to give 1.4 g (100%) of **2**. After recrystallization from cyclohexane, the melting point was 131–134°.

Anal. Calcd for $C_7H_8Cl_2OS$: C, 39.8; H, 3.81; Cl, 33.6; S, 15.2. Found: C, 40.1; H, 3.89; Cl, 33.4; S, 15.1.

The purity of **2** was verified by gas chromatographic and infrared analysis which identifies this sulfoxide with the minor component of the crude sulfoxide mixture. The sulfur–oxygen stretching frequency of **2** in carbon disulfide (2%) is at 1057 cm^{-1}.

To a solution of 97 mg (0.0005 mole) of **2** in 2 ml of glacial acetic acid was added 30 mg of 50% of aqueous hydrogen peroxide. After evaporation and sublimation, 80 mg (75%) of **4** was obtained, identified by mixture melting point and infrared absorption. Similarly, 97 mg of **3** in 2 ml of glacial acetic acid gave 73 mg (70%) of **4**, identified by mixture melting point and infrared absorption.

Reaction of 1 with Methyl Iodide.—A solution of 3.9 g (0.02 mole) of the sulfide **1** in 50 ml of methyl iodide was refluxed for 54 hr after which the excess of methyl iodide was allowed to evaporate. The crystalline residue, 3.7 g, mp 42–44°, was identified by its infrared absorption and mixture melting point as unchanged **1**. The crude product was completely soluble in pentane.

Desulfurization of 1.—To a stirred suspension of 172 g of Raney nickel in 250 ml of ethanol was added 25 g (0.128 mole) of **1**. The mixture warmed up immediately and gas chromatographic analysis indicated the absence of starting material 1 hr after the components had been mixed. The Raney nickel was filtered off and washed with ethanol. The combined alcoholic solution was diluted with 200 ml of water and continuously extracted with pentane, and the pentane solution was washed with water to remove ethanol, dried with magnesium sulfate, and distilled to leave 8 g of crude product. Distillation through a 3-in. Vigreux column gave the following fractions at 760 mm: (a) 3 g, bp 94–102°; (b) 2 g, bp 102–110°; (c) 1 g, bp 110–163°. Redistillation of fraction c gave 2-chloronorbornane with bp 162°, mp −5°,[15,16] and an infrared spectrum identical with that reported.[17]

Preparative-scale chromatography and subsequent identification by infrared and nmr spectroscopy characterized the desulfurization components as norbornene, norbornadiene, and norbornane. Approximate gas chromatographic analysis showed 10% chloronorbornane, 50% norbornadiene, 20% norbornene, and 20% norbornane.

Acknowledgment.—The author is greatly indebted to Professor J. K. Stille for the discussion of various aspects of this work, to Professor D. B. MacLean for the recording of the mass spectrum, to Professor G. F. Wright for allowing the use of the instrument for measuring dipole moments,[18,19] and to Dr. R. T. Woodhams for encouragement and his interest in this work.

(15) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 195 (1946).
(16) E. C. Kooijman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).
(17) J. D. Roberts, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950).
(18) C. C. Meredith, L. Westland, and G. F. Wright, *ibid.*, **79**, 2385 (1957).
(19) C. C. Meredith and G. F. Wright, *Can. J. Technol.*, **33**, 182 (1955).

Bridged Ring Compounds. XIII.[1-3] The Reaction of N,N-Dibromobenzenesulfonamide with Bicyclo[2 2.1]heptene, Bicyclo[2.2.2]octene, and *endo*-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic Anhydride

