over platinum oxide catalyst in acetic acid at 100 atm. The reduced acid was obtained as a clear liquid, b.p. 134–136° (24 mm.), $n^{20}D$ 1.4568. An $n^{25}D$ 1.4566 has been reported[16] for a 74:26 *cis-trans* mixture. Larger batches were prepared more conveniently by reduction of the ethyl ester followed by hydrolysis of the ester by the procedure described for the 2-methylcyclohexanecarboxylic acid.

3-Bromo-1-methylcyclohexane (II). A. Hunsdiecker Method.—The silver salt of 3-methylcyclohexanecarboxylic acid was allowed to react with bromine according to the procedure described under I. The bromide, b.p. 56° (10 mm.), $n^{25}D$ 1.4844, was distilled through a 14-in. Vigreux column. It was obtained in 70% crude yield and 26% yield in pure form. Infrared absorption occurs at 1463 s, 1381 m, 1335 m, 1260 s, 1224 m, 1195 s, 1032 m, 945 m, 878 w, 692 s, 662 sh, 581 w, 524 s, 510 sh, 475 m, 438 w, 428 w, 406 w. The n.m.r. spectrum exhibits an ill-defined quintet (J = 3.5 c.p.s.) at τ 5.5, a broad multiplet (triplet of triplets, J = 4, 11 c.p.s.) at 6.13, a sharp doublet (J = 6 c.p.s.) at 9.10, and a series of peaks between 7.6 and 8.85.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40. Found: C, 47.70; H, 7.45.

B. Cristol Modification.—A 3.72-g. sample of 3-methylcyclohexanecarboxylic acid was treated with mercuric oxide and bromine according to the procedure of Cristol and Firth.[15] The product showed a tendency to decompose during distillation, and a low yield 0.97 g. of bromide, b.p. *ca.* 45° (15 mm.), $n^{20}D$ 1.4909 was isolated. The infrared spectrum was identical with that from the Hunsdiecker reaction in the sodium chloride region, except for a small peak at 1720 and bands at 837 and 780 cm.$^{-1}$.

C. Cleavage of Mercury Salt.—A sample of 3-methylcyclohexylmercuric bromide was prepared according to the method described for the 2-isomer. After recrystallization from hexane–benzene, the salt melted at 88–90°. Cleavage of 7.3 g. of the mercury salt by the pyridine–bromine method[3] gave 84% of a clear liquid, b.p. *ca.* 55–60° (10 mm.), $n^{20}D$ 1.4860. Except for a lower intensity for the infrared band at 581 cm.$^{-1}$, the infrared and n.m.r. spectra of the Hunsdiecker and this product were identical.

Conversion to Ketones.—Dry oxygen was bubbled through a cold solution of Grignard reagent (from I or II) in ether for several hours.[23] The alcohol obtained (35–50% yield after distillation) was identified by g.p.c. using a 6-ft. type A column and comparison with internal standards. Since the separation of the two alcohols was incomplete, they were oxidized (dichromate) to the respective ketones and again checked for identity on a 6-ft. type A column. I gave 2-methylcyclohexanone and II gave 3-methylcyclohexanone.

4-Bromo-1-methylcyclohexane (IV). A. Cleavage of Mercury Salt.—A sample of the *trans* isomer was prepared by the method of Jensen and Gale.[3] The product, m.p. *ca.* 25°, showed an n.m.r. spectrum with a triplet of triplets (J = 4.0, 10.5 c.p.s.) at τ 6.18, a sharp doublet (J = 5.0 c.p.s.) at 9.16, and a series of ill-resolved peaks between 7.5–9.0.

B. Landauer and Rydon's Method.—A mixture containing 100 g. (0.58 mole) of benzyl bromide and 190 g. (0.61 mole) of triphenyl phosphite was heated at 155–160° for 5 days. The bronze-colored solid product was triturated with hexane, and the residual solid was dried *in vacuo*. A portion, 105 g., of the solid was mixed with 25 g. of 4-methylcyclohexanol and the mixture was allowed to stand at 70° for 24 hr. The volatile product was removed from the reaction mixture under reduced pressure, washed with dilute sodium hydroxide solution, and dried over anhydrous sodium sulfate. The bromide was distilled using a 24-in. concentric tube column: b.p. 49–51° (8 mm.), $n^{25}D$ 1.4810. Infrared absorption bands appear at 1462 s, 1384 w, 1359 w, 1310 w, 1254 s, 1245 s, 1190 s, 1105 w, 1030 m, 970 m, 950 m, 850 m, 702 m, 689 s. The n.m.r. spectrum consisted of a quintet (J = 4 c.p.s.) at τ 5.58, a sharp doublet (J = 6.0 c.p.s.) at 9.11, a second sharp doublet of lower intensity (J = 6.0 c.p.s.) at 9.13, and two poorly resolved multiplets between 7.9 and 8.7. A weak singlet τ at 2.25 and a series of peaks at 2.6–3.0 as well as absorption at 3320 cm.$^{-1}$ indicated contamination by phenol.

C. Phosphorus Tribromide Method.—A sample of 4-methylcyclohexanol, free from isomers by g.p.c. analysis, was treated with phosphorus tribromide according to the procedure described for I. The product was identical (except for the contamination by phenol) with that obtained by Landauer and Rydon's method.

Infrared Spectra.—All spectra in the sodium chloride region were run on neat samples in sandwich cells using a Perkin-Elmer Model 21. Spectra in the potassium bromide region were run on neat samples in a 0.05-mm. fixed cell using a Beckman IR-7.

N.m.r. Spectra[24]—All spectra were taken on a Varian A-60 proton magnetic resonance spectrometer using tetramethylsilane as an internal reference. Samples were run in varying concentrations in carbon tetrachloride solution.

Gas Chromatography.—Analysis by gas chromatography was made on a Perkin-Elmer Model 154 C instrument using helium as carrier gas. The alcohols were analyzed on a commercial type K column and the bromides on a 6 ft. × 0.25 in. column containing 15% trifluoromethylsilicone (Dow-Corning FS 1265) on Chromosorb.

