States-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

Registry No. **1H**, 14604-48-9; **2Si**, 80631-00-1; **2C**, 50457-57-3; **3Si**, 80631-01-2; **3C**, 80631-02-3; **4H**, 62698-25-3; **5Si**, 80631-03-4; **5C**, 80631-04-5; **6Si**, 80631-05-6; **6C**, 80631-06-7; **7H**, 74-85-1; **8Si**, 7291-09-0; **8C**, 115-07-1; **9Si**, 754-05-2; **9C**, 558-37-2; **10H**, 689-97-4; **11Si**, 59923-57-8; **11C**, 646-05-9; **12Si**, 2696-32-4; **12C**, 4911-58-4; **13H**, 557-75-5; **14Si**, 80631-07-8; **14C**, 29456-04-0; **15Si**, 80631-08-9; **15C**, 79144-28-8.

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Quadricyclene

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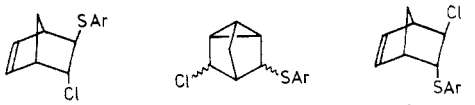
The treatment of quadricyclene with 2,4-dinitrobenzenesulfenyl chloride has been reinvestigated and chloro adducts **1-A** and **2b-A** as well as acetates **4a-A**, **4b-A**, **6**, and **7** have been obtained. Establishing **2b-A** with *endo*-chloride led to the important conclusion that *endo*-chloride attack occurs by collapse of an ion pair. Monitoring changes in the proportions of acetates, especially with added $LiClO_4$, has allowed conclusions about the degree of development of the carbocation intermediates. These conclusions were proposed on the basis of the previously published ideas of stereocontrol by an ion pair.

The addition of sulfenyl chlorides to norbornadiene has received considerable attention.[1-8] These studies may be summarized as follows (despite differences in opinion on the stereochemistry of one addition product and thus the attendant mechanism). First, the relative proportions of products are extremely sensitive to the polarity of the solvent used. Second, products have been observed with stereochemistry that may be suprising to some. Third, the second double bond can interact with the incipient carbocation center, possibly stabilizing the intermediate and in many cases clearly allowing rearrangement to nortricyclene-structure adducts. These combined observations have led to important mechanistic conclusions[4,9,10] for 2,4-dinitrobenzenesulfenyl chloride (DNBSC) additions.

Let us expand upon these observations. Early papers described the formation in nonpolar solvents of *trans*-chloro sulfides (type 1, *endo*-Cl) mixed with minor

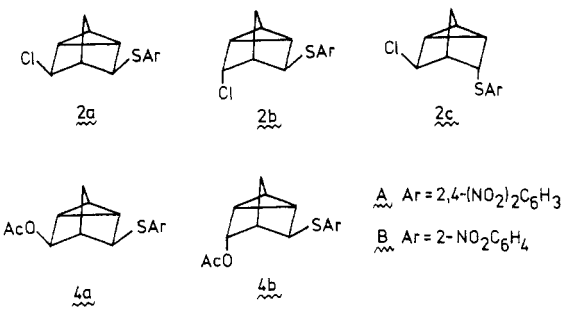


1 2 3

A Ar = 2,4-$(NO_2)_2C_6H_3$; B Ar = 2-$NO_2C_6H_4$

amounts of isomeric adducts with nortricyclene skeletons.

Chart I



2a 2b 2c

4a 4b

More recently, the reports by the research groups of Zefirov and Morrill[4] and of Garratt[5] revealed a more complex picture. First, additions carried out in carbon tetrachloride and in dichloromethane solvents yield three major products, specifically adducts **1** and **2** as well as olefinic *trans*-chloro sulfide **3** with the SAr and Cl groups in a configuration opposite that of **1**. The structure of **3-B** has been established by X-ray diffraction.[6] Adduct **3** indicates that the diene has been attacked by electrophilic sulfur on the endo side.

