(20) Cl_2 was first condensed into a tared cold trap from which it was revaporized and condensed into the phosphine solution via a Dry Ice condenser. Alternatively, the Cl_2 was delivered as a solution in CH_3CN, the concentration of which was determined by iodometric titration.
(21) These concentrations represent the approximate limit of solubility of **2** in these solvents.
(22) Solutions of **3** were prepared in a volumetric flask with solid **3** and CH_2Cl_2; in situ preparation of a solution was not feasible because of difficulty in removal of any excess BF_3. A 1.15 *M* solution of **3** in CH_2Cl_2 was assayed by hydrolysis in 0.1 *M* NaOH (~0.75 equiv) followed by titration of this aqueous solution with dilute NaOH to a phenolphthalein endpoint. Two trials gave a molarity of 1.16 *M* (±0.00), based on the release of 5 mol of acid per mole of **3**.
(23) J. S. Hartman and G. J. Schrobilgen, *Can. J. Chem.*, **50**, 713 (1972).
(24) Pure $Ph_3PO{\cdot}BF_3$ was formed after several hours of exposure of solid **3** to the air.
(25) This ester has been reported previously [D. L. Dull, I. Baxter, and H. S. Mosher, *J. Org. Chem.*, **32** 1622 (1967)], but was apparently isolated as a mixture of the isomers [bp 75–82° (1.5 mm), $n^{22}D$ 1.4660].
(26) F. E. Herkes and D. J. Burton, *J. Org. Chem.*, **32**, 1311 (1967).
(27) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).
(28) O. Stellung, *Z. Phys. Chem. (Leipzig)*, **117**, 170 (1925).
(29) Alternatively, *n*-BuOH was used as a trap for CF_3COCl, in which case the amount of CF_3COOBu-*n* was determined by GLC analysis.
(30) G. T. Morgan and C. R. Porter, *J. Chem. Soc.*, 1256 (1926).
(31) Residual solvent from the preparation of **2**.
(32) M. J. Frazer, W. Gerrard, and R. Twaits, *J. Inorg. Nucl. Chem.*, **25**, 637 (1963).
(33) Residual solvent from the preparation of **3**.
(34) The amount of *n*-BuCl in the solution was not calculated because of the interference from decomposition of the ammonium salts in the gas chromatograph, which also produces *n*-BuCl.
(35) The average of two to three analyses is given followed by, in parentheses, the average deviation.
(36) This yield is based on the amount of $CF_2ClCOOMe$ initially present. It indicates that decarboxylation of CF_2ClCOO^- occurred with the release of Cl^-, since the amount of $(n\text{-}Bu)_4N^+Cl^-$ present is insufficient to account for all of the CH_3Cl formed.
(37) The butyl chloride peak due to decomposition of the ammonium salts in the gas chromatograph tailed slightly into the ethyl ester peak.
(38) H. Gross, A. Reiche, and E. Höft, *Chem. Ber.*, **94**, 544 (1961).
(39) L. Heslinga, G. J. Katerberg, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **76**, 969 (1957).

Stereochemistry and Mechanism of Ionic Cyclopropane Ring Cleavage by Arenesulfenyl Chloride Addenda in Quadricyclene Systems

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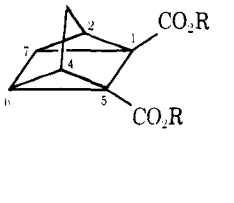
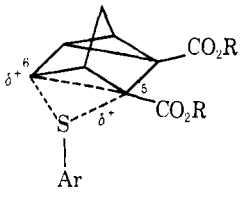
Received March 3, 1975

Addition of benzenesulfenyl chloride to quadricyclenedicarboxylic acid (**1a**) and to the corresponding dimethyl ester (**1b**) gave adducts [*exo*-5-chloro-*endo*-3-phenylthiotricyclo[2.2.1.$0^{2,6}$]heptane-2,*exo*-3-dicarboxylic acid (**3a**) and the C-3 epimer (**4a**) from **1a** and the corresponding dimethyl esters from **1b**, **3b**:**4b**, ca. 1:1]; these are the result of electrophilic cleavage of a cyclopropane ring in this system by retention and inversion processes (in nearly equal amounts). The addition of toluenesulfenyl chloride to **1b** gives analogous results. All such results demonstrate the lack of bridged sulfonium ions (e.g., **2**) as the sole product precursors and indicate that corner-attached electrophilic addition intermediates, relative to the corresponding edge-attached species, may have a far greater importance than previously suspected. The stereochemistry of the adducts was confirmed by spectral (largely proton magnetic resonance) and chemical (lactone formation) studies.

Although the ionic cleavage of cyclopropanes has been the subject of a large amount of research,[1] the stereochemical role of the electrophile has not been totally established. The vast majority of studies show that cyclopropane ring cleavages by nucleophile have occurred by inversion,[1,2] whereas electrophilic ring cleavage stereochemistry has been reported to involve each of retention,[1,3,4] inversion, and mixed retention–inversion processes.[1,5,6] Completion of our work[5] on the ionic cleavage of a cyclopropane in quadricyclenedicarboxylic acid with hydrogen chloride implied that the stereochemistry of new proton position in our final adduct was not a result of *direct* cyclopropane ring cleavage. We thus decided to investigate the arenesulfenyl chloride cyclopropane ring cleavage of quadricyclenedicarboxylic acid (**1a**, tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane-1,5-dicarboxylic acid) and ultimately its dimethyl ester (**1b**). This combination seemed ideal because of the known propensity for C_5–C_6 (C_1–C_7) bond cleavage in this system[5,7] and the great driving force for sulfenyl halides to add via a bridged sulfonium ion.[8] We felt that the possibility of the latter would enhance the chances of direct electrophilic attack on the carbon atoms of the cyclopropane ring skeleton, perhaps to the exclusive formation of ion **2**, which should result in the exclusive formation of **3**.[9] The work described below shows that such an exclusive pathway is *not* the case, but that one, in all cases, obtains quantities of **4** essentially equivalent to the amount of **3** formed. This implies, as far as comparisons can be made between theoretical considerations of protonated cyclopropanes and cyclopropane cleavage intermediates involving other electrophiles, that the balance may lie much more heavily toward corner-attached species (as opposed to edge-attached species) than previously suspected.[1,10,11]