(23) M. T. Goebel and C. S. Marvel, *J. Am. Chem. Soc.*, **55**, 1693 (1933).

(24) We are indebted to the National Science Foundation for partial financial support toward the purchase of this instrument.

The Structure and Reactions of the 1:1 Adduct of Benzenesulfonyl Azide and Bicyclo[2.2.1]heptene

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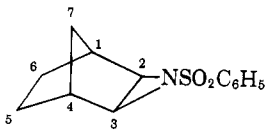
Nuclear magnetic resonance and chemical evidence are presented which support an aziridine structure for the 1:1 adduct formed from benzenesulfonyl azide and bicyclo[2.2.1]heptene. Potassium thiophenate reacted smoothly with the adduct to afford 2-*endo*-thiophenoxy-3-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane which was readily converted to 2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane by Raney nickel treatment. Lithium aluminum hydride reduction of the adduct produced the 2-*exo*-sulfonamide directly. The reaction of the aziridine with thiophenol under acidic conditions followed by desulfurization yielded 7-benzenesulfonamidobicyclo[2.2.1]heptane as the major product. The n.m.r. spectrum of the aziridine prepared from 2,3-dideuteriobicyclo[2.2.1]-2-heptene and benzenesulfonyl azide conclusively established that rearrangement did not occur during this reaction and that carbonium ion intermediates were not involved. A mechanism analogous to epoxidation is proposed

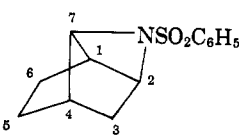
In a preliminary communication[1] the reactions of various sulfonyl and phosphoryl azides with several olefins were reported. It was proposed that the 1:1 adduct formed from benzenesulfonyl azide and bicyclo[2.2.1]heptene is the aziridine (Ia) rather than the azetidine (Ib). One basis for this conclusion is the similarity in the nuclear magnetic resonance spectrum of I with that of 2,3-*exo*-epoxybicyclo[2.2.1]heptane. Although this correlation has been described[2] as being

(1) J. E. Franz and C. Osuch, *Tetrahedron Letters*, 837 (1963).

(2) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963), ref. 8.



Ia



Ib

"fortuitous," the following evidence indicates that Ia is entirely consistent with the data.

The proton magnetic resonance spectra of 2,3-*exo*-epoxybicyclo[2.2.1]heptane and adduct I are reproduced in Fig. 1 (both as 7.5% solutions in benzene). The epoxide (Fig. 1a) shows well-resolved signals from $H_{2,3}$ at 2.70 (2H), $H_{1,4}$ at 2.13 (2H), *syn*-H_7 at 1.44 (1H), *anti*-H_7 at 0.43 (1H),[3] and a complex multiplet from $H_{5,6}$ centered at 0.98 p.p.m. (4H). The peaks from $H_{2,3}$ and $H_{1,4}$ are broadened singlets, while the peaks from *syn*- and *anti*-H_7 are doublets ($J_{syn\text{-}H_7\text{-}anti\text{-}H_7}$ = 9.5 c.p.s.). The peak from the *syn*-H_7 shows an additional small coupling with other unidentified protons in the molecule to give pentuplets. The aliphatic portion of the spectrum of our 1:1 adduct I (Fig. 1b) shows identical features with those of the epoxide. Well-resolved signals are present for $H_{2,3}$ at 2.84 (2H), $H_{1,4}$ at 1.97 (2H), *syn*-H_7 at 1.38 (1H), *anti*-H_7 at 0.30 (1H), and a complex multiplet for $H_{5,6}$ at 0.86 p.p.m. (4H).

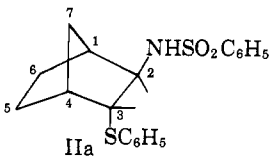
Owing to uncertainty of the bond angles in structures I, neither a nor b can be excluded using only comparisons of the observed coupling constants with those reported for substituted bicyclo[2.2.1]heptanes.[5]

Some of the features observed in the spectrum of I, however, are difficult to explain on the basis of the azetidine structure (Ib). These are the observed equivalence of the 2,7 protons, the absence of a 3.8–4.4-c.p.s. coupling between the 3-*exo* and the bridgehead 4-proton, and the absence of any appreciable coupling between the 2-*endo* and either of the 3-position protons. The objection to the aziridine structure (Ia) raised by Zalkow and Oehlschlager,[2] that the doublet for the *anti*-H_7 proton is at too high field for this type of proton, is seen to be invalid since both 2,3-*exo*-epoxybicyclo-[2.2.1]heptane and 3,3-*exo*-dichlorotricyclo[3.2.1.$0^{2,4}$]-octane[4a] have this type of high-field absorption for one of the bridge protons.

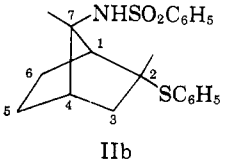
The possibility of a nortricyclene type structure for I was excluded on the basis of the proton area ratio obtained from the n.m.r. spectrum of I in CCl_4 (five aromatic protons to ten aliphatic protons). Despite arguments presented by Zalkow and Oehlschlager[2] in favor of the azetidine structure (Ib), we will present physical and chemical evidence which confirms the correctness of our original aziridine (Ia) assignment.

Adduct I reacted readily with potassium thiophenate in refluxing *t*-butyl alcohol to yield a new compound, $C_{19}H_{21}NO_2S_2$ (II), in 92% yield. The infrared spectrum of the latter product (Fig. 2A) showed the expected –NH and $-SO_2-$ bands.

