversion relative to the seven quasi-planar tropylium positions, they do not provide data adequate to unveil the nature of this rearrangement.

Results of Dideuteration. The thermal isomerization of **10** to **11** requires temporary interruption of homoaromatic stabilization. Such endo-exo scrambling of the bridged methylene positions could be the direct result of inversion through a virtually planar classical cyclooctatrienyl cation[3] or of ring circumambulation, the latter process requiring for reasons of orbital symmetry conservation an interchange of the 8-endo and 8-exo hydrogens at each suprafacial step.[15,16] From their examination of homotropylium-*4-d* and 8-*exo*-carbethoxyhomotropylium-*2-d*$_1$, Berson and Jenkins concluded the most likely mechanism for epimerization at C_8 to be conformational isomerization, ring circumambulation apparently requiring in excess of 26 kcal/mol.[12]

Species **10** is distinguished from other known homotropylium ions by the fact that it contains an exceedingly bulky 8-endo substituent which is obviously not in the thermodynamically favored orientation. Equilibration to the exo isomer is particularly favorable, but the relative importance of the two possible mechanisms for configurational inversion remained to be assessed. To this end, two dideuterated derivatives of **10** have been prepared and subjected to variable temperature NMR scrutiny.

The ^{1}H NMR spectra of **12** and **13** in SO_2 containing 2.5 equiv of SbF_5 at −53° provide evidence for generation of the homotropylium complexes **14** (Figure 2) and **15** (Figure 3), respectively. H_{8exo} deuteration in both species is revealed clearly by the appearance of the signals due to H_1 and H_7 as clean doublets as the result of residual spin-spin interaction with H_2 and H_6. That **14** and **15** possess differing arrangements of ring deuterium labeling also does not escape notice. The diminution in intensity of the lower half of the δ 8.0–9.0 multiplet in **14** provides indication that H_3

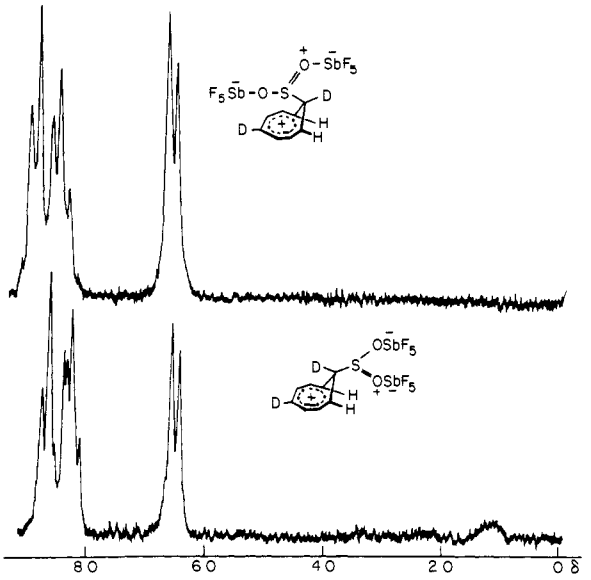
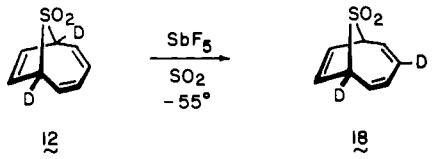


Figure 3. ^{1}H NMR spectra (60 MHz) of: (top) the *endo*-8-homotropylium-*4,8-d*$_2$-sulfinate complex **15** in SO_2 at −53°; (bottom) the epimeric exo complex **17** recorded under identical conditions.

(and H_5 for symmetry reasons) are more downfield shifted than the even-numbered protons ($H_{2,4,6}$). This conclusion, which is supported nicely by the multiplicities and relative intensities seen for this absorption region in the spectrum of **15,** agrees with relative electron densities expected to prevail in homotropylium cations.[17]

As observation of these solutions was continued during warming to room temperature, equilibration to the respective *exo*-homotropylium-*d*$_2$-sulfinate complexes **16** and **17** was evident. In the case of **17,** the vestiges of incomplete deuteration were now visible in the form of a broad upfield peak of weak intensity at δ 1.1 (Figure 3). Of vastly greater import, the spectra of the exo ions differ only slightly in their individual olefinic regions from those of their progenitor endo isomers. Because a single symmetry-allowed circumambulatory [1,6] migration of C_8 would necessarily alter the position of the ring deuterium relative to the stereochemically inverting bridge, scrambling of *3-d* to *2-d* and/or *4-d* and vice versa should be encountered if this mechanism is operative. Continued rearrangement of this type would simply distribute the isotope more extensively to include positions 1 and 7. Since the spectra of **14** and **15** define unmistakably the locus of ring deuterium substitution and, because the signals and peak areas from the respective exo ions do not give evidence of positional permutation, then endo-exo isomerization necessarily occurs with maintenance of the integrity of the seven tropylium positions. Even when the solutions are allowed to stand for more prolonged periods at room temperature, the downfield multiplets remain unaltered. Seemingly, therefore, inversion through the planar cyclooctatrienyl cation is the low energy pathway to C_8 epimerization.