1a, R = H
b, R = CH_3



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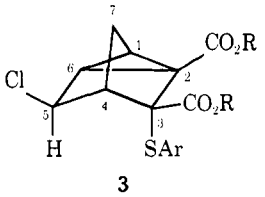

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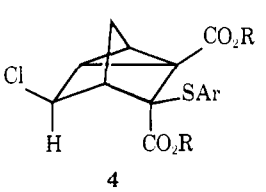

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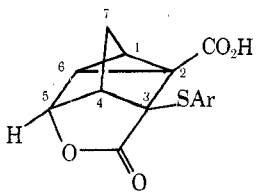
2–4a, R = H; Ar = C_6H_5
b, R = CH_3; Ar = C_6H_5
c, R = H; Ar = *p*-$CH_3C_6H_4$
d, R = CH_3; Ar = *p*-$CH_3C_6H_4$

The preparation of the quadricyclene diacid (**1a**) was carried out as has been described earlier.[5,12] Treatment of diacid **1a** (in dioxane at room temperature) with benzenesulfenyl chloride[13] resulted in quantitative yields of ad-

ducts (**3a–4a**) after 5 min. The sample quantitatively analyzed (see Experimental Section) for a 1:1 adduct and displayed an NMR spectrum characteristic of a nortricyclene skeleton. The NMR spectrum showed two signals in the region consistent for protons α to chlorine (δ 4.1, 0.5 H; 4.9, 0.5 H) implicating the existence of (at least) two adduct isomers.[5] Previous studies[5,9] imply that the isomer pair would be the C-3 epimers: *exo*-5-chloro-*endo*-3-phenylthiotricyclo[2.2.1.$0^{2,6}$]-heptane-2,*exo*-3-dicarboxylic acid (**3a**), and the *exo*-3-thiophenyl-*endo*-3-carboxyl isomer (**4a**). Arguments have been outlined earlier[5] that speak against the other two epimers (endo chlorine) possible. The chemical and spectral evidence described below confirm the structures and rule out other regioisomers.[9]

The diacid adduct (**3a–4a**) mixture (from above) was treated under conditions expected to give rise to lactone.[5] The resulting solids led to a characterizable product (mp 189–190°), the infrared of which showed a band at 5.5 μm (1818 cm^{-1}) consistent with lactone formation (**5a**).[5,7]



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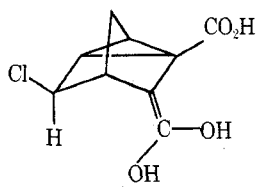

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5a, Ar = C_6H_5; **c**, Ar = *p*-$CH_3C_6H_4$

The NMR spectrum of the isolated sample is very similar to that of the diacid precursors (**3a–4a**) except that the δ 4.10 signal had disappeared and the signal at δ 4.85 integrated for one proton. This implies a **5a–3a** mixture with superimposition of the 5-H signal of **5a** upon the 5-H signal of **3a**. Quantitative elemental analysis is consistent with a **5a–3a** mixture (see Experimental Section). Formation of lactone **5a** confirms the identity of adduct **4a**[5,7] and the NMR spectra of the mixtures and known general ring opening routes[1] argue for concurrent formation of adduct **3a**.

In view of the known mechanism for hydrogen chloride opening of **1a**,[5] a possible mechanism for the benzenesulfenyl chloride ring opening of **1a** was (a) formation of hydrogen chloride from the reaction of benzenesulfenyl chloride with the dicarboxylic acid followed by (b) cleavage of **1a** with hydrogen chloride to form enediol **6**; the nearly equally available faces of the C=C unit in **6** would predict that (c) the addition to **6** of benzenesulfenyl chloride,[8] followed by deprotonation, should give a nearly 50:50 ratio of **3a–4a**. Thus further addition reactions were carried out on quadricyclene diacid dimethyl ester (**1b**) to preclude such possibilities.

Although the preparation of quadricyclenedicarboxylic acid dimethyl ester (**1b**) has been reported,[12] we have prepared our diester by a different method.[14] Thus treatment of diacid **1a** with an acetone solution of dimethyl sulfate and potassium carbonate resulted in **1b**.