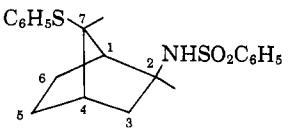
Assuming an SN2 attack of the strongly nucleophilic thiophenate anion on Ia or Ib, II could reasonably be represented by structures IIa, IIb, or IIc. Attack of



IIa



IIb



IIc

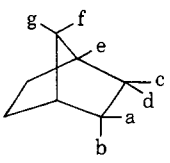
a nucleophile at the 7-position to yield IIc, however, is highly unlikely.[7]

The pertinent portions of the n.m.r. spectrum of II are shown in Fig. 3 (a in $CDCl_3$ and b in $CDCl_3$ containing 5% CF_3CO_2H). In IIb, the doublet at 5.85 p.p.m. has disappeared and the multiplet at 2.94 p.p.m. has collapsed to a doublet. The former, therefore, represents the proton on N and the latter the proton on the carbon adjacent to the –NH group.[8] The only other nonaromatic proton appearing below 2.1 is at 3.22 p.p.m. and must therefore represent the proton on the carbon bearing the thiophenoxy group. Either 7-substituted derivative (IIb or IIc) would be expected to show a complex band for H_2 due to coupling of this proton with the two H_3 protons and, in IIb, further coupling between H_2 and H_1.[5] In structure IIa, H_2 is expected to be a doublet (in acid solution) coupled to H_3 with a J of 2.2–5.2 c.p.s. with further small coupling possible with H_1, while H_3 should be a doubled doublet or a triplet showing coupling to H_2 and H_4 ($J_{2,3} \cong J_{3,4}$ = 2.2–5.6 c.p.s.). The spectra obtained fit the predictions for IIa. Removal of the thiophenoxy group of II was readily accomplished with Raney nickel to give a product (III), $C_{13}H_{17}NSO_2$, in 80% yield. Considering structures IIa and IIb as its precursor, III would have to

(3) The relative assignments of *anti*-H_7 and *syn*-H_7 are based on similar assignments for the *syn*- and *anti*-C-8 protons of 3,3-*exo*-dichlorotricyclo-[3.2.1.$0^{2,4}$]octane reported by Moore, Moser, and LaPrade.[4a] Since the initial preparation of this manuscript, the n.m.r. spectrum of norbornene oxide has been published.[4b] These workers used $CDCl_3$ as solvent and did not separate the *syn*-H_7 from the $H_{5,6}$ protons. It should be noted that in benzene (Fig. 1) all the protons except the *syn*-H_7 are shifted upfield. A similar observation was reported by Moore and co-workers[4a] for their adduct. For a discussion of solvent effects in the norbornene system see Laszlo and Schleyer.[6]

(4) (a) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (b) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 559 (1964).

(5) N.m.r. spectra of bicyclo[2.2.1]heptane derivatives have been studied extensively. In the absence of additional fused rings, which may perturb the molecular geometry, consistent values for the major coupling constants between various potons have been determined. These values (c.p.s.) have the ranges shown.[4,6] Additional small (1–2 c.p.s.) couplings between protons f,g and other protons in the molecule have also been reported.



J_{ac} = 7.4–11.4 J_{ce} = 3.8–5.6
J_{bd} = 5.1–8.9 J_{de} = *ca.* 1
J_{ad} = 2.4–6.0 J_{fg} = 7.2–11.2
J_{bc} = 2.2–5.2 J_{cd} = 12.6–13.3

(6) For a recent review and leading references, see P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(7) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956), and references cited therein.

(8) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

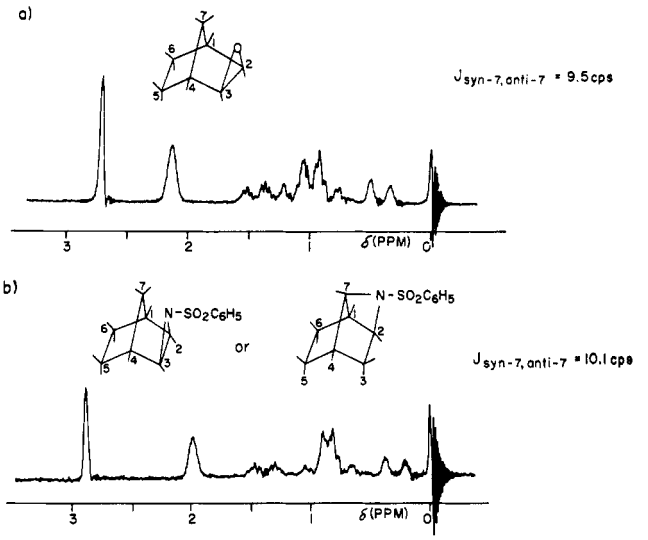


Fig. 1.—Proton n.m.r. spectra of bicyclo[2.2.1]heptane derivatives: a, 2,3-*exo*-epoxybicyclo[2.2.1]heptane; b, aliphatic portion of adduct I. Both were run in benzene (7.5%) with tetramethylsilane as internal standard.