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N,N-Dibromobenzenesulfonamide (NNDBS) reacts vigorously with bicyclo[2.2.1]heptene in benzene at room temperature to give 3-bromotricyclo[2.2.1.$0^{2,6}$]heptane, 7-*syn*-bromo-2-exo-benzenesulfonamido- and 7-*anti*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane, but none of the 2-*exo*-bromo-3-*endo*-benzenesulfonamido isomer could be detected. These results are contrasted with those obtained in the reaction of norbornylene with molecular bromine and the mechanistic implications discussed. Under similar conditions, bicyclo[2.2.2]octene gave 8-*syn*-bromobicyclo[3.2.1]-2-octene, 2-*exo*-bromo-3-*endo*-benzenesulfonamidobicyclo[2.2.2]octane, and 7-*syn*-bromo-2-*exo*-benzenesulfonamidobicyclo[3.2.1]octane. Thus, in the case of bicyclo[2.2.2]octene the halogen-bridged cation is a product forming intermediate, whereas in the case of norbornylene it is not. *endo*-Bicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic anhydride was found to react with NNDBS to give 5-*exo*-bromo-6-*exo*-benzenesulfonamido-2,3-*endo-cis*-dicarboxybicyclo[2.2.1]heptane anhydride. The solvolysis of 7-*anti*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane was found to yield the rearranged product 7-*syn*-benzenesulfonamido-2-*endo*-hydroxybicyclo[2.2.1]heptane and the fragmented product 3-cyclopentenylacetaldehyde, whereas the isomeric 7-*syn*-bromo-2-*exo*-benzenesulfonamido derivative was unchanged on solvolysis.

Kharasch and Priestley[6] observed that N,N-dibromoarenesulfonamides (I) added to unsymmetrical alkenes to yield products in which the bromine atom took the position expected in a process involving positive bromine, as in II. The second bromine atom of the N,N-dibromoarenesulfonamide appeared as a vinyl bromide, III.

$$2RCH{=}CH_2 + \underset{\text{I}}{ArSO_2NBr_2} \longrightarrow \underset{\text{II}}{RCHCH_2Br}\,(HNSO_2Ar) + \underset{\text{III}}{RC_2H_2Br}$$

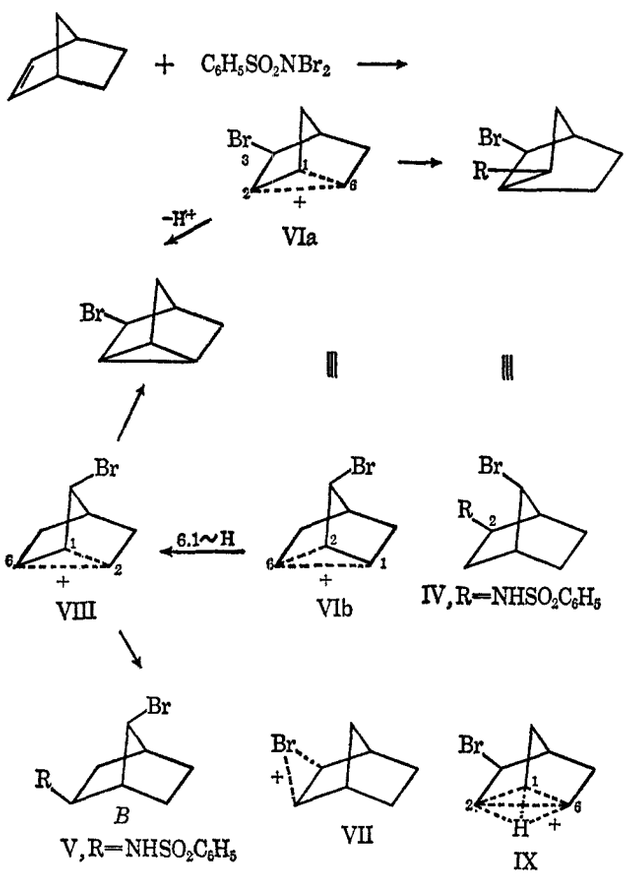
R = alkyl or aryl group

Since a great deal of information on ionic additions to bicyclo[2.2.1]heptene derivatives and to bicyclo-[2.2.2]octene has been recorded,[7] we were interested in extending the reaction of N,N-dibromobenzenesulfonamide (NNDBS) to these alkenes. We were particularly interested in comparing the results obtained in this case with the results obtained in the addition of other positive halogen compounds to such compounds.