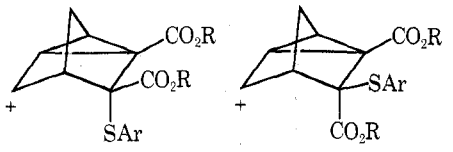
Treatment of diester **1b** with benzenesulfenyl chloride[13] in methylene chloride at room temperature for 2 days results in formation of adduct (**3b + 4b**, see below); after isolation by dry column chromatography,[16] an 82% yield of adduct (**3b–4b**, see below) was realized. The NMR spectrum ($CDCl_3$) of the product mixture was very similar to that we had observed (above) for the (diacid) adducts from **1** (**3a–4a**); the observation of signals at δ 3.91 and 4.95, each integrating for ca. 0.5 H, was especially significant and strongly implied a 50:50 mixture of **3b** and **4b**. The nortricyclene skeleton was confirmed by observation of a near-infrared band[17] at 1.663 μm. Repeated dry column chromatography[16] lead to separation of the two adducts (**3b–4b**); this separation was confirmed by NMR since one sample displayed a δ 3.91 signal[5] and the other a δ 4.95 signal (1 H).[18] Saponification of the **3b** and **4b** samples (individually and mixed) gave rise to diacids **3a** and lactone **5a**; the ester sample with the NMR signal ($CDCl_3$) at δ 3.91 (1 H) gave rise to lactone **5a**; the ester sample with the signal at δ 4.95 gave rise to diacid with the signal at δ 4.95. Lactone characterization procedures are well described[5,7] (ir shows high-energy C=O stretch; see Experimental Section). It has been clearly established that such lactone formation requires exo (C-5) chlorine and endo (C-3) carboxyl groups[19] and thus the δ 4.00 diacid sample is **4a**, the δ 3.91 diester sample is **4b**, the δ 4.95 diacid sample is **3a**, and the δ 4.95 diester sample is **3b**. In view of the known[20] deshielding effect of CO_2R groups (R = alkyl) when endo at C-3 (or C-5) upon endo protons at C-5 (or C-3), the preceding assignment was surprising. We can only speculate that the phenylthio group imposes an unusual conformational orientation upon the geminal carbomethoxy or carboxyl group such that the proton α to chlorine is thrust into the shielding cone of the endo carbonyl group of **4a** and **4b**.

In view of the varied stereochemical results that predictably depend upon the nature of the sulfenyl halide addendum,[8,21] we felt that the addition of *p*-toluenesulfenyl chloride to **1b** offered a better possibility for reaction solely via bridged ion **2d** (and thus production of product **3d** only). That this is not the case is shown in the Experimental Section and discussed here. Addition of *p*-toluenesulfenyl chloride to **1b** proceeded smoothly, in substantial yield, to give adduct which was identified as a mixture of **3d–4d** (ca. 1:1) by the same investigational procedure described above for the **3b–4b** mixture. Briefly, **3d–4d** displayed an NMR spectrum (generally similar to the spectrum of the **3b–4b** mixture) with chemical shifts at δ 3.87 (0.5 H) and at δ 4.96 (0.5 H), assigned (based on arguments above and evidence below) to the proton α to Cl in **4d** and **3d**, respectively. These isomers were separable by fractional crystallization; saponification of the separated esters lead to diacid **3c** (from **3d**) and lactone **5c** (from **4d**). Saponification of these isomers also showed that the ester with the more downfield NMR signal for the proton α to chlorine (**3d**) corresponded to the acid (**3c**) with the more downfield NMR signal for the proton α to chlorine; acid **4c** was never isolated. Kinetic control is supported since the adducts (**4d** and **3d**), when treated under addition reaction conditions, did not interconvert. Thus ionic cleavage of the cyclopropane ring with *p*-toluenesulfenyl chloride, as well as with benzenesulfenyl chloride, resulted in electrophilic cleavage of the ring with retention (**3** type products) and inversion (**4** type products) processes[1] and with nearly equal amounts of the two processes occurring in each of the two addition reactions.

The results observed here can be interpreted in the light of previous discussions.[1,2] In view of the two highly electron-withdrawing carbomethoxy (or carboxyl) groups, the substantially stabilized carbocation apparently necessary[1-3] for nucleophilic cleavage retention product (endo C-5-chlorine) is not available; previous nucleophile cleavage studies on the same carbon skeleton experimentally support this idea.[5] Cleavage of the 5–6 (or 1–7) bond in **1** (**a** or **b**) is not surprising in view of the approximately 40 kcal/mol in stability gained by loss of ring strain.[22]

The approximately 1:1 (**3:4**) product ratios clearly preclude **2** type precursors as the sole stereochemistry-determining intermediates; this was somewhat surprising in view of the known excellent bridging ability of vicinal sul-

fur.[8,20,21,23] The reaction has shunned the edge-attached (2 intermediate) pathway for a pathway that likely involves corner-attached species such as 7 and 8 (formed in nearly



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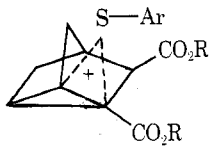

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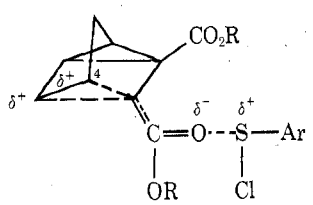
equal amounts). These intermediates likely are an order of magnitude[23] more stable than previously anticipated.[1,10,11] Based upon experimental results, we cannot rule out edge-attached species (2 and 9) as transition states leading to the corner-attached intermediates (7 and 8, respectively), but there does not seem to be any clear reason to retain both types. Finally, we should also consider polarized interactions (e.g., 10) analogous to the proposed[5] precursors to the enediol intermediates (e.g., 6). Such interaction would be consistent[5] with the nucleophile cleavage process (inversion) reported herein but the requisite analog to the enediol (6)[5] intermediate, 11, seems very unlikely. Thus, our results are most easily interpreted in terms of intermediates such as 7 or 8 (or 10).[5,24]



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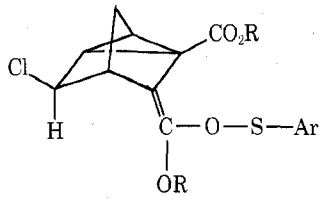

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Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 257 instrument. Proton magnetic resonance (^{1}H NMR) spectra were obtained on a Perkin-Elmer R-20 (60 MHz) instrument. Chemical shifts are expressed as parts per million relative to Me_4Si (δ 0.00). Mass spectra were obtained from a Perkin-Elmer RMU-6E instrument. Microanalyses were done by Baron Consulting, Orange, Conn. NMR notations: s, singlet; d, doublet; t, triplet; brs, broadened singlet.