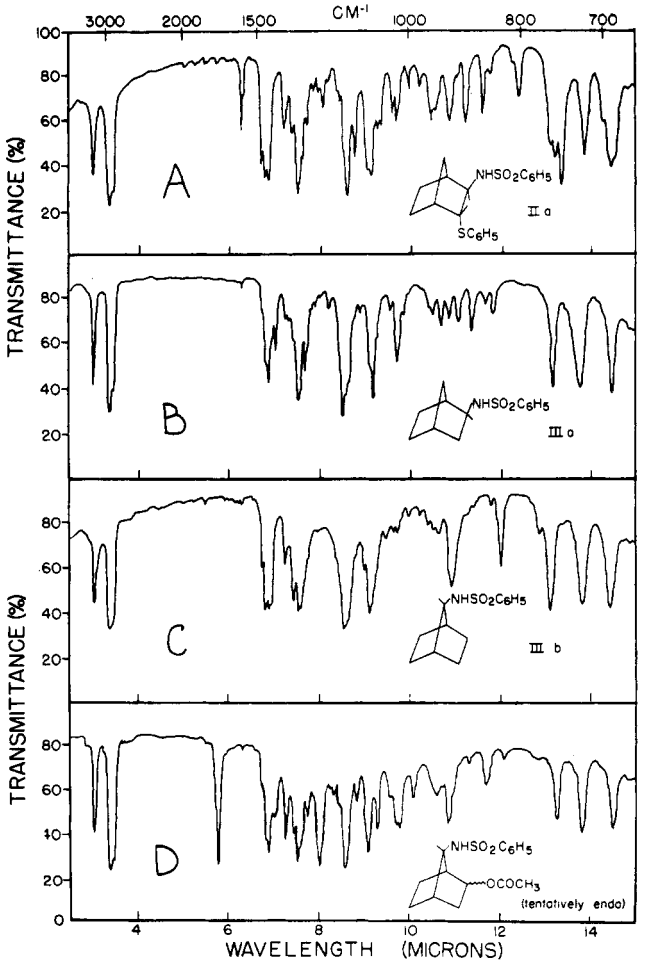


Fig. 2.—Infrared spectra of benzenesulfonamidobicyclo[2.2.1]-heptane derivatives (as mineral oil mulls).

be *exo*-2-benzenesulfonamido[2.2.1]heptane (IIIa) or the 7-derivative (IIIb). The n.m.r. spectrum of III (Fig. 4) is consistent only with the IIIa structure on the basis of the following analysis. The H_2 proton should be split by H_N, H_{exo-3} (J = 2.2–5.2 c.p.s.), H_{endo-3} (J = 5.1–8.9 c.p.s.), and H_1 ($J \approx 1$ c.p.s.). Furthermore,

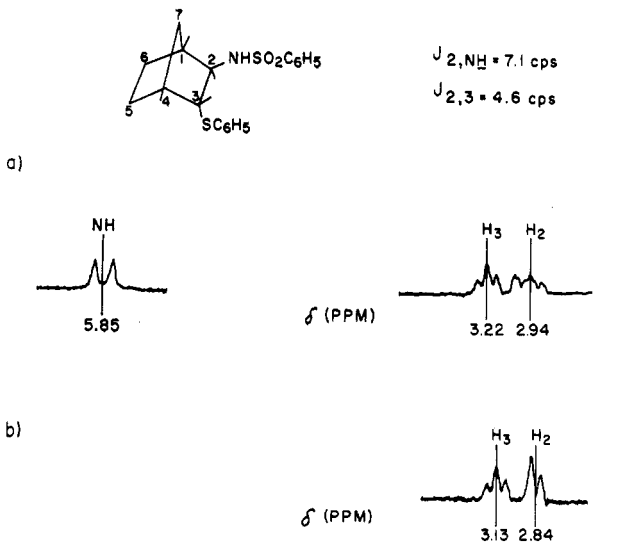


Fig. 3.—Slow sweep of the 2-, 3-, and NH-proton regions of the thiophenol adduct II: a, in $CDCl_3$; b, in $CDCl_3$ containing about 5% CF_3CO_2H.

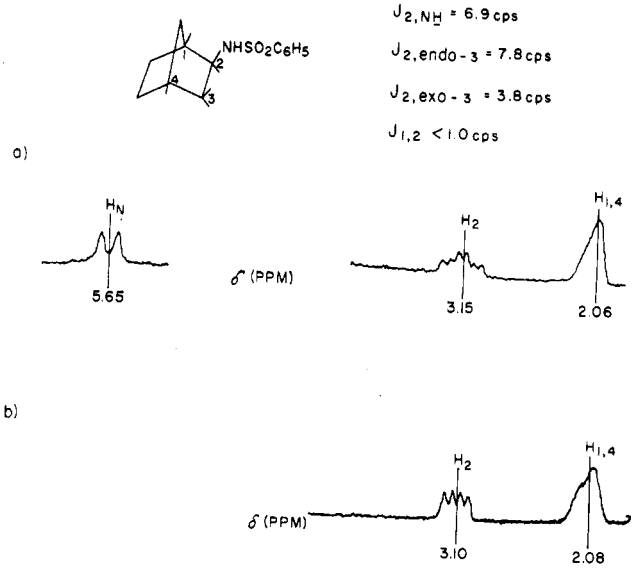
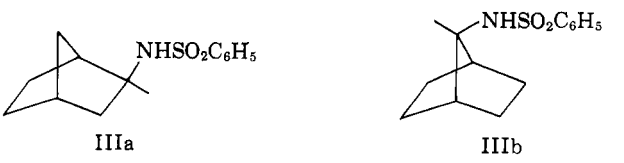


Fig. 4.—Slow sweep of the 1-, 2-, 4-, and NH-proton regions of the sulfonamide IIIa obtained by Raney nickel desulfurization of II: a, in $CDCl_3$; b, in $CDCl_3$ containing about 5% CF_3CO_2H.

some nonequivalence might be expected in the 1,4-protons. In the presence of acid H_2 would be split by H_{exo-3} and H_{endo-3} (with different J values), thus giving rise to a double doublet. The 7-proton of IIIb is expected to be a simple doublet, collapsing to a singlet on acidification. Finally, we have found the n.m.r. and infrared spectra (Fig. 2) of III to be identical with those of the benzenesulfonamide prepared from authentic 2-*exo*-aminobicyclo[2.2.1]heptane.[9]



The hydrogenolysis of 2,3-*exo*-epoxybicyclo[2.2.1]-heptane with lithium aluminum hydride was described[10]

(9) W. R. Boehme and E. Schippia, *J. Am. Chem. Soc.*, **80**, 5488 (1958).

recently. The major product obtained in this reaction was 2-*exo*-hydroxybicyclo[2.2.1]heptane, the result of an electrophilically assisted SN2 attack of the hydride ion at the 2-position of the bicyclic ring. Using similar reaction conditions, Ia yielded a 3:1 mixture of IIIa and IIa. Separation of IIa from IIIa could be effected by gas–liquid phase chromatography or by treatment of the reaction mixture with Raney nickel in hot isopropyl alcohol. The origin of IIa in this reaction is not known with certainty, but reduction of Ia or IIIa[11] to thiophenol followed by further reaction of the latter product with Ia would account for the results observed.