Second, yields of nortricyclene chloro sulfides **2** increase sharply with an increase in solvent polarity, and type-**2** adducts predominate in acetic acid[4,11] and in liquid sulfur dioxide.[8] Garratt and Beaulieu[5] have assigned configuration **2a** (*exo*-chlorine, *exo*-thioether, Chart I) to their product on the basis of ^{13}C NMR data. More recently Zefirov and Morrill[4] published results leading to a different structure for this product; configuration **2b** was assigned (*exo*-thioether, *endo*-chlorine) on the basis of single-crystal X-ray studies of **2b-A**.[4,7]

Formation of adduct **2b-A** has been interpreted in terms of an ion-pair mechanism; this has evolved from the concept of "stereocontrol of addition" by ion pairs.[4,9,12] Under "doping" conditions[9,10,13] ($LiClO_4$ in the acetic acid), the

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(11) (a) Even the addition of small amounts of cosolvent acetic acid to dichloromethane (acetic acid/2-$NO_2C_6H_5SCl$, 2:1) leads to drastic product changes: the proportion of **1-B** decreases and an increasing proportion of **2b-B** to **1B** was observed. (b) L. A. Andreeva, personal communication.
(12) N. S. Zefirov, N. K. Sadovaja, R. S. Akhmedova, and I. V. Bodrikov, *Khim.*, **15**, 217 (1979).

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major addition pathway is formation of two nortricyclenic adducts (**4a** and **4b** in both **A** and **B** series). X-ray data[14] for acetoxy thioethers **4a** and **4b** show them to both have *exo*-sulfide groups and to have, respectively, *exo*- and *endo*-acetoxy groups. Detection of these two isomers suggests that here the carbocation center is well developed.

The stereochemistry of type-**2** adducts arising from additions to norbornadiene has been used for comparison to corresponding additions to quadricyclene (tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane). Electrophilic cleavage of single carbon–carbon bonds in strained quadricyclene systems has been described.[15,16] In particular, the extensive study by Garratt[16] indicates formation of three major products (all chloro sulfides): type **1** (10–46%), type **2a** (25–66%), and type **2c** (0–59%). If, however, the new assignment (**2b-A**) for the chloro sulfide from dinitrobenzenesulfenyl halide addition is accepted (as opposed to configuration **2a-A**[5,16]), the mechanistic interpretation for this reaction must be revised.

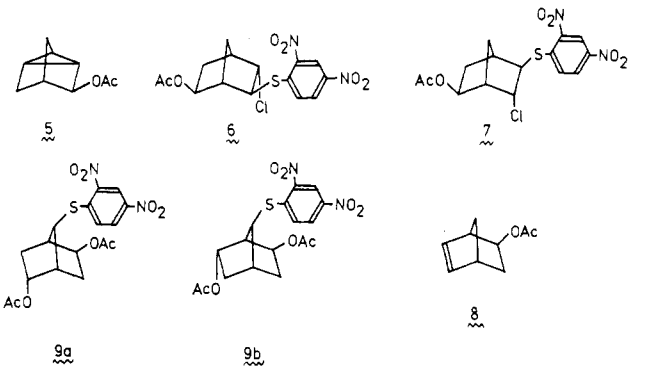
In this study we have examined the addition of 2,4-dinitrobenzenesulfenyl chloride to quadricyclene for two reasons. First, we wished to establish the configurations of adducts with nortricyclene skeletons by relating them to structure **2b-A** for which the X-ray results are known.[4,7] Second, it was of interest to determine the effect upon product composition of doping[4] with lithium perchlorate.

Results

In order to be sure of the configurational assignments, it was important to develop a method of synthesis for **2a-A** and **2a-B** (both with *exo*-chlorine) so they could be compared to the compounds in the **2b** series. As described above, the doped addition to norbornadiene proceeded nonstereospecifically to give both acetates **4a** and **4b** (in both series **A** and **B**). We have now found that LiCl-doped addition of both DNBSC and 2-nitrobenzenesulfenyl chloride (NBSC) to norbornadiene gives, in each series, both **2a** and **2b**; these isomers are formed in comparable yields and can be isolated by preparative TLC. The configurational assignments are partly based on the upfield shift (~0.5 ppm) of the ^{1}H NMR signal of the H–C–S proton of **2a** compared to that of **2b**.[4,9,17] In addition, the structure of **2a-B** has been recently established by X-ray analysis.[18]

In view of the differences in opinion regarding the configurations of some (nortricyclene) type-**2** adducts,[4,5,16] we will briefly review other publications[4,16] leading to configuration assignments that disagree with ours. Garratt's group has routinely reported kinetic control results based on immediate ^{1}H and ^{13}C NMR analyses of reaction products. When DNBSC was added to quadricyclene in dichloromethane, a ratio of **1**/**2a**/**2c** of 30:66:4 was reported. No evidence for isomeric olefinic adducts **3** or Wagner–Meerwein rearrangement was reported. Although it was stated that the individual adducts were isolated by preparative TLC, no preparative yields, melting points, or ^{1}H NMR results were reported. In fact, only the ^{13}C NMR shifts for the compounds reported to be **2a**[5] and **2c**[16] were reported.