(1) Part XII: A. C. Oehlschlager and L. H. Zalkow, *Chem. Commun.*, 5 (1966).
(2) For a preliminary account of a part of this work, see L. H. Zalkow and A. C. Oehlschlager, *J. Am. Chem. Soc.*, **86**, 4208 (1964), and ref 3.
(3) A. C. Oehlschlager and L. H. Zalkow, *Tetrahedron Letters*, 2663 (1964).
(4) National Defense Education Act Fellow, 1962–1965. Taken from the Ph.D. Thesis of A. C. Oelschlager, submitted April 1965, Oklahoma State University.
(5) To whom inquiries should be addressed: School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.
(6) M. S. Kharasch and H. M. Priestley, *J. Am. Chem. Soc.*, **61**, 3425 (1939).
(7) J. A. Berson in "Molecular Rearrangements," Part One, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, and references therein.

As described in a preliminary publication,[3] the reaction of bicyclo[2.2.1]heptene with NNDBS was found to yield, in addition to 3-bromotricyclo[2.2.1.-$0^{2,6}$]heptane and unidentified bicyclo[2.2.1]heptyl dibromides, two addition products which have been assigned structures IV and V (see Scheme I). Although IV was to be expected by analogy with the results obtained in reactions with other positive bromine reagents,[8,9] the isolation of V and absence of the 2-*exo*-bromo-3-*endo*-benzenesulfonamido isomer were of particular interest.

SCHEME I



The nmr spectra[10] of IV and V were indicative of their structures, but in addition firm chemical evidence was provided for these structures as follows. Both IV and V were converted into the known[11] 2-*exo*-aminobicyclo-[2.2.1]heptane under nonepimerizing conditions and IV was further transformed into the known[9] *syn*-7-bromobicyclo[2.2.1]heptanone while V was transformed into *anti*-7-bromobicyclo[2.2.1]heptanone. The latter ketone was independently synthesized from the previously described[12] analogous alcohol.

It is of interest to examine in more detail the nmr spectra of IV and V, and in particular the signals arising from H^2 in each case. As mentioned previously,[3] H^2 in V appeared as a quartet which can now be assigned as $J_{2,3\text{-}trans} = 3.9$ cps and $J_{2,3\text{-}cis} = 8.1$ cps. On the other hand, in IV and in 2-*exo*-hydroxy- and 2-*exo*-bromo-7-*syn*-bromobicyclo[2.2.1]heptane H^2 appears as a triplet. This, of course, means that in these compounds $J_{2,3\text{-}trans} = J_{2,3\text{-}cis}$. In such compounds nonbonded repulsions between the 2-*exo* and 7-*syn* substituents would be expected to lead to a rocking of the C-2 substituent about the C-2,3 bond. The effect of this rocking would be to increase the *cis* and *trans* dihedral angles but to decrease $J_{2,3\text{-}cis}$ and increase $J_{2,3\text{-}trans}$, resulting fortuitously in coupling constants of 6 cps for each of these in V.[10]

The formation of V and the apparent absence of any appreciable amount (94% of the norbornylene consumed was accounted for) of 2-*exo*-bromo-3-*endo*-benzenesulfonamidobicyclo[2.2.1]heptane in the reaction of NNDBS with norbornylene indicate that the carbon-bridged cation VI (see Scheme I) is the reactive intermediate rather than the halogen-bridged cation VII since the latter would be expected to lead with the 2,3-*trans* product. Intermediate IX would likewise satisfactorily account for products IV and V, but, if it were the sole reactive intermediate, it would be difficult to explain the almost 2:1 yield of IV compared with V.[13] An explanation for the 2,6-hydride shift required in the formation of V may be found in the relative sluggishness of the nucleophile ($R^-\ddot{N}SO_2C_6H_5$) involved, which would allow the slow[7] hydride shift to occur before attack of the nucleophile.