The preparations of diacid **1a** and diester **1b** are modifications of known procedures.[12,25]

Preparation of the Dimethyl Ester of Quadricyclenedicarboxylic Acid (1b). The methyl sulfate (dimethyl sulfate) to be used in this preparation should be carefully purified by both of the procedures described by Vogel.[26] A solution of 4.0 g (0.020 mol) of quadricyclenedicarboxylic acid (**1a**) and 8.4 g (0.060 mol) of anhydrous potassium carbonate, suspended in 180 ml of anhydrous acetone, was prepared. To this stirred mixture was added 4.8 ml (0.050 mol) of the purified dimethyl sulfate. This solution was allowed to reflux for 14 hr. To this warm solution was added 0.4 ml (0.010 mol) of concentrated ammonium hydroxide and the reflux procedure was continued for an additional 10 min. The solution was evaporated to dryness (rotary evaporator) and the resulting materials were dissolved in 25 ml of water. This aqueous solution was extracted with 8 × 75 ml of chloroform. Any solids that resulted from this work-up were filtered off and washed with chloroform and the chloroform washings were added to the chloroform extracts. The combined chloroform solutions were extracted with 2 × 250 ml of saturated sodium chloride and once with water (250 ml) and dried over magnesium sulfate. Filtration and solvent removal (rotary evaporator) resulted in a yellow oil. Distillation at 110–115° (0.45 Torr) resulted in pure (79% yield) quadricyclene diester (**1b**); the pot temperature must *not* be allowed to exceed 135°. Use of a Rinco Kugelrohr (horizontal) distillation apparatus allows vacuum distillation that does not require severe pot temperatures. Multiple distillations often lead to samples that spontaneously crystallize (various melting points in the area of 52–58°, some ranges as narrow as 3°). Liquid samples resulted in accurate quantitative elemental (C, H) analyses (C, 63.18; H, 5.98; calcd C, 63.45; H, 5.81) and were used for spectral analyses: ir (thin liquid film) 3080, 2990, 2950, 2860 (C–H stretch), 1715 (C=O stretch), 1440 ($\delta_{as}CH_3$), 1383 (δ_sCH_3), 1300 (ring skeleton C–H bend), 1230 [C(CO)–O "C–O" stretch], 1108 cm^{-1} (O–CH_3 stretch); NMR ($CDCl_3$) m, δ 2.2–2.55 (6 H, ring skeleton); s, δ 3.68 (6 H, CO_2CH_3); n^{23}D 1.4995 (lit.[12] n^{20}D 1.5022, n^{25}D 1.5022).

Addition of Benzenesulfenyl Chloride to Dimethyl Ester of Quadricyclenedicarboxylic Acid (1b). To a solution of 1.11 g (5.3 mmol) of the dimethyl ester of quadricyclenedicarboxylic acid (**1b**) in 40 ml of dry methylene chloride at room temperature, the freshly distilled benzenesulfenyl chloride[13] (0.763 g, 5.3 mmol) was added dropwise. The first and second drops of red benzenesulfenyl chloride added to the reaction flask were decolorized immediately. The red color of the reagent upon mixing changed to yellow during the remaining addition. By the end of the addition, the reaction temperature had risen from 29° to 45°. The mixture was stirred for another 8 hr at room temperature, resulting in a slightly yellow solution. The solvent was then removed (rotary evaporator) to yield a pale, yellow, viscous liquid (mixture of isomers **3b, 4b**), 1.8 g (100% crude yield). NMR data (solvent $CDCl_3$): m, δ 1.4–2.8, 5 H, nortricyclene skeleton protons; s, δ 3.64, 3 H, CO_2CH_3; s, δ 3.70, 3 H, CO_2CH_3; brs, δ 3.91, 0.5 H, H α to Cl in **4b**; brs, δ 4.95, 0.5 H, α to Cl in **3b**; m, δ 7.2–7.8, 5 H, aromatic protons.

The reaction product was fractionated (see below) by dry column chromatography[16] (silica gel) to yield 1.53 g (82%) of two liquid isomers, **3b** and **4b**, in the ratio of 50:50 as demonstrated by NMR. One (isomer **3b**) is a colorless, viscous liquid, n^{25}D 1.5617, while the other (isomer **4b**) crystallized spontaneously (mp 110–113°). The ester adducts (**3b, 4b**) gave a negative test for chlorine upon reaction with alcoholic silver nitrate while a positive chlorine test was obtained from a sodium fusion test.

Anal. Calcd for $C_{17}H_{17}O_4SCl$: C, 57.86; H, 4.85; O, 18.13; Cl, 10.05; S, 9.08. Found: C, 57.58; H, 4.57; O, 18.9; Cl, 10.15; S, 8.80.

NMR data of solid isomer (**4b**) (solvent $CDCl_3$): m, δ 2.1–2.8, 5 H, nortricyclene skeleton protons; s, δ 3.64, 3 H, CO_2CH_3; s, δ 3.7, 3 H, CO_2CH_3; brs δ 3.92, 1 H, H α to Cl; m, δ 7.2–7.8, 5 H, aromatic protons.

NMR data of liquid isomer (**3b**) (solvent $CDCl_3$): m, δ 1.6–2.4, 5 H, nortricyclene skeleton protons; s, δ 3.64, 3 H, CO_2CH_3; s, δ 3.7, 3 H, CO_2CH_3; brs, δ 4.95, 1 H, H α to Cl; m, δ 7.2–7.8, 5 H, aromatic protons.