Chart II



We have repeated the addition of DNBSC to quadricyclene in dichloromethane as had been described.[16] In our hands this reaction resulted in two major adducts in a ratio of 35:65 (^{1}H NMR). The 35% product proved to be the trans adduct (**1-A**) in agreement with the published assignment for Garratt's 30% isomer. The major product, however, proved to be **2b-A** rather than **2a-A**. A similar result was obtained in carbon tetrachloride solvent; **1-A** and **2b-A** were isolated in, respectively, 47% and 20% yields. A third adduct, apparently possessing a nortricyclene skeleton, was also observed but in very low (4%) yield (note the similarity in yield to the third product described above in Garratt's work[16]). The analysis of the reaction mixture showed a number of spots corresponding to yields in the 2–5% range; one of these spots did have an R_f identical with that of **2a-A**. Due to the low yields and incomplete characterization of these products we cannot determine these structures or draw conclusions as to the implications for kinetic control of the minor products.

Treatment of quadricyclene with DNBSC in acetic acid (20 °C) resulted in chloro sulfides **1-A**, **2-aA**, and **2b-A** in 16%, 5%, and 35% yields, respectively. In addition, five acetates were formed in a combined yield of 36%. Two of them proved to acetoxy thioether **4a-A** (7% yield; exo,exo) and **4b-A** (8% yield; *exo*-thioether, *endo*-acetoxy).[4] A third acetate was found to be 3-acetoxynortricyclene (**5**),[19] and the last two were found to be trisubstituted norbornanes **6** and **7** (Chart II). The structures **6** and **7** were deduced from their ^{1}H NMR spectra. Compound **6** exhibits signals at δ 3.19 (broadened d, J = 4.4 Hz, H–C–S), 4.1 (dt, J = 4.4 Hz, H–C–Cl), 4.88 (dd, J = 7.6, 3.2 Hz, H–C–O). Double resonance indicates that the 4.4-Hz coupling is vicinal coupling ($J_{2,3}$) which supports the vicinal relationship of SAr and Cl. The magnitude of the coupling constant (4.4 Hz) supports the trans relationship of SAr and Cl. The ^{1}H NMR spectrum of **7** (see the Experimental Section) similarly supports a trans-vicinal relationship of SAr and Cl. The deshielded position (δ 5.34) of the H–C–O proton of **7** suggests that the *endo*-chlorine is closer to this proton than to the corresponding proton (δ 4.88) in **6**.[20] The exo configuration of

(13) N. S. Zefirov, N. K. Sadovaja, A. M. Maggerramov, I. V. Bodrikov, *ibid.*, **13**, 245 (1977); N. S. Zefirov, N. K. Sadovaja, L. A. Novgorodtseva, and I. V. Bodrikov, *ibid.* **14**, 463 (1978).

(14) The crystal data for **4a-B**: a = 27.92 (2) Å, b = 7.419 (8) Å, c = 14.00 (1) Å; space group P_{bca}, Z = 8, R_{hkl} = 0.065 (T. F. Rau, V. G. Rau, K. A. Potekhin, Y. T. Struchkov, R. S. Akhmedova, N. S. Zefirov, And N. K. Sadovaja, accepted for publication in *Cryst. Struct. Commun.*). X-ray data for **4b-B** see B. B. Sedov, T. F. Rau, Y. T. Struchkov, R. S. Akhmedova, N. S. Zefirov, and N. K. Sadovaja, *ibid.*, **9**, 639 (1980).

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(16) P. L. Beaulieu, A. Kabo, and D. S. Garratt, *Can. J. Chem.*, **58**, 1014 (1980).

(17) N. S. Zefirov, N. K. Sadovaja, L. A. Novgorodtseva, I. V. Bodrikov, *Tetrahedron*, **14**, 1373 (1978).