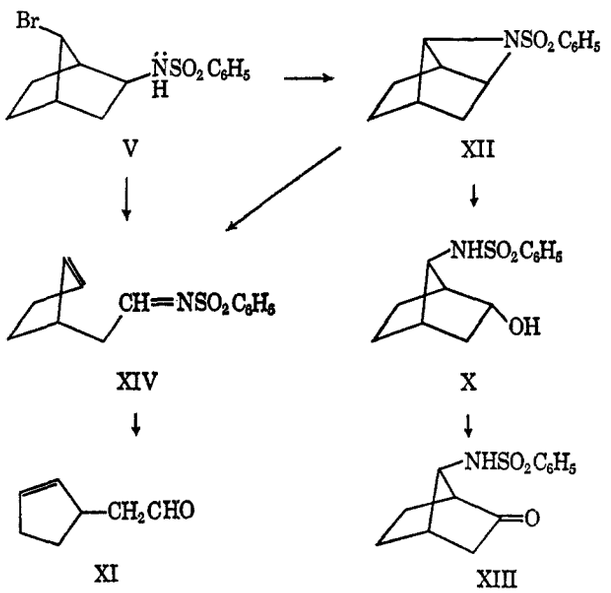
Bromination of bicyclo[2.2.1]heptene with molecular bromine in carbon tetrachloride or in carbon tetrachloride containing pyridine has been shown to yield approximately 15% of the *trans*-2,3 dibromide, but in the more polar solvent almost twice as much of the 2-*exo*-7-*syn* dibromide was formed compared with the less polar solvent.[7,14] It does not appear likely that the absence of any appreciable amount of the *trans*-2,3 product in the present case is a result only of the solvent (benzene) used. All of the reported reactions of bicyclo[2.2.1]heptene with positive bromine reagents can be reconciled if one assumes that the halogen-bridged cation VII is initially formed and this may suffer attack by a relatively good nucleophile such as Br^-, but competing with this is the participation of the electrons of the C-1,6 bond which leads to VI. The more sluggish nucleophiles, such as $H\ddot{N}SO_2C_6H_5^-$, would capture VI, or the further rearranged intermediate VIII. What is postulated is that VII and VI are not in equilibrium[14] and the product distribution is a measure of comparative rates rather than equilibrium distribution of VII and VI. In the present case, nortricyclene bromide is formed rather than a vinylic bromide as observed by Kharasch[6] and Priestley.

As previously mentioned,[2] solvolysis of V gives the rearranged product X, identified by conversion to the known[11] ketone XIII and 3-cyclopentenylacetyldehyde (XI) (Scheme II). The latter product arises by a now familiar fragmentation reaction.[15] In contrast to V, IV was unchanged on refluxing in 5% aqueous alcoholic sodium hydroxide for 60 hr.

The reaction of NNDBS with bicyclo[2.2.2]octene (XV) in benzene at room temperature also led to small amounts of addition products and 8-*syn*-bromobicyclo-[3.2.1]-2-octene (XVI) as the major product. Chrom-

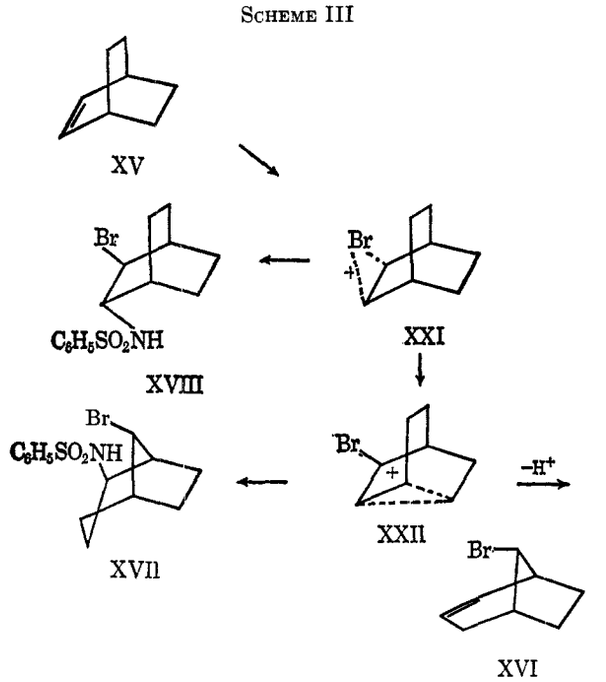
(8) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954).
(9) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **29**, 1625 (1964).
(10) P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).
(11) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).
(12) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5678 (1956).
(13) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).
(14) L. Kaplan, H. Kwart, and P. v. R. Schleyer, *ibid.*, **82**, 2341 (1960).
(15) C. A. Grob, *Gazz. Chim. Ital.*, **92**, 902 (1962).