By implication, the previously demonstrated reclosure of **10** to **6** should have a parallel in neutralization reactions of **14.** However, the latter endo homotropylium complex does not possess comparable symmetry, with the result that C–S bond formation at C_3 and C_5 will provide differently labeled sulfones. Such an experiment would have the important consequence of establishing by chemical methods the involvement of a ring-opened intermediate. When an SO_2 solution of **12** having concentration levels approaching those employed for the NMR spectral measurements (more dilute conditions proved less effective) was treated with



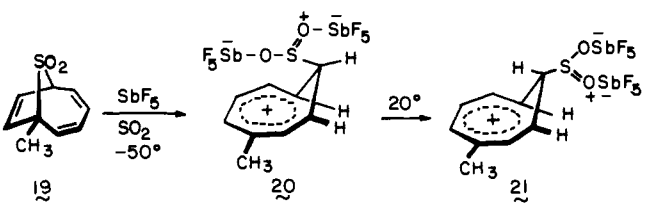
12 18

SbF_5 at −55° for 3.5 hr, the sulfone sample subsequently recovered was shown by ^{1}H NMR Fourier transform methods to have suffered a 28% influx of hydrogen to one bridgehead position together with a parallel diminution in olefin absorption intensity. We have considered this to arise by partial conversion to **18,** although it has not been possible to establish precisely the site of sp^2-bound deuterium due to the narrow width of the composite olefinic proton signal. The level to which **18** is formed is too low to reflect the H–D fractionation factor operating during closure of **14.** Rather, this excessive weighting in favor of **12** likely means that a portion of this starting sulfone has remained intact throughout the reaction period.

To the critical reader, the great similarity of the spectra shown in Figures 2 and 3 could conceivably raise the question that they represent one and the same compound. Although the findings with the protio counterparts (Figure 1) render this presumption unlikely, supportive chemical evidence was unquestionably needed. The recovery of **6** and **18** from solutions of **10** and **14** maintained at −50° and below has been discussed previously. This capability for reclosure of the *endo*-8-sulfinate complexes to 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxides has proved general. In contrast, quenching experiments conducted subsequent to thermal equilibration at 25° have not led to cyclic sulfone products. Rather, water soluble substances which may be sulfinic acids are formed; to this time, their complete characterization has eluded us. Importantly, however, solutions of **16** and **17** gave rise to such products when quenched with water.

Consequences of Monomethylation. Stepwise treatment of **6** with 1 equiv of *n*-butyllithium in anhydrous tetrahydrofuran at −78° and excess methyl iodide afforded **19** which was obtained in a pure state by high pressure liquid chromatography on silica gel. The low temperature ^{1}H NMR spectrum of this sulfone dissolved in SbF_5–SO_2 is shown in Figure 4. When the sample was allowed to warm to room temperature, the δ 5.7 signal was replaced by a multiplet of equal area (1 H) at 1.67. This strong upfield shifting is precisely the behavior expected for migration of an 8-exo hydrogen to the endo environment of the bridging carbon. An additional intriguing aspect of these spectra concerns the location of the methyl peak (δ 2.58) and the almost negligible impact of conformational isomerization upon the chemical shift of this signal and those of the olefinic multiplets. These observations give one considerable insight into the specificity of ring opening in **19,** the available data compelling interpretation in favor of cleavage of the S^{IV}–C_5 bond with placement of the methyl group uniquely at C_3.

The remaining absorptions in the spectra of **20** and **21** [δ

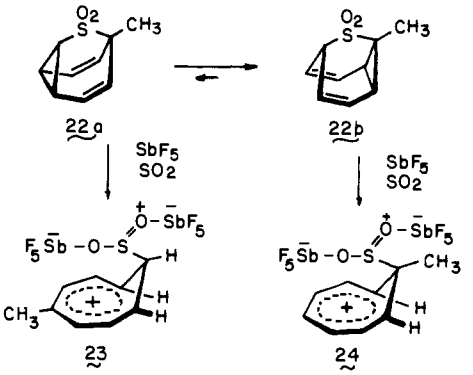


19 20 21

8.13–8.50 (H_5), 7.40–8.00 ($H_{2,4,6}$), and 6.12–6.61 ($H_{1,7}$)] are then assignable by analogy. The unsymmetrical nature of these complexes is easily recognized and is further sig-

naled by the increased shielding of the ring protons (except H_5) which likely results from diminished positive charge in these segments of the homotropylium ion.