(18) The crystal data for **2a-B**: α = 10.064 (2) Å, b = 13.368 (1) Å, c = 10.42 (3) Å, V = 1278.6 cm^3, β = 114.2 (1)°; space group $P2_{1/c}$, R_{hkl} = 0.071, R_w = 0.074. (A. M. Nersisyan, A. I. Yanovsky, Y. T. Struchkov, L. A. Andreeva, N. S. Zefirov, and N. K. Sadovaja, accepted for publication in *Cryst. Struct. Commun.*)

(19) W. Dauben, and R. Cargill *Tetrahedron*, **15**, 197 (1961); J. Tabashi, K. Yamamure, and A. Togashi, *J. Org. Chem.*, **41**, 2169 (1976).

(20) H. Christol, F. Plenat, and J. Revel, *Bull. Soc. Chim. Fr.* **1971**, 4537.

Table I. Preparative Yields of the Addition Products of DNBSC to Quadricyclene at 20 °C

solvents	addition product yields, %								
	1-A	2a-A	2b-A	4a-A	4b-A	5	6	7	8
CCl_4	47		19						
CH_2Cl_2	(35)[a]		(65)[a]						
CH_3COOH	15	5	35	7	8	10	7	4	
$CH_3COOH + LiClO_4$[b]		8[c]		9	trace	40	6[d]		18

[a] Ratio by NMR. [b] $LiClO_4$/DNBSC ratio is 5:1. [c] Yield of **1-A**, **2a-A**, and **2b-A**. [d] Yield of **6** and **7**.

the acetoxy group in both **6** and **7** seems reasonable as olefinic acetate **8** (with *exo*-acetoxy; see below) is likely the precursor to **6** and **7**.

It has been reported[19] that acetic acid readily adds to quadricyclene (at 20 °C) to give comparable amounts of 3-acetoxynortricyclene (**5**) and 5-*exo*-acetoxynorbornene (**8**). We have found that under our experimental conditions (20 °C, 2 h, 0.2 M quadricyclene) in the absence of sulfenyl halide, acetic acid adds to form a mixture of **5** and **8** (detected by NMR). Thus it seems reasonable to assume that **8** is the precursor to diadducts **6** and **7**. The addition of DNBSC to the double bond of **8** thus appears to be a trans addition (without Wagner–Meerwein rearrangement) involving exo attack of sulfur which occurs with two different kinds of regiospecificity.

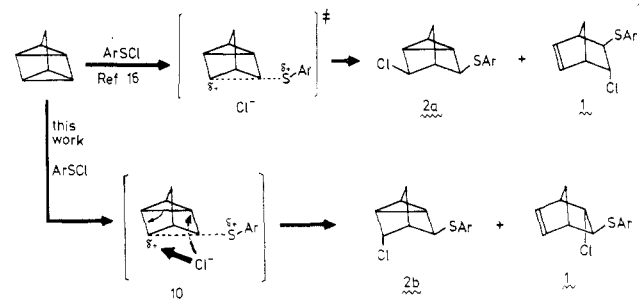
Treatment of quadricyclene with DNBSC in acetic acid doped with $LiClO_4$ gives different results: the major single product is acetate **5** (40% yield), and the total yield of products of DNBSC addition is only 40%. The presence of $LiClO_4$ greatly favors production of acetates **5** and **8**,[21] the latter being formed in 18% yield. DNBSC addition leads to acetate **4a-A** (9% yield, plus a trace of isomer **4b-A** indicated by TLC), a mixture of diadducts **6** and **7** (6%), and diacetate **9**. The structure of **9** is tentatively assigned by ^1H NMR. A singlet at δ 3.41 (H–C–S) places the SAr group at C-7,[9,17] and thus Wagner–Meerwein rearrangement is indicated. The two acetoxy groups should have different configurations as indicated by the two different H–C–O signals, one at δ 5.11 ($w_{1/2}$ = 20 Hz) and the other at δ 4.75 ($w_{1/2}$ = 14 Hz). Thus **9** is apparently the result of addition of DNBSC to olefinic acetate **8** followed by Wagner–Meerwein rearrangement and attack of external nucleophile (acetic acid) to form **9**.[9,13,17] Structure **9a** or **9b** is possible, depending upon the regiospecificity of DNBSC attack upon **8**. These data do not permit an unambiguous choice, although **9a** might be predicted on the basis of mechanism.