Near-infrared of each isomer (**3b, 4b**) (solvent CCl_4), instrument Beckman DK-2A, tungsten lamp, 0.5 *M*) each showed a peak at 1.663 μm indicative of a nortricyclene structure.[17]

A mass spectrum of a **3c–4c** (1:1) mixture showed a molecular ion (*m/e* 352) of intensity 49% (base peak, *m/e* 211, 100%). Defining the molecular ion as 100% results in *m/e* 353 (M + 1) and 354 (M + 2) peaks of, respectively, 20.9 and 40.4% (calcd for $C_{17}H_{17}O_4SCl$: M + 1, 19.8; M + 2, 39.6).

Separation of the Isomeric *exo*-5-chloro-*exo*- (4b) and *endo*- (3b) -3-phenylthio-2,3-*exo*- (and *endo*-) dicarbomethoxytricyclo[2.2.1.0^{2,6}]heptanes by Dry Column Chromatography.[16] A nylon dry column with 2-in. diameter and 16-in. length was used for the mixture of 2.3 g of isomers **3b** and **4b**. The column was sealed and packed with silica gel.[16] The liquid mixture of ester adducts **3b** and **4b** was dissolved in 20 ml of anhydrous ether and 11.5 g of silica gel (five times the weight of the mixture) was added to the solution. The solvent was then removed (rotary evaporator) at 30–40°. The dry compound–silica gel mixture was deposited on the top of the column which then was covered with a layer (0.5 in.) of sand. A mixture of 20% ether and 80% petroleum ether (determined by TLC as a suitable developing solvent) was allowed to drop from a separatory funnel to the column under a constant liquid head of 5.0 cm. When the solvent reached the bottom of the column, the only band (located by ultraviolet light) present on the column was sliced into five segments. Each segment was extracted with anhydrous ether. The first three segments (top site) yielded 1.195 g of the colorless liquid (isomer **3b**), the fourth segment gave 0.895 g of the mixture of two isomers, whereas 0.387 g of isomer **4b** was obtained from the last segment (total yield was 84%).

Saponification of Diester 3b. To a solution of 0.376 (1 mmol) of liquid ester adduct **3b** in 20 ml of 100% ethanol, 1.8 g of 85% potassium hydroxide in water was added. The mixture was stirred at

room temperature for 2.5 days. An orange solution with a white precipitate was obtained at the end of this period. To this mixture, 200 ml of water was added which dissolved the precipitate. The solution was acidified (Congo Red indicator paper) with 5% hydrochloric acid and was left at room temperature for 1 day (a light brown solid precipitated). The crude product was recrystallized from anhydrous ether and decolorized with charcoal to give 0.121 g of white, solid, diacid product (**3a**). In addition, 0.210 g of white solid was obtained from extraction of the aqueous solution with anhydrous ether, decolorization with charcoal, and drying over magnesium sulfate, followed by evaporation of solvent (rotary evaporator) (95% total yield). This solid melted (with foaming) at 234–238° and stopped foaming and turned brown at 241°. NMR data (solvent, polysol-*d*): m, δ 1.1–2.4, 5 H, nortricyclene skeleton protons; s, δ 4.87, 1 H, H α to Cl; m, δ 7.2–7.8, 5 H, aromatic protons; s, δ 10.0, 2 H, COOH. Ir (Nujol): 5.82 and 6.15 μm (1718 and 1626 cm^{-1}) (C=O stretch). Anal. Calcd for $C_{15}H_{13}O_4ClS$: C, 55.46; H, 4.03; O, 19.70; Cl, 10.91; S, 9.87. Found: C, 55.65; H, 4.15; O, 19.87; Cl, 10.67; S, 9.66.

Attempted Lactonization of *exo*-5-Chloro-*endo*-3-phenylthiotricyclo[2.2.1.$0^{2,6}$]heptane-2,*exo*-3-Dicarboxylic Acid (3a). This is a modification of the procedure of Cristol and LaLonde.[12] A suspension of 0.20 g of acid adduct **3a** in 200 ml of water was allowed to reflux for 2 hr. During this time the solid dissolved. The water was then removed (rotary evaporator) and the resulting solid was vacuum dried to give 0.20 g (100% yield) of starting material (**3a**). The melting point, infrared, and NMR (including proton α to Cl at δ 4.95, polysol-*d* solvent) spectra of the resulting solid were exactly the same as of the acid adduct **3a**. There was no lactone absorption[12] in the infrared spectrum.

Saponification of *exo*-5-Chloro-*exo*-3-phenylthiotricyclo-[2.2.1.$0^{2,6}$]heptane-2,*endo*-3-dicarboxylic Acid Dimethyl Ester (4b). To a solution of 1.54 g (4 mmol) of solid ester adduct **4b** in 50 ml of 100% ethanol, 4.4 g of 85% potassium hydroxide in water was added. The mixture was stirred at room temperature for 2.5 days. At the end of this period, the orange solution with a white precipitate was obtained. To this saponification mixture, 250 ml of water was added to dissolve the precipitate. The solution was acidified (Congo Red indicator paper) with 5% hydrochloric acid and was left at room temperature for 1 day. A 0.285-g precipitate of mixed dark brown and white solids formed. The crude precipitate was recrystallized from water (reflux) and decolorized with charcoal to give 0.18 g of white solid of the lactone **5a**, mp 198–200°. An additional 0.677 g of white solid was obtained from extraction of the aqueous layer with ether, decolorization with charcoal, drying over magnesium sulfate, evaporation of solvent, and recrystallization in water (76% total yield). The NMR spectra taken before and after purification were the same.

NMR (solvent polysol-*d*): m, δ 1.7–2.7, 5 H, nortricyclene skeleton protons; brs, δ 4.87, 1 H, HCO of lactone; m, δ 7.2–7.7, 5 H, aromatic proton; brs, δ 8.85, 1 H, COOH. Ir (Nujol): 5.62 μm (1779 cm^{-1}) (C=O stretch of lactone),[7] 5.92 μm (1689 cm^{-1}) (C=O stretch of COOH group).