Although monomethylation of the 9-thiabarbaralane dioxide ring system as in **22** will affect the energetics of the Cope rearrangement, the influence of the alkyl group on this particular process is expected to be minimal. On the other hand, the rearrangement is no longer degenerate and an equilibrium imbalance in favor of **22b** can be expected.[18]



In fact, controlled alkylation of **7** does provide a monomethyl derivative which exists predominantly as **22b** at room temperature.[19] Possible regioselectivity of the SbF_5-promoted ring opening of **22** now becomes a mechanistic question of some interest. Fortunately, an experimental assessment of the situation is possible since ring opening of bridgehead substituted form **22a** should provide symmetrical ring methylated cation **23,** while **22b** should experience conversion to **24** under these reaction conditions.

^1H NMR spectra of **22** in SbF_5-SO_2 recorded at −50° display multiplet resonances at δ 7.8–8.5, 5.17–6.14, and 1.15–1.53 together with a pair of somewhat broadened methyl singlets of approximately equal intensity at 2.45 and 2.13. Although the spectra are complicated by the presence of an unexplained weak intensity high-field multiplet (δ 1.15–1.53),[20] the remaining features support the notion that **23** and **24** are formed competitively. These spectra proved stable for several hours at −50°. On warming briefly (15 min) to room temperature, however, all features of the spectra sharpened noticeably and the methyl signal at 2.13 as well as the upfield multiplet were no longer present. The remaining absorptions [δ 7.55–8.37 (m, $H_{2,3,5,6}$), 5.62–6.25 (m, $H_{1,7}$), 5.08–5.62 (m, H_8), and 2.34 (br s, $-CH_3$)] comprise a pattern fully consistent with that anticipated for **23**. We have not found it possible to establish that **24** undergoes conversion to **23** at the more elevated temperatures. Alternatively of course, this homotropylium ion could be experiencing rapid selective destruction. Interestingly, when the solution containing **23** was left at room temperature for periods up to 1 hr, the onset of decomposition was noted but conformational isomerization was clearly nonoperational. The H_{8exo} resonance at δ 5.08–5.62 did not fade more rapidly than the others and in particular was not replaced by an H_{8endo} signal at higher field. It is enticing to speculate that the increased positive charge density at C_4 in **23** which results from its tertiary nature may be of such proportions that electrostatic interaction with the *endo*-8-sulfinate group becomes adequate to deter its migration to the exterior of the molecule.

In an attempt to gain somewhat more direct access to such methyl substituted homotropylium cations, the reaction of methylcyclooctatetraene with SbF_5 in liquid sulfur dioxide was examined. Solutions prepared from this polyolefin in the standard manner showed a very complex methyl region. The prevailing intricacy was not obviated when

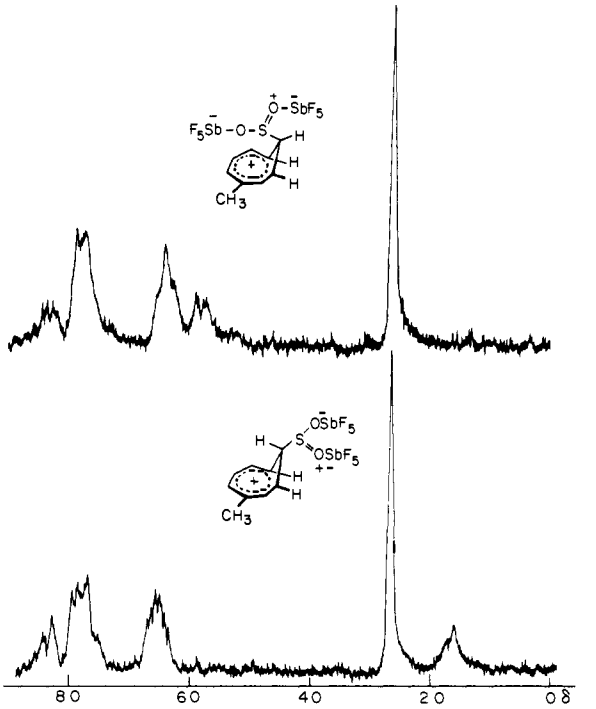
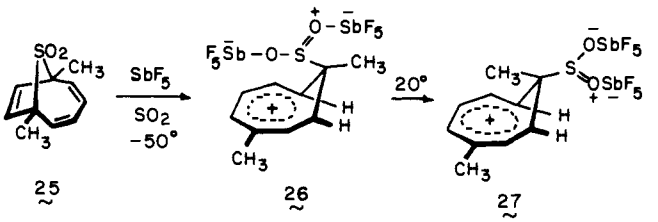


Figure 4. ^1H NMR spectra (60 MHz) of: (top) *endo*- and (bottom) *exo*-3-methyl-8-homotropyliumsulfinate complexes (**20** and **21**) in SO_2 at −50°.

the tubes were allowed to remain at 25° for varying periods of time. Consequently, this approach did not provide useful synthetic methodology but was the source of meaningful mechanistic insight (see below).