Discussion

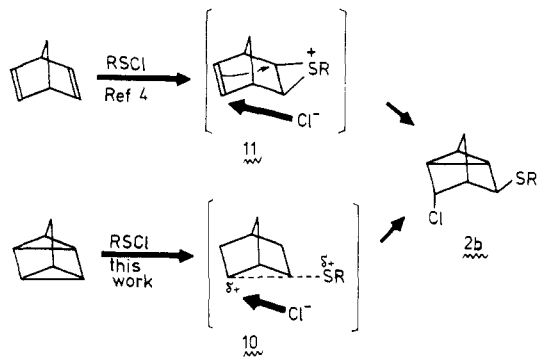
The following are the more important aspects of this study: (a) the reaction of DNBSC with quadricyclene results in smooth cleavage of the cyclopropane ring, and the ratio of products obtained depends upon the polarity of the solvent; (b) configuration of the major product arising from cleavage by sulfur electrophile is **2b-A** with an *endo*-chlorine which indicates retention of configuration at this position, which is inconsistent with previous reports[16] but which supports our ion-pair mechanism;[4] (c) the process in acetic acid seems to involve competitive additions of DNBSC and acetic acid to quadricyclene, the latter becoming dominant under doping conditions.

Garratt has pointed out that the minor or negligible proportions of olefinic or nortricyclenic adducts formed as the result of endo attack by sulfur is effectively negative evidence for "edge-attack" by sulfur.[16] He has used a

Scheme I



Scheme II



"corner attached" (*exo*-sulfur) species (see Scheme I, first-formed species)[16,22] as a precursor to both **2a** and, through an exo-bridged sulfonium ion, to olefinic product **1**. The basic argument for corner attack is the fact that electrophilic cleavage occurs with inversion.[23]

Since we find **1A** and **2b-A** (both with *exo*-SAr), we are in agreement with the corner-attack concept. We do feel, however, that it should be modified to involve an ion-pair intermediate (**10**, Scheme I) that partitions between **2b** and **1** rather than the activated complex (Garratt[16,22] uses a ‡ notation) that leads to **2a** or eventually to **1**. The proximity of the anion for endo attack in our ion pair seems plausible here as well as in our previous studies.[4,9] As discussed earlier, a greater proportion of chlorides to acetates is an indication of the greater importance of ion pairing. The data of Table I summarize the prefered formation of chlorides (**1A** + **2b-A**, 55%) vs. acetates (**4a-A** + **4b-A**, 13%) in acetic acid in the absence of $LiClO_4$. Thus in the absence of $LiClO_4$, ion pairing is more important, and in the chlorinated solvent the ion pair is even tighter, leading to even larger proportions of chlorides.

(21) (a) We have found also that the AcOH + $LiClO_4$ system readily isomerized 1,1-dimethylcyclopropane into 2-methylbut-2-ene.[21b] (b) N. S. Zefirov, N. V. Zyk, and A. V. Nikulin, unpublished result.

(22) P. L. Beaulieu, V. M. Morisset, D. S. Garratt, *Can. J. Chem.*, **58**, 1005 (1980).

(23) Although **2c-A**, in 4% yield, has been reported,[16] we could not detect this compound by ^1H NMR; TLC data seem to indicate, however, minor amounts of **2a-A**. For other arenesulfenyl chlorides, yields of **2c** in the range of 30–50% have been reported. In our hands the addition of *p*-ClC_6H_4SCl did not give the reported products[16] but rather **2b**- and **3**-type adducts as well as diadducts and no trace of **2c**-type product. In view of our results the products and mechanisms described in ref 16 should be throughly reinvestigated.

Indeed, in acetic acid the process seems to involve a freer carbocation than in the chlorinated solvents as evidenced by the emergence of product with an *exo*-chloro group (**2a-A**) and of product acetates (**4a-A** and **4b-A**). We thus simply propose ion pair **10** without any greater detail as to the "tightness" of this intermediate.

The idea that a well-developed or freer carbocation should give rise to both epimers (*exo*- and *endo*-chlorine) has been discussed by others.[16,24] Thus we associate primarily endo capture with a less well developed cation.[4,9,12] Specifically, the doped addition of ArSCl to norbornadiene in acetic acid gave both **4a** and **4b**. In the absence of $LiClO_4$, norbornadiene gave rise to only one chloride (**2b**, in both the **A** and **B** series), and this was explained by the ion-pair process at the top of Scheme II. The new results for quadricyclene described herein are analogous and lend support to the similar process in Scheme II (**10** → **2b-A**). Both processes assumedly involve quick endo attack of the internal chloride ion.[25]

Treatment of quadricyclene with DNBSC in acetic acid proceeds along two successive paths: one is the addition of acetic acid solvent to produce acetates **5** and **8**, and the other is the subsequent attack of these acetates by DNBSC. This second attack displays characteristics typical of well-developed carbocations, namely, (a) the occurrence of Wagner–Meerwein rearrangement (see product **9**, Table I) and (b) the incorporation of acetic acid solvent, presumably in the final step leading to **9**, from solvent external to the ion-paired chloride. The use of "doping" conditions has thus led to a method of "separating" an ion pair and subsequently to a way of testing reaction intermediates.