Attempts to hydrolyze IIIa to 2-*exo*-aminobicyclo-[2.2.1]heptane under acidic conditions were complicated by elimination reactions. The major product isolated in most cases was benzenesulfonamide along with various unidentified mixtures of alcoholic and ketonic products. In one instance, a low yield of amine hydrochloride was obtained which formed a chloroacetyl derivative melting at 117–123°. The reported melting point of 2-*exo*-chloroacetylaminobicyclo[2.2.1]heptane is 120–121°[2] (126–127°),[12] whereas the melting points[12] of both the 2-*endo* and 7-derivatives are below 110°.

Acid-catalyzed SN1 ring opening of Ia with thiophenol was found to yield a mixture of products in contrast to the single pure component obtained under basic conditions. The 7-sulfonamide derivative was expected to be the major adduct formed and the n.m.r. spectrum of the crude mixture supported this conclusion. The latter product was readily reduced by Raney nickel to yield a mixture of sulfonamides whose n.m.r. spectrum indicated that 7-benzenesulfonamidobicyclo[2.2.1]heptane (IIIb) was the major constituent. The pertinent portions of the spectra shown in Fig. 5 are in full agreement with prediction. Thus, the 7-proton was split only by the adjacent NH to give a doublet (J = 5.4 c.p.s.) which collapsed to a reasonably sharp singlet on acidification.

The reaction of glacial acetic acid with the aziridine Ia gave a viscous oil which could not be separated into pure components by chromatography on Attapulgus earth. Five constituents were indicated by gas–liquid chromatography with the following relative peak areas: 1.3, 5.2, 49.7, 32.0, and 11.8%. The two major fractions were collected separately and isolated as crystalline solids. The n.m.r. spectrum (Fig. 6) of the major product, m.p. 136°, shows the H_2 proton as what could be a partially resolved doubled doublet (compare with H_2 of Fig. 3b), suggesting the 2-*exo*-acetoxy-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane configuration.[13] The 32% fraction is tentatively assigned the *endo* configuration (see Fig. 2D).

The formation of the aziridine Ia in the reaction of benzenesulfonyl azide with bicyclo[2.2.1]heptene indicates that rearrangements do not occur in this reaction. This point was conclusively established by an n.m.r. examination of the adduct obtained at room

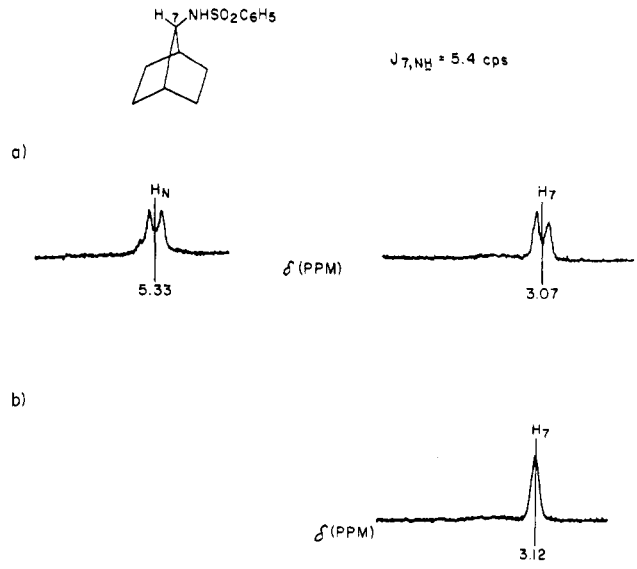


Fig. 5.—Slow sweep of the 7- and NH-proton regions of 7-benzenesulfonamidobicyclo[2.2.1]heptane (IIIb): a, in $CDCl_3$; b, in $CDCl_3$ containing about 5% CF_3CO_2H.

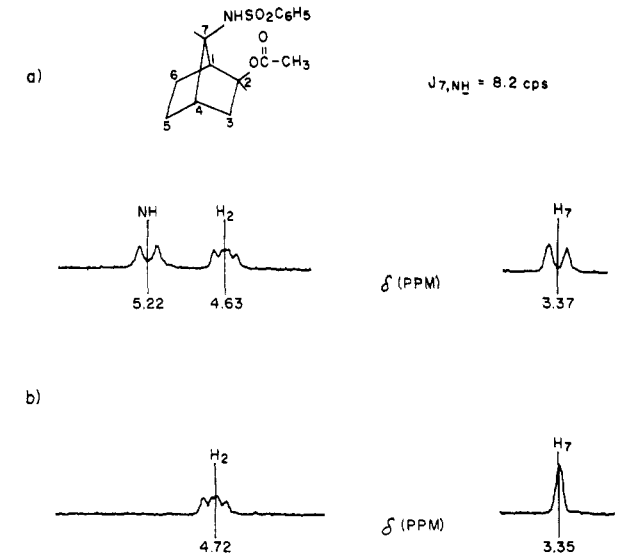
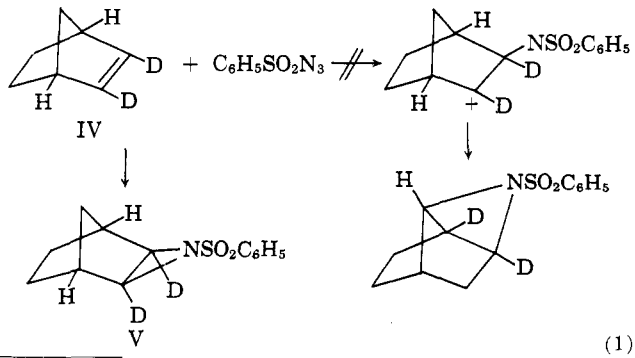


Fig. 6.—Slow sweep of the 2-, 7-, and NH-proton regions of the acetic acid adduct (m.p. 136°) of I: a, in $CDCl_3$; b, in $CDCl_3$ containing about 5% CF_3CO_2H.

temperature in benzene solution from benzenesulfonyl azide and deuteriobicyclo[2.2.1]heptene (IV) in which 78.5% of the olefinic protons had been replaced with deuterium. The latter product was readily prepared by reaction of norbornene with butyl sodium[14] followed by D_2O hydrolysis.