Dimethyl Derivatives. Dimethyl sulfone **25,** prepared from the dianion of **6**[11] and excess methyl iodide, was treated with incrementally greater molar equivalents of SbF_5 in SO_2 solution (−50°) to gain information on the effect of differing relative amounts of the Lewis acid. At the low end of the concentration range (1 mol equiv), the spectrum consisted of a somewhat broadened methyl signal at δ 1.00 and a six-proton absorption in the 5.1–5.9 region. Although coordination was apparent, ring opening had clearly not taken place.[21] As the level of SbF_5 was increased, this spectrum was gradually replaced with that expected for **26.** Once 2.5 equiv of SbF_5 had been introduced, no further spectral changes were seen. The well-resolved features now consisted of multiplets at δ 7.8–9.0 (4 H) and 5.9–6.5 (2 H), as well as methyl peaks at 2.72 and 2.03 (Figure 5). The latter two signals were not clean singlets; low intensity spikes of unknown origin invariably appeared on either side of the principal absorption.[20] Brief warming (15–30 min) of these solutions to room temperature resulted in partial conversion to **27,** as reflected by the reduction in intensity of



the δ 5.9–6.5 multiplet and the 2.03 singlet in tandem with the "growing in" of new signals of proportionate area at 5.4–5.9 and −0.28. After 55 min at 20°, the new spectrum also began to decay, thus suggesting that **27** may be somewhat less stable than its lower methylated analogs.

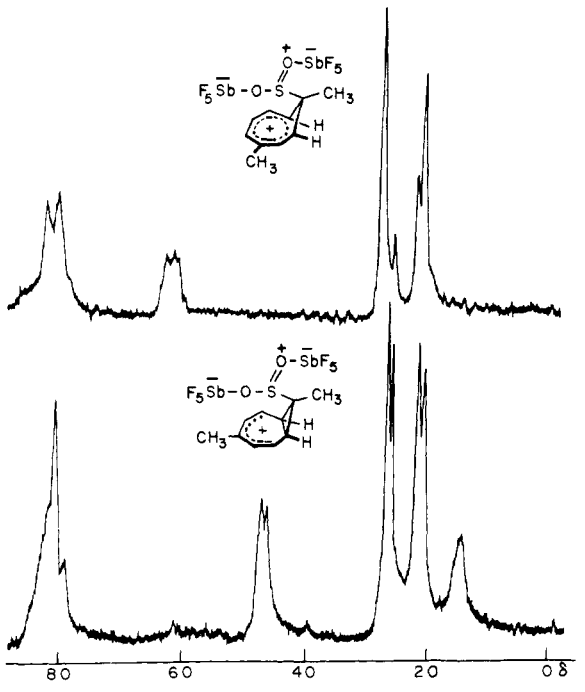
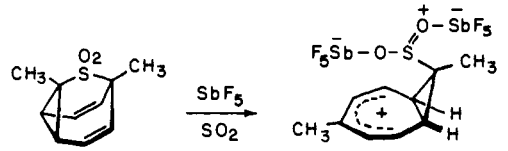


Figure 5. ^{1}H NMR spectra (60 MHz) of: (top) ion **26** in SO_2 at −50°; (bottom) ion **29** under the same conditions. Both spectra were recorded after approximately 1 hr at this temperature.

Due to the prevailing rapid Cope rearrangement, dimethylsulfone **28** displays (in $CDCl_3$) a lone methyl singlet (δ 1.54), a time-averaged cyclopropyl-olefinic absorption (m, 4 H, 4.0–4.32), and a permanently olefinic pair of protons (m, 5.63–6.08). Using **25** as a prototype, **28** was similarly



28 **29**

treated with 2.4 equiv of SbF_5. The spectrum so generated consisted of narrow multiplets at δ 7.8–8.5 (4 H) and 4.3–4.9 (2 H), together with twinned methyl singlets at 2.67 and 2.17 (more intense) as well as 2.60 and 2.08 (lesser intensity) (Figure 5). No changes were evident after 90 min at this temperature. Upon warming to 20° for 12 min, the two multiplets remained essentially unaltered. However, the relative intensities of the pairs of methyl peaks were now reversed.

It is evident from the NMR data that the zwitterion generated in these experiments maintains symmetry through carbons C_1 and C_5. However, the two methyl substituents do not remain identical. Furthermore, the chemical shift of H_1 and H_7 denotes that homotropylium character has not been attained since their location (δ 4.3–4.9) is approximately 1.5–2 ppm to higher field than normally encountered in such homoaromatic systems. These facts, together with the observation that H-2,3,5,6 must necessarily bear some degree of positive charge,[22,23] are best explained in terms of closed ion **29**. Some measure of additional support for this assignment was derived from the finding that **28** could be recovered in good yield when hydrolysis was effected after 3.5 hr at −70°. Thus, in contrast to the behavior of **7**, isomerization to a [4.2.1]bicyclic frame does not operate, likely because of the prohibitive constraints present in **29**.