In summary, we stress that the unambiguous determination of nortricyclene **2b-A** has been crucial to this and our previous report.[4] Indeed, basing the configurational assignments for substituted nortricyclenes on relative chemical shifts in ^1H NMR spectra has been misleading before[15] and, more recently with ^{13}C NMR, has again been misleading.[5,16] At present we cannot generalize on the entire series of ArSCl[16] and ArSeCl additions to norbornadiene and to quadricyclene. It does seem clear that the entire mechanistic picture should cautiously be reinvestigated.

Experimental Section

All products were separated and purified by preparative TLC with Silpearl silica gel and L5/40μ. The ^1H NMR spectra were obtained from Varian C-60-H and JNM-MH-100 spectrometers by using $CDCl_3$ and CCl_4 solvents with Me_4Si (δ 0.00) as an internal standard. Acetic acid was purified as previously reported.[26]

Synthesis of *exo*-Chloro Sulfides 2a-A and 2a-B. (a) To a stirred solution of LiCl (1.3 g, 31 mmol), $LiClO_4$ (1.5 g, 14 mmol), and norbornadiene (0.12 g, 1.3 mmol) in 20 mL of acetic acid was added 0.3 g (1.3 mmol) of DNBSC. This mixture was stirred 5 min, poured into water, and extracted with chloroform. The combined chloroform extracts were dried ($MgSO_4$), and the solvent was removed, allowing chromatographic (TLC) separation of the resulting residue with hexane/ether (1:1). This TLC yielded 0.04 g (9% yield) of olefinic adduct **1-A**, 0.9 g (22% yield) of *endo*-chloro adduct **2b-A**, and 0.9 g (22% yield) of adduct **2a-A**: mp 111–112 °C (from CCl_4); ^1H NMR δ 3.52 (s, 1 H, H–C–S), 4.16 (s, 1 H, H–C–Cl). Anal. Calcd for $C_{13}H_{11}ClN_2O_4S$: C, 47.77; H, 3.37; S, 9.81. Found: C, 47.50; H, 3.41; S, 10.11. In addition, a 30% yield of acetates **4a-A** and **4b-A** (2.5:1 ratio) was obtained.

(b) To a stirred solution of 1 g of LiCl, 1.6 g of $LiClO_4$, and 0.46 g (5.0 mmol) of norbornadiene in 20 mL of acetic acid was added 0.94 g (5.0 mmol) of 2-nitrobenzenesulfenyl chloride. A workup and TLC as described above gave 0.49 g (35% yield) of a mixture of chloro sulfides **1B** and **2b-B** and 0.24 g (17%) of chloro sulfide **2a-B**: mp 106–107 °C (from CCl_4); ^1H NMR δ 3.34 (s, 1 H, H–C–S), 4.03 (s, 1 H, H–C–Cl). Anal. Calcd for $C_{13}H_{12}ClNO_2S$: C, 55.42; H, 4.29; S, 11.38. Found: C, 55.11; H, 4.32; S, 11.60. In addition, 0.3 g (22%) of acetates **4a-B** and **4b-B** were obtained (3:1 ratio).

Addition of DNBSC to Quadricyclene. (a) A mixture of quadricyclene (0.40 g, 4.34 mmol) and DNBSC (1.02 g, 4.35 mmol) in 20 mL of CCl_4 was stirred at 20 °C for 2 h. Removal of the solvent and ^1H NMR analysis of the residue revealed a 2.5:1 ratio of **1-A** to **2b-A**. These were separated by TLC (hexane/ether, 1:1.5) to give 0.46 g of **1-A** and 0.30 g of **2b-A**.

(b) Treatment of quadricyclene (0.10 g, 1.1 mmol) with DNBSC (0.26 g, 1.1 mmol) in dichloromethane for 2 h at 20 °C gave a 1:2.2 ratio of **1-A**/**2b-A** as detected by ^1H NMR.