(1)

(10) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

(11) Further reduction of IIIa by lithium aluminum hydride is possible since this sulfonamide does not readily form a salt even in strongly alkaline solution from which it can be extracted with ether.

(12) W. R. Boehme and J. Nichols, U. S. Patent 2,296,172 (1961).

(13) This compound has been assigned the 2-*endo* structure by others[2] based on the direction of ring opening expected from an SN2 attack of hydroxide ion on the azetidine Ib. However, the n.m.r. of the *endo* isomer would be expected to show H_2 as a more complex band.

(14) R. A. Finnegan and R. S. McNees, *Chem. Ind.* (London), 1450 (1961).

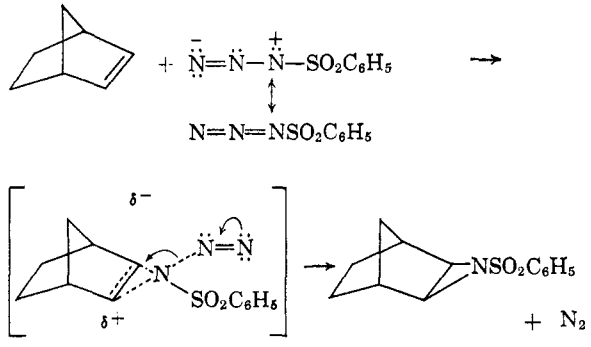
TABLE I

Proton type	Protons/molecule IV	V
$H_{2,3}$	0.43 ± 0.01[a]	0.42 ± 0.05[b]
$H_{1,4}$	1.98 ± 0.05	1.94 ± 0.05
$H_{5,6,7}$	6.02 ± 0.05	6.04 ± 0.11

[a] Calculations based on $H_{1,4} + H_{5,6,7} = 8.00$ protons. [b] Calculations based on 5.00 aromatic protons/molecule.

Integration of the n.m.r. spectra of the starting deuterionorbornene (IV) and the azide adduct (V) revealed that the ratio of protons at the 1,4-, the 2,3-, and the 5,6,7-positions remained constant (Table I). Rearrangement to an azetidine would have resulted in a substantial decrease in the number of 1,4-protons and a similar increase in the number of protons adjacent to the nitrogen atom of the azetidine ring as indicated in equation sequence 1. This evidence indicates that carbonium ion intermediates are not involved and that deuterium scrambling does not occur during this reaction.

Although a triazoline may be an intermediate, the mechanism of aziridine formation probably parallels that of epoxidation[15] involving a concerted addition of the azide to the double bond of the olefin with the concomitant loss of nitrogen. Additional work bearing on this and related problems are in progress.



Experimental[16]

Preparation of N-Benzenesulfonyl-3-azatricyclo[3.2.1.0$^{2,4-exo}$]-octane (Ia).—This material was prepared as described earlier.[1] The benzenesulfonyl azide was prepared by the method of Boyer[17] and co-workers. The norbornylene used was a research sample supplied by Esso Research and Engineering Co.

Preparation of 2-*endo*-Thiophenoxy-3-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane (IIa).—To 2.5 g. (0.01 mole) of adduct (Ia) there was added 2.0 g. (0.018 mole) of thiophenol and 20 ml. of approximately 0.1 *N* potassium *t*-butoxide in *t*-butyl alcohol. The mixture was refluxed overnight and then poured onto water. After neutralizing with Dry Ice, the product was extracted with ether, the ether layer was dried over magnesium sulfate, and then the solvent and excess thiol were removed under vacuum. The crude product was washed with *n*-hexane to give 3.3 g. (92%) of nearly white crystalline material, m.p. 113–114.5°. The analytical sample was obtained by recrystallization from chloroform–*n*-hexane, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{19}H_{21}NO_2S_2$: C, 63.48; H, 5.89; N, 3.90. Found: C, 63.67; H, 6.05; N, 4.07.

Preparation of 2-*exo*-Benzenesulfonamidobicyclo[2.2.1]heptane (IIIa). A. By Raney Nickel Reduction of IIa.—The thiophenol addition product (IIa, 1.50 g.) was refluxed 4 hr. with 12.5 g. of a slurry of Raney nickel in 2-propanol and 30 ml. of 2-propanol. The clear solution was decanted, and the Raney nickel was washed several times with hot 2-propanol. The combined washings were filtered to remove nickel and the solvent was removed under reduced pressure. The crude oil, 1.03 g., solidified on scratching to give a solid, m.p. 71–77°. Washing with *n*-hexane gave 0.84 g. (80%), m.p. 82–84°.[18] The analytical sample was prepared by recrystallization from *n*-hexane, m.p. 84–86.0°.

Anal. Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 61.95, 62.30; H, 6.71, 6.95; N, 5.44, 5.69.