Interpretation of the changes in the methyl region necessarily borders on the speculative. It is plausible, however, that the degree and locus of methyl substitution in **29** may be adequate to effect restricted rotation about the C–S bond. Because of the rigid geometry of the sulfone group in **28**, the spatial directionality achieved upon initial coordination of SbF_5 to oxygen may not be that which is most energetically satisfying to **29**. But whereas the preferred equilibrium orientation is easily reached in the homotropylium-8-sulfinate complexes, the combination of bicyclic character and disubstitution at C_4 and C_8 in **29** could reasonably attain restrictive levels. As expected of this phenomenon, the intensities of the four original methyl signals undergo synchronized alterations in relative intensity.

Direct treatment of 1,4- and 1,5-dimethylcyclooctatetraenes[24] with SbF_5–SO_2 did not give evidence of providing either **26** or **29**. This was anticipated since electrophilic attack at one of the methyl bearing ring carbons would be required, an unlikely event. Rather, the principal absorptions witnessed after 15 min at −50° appear at δ 7.5–8.7, 5.4–6.5, and 2.1–2.9. The complexity of these spectra is comparable to that realized from methylcyclooctatetraene. Together, they point up clearly that homotropylium-8-sulfinate complexes do not undergo ready dissociation to their cyclooctatetraene counterparts (and subsequent recombination) under the experimental conditions followed herein.

Discussion

The fact that sulfones **6** and **7** are produced upon reaction of cyclooctatetraene with the 1:1 SO_2–SbF_5 complex[25] suggests that ring closure may proceed via hypothetical homotropylium species such as **4** and **5** (XY^- = $-S(O)OSb^-F_5$).[6e,7] When interaction with a second mole of SbF_5 becomes possible, the anionic moieties (cf. **10**, **11**, etc.) now become sufficiently stabilized that maintenance of zwitterionic character is made possible. As a direct consequence of the demonstrated stoichiometry requirements, therefore, the homotropylium-8-sulfinate species generated in this study have been formulated as 2:1 complexes. Since both 9-thiabicyclo[4.2.1]nona-2,4,7-triene and 9-thiabarbaralane 9,9-dioxide structures can act as serviceable precursors to these ions, it is clear that the isomeric frameworks share the common characteristic of facile electrophilic ring opening.

With the exception of **29**, the quite large chemical shift difference observed for 8_{exo} (deshielded) and 8_{endo} (shielded) substituents attests to the operation of a ring current. Classical bicyclic structures such as the bicyclo[3.1.0]hexenyl[26] and bicyclo[5.1.0]octadienyliron tricarbonyl cations[27] are known not to exhibit comparable anisotropic effects. In most of the examples studied, endo–exo isomerization of the C_8 center occurred readily. When one of the tropylium sites was substituted by deuterium or methyl, positional integrity of the ring positions was maintained during such stereochemical inversion. Consequently, the process cannot be defined as a circumambulatory rearrangement. Rather, inversion through a planar cyclooctatrienyl cation appears to be the low-energy pathway. Theoretical assessment of the energetics for degenerate circumambulatory rearrangement in the parent homotropylium cation has projected an energy barrier of 43 kcal/mol.[16] Although suitable substitution of C_8 might reduce the magnitude of this activation energy, it remains difficult to decrease matters below the 22–23 kcal/mol level where ring flattening and attainment of cyclooctatrienyl character can develop.[3,12] Since *endo*-homotropylium-8-sulfinate complexes are not exceptions to this trend, this type of bulky 8-endo substituent does not provide a perturbation

which leads to mechanistic crossover. However, adverse electronic effects may operate against [1,6] suprafacial migration in our examples.[16]

The positive charge in homotropylium structures formally resides on the seven-membered ring. The introduction of methyl groups at these positions should exert a stabilizing inductive influence on the ground state, while similar substitution at C_8 should have lesser import, perhaps of a steric nature only. The experimental results show that the 3-methyl substitution plan adopted by **20** and **26,** although the source of some spectral alterations, neither perturbs measurably the inherent delocalization of the system nor the facility (qualitative) with which ring flipping occurs. Also, any distortion which the exo-8-methyl group in **26** may bring to this zwitterion is not apparent.