Anal. Calcd for $C_{15}H_{12}O_4S$: C, 62.48; H, 4.20; O, 27.20; S, 11.12. Found: C, 62.30; H, 4.34; O, 22.44; S, 10.92.

Preparation of *p*-Toluenesulfenyl Chloride. To a three-necked flask, equipped with a condenser (topped by a $CaCl_2$ drying tube), a thermometer, and a magnetic stirrer, was added 3.46 g (1.54 mmol) of *p*-tolyl disulfide (Aldrich). The solid disulfide was dissolved in 9.0 ml of methylene chloride (freshly distilled from calcium chloride); to this stirred, aluminum foil jacketed, yellow-green solution was added 1.14 ml (1.40 mmol) of freshly distilled (bp 69–70°) sulfuryl chloride (Eastman). Stirring this solution for 2 days at room temperature resulted in an orange solution; solvent removal (rotary evaporator) yielded a reddish-yellow solid and a red liquid. The red liquid was decanted and passed through a glass sintered funnel into a vacuum distillation apparatus. Red liquid fractions (combined yield 44%) boiling at ca. 55° (0.45 Torr) were stored (refrigerator) and used for analysis and preparative purposes. NMR ($CDCl_3$): δ 2.36, s, 3 H, CH_3; δ 7.20, apparent doublet, 2 H; δ 7.60, apparent doublet, 2 H, aromatic AA'BB' system; ir (thin film) 3000 (aromatic C–H stretch), 2895, 2830 (aliphatic C–H stretch); 1582, 1478 (aromatic C=C stretch); 1388, 1366 (methyl C–H bend); 791 (aromatic C–H bend); 640 (C–S stretch); 500 cm^{-1} (S–Cl stretch). The methyl group (NMR) of the disulfide precursor (δ 2.29, $CDCl_3$) was undetected in these samples.

Addition of *p*-Toluenesulfenyl Chloride to Diester 1b. A solution of 4.80 g (0.023 mol) of diester **1b** in 80 ml of methylene chloride was placed in the same type of apparatus as used in the preceding experiment. To this pale yellow solution, 3.64 g (0.023 mol) of *p*-toluenesulfenyl chloride was added dropwise over a period of 5 min. This red-orange solution was stirred at room temperature for 3 hr, whereupon the color had returned to pale yellow. Stirring was continued for 48 hr (room temperature); solvent removal (rotary evaporator) resulted in 8.5 g (ca. 100% crude yield) of an amorphous substance. The NMR spectrum of this substance indicated that it was primarily **4d** and **3d** (in nearly equal amounts). Treatment of the amorphous material with several small (ca. 2 ml) portions of anhydrous ether resulted in a fine, powdery, white precipitate (**4d**, mp 122.5–127.5°) which was removed with a glass-sintered filter; the remaining solution yielded a rigid, brown powder (**3d**, mp 53–62°) upon solvent removal. Compound **4d** could be recrystallized from ether: mp 130–133°; ir (KBr pellet) 3070 (cyclopropane C–H stretch); 3010, 2990 (aromatic C–H stretch); 2945, 2908 (aliphatic C–H stretch); 1712 (broad) (C=O stretch); 1593 (C=C stretch); 1484, δ CH_2; 1428, δ_{as} CH_3; 1367, δ_s CH_3; multiple complex bands 1260–1150 (C–O "alcohol" stretch of esters); 1127, 1105 (C(C=O)O stretch of esters); 797 ("nortricyclene" band);[27] 840, 777 (out-of-plane, aromatic C–H bend); 690 cm^{-1} (C–Cl and/or C–S stretch). Ir of **3d** (KBr pellet): 3067 (cyclopropane C–H stretch), 3008 (aromatic C–H stretch); 2950, 2930, 2880, 2860 (aliphatic C–H stretch); 1491, δ CH_2; 1438, δ_{as} CH_3; 1374, δ_s CH_3; multiple, complex bands 1260–1150 (C–O "alcohol" stretch of ester); 1163, 1130, 1112 (C(C=O)O stretch); 842, 809, 750 (out-of-plane, aromatic C–H bend); 772 ("nortricyclene" band);[30] 705, 692 cm^{-1} (C–Cl and C–S stretch). NMR spectrum of **4d** ($CDCl_3$): δ 2.03–2.79, m, 5 H, nortricyclene ring skeleton; δ 2.34, s, 3 H, $ArCH_3$; δ 3.67, s, 3 H, CO_2CH_3; δ 3.73, s, 3 H, CO_2CH_3; δ 3.89, brs, 1 H, CHCl; δ 7.07–7.37, apparent doublet, 2 H, benzenoid, ortho to CH_3 group; δ 7.37–7.59, apparent doublet, 2 H, benzenoid, ortho to SR group. NMR spectrum of **3d** ($CDCl_3$): δ 1.83–2.57, m, 5 H, nortricyclene ring skeleton; δ 2.33, s, 3 H, $ArCH_3$; δ 3.66, s, 3 H, CO_2CH_3; δ 3.71, s, 3 H, CO_2CH_3; δ 4.96, brs, 1 H, CHCl; δ 7.00–7.36, distorted apparent doublet, 2 H, benzenoid, ortho to CH_3 group, apparent doublet, 2 H, benzenoid, ortho to SR group. The NMR spectrum of this sample of **3d** showed a trace amount of the CHCl signal of **4d**, indicating a small amount of contamination by **4d**.