B. From Authentic 2-*exo*-Aminobicyclo[2.2.1]heptane.—Following the procedure of Boehme and co-workers,[9] 51 g. (0.43 mole) of 5-*exo*-cyanobicyclo[2.2.1]heptene-2, 10 g. (0.43 g.-atom) of sodium, and 750 ml.of dry ammonia yielded 25 g. of 5-*exo*-carbamylbicyclo[2.2.1]heptene-2 and 17 g. of 5-*exo*-carboxybicyclo[2.2.1]heptene-2. 5-*exo*-Carbamylbicyclo[2.2.1]heptane was obtained in quantitative yield after catalytic reduction of the unsaturated derivative in ethanol using a platinum-on-carbon catalyst. After recrystallization from water the product melted at 189–191°. The Hofmann reaction was carried out as described using 8.2 g. (0.06 mole) of 2-*exo*-carbamylbicyclo[2.2.1]heptane, 4.5 ml. of bromine, 13.5 g. (0.34 mole) of sodium hydroxide, and 130 ml. of water. The crude oily product (7 g.) obtained in this reaction contained both a ketone and an imine as indicated by the infrared spectrum. The ketone was identified as norcamphor (1 g.) after extraction of the mixture with dilute HCl. After neutralization of the acid solution, extraction with ether afforded 5 g. of an oil possessing a strong imine absorption band at 5.92 μ in the infrared spectrum. The oil was hydrolyzed by refluxing it for 24 hr. with 4 *N* H_2SO_4. The insoluble product (1.6 g.) which formed in this reaction was found to be norcamphor. The acidic solution was made strongly basic with sodium hydroxide and then extracted with ether. The ether extract was dried over magnesium sulfate and finally saturated with dry hydrogen chloride. The white crystalline amine hydrochloride was collected and recrystallized from methanol–ethyl acetate. The product did not melt below 315°.[19] The n.m.r. spectrum in $CDCl_3$ indicated that the major product was the *exo* derivative contaminated with some *endo* isomer. The *endo–exo* mixture of sulfonamides was prepared by shaking 0.25 g. (0.002 mole) of amine hydrochloride and 0.7 g. (0.004 mole) of benzenesulfonyl chloride with 10 ml. of 5% sodium hydroxide solution. The crude product melted at 55–60° and was obtained in quantitative yield. After several recrystallizations from dilute methanol the product had a melting point of 78–81°. The infrared and n.m.r. spectra of the latter material were identical with those obtained with the sulfonamide prepared by the Raney nickel desulfurization described in A.

C. From Lithium Aluminum Hydride Reduction of Adduct Ia.—A solution of 2.5 g. (0.01 mole) of aziridine (Ia) in 25 ml. of freshly distilled tetrahydrofuran and 1.0 g. of lithium aluminum hydride was refluxed 55 hr. The reaction mixture was poured cautiously onto ice, ammonium chloride was added, and the product was extracted with ether. After drying, the solvent was removed under vacuum to leave 2 g. of a crude oil. One gram of this material was chromatographed on a silica gel column and similar fractions (by infrared analysis) were combined and decolorized with carbon, and the solvent was removed to leave 620 mg. of colorless oil. Proton n.m.r. showed this material to have two distinct NH absorptions. A sample was chromatographed by gas–liquid partition techniques using a 2-m. silicone (SE-52) column.

Two peaks were observed and samples were collected. One peak representing 76% of the material, m.p. 80–81.5°, was undepressed on mixing with authentic 2-*exo*-benzenesulfonamido-

(15) D. Swern, *Org. Reactions*, **7**, 386 (1953).

(16) All melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. Nuclear magnetic resonance spectra were obtained on a Varian HR 60 n.m.r. spectrometer at 60 Mc./sec. with tetramethylsilane as reference.

(17) J. H. Boyer, C. H. Mack, N. Goebel, and L. R. Morgan, Jr., *J. Org. Chem.*, **23**, 1051 (1958).

(18) This material appeared as a single peak when chromatographed by g.l.c. on either a silicone (SE-52) or a polyester (NPGS) column. Analysis of the *n*-hexane soluble oil by g.l.c. on a 2-m. SE-52 column showed the presence of the 2-*exo*-sulfonamide (65%) along with unreacted thiol adduct IIa (33%).

(19) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934).

bicyclo[2.2.1]heptane (IIIa). The other peak, 24% of the sample, had m.p. 113–115° alone and when mixed with authentic IIa prepared from aziridine (Ia) and thiophenol. The retention times of these two fractions also agreed with those of authentic samples. Reduction of the crude mixture with Raney nickel in hot 2-propanol yielded the *exo* isomer, m.p. 82–84°, as the only sulfonamide product.

Hydrolysis of 2-*exo*-Benzenesulfonamidobicyclo[2.2.1]heptane (IIIa). A. With Dilute HCl.—A mixture of sulfonamide (IIIa), 191 mg., and 1.5 ml. of 10% HCl was heated in a sealed tube for 16 hr. After extraction of the aqueous acid with ether, the water layer was basified with 20% NaOH and extracted with ether. The dried ($MgSO_4$) layer was treated with gaseous HCl to give a small quantity, 23 mg., of crystalline solid. This solid was suspended in benzene, pyridine was added, and the mixture was treated with chloroacetyl chloride. After standing overnight the benzene solution was washed with water, dilute acid, and water, and dried over $MgSO_4$; the solvent was evaporated. Sublimation of the residue afforded white needles, m.p. 117–123°, of 2-*exo*-chloroacetylaminobicyclo[2.2.1]heptane.[12]

B. With HBr.—Sulfonamide (IIIa, 250 mg.) was mixed with 5 g. of phenol and 3.75 ml. of 48% HBr. After 1 hr. of refluxing, the acidic solution was extracted with ether and the washed aqueous layer was neutralized with 20% NaOH. Extraction of the basic layer with ether, drying and removal of the solvent left only 16 mg. of material which appeared from the infrared spectrum to be predominantly benzenesulfonamide.

C. With 25% HCl.—A mixture of 250 mg. of sulfonamide (IIIa) and 10 ml. of 25% HCl was refluxed for 3 days. Extraction of the acid mixture with ether resulted in the recovery of 97 mg. (61.8%) of benzenesulfonamide. The ether extract of the neutralized aqueous solution yielded 38 mg. of crude oil which did not yield an amide derivative on treatment with chloroacety chloride.