Placement of a methyl group at C_4 is quite another matter. In light of our experience with **23,** it seems that a greater part of the positive charge now becomes localized at this site with the result that configurational inversion at C_8 does not operate. We might visualize this as the result of a perturbation transmitted to the basal carbons at positions **1** and **7** such that their hybridization status is somehow altered.[16,28] Proton chemical shift data do not resolve this issue. However, electrostatic attraction may also develop between C_4 and the endo-oriented sulfur substituent which is of adequate proportions to deter conformational inversion. Most intriguing is the finding that introduction of a second methyl group at the 8-exo site leading to **29** results in loss of homoaromatic character. Such a dampening effect points up the rather narrow width of the interfacing which separates homoaromatic ions from their more classical counterparts,[29] a phenomenon which is certain to be still more apparent in *neutral* molecules which lack the added driving force to delocalization provided by an electrical charge.[30] As a direct result of the positional specificity provided by the present method, some glimpse of substituent effects on homoaromatic character has been made possible. Because the sulfinate moiety present in our complexes is likely to be considered by many as an unknown ingredient having bothersome complexity, attention should now be turned to a range of simpler isomeric mono- and disubstituted homotropylium ions. Although some exploratory effort has been made in this direction,[31] it is our intention that the present results provide the impetus necessary to foster requisite interest in the elucidation of these various factors.

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer; apparent splittings are given in all cases. Infrared spectra were determined on a Perkin-Elmer 467 instrument. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Reaction of Cyclooctatetraene with Antimony Pentafluoride in Liquid Sulfur Dioxide. Into a 1-l. three-necked flask fitted with a dry ice condenser, an overhead stirrer, and a jacketed addition funnel was condensed 100 ml of sulfur dioxide at −70° under a nitrogen atmosphere. Freshly distilled cyclooctatetraene (11.5 g, 0.11 mol) was added. Antimony pentafluoride (24 g, 0.11 mol) was weighed into a 250-ml three-necked flask equipped with a dry ice condenser and stirring bar. After the condensation of 150 ml of sulfur dioxide at −50° and dissolution, transfer to the addition funnel was made at −60°. This reagent was added dropwise during 45-60 min to the yellow COT-SO_2 solution. The resulting mixture was stirred for 2.5 hr at −70° under nitrogen, the sulfur dioxide was removed at 10-20 mm and −40 to −60°, cold (−30°) methylene chloride was introduced, and all was poured in a slow stream into a vigorously stirred saturated sodium bicarbonate solution (600 ml) cooled in an ice bath. The layers were allowed to separate, and the aqueous phase was extracted with methylene chloride. The combined organic layers were washed several times with water and brine, dried, and concentrated in vacuo. Three recrystallizations of the resulting light yellow solid (13.1 g, 70.5%) from chloroform-hexane afforded pure **6** (4.63 g), mp 193-193.5°. Chromatography of the combined mother liquors on silica gel (elution with chloroform-ether (9:1)) furnished an additional 2.46 g of **6** (total yield 38%). The slower moving component proved to be **7**: mp 166-166.5° (0.46 g, 2.5%); δ_{Me_4Si} ($CDCl_3$) 5.96 (pseudo t, 2, olefinic), 4.48 (pseudo t, 4, cyclopropyl ⇄ olefinic), and 3.33 (pseudo t, 2, methine); ν_{max} ($CHCl_3$) 1306, 1286, and 1121 cm^{-1}.

Anal. ($C_8H_8O_2S$) C, H, S.

Method for Obtaining ^1H NMR Spectra in Sulfur Dioxide. An accurately weighed sample of antimony pentafluoride under nitrogen was cooled to −60°, while sulfur dioxide was condensed (−60°) to provide approximately 0.5 ml of solution. After complete dissolution of the Lewis acid (best achieved at −20°), the sulfone was added in one portion at −60° with agitation from a glass rod. The micro reaction vessel was so designed that it could now be connected via a transfer adapter simultaneously to a vacuum line and an NMR tube. While cooled in liquid nitrogen, the vessel was evacuated and dry nitrogen was introduced to a level of 100 mm. Transfer to the tube was achieved by gravity and differential cooling (liquid N_2). Subsequently, the sample was degassed using standard techniques and sealed under high vacuum.

9-Thiabicyclo[4.2.1]nona-2,4,7-triene-*1,6-d*$_2$ 9,9-Dioxide (12). To a stirred solution of **6** (168 mg, 1.00 mmol) in dry tetrahydrofuran (15 ml) was added 2.25 mol equiv of *n*-butyllithium dissolved in pentane at −70° under nitrogen over a period of 2 min. After stirring for 6 min at this temperature, an appreciable excess of acetic acid-*O-d* was introduced and the cooling bath removed. Dichloromethane was added after solvent removal, and the mixture was washed several times with water before drying, concentration, and sublimation [120° (0.2 mm)]. There was obtained 117 mg (68%) of **12**: mp 194-194.5°; δ_{Me_4Si} ($CDCl_3$) 6.03 (s, olefinic).