Saponification of Diester Adduct 4d (Leading to Lactone 5c). A charge of 5.6 g of reagent grade (Baker) potassium hydroxide was added (with magnetic stirring) to a solution of 1.6 g of adduct **4d** in 50 ml of (Fisher reagent) methanol; this procedure was carried out in the 500-ml round-bottom flask portion of a standard reflux apparatus. Continual stirring for 2 days (room temperature) did not result in a homogeneous solution; homogenization was effected by reflux for 15 min. Since color formation implied substantial reaction, the solution was acidified (to litmus) with aqueous hydrogen chloride. This solution was allowed to reflux for 2 days; methanol removal (rotary evaporator) afforded 0.15 g of a tan powder (presumably lactone **5c**) which precipitated from the aqueous system. Acetone was added to effect dissolution resulting in precipitation of a new white solid (assumedly potassium chloride); after removal of the solid, the solution was extracted with 4 × 150 ml of ether. Solvent removal gave 0.90 g of yellow powder (combined, crude yield 1.05 g, 85%). The combined solids were recrystallized from ether to give 0.80 g of lactone **5c**, mp 213–215°, 68.5% yield; ir (KBr pellet) 3650–2400 (max at 3422) (O–H stretch of CO_2H), 1787 (C=O stretch of lactone),[5] 1693 cm^{-1} (C=O stretch of CO_2H); NMR (dimethyl sulfoxide-d_6) δ 1.89–2.76, ca. 5 H, m, ring skeleton protons plus CD_3SOCD_2H; δ 2.30, s, 3 H, $ArCH_3$; δ 4.60, brs, 1 H, CO_2H (and/or water); δ 4.93, 1 H, brs, CHO– of lactone moiety;[5] δ 7.06–7.56, 4 H, pair of apparent doublets, aromatic protons, AA'BB'; system.

Saponification of Diester Adduct 3d (Leading to Diacid Formation). Exactly the same procedure was used here as for the isomer **4d** above, up to the point of ether solvent removal; this afforded a tan powder (0.70 g, 56% yield, mp 203.5–207°). This tan powder was spectrally consistent with one of the two half-esters of **3d**; ir spectrum (KBr pellet) 3600–2300 (O–H stretch of CO_2H), 1739 cm^{-1} [C=O stretch of ester group, overlaps with 1712 (C=O stretch of carboxylic acid group)]; NMR spectrum (dimethyl sulfoxide-d_6) δ 1.25–2.60, ca. 7 H, m, ring skeleton protons plus CD_3SOCD_2H; δ 3.66, s, 3 H, CO_2CH_3; δ 4.96, 1 H, brs, CHCl; δ 7.10–7.72, 4 H, pair of apparent doublets, aromatic protons, AA'BB' system.

Virtually all of this sample of tan powder was placed under the same type of experimental conditions as above, except that it was subjected to 0.50 g (2.84 mmol, 2 equiv) of potassium hydroxide; this solution was stirred for 1.5 weeks (room temperature). The solution was then heated (steam bath) to reflux for 0.5 hr. Neutral-

ization (as above) was followed by solvent removal (rotary evaporator). The resulting tan precipitate was filtered off and dissolved in ether and the new solution was dried (magnesium sulfate). Solvent removal (rotary evaporator) afforded a semiamorphous, tan powder (0.43 g, 31% crude yield). The NMR spectrum (dimethyl sulfoxide-d_6) showed no signal at δ 3.66 and was consistent with diacid **3c**: δ 1.54–2.68, m, ca. 5 H, ring skeleton protons plus solvent impurities, δ 2.33, 3 H, s, $ArCH_3$; δ 4.88, brs, 1 H, CHCl; δ 7.10–7.71, 4 H, pair of apparent doublets, aromatic protons, AA'BB' system.

This sample (presumably diacid adduct **3c**) was allowed to reflux in water for 8 hr. Ether extraction (3 × 100 ml) and solvent removal (rotary evaporator) afforded 100% yield of a semiamorphous, brown solid that had NMR ($CDCl_3$) and infrared signals attributable to diacid **3c** only.

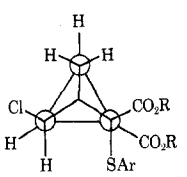
Kinetic Control Determinations on Diester Adducts 4d and 3d. A solution of 0.15 g (0.41 mmol) of adduct **4d** and 0.060 g of *p*-toluenesulfenyl chloride in 15 ml of methylene chloride was allowed to stir for 4 days in a system protected from light (aluminum foil on outer surface of flask) and from water (calcium chloride drying tube). NMR analysis ($CDCl_3$) of the sample (obtained upon solvent removal did not reveal the presence of **3d** (no signal near δ 4.90); only signals attributable to the reagents and/or *p*-toluene disulfide were observed. An experiment that was nearly identical with the preceding (except that 3.69 mmol of each of **3d** and the arenesulfenyl halide were combined in 25 ml of methylene chloride for 2.5 days) was carried out. Solvent removal afforded a sample which demonstrated (NMR, $CDCl_3$) that no change (within experimental error estimated at ±10%) had occurred in the minor proportion (ca. 20%) of isomer **4d** (δ 3.90 signal) in this sample of adduct **3d** (δ 4.98 signal).

Acknowledgments. We would like to acknowledge the following sources of financial support: College of Science Dean's Fellowship (T.C.M.), National Science Foundation Grant GU 3570 (K.M.W., Undergraduate Research Participant), a training grant from the U.S. Agency for International Development (S.M.), and the Research Corporation (B.E.G.). We would also like to indicate appreciation for the technical assistance and theoretical discussions arising from Mr. Harold C. Warren and Mr. Robert J. Opitz.

Registry No.—**1a**, 30715-39-0; **1b**, 714-53-4; **3a**, 55925-65-0; **3b**, 56084-09-4; **3c**, 55975-75-2; **3d**, 55925-66-1; **4b**, 55925-67-2; **4d**, 55954-93-3; **5a**, 55925-68-3; **5c**, 55925-69-4; benzenesulfonyl chloride, 931-59-9; *p*-toluenesulfonyl chloride, 933-00-6.