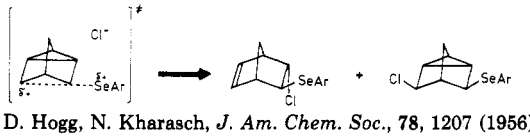
(c) A mixture of quadricyclene (0.40 g, 4.3 mmol) and DNBSC (1.04 g, 4.4 mmol) in acetic acid was stirred at 20 °C for 2 h and then poured in water. This was extracted with chloroform, and the chloroform solution was dried ($MgSO_4$), the solvent removed, and the residue chromatographed (hexane/ethyl acetate, 5:1) to give (in order of decreasing R_f value): 0.065 g (yields in Table I) of acetate **8** [bp 90° (bath temperature; 6 mm); n^D_{20} 1.4711; ^1H NMR δ 4.53, (s, 1 H, H–C–O). Anal. Calcd for $C_9H_{12}O_2$: C, 71.05; H, 7.89. Found: C, 71.48; H, 8.11], chloro sulfides **1-A** (0.22 g), **2b-A** (0.5 g), and **2a-A** (0.07 g) which proved to be identical with samples we have previously described,[4] acetoxychloro sulfides **4a-A** (0.18 g) and **4b-A** (0.1 g), again identical with earlier samples,[4] diadduct **6** [mp 165–166 °C (from heptane–benzene); ^1H NMR δ 3.19 (d, J = 4.4 Hz, 1 H, H–C–S), 4.1 (dt, J_d = 4.4 Hz, 1 H, H–C–Cl), 4.88 (dd, J = 7.6, 3.2 Hz, 1 H, H–C–O). Anal. Calcd for $C_{15}H_{15}ClN_2O_6S$: C, 46.58; H, 3.91; S, 8.29. Found: C, 46.24; H, 4.03; S, 8.44], and diadduct **7**: 0.06 g; mp 132–134 °C; ^1H NMR δ 3.31 (dd, J = 4.0 Hz, 1 H, H–C–S), 4.18 (t, 1 H, H–C–Cl), 5.34 (dd, J = 7.6, 3.0 Hz, 1 H, H–C–O).

(d) DNBSC (1.04 g, 4.44 mmol) was added to a stirred solution of $LiClO_4$ (2.2 g, 20.7 mmols) and quadricyclene (0.4 g, 4.35 mmol) in 20 mL of acetic acid, and this mixture was stirred for 2 h at 20 °C and then subjected to the workup described above. Chromatography (heptane/ethyl acetate, 1.5:1) gave the compounds listed in Table I, all of which have been characterized as described above with the exception of diadduct **9**: 0.28 g; mp 146–147 °C (from ethanol); ^1H NMR δ 3.41 (s, 1 H, H–C–S), 4.75 (m, 1 H, H–C–O), 5.11 (m, 1 H, H–C–O). Anal. Calcd for $C_{17}H_{18}N_2O_8S$: C, 49.79; H, 4.42; S, 7.81. Found: C, 50.20; H, 4.56; S, 7.89.

Registry No. **1-A**, 66887-41-0; **1-B**, 71040-85-2; **2a-A**, 71075-02-0; **2a-B**, 71040-98-7; **2b-A**, 73464-48-9; **2b-B**, 74524-52-0; **4a-A**, 66965-67-1; **4a-B**, 74502-32-2; **4b-A**, 66887-43-2; **4b-B**, 74524-51-9; **5**, 876-10-8; **6**, 80698-18-6; **7**, 80698-19-7; **8**, 5257-37-4; **9a**, 80698-20-0; norbornadiene, 121-46-0; quadricyclene, 278-06-8; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; 2-nitrobenzenesulfenyl chhloride, 7669-54-7.

(24) S. J. Cristol, J. K. Harrington, and M. S. Singer, *J. Am. Chem. Soc.*, **88**, 1529 (1966).

(25) These results place some constraints upon the ion-pair structure. Although the position of the counter ion (here Cl^-) cannot be placed with certainty, the stereochemistry of the products does shed some light upon its position. The position of the counter ion in Scheme II correlates with the structure of the products. On the other hand, the reported addition of ArSeCl to quadricyclene[21] implies a different scheme as shown below. In such selenium additions there does not appear to be an ion pair for stereocontrol of the products but rather attack by external nucleophile only.



(26) D. Hogg, N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1207 (1956).