9-Thiabarbaralane-*1,5-d*$_2$ 9,9-Dioxide (13). Comparable treatment of **7** (300 mg, 1.79 mmol) in 35 ml of anhydrous tetrahydrofuran with 2.68 ml of 2.0 *M* *n*-butyllithium (5.4 mmol) at −70° for 5 min, followed by quenching with acetic-d_4 acid (1.2 ml) gave 250 mg (82.2%) of sulfone. NMR analysis indicated deuterium exchange to be incomplete, but this was achieved after a second pass (220 mg, 72.3%). Recrystallization from chloroform-hexane gave white crystals: mp 165.5-166°; δ_{Me_4Si} ($CDCl_3$) 5.76-6.18 (pseudo t, 2, olefinic) and 4.47 (pseudo d, 4, olefinic ⇄ cyclopropyl).

1-Methyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (19). To a stirred suspension of **6** (99.8 mg, 0.594 mmol) in 10 ml of anhydrous tetrahydrofuran cooled to −78° under nitrogen was added 0.22 ml of 2.715 *M* *n*-butyllithium-hexane solution (0.594 mmol). The dark brown solution was allowed to stir for 30-35 sec before quenching with 0.6 ml of methyl iodide. The resulting light yellow solution was evaporated in vacuo (20°), and the residue was taken up in water and dichloromethane. The organic layer was washed several times with water, dried, and evaporated to leave 89.4 mg of yellow oil. The products from a total of six such methylations were combined and subjected to high pressure liquid chromatography on silica gel (elution with 10% ether in chloroform). The more rapidly eluted component was **25** (49.0 mg), identified by direct comparison with the substance prepared below. There followed 254.5 mg of **19** and ultimately 66.7 mg of recovered **6**. Recrystallization of the desired product from chloroform-hexane afforded white crystals: mp 115-116°; δ_{Me_4Si} ($CDCl_3$) 5.45-6.24 (m, 6, olefinic), 3.83-4.10 (m, 1, bridgehead), and 1.52 (s, 3, methyl).

Anal. ($C_9H_{10}O_2S$) C, H, S.

1(5)-Methyl-9-thiabarbaralane 9,9-Dioxide (22). To a stirred solution of **7** (52.8 mg, 0.314 mmol) in 8 ml of anhydrous tetrahydrofuran was added 0.116 ml (0.314 mmol) of 2.715 *M* *n*-butyllithium-hexane solution via syringe at −78° under nitrogen. The yellow solution was allowed to stir for 45 sec before the addition of methyl iodide (0.3 ml). Work-up in the predescribed fashion produced 52.4 mg (91.8%) of pale yellow solid. From a total of four such runs, the combined products were subjected to high pressure liquid chromatography on silica gel (elution with chloroform-ether (9:1)). In order of elution, there were isolated 23.1 mg of **28,** 70.7 mg of **22,** and 32.9 mg of recovered **7**. The desired sulfone was obtained as white crystals: mp 225.5-226° dec, from chloroform-hexane; δ_{Me_4Si} ($CDCl_3$) 5.66-6.07 (m, 2, olefinic), 4.96-5.34 (m, 2), 3.30-3.62 (m, 3), and 1.56 (s, 3, methyl).

Anal. ($C_9H_{10}O_2S$) C, H, S.

1,6-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (**25**) was available from a previous study.[24]

1,5-Dimethyl-9-thiabarbaralene 9,9-Dioxide (**28**). Following previous methodology, a solution of **7** (830 mg, 4.94 mmol) in 60 ml of anhydrous tetrahydrofuran was treated sequentially at −70° with 7.5 ml of 2.0 *M* *n*-butyllithium–hexane solution (16.5 mmol) and 5 ml of methyl iodide. There was obtained 890 mg (92%) of crude **28** which was recrystallized from chloroform–hexane: hard white crystals; mp 237° dec; δ_{Me_4Si} ($CDCl_3$) 5.63–6.08 (m, 2, olefinic), 4.0–4.32 (m, 4, cyclopropyl ⇄ olefinic), and 1.54 (s, 6, methyl).

Anal. ($C_{10}H_{12}O_2S$) C, H, S.

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References and Notes

(1) J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

(2) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965); (b) C. E. Keller and R. Pettit, *ibid.*, **88**, 604, 606 (1966); (c) L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *ibid.*, **95**, 3386 (1973).

(3) S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 2047 (1966).

(4) L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Am. Chem. Soc.*, **93**, 4503 (1971).

(5) (a) R. Huisgen, G. Boche, and H. Huber, *J. Am. Chem. Soc.*, **89**, 3345 (1967); (b) R. Hulsgen and J. Gasteiger, *Angew. Chem.*, **84**, 1187 (1972); *Tetrahedron Lett.*, 3661 (1972).