Preparation of 2-Acetoxy-7-benzenesulfonamidobicyclo[2.2.1]-heptane.—Glacial acetic acid, 10 ml. was added to 1.456 g. of aziridine (Ia) and heated on the steam bath for 2 hr. The excess acid was removed under reduced pressure and the oily residue was dissolved in ether. The organic layer was extracted with dilute aqueous sodium carbonate, washed with water, and dried over $MgSO_4$. After removal of solvent the product was obtained as a viscous, colorless oil, 1.692 g., 94.3% of theory. A portion, 1.0 g., of this oil was chromatographed on an Attapulgus earth column. Two major fractions were collected, 275 mg. and 407 mg., both of which solidified on long standing (2 weeks). The fraction weighing 407 mg. was triturated in ether to give 184 mg. of insoluble material, m.p. 85–125°. After one recrystallization from $CHCl_3$–$(C_2H_5)_2O$ there was obtained 116 mg. of material, m.p. 135–138° (lit.[2] m.p. 135–136° for 2-acetoxy-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane). The infrared spectrum of this material (as mineral oil mull) agreed closely with that reported by Zalkow and Oehlschlager.[2] The ether soluble fraction from the 407 mg. of crude material was diluted with *n*-hexane to give 69 mg. of crystals, m.p. 99–104°. One recrystallization from $CHCl_3$–$(C_2H_5)_2O$–*n*-hexane gave 23 mg. of needles, m.p. 106–107°.

Anal. Calcd. for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19. Found: C, 58.22; H, 6.45.

An additional small amount of this material was obtained from the 275-mg. fraction from the column chromatograph. The proton n.m.r. spectrum obtained was not conclusive but suggested that the latter product was the 2-*endo*-acetoxyl derivative. The infrared spectrum (see Fig. 2D) is similar to, but not identical with, the high-melting isomer.

A sample of the original, crude 1.692 g. of material was analyzed by gas–liquid phase chromatography on a 2-m. column packed with silicone (SE-52). Five peaks were eluted with relative area ratios of 1.3, 5.2, 49.7, 32.0, and 11.8%. The material melting at 135–138° had the same retention time and infrared absorption spectrum as peak 3, while the lower-melting fraction, 106–107°, had the same retention time and infrared curve as peak 4. Peak 5 was collected and the infrared spectrum appeared to be that of an acetoxy sulfonamide compound, but the material was not sufficiently pure to further characterize. Peak 2, m.p. 72.5–75.0°, did not possess carbonyl absorption in the infrared spectrum and was not further investigated.

Preparation of 7-Benzenesulfonamidobicyclo[2.2.1]heptane.—A mixture of 0.5605 g. (0.002 mole) of Ia, 0.5840 g. (0.005 mole) of thiophenol, and 3 small drops of boron trifluoride etherate was warmed on the steam bath and then allowed to remain overnight. Excess thiophenol was removed under reduced pressure at 100° and the crude product (0.8530 g.) was dissolved in hot isopropyl alcohol. The isopropyl alcohol solution was refluxed for 1.5 hr. with 12 g. of Raney nickel and then filtered. After drying over magnesium sulfate and concentrating the solution, there was obtained 0.461 g. (81%) of crude product which crystallized on standing. The latter was washed with petroleum ether (b.p. 30–60°) to yield material which melted at 82–95°. The n.m.r. spectrum of this product indicated that the major constituent was 7-benzenesulfonamidobicyclo[2.2.1]heptane. The product obtained after recrystallization from hexane melted at 89–95°.[20] Recrystallization of the thiophenol adduct before reduction with Raney nickel yielded a fraction which melted sharply at 148.5–150.5°. This material has not been positively identified.

Preparation of 2,3-Dideuteriobicyclo[2.2.1]-2-heptene.—Norbornene, 18.8 g., 0.2 mole, dissolved in petroleum ether was added slowly to approximately 0.25 mole of butyl sodium in petroleum ether.[14] After stirring 6 hr., the slurry was decomposed by careful addition of excess deuterium oxide. On work-up (dilution with water, extraction, drying, and distillation), 9.1 g. of norbornene was obtained boiling at 94–95° at atmospheric pressure. Analysis by n.m.r. indicated that approximately 0.7 deuterium atoms had been introduced. This material was treated again with excess butyl sodium followed by D_2O. The resulting product was purified by preparative gas–liquid phase chromatography and shown to be a single component as indicated by a single peak from a capillary g.l.c. column.[21] The melting point of the product obtained was 44–45.5° (sealed capillary), lit.[22] m.p. 46.0–46.5° for norbornene. Proton analysis by n.m.r. is shown in Table I.

Preparation of N-Benzenesulfonyl-3-Azatricyclo[3.2.1.$0^{2,4\text{-}exo}$]-2,4-dideuteriooctane.—A benzene solution of 1.0 g. of deuterionorbornene and 0.950 g. of benzenesulfonyl azide was allowed to stand at room temperature overnight. On work-up, there was obtained 0.696 g. (53.3%) of product,[23] m.p. 99–106°; one recrystallization gave m.p. 105.5–107.0°. The infrared and n.m.r. spectra of the crude and recrystallized samples were identical. Detailed analysis of the n.m.r. spectrum is shown in Table I.

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(20) Analysis of this material by g.l.c. on a silicone (SE-52) column showed a single peak. However, when a polyester (NPGS) column was used, two peaks were obtained. The major peak, 81.4%, was collected and shown by infrared and melting point (96–102° on Kofler hot stage) to be the 7-isomer. The minor peak, 18.6%, is an as yet unidentified sulfonamide. The oils obtained from the purification steps were analyzed by g.l.c. and shown to contain predominately these same two components (95.4% of total).

(21) Although this method seems to be capable of excellent yields, we found high losses due to the high vapor pressure of norbornene. For example, liquid nitrogen traps used with the Megachrom failed to trap all the norbornene, probably owing to the high rate of gas flow in the system.

(22) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

(23) The infrared spectrum of the crude oil representing the remainder of the material indicated that no unreacted azide was present. A strong 6.1-μ band indicated the presence of imine (see ref. 1).