References and Notes

(1) For a leading reference, see S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Am. Chem. Soc.*, **92**, 4013 (1970).
(2) Nucleophilic cyclopropane ring cleavages accompanied by retention have been reported.[1] Ion-pair intermediates are apparently intimately involved.[1,3]
(3) J. B. Hendrickson and R. K. Boeckman, Jr., *J. Am. Chem. Soc.*, **93**, 4491 (1971).
(4) R. J. Warnet and D. M. S. Wheeler, *Chem. Commun.*, 547 (1971).
(5) S. J. Cristol, J. K. Harrington, Jr., T. C. Morrill, and B. E. Greenwald, *J. Org. Chem.*, **36**, 2773 (1971).
(6) C. H. DePuy and R. H. McGirk, *J. Am. Chem. Soc.*, **95**, 2366 (1973).
(7) S. J. Cristol and R. T. LaLonde, *J. Am. Chem. Soc.*, **80**, 4355 (1958).
(8) W. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).
(9) (a) The *regiospecificity*[9b] implied by the formation of **3** (and **4**) in the absence of chloride attack at position **5** of **2** is expected because of the minimal positive charge at this position due to the electron-withdrawing carboxyl groups. This has been confirmed experimentally.[5,7] (b) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).
(10) G. Klopman, *J. Am. Chem. Soc.*, **91**, 89 (1969).
(11) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 3954, 3956 (1969).
(12) S. J. Cristol and R. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958).
(13) Arenesulfenyl halides were prepared by the method of W. M. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2080 (1968).
(14) The dimethyl ester **1b** has been reportedly[12] synthesized by diazomethane treatment of **1a**. In our hands, the procedure resulted in a sample of refractive index ($n^{23}D$ 1.4800) quite different from that reported earlier;[12] this sample showed two (or more) NMR signals in the CH_3O region (δ 3.5–4.0) and three gas chromatographic peaks.
(15) Our methylation procedure is an adaptation of the procedure used by Mirrington to methylate phenols. The procedure is especially useful for acid-sensitive substrates: R. N. Mirrington and G. I. Feutrill, *Tetrahedron Lett.*, 1327 (1970). We used acetone, rather than *N,N*-dimethylformamide, as a solvent. In view of the sensitivity of the rings in **1a** to acid and base cleavage our results demonstrate the utility of this procedure under such demands.
(16) B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967).
(17) It has been shown that the nortricyclene, quadricyclene, and corresponding olefinic isomers all give unique near-infrared bands: P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965).
(18) This separation[16] is impressive in view of the fact that diastereoisomers **3b** and **4b** have very subtle structure differences (replacement of Cl by



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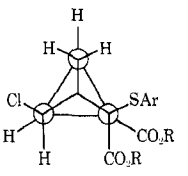

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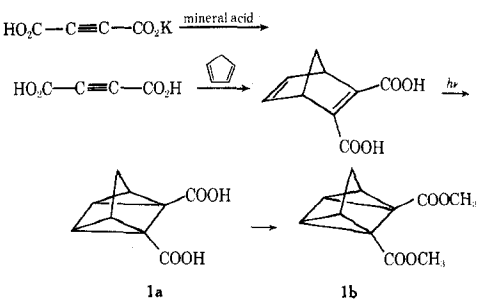
H in **3b** and **4b** gives rise to enantiomers) and thus they would be expected to have minute dipolar differences. The signals of δ 3.91 and 4.18 are assumed to be due to protons on carbon bearing chlorine.
(19) S. J. Cristol, J. K. Harrington, Jr., and M. S. Singer, *J. Am. Chem. Soc.*, **88**, 1529 (1966).
(20) J. K. Stille and L. F. Hines, *J. Am. Chem. Soc.*, **92**, 1798 (1970); D. R. Coulson, *ibid.*, **91**, 200 (1969).
(21) (a) S. J. Cristol, et al., *J. Am. Chem. Soc.*, **79**, 6035 (1957); (b) T. C. Morrill and N. D. Saraceno, "The Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Norbornadiene: The Absence of Results Directed by a Bridged Sulfonium Ion", Abstract 259, XXIII IUPAC Meeting, Boston, Mass., July 25–30, 1971. These works suggest that the methyl group on the aryl group should provide greater positive charge stabilization, thus enhancing bridging.
(22) The strain energy of nortricyclene has recently been reestimated to be 38.8 kcal/mol and that of quadricyclene to be 78.7 kcal/mol: H. K. Hall, Jr., et al., *J. Am. Chem. Soc.*, **95**, 3197 (1973).
(23) The thermodynamic function L_0 estimates that a neighboring group with sulfur (appropriately arranged for) bridging results in stabilizing the intermediate by 13 kcal/mol (the largest value so reported): S. Winstein et al., *J. Am. Chem. Soc.*, **70**, 821, 828 (1948).
(24) The second site of positive charge (delocalization to C-4) in **10** is possible in view of earlier studies;[5] there is no evidence, however, of the (highly strained) product that would arise as a result of nucleophilic attack at that position.
(25) The sequence



1a 1b

has been described.[7] We have not included our preparation descriptions, in order to preserve space, but it should be pointed out that we have improved upon the procedure in all steps and the procedure used earlier[12] to prepare **1b** was likely not completely successful.[14]
(26) A. J. Vogel, "Practical Organic Chemistry", 3rd ed, Longmans, Green and Co., New York, N.Y., 1956, p 804.
(27) G. T. Youngblood et al., *J. Org. Chem.*, **23**, 684 (1958); also note the discussion in ref 17.