(6) (a) L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967); (b) L. A. Paquette, J. R. Malpass, and T. J. Barton, *ibid.*, **91**, 4714 (1969); (c) R. Huisgen, W. E. Konz, and U. Schnegg, *Angew. Chem.*, **84**, 765 (1972); (d) J. Gasteiger and R. Hulsgen, *ibid.*, **84**, 766 (1972); (e) J. Gasteiger and R. Huisgen, *J. Am. Chem. Soc.*, **94**, 6541 (1972); (f) L. A. Paquette, D. R. James, and G. H. Birnberg, *ibid.*, **96**, 7454 (1974).

(7) L. A. Paquette, U. Jacobsson, and M. Oku, *J. Chem. Soc., Chem. Commun.*, 115 (1975).

(8) The ^1H and ^{13}C NMR spectral properties of sulfone **7** clearly reveal this molecule to be in a state of rapid flux.[7,9] Although a single structural representation of **7** will be utilized herein to economize space, the reader should recognize that **7** is subject to facile degenerate rearrangement at ordinary temperatures.

(9) A. G. Anastassiou, E. Reichmanis, and J. C. Wetzel, private communication. We thank Professor Anastassiou for informing us of his findings in advance of publication.

(10) (a) T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *J. Am. Chem. Soc.*, **92**, 734 (1970); (b) A. G. Anastassiou and B. Y.-H. Chao, *J. Chem. Soc., Chem. Commun.*, 277 (1972); (c) A. G. Anastassiou, A. E. Winston, and E. Reichmanis, *ibid.*, 779 (1973).

(11) L. A. Paquette, R. H. Meisinger, and R. Gleiter, *J. Am. Chem. Soc.*, **95**, 5414 (1973).

(12) J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8907 (1972).

(13) Except where indicated to the contrary, 2.4–2.5 equiv of SbF_5 was the quantity routinely employed in this study.

(14) G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *J. Am. Chem. Soc.*, **89**, 3344 (1967).

(15) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1969.

(16) W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 8908 (1972); **96**, 5207 (1974).

(17) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

(18) D. R. James, G. H. Birnberg, and L. A. Paquette, *J. Chem. Soc., Chem. Commun.*, 722 (1974); *J. Am. Chem. Soc.*, **96**, 7465 (1974).

(19) U. Jacobsson, unpublished observations.

(20) These and other weak extraneous peaks which are sometimes encountered may owe their origin to the presence of low concentrations of complexes having stoichiometry differing from the depicted 2:1 ratio. Alternatively, these signals may reflect the presence of bicyclic species which ring-open upon warming.

(21) The species thus generated remained unchanged for several hours at this temperature. When the sample was allowed to warm to 25° for 30 min, however, some conversion to **26** was noted.

(22) Although cycloheptadienyl cations seem not to have been examined spectroscopically in superacid media, data on cycloheptenyl cations are available: G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **94**, 6434 (1972).

(23) For data on the 1,3-bishomotropylium cation, consult: L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *J. Am. Chem. Soc.*, **95**, 3386 (1973). Other relevant references have been summarized in L. A. Paquette, M. Oku, W. B. Farnham, G. A. Olah, and G. Liang, *J. Org. Chem.*, **40**, 700 (1975).

(24) L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Am. Chem. Soc.*, **96**, 5806 (1974).

(25) J. W. Moore, H. W. Baird, and H. B. Miller, *J. Am. Chem. Soc.*, **90**, 1358 (1968).

(26) (a) R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7144 (1968); (b) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969); (c) R. F. Childs and B. Parrington, *ibid.*, 1540 (1970); (d) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Am. Chem. Soc.*, **93**, 1551 (1971).

(27) M. Brookhart, E. R. Davis, and D. L. Harris, *J. Am. Chem. Soc.*, **94**, 7853 (1972), and references cited therein.

(28) W. J. Hehre, *J. Am. Chem. Soc.*, **95**, 5807 (1973).

(29) R. C. Haddon, *Tetrahedron Lett.*, 2797 (1974); 863 (1975).

(30) L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Am. Chem. Soc.*, **94**, 4739 (1972); H. Gunther, H. Schmickler, U. H. Brinker, K. Nachtkamp, J. Wassen, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **12**, 760 (1973); L. A. Paquette, H. C. Berk, and S. V. Ley, *J. Org. Chem.*, **40**, 902 (1975).

(31) S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 141 (1969); H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966); M. Brookhart, M. Ogliaruso, and S. Winstein, *ibid.*, **89**, 1965 (1967); G. D. Mateescu, C. D. Nenitzescu, and G. A. Olah, *ibid.*, **90**, 6235 (1968); O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969); P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 2146 (1970); Y. Sugimura and N. Soma, *Tetrahedron Lett.*, 1721 (1970); R. F. Childs, M. A. Brown, F. A. L. Anet, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2175 (1972); M. S. Brookhart and M. A. M. Atwater, *Tetrahedron Lett.*, 4399 (1972).