SCHEME II



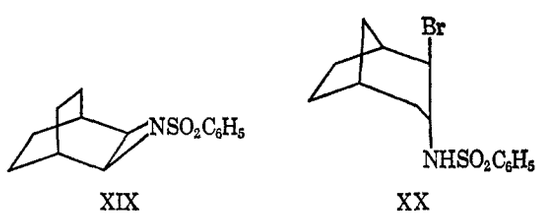
atography of the crude reaction product on alumina led to a ready separation of XVI, which was identified by comparison with an authentic sample,[9] and the addition products which could be separated into individual compounds only by repeated and tedious chromatography. By analogy with the addition of bromine to XV,[16] one might expect XVII and XVIII as products in the present case and indeed products corresponding to these structures were isolated (see Scheme III).

SCHEME III



The nmr spectrum of the least polar of the addition products (XVII) showed a triplet (J = 4 cps) centered at δ 4.08 for the proton attached to the bromine-bearing carbon exactly analogous to the C-8 proton in XVI. Treatment of XVII with aqueous hydrochloric acid in a sealed tube at 175° gave a bromoamine which was subsequently converted into the corresponding dimethylamine oxide. Pyrolysis of the latter gave XVI, thus establishing the skeleton of XVII and the position and stereochemistry of the bromine atom in XVII. Reduction of XVII with sodium in alcohol gave 2-aminobicyclo[3.2.1]octane which upon oxidation gave the known[17] bicyclo[3.2.1]-2-octanone, thus establishing the position of the benzenesulfonamido group in XVII. The stereochemistry of the latter group was established by converting the 2-aminobicyclo[3.2.1]-octane, described above, into its acetate. The 2-acetamidobicyclo[3.2.1]octane thus obtained was shown to be different from 2-*endo*-acetamidobicyclo[3.2.1]-octane obtained by lithium aluminum hydride reduction of the oxime of bicyclo[3.2.1]-2-octanone followed by acetylation. Since reduction of bicyclo[3.2.1]-2-octanone by lithium aluminum hydride is known[17] to yield the equatorial alcohol (*endo*), it can be assumed that reduction of the corresponding oxime, under identical conditions, would proceed in a similar manner. Therefore, the benzenesulfonamido group in XVII must be axial (*exo*), as would be expected on mechanistic grounds.

A second addition product was shown to be XVIII as follows. Reduction of XVIII with sodium in *sec*-butyl alcohol gave 2-aminobicyclo[2.2.2]octane, identified as its acetate, and XVIII was shown to be identical with one of the products obtained in the treatment of aziridine XIX with hydrogen bromide in carbon tetra-



chloride.[18] A third adduct, isolated in extremely low yield, has been tentatively assigned structure XX. Reduction of XX with sodium and alcohol gave an amine which on oxidation gave the known[19] bicyclo-[3.2.1]-3-octanone. This product (XX) undoubtedly arises from the reaction of NNDBS with bicyclo[3.2.1]-2-octene, present as a contaminant[16] in the starting bicyclo[2.2.2]octene.

It is interesting to compare the results obtained in the reaction of NNDBS with norbornylene and with bicyclo[2.2.2]octene, respectively. In the latter case, the formation of the *trans*-2,3 product XVIII indicates the intermediacy of the halogen-bridged cation XXI, in contrast to the former reaction where such an intermediate (VII) was not product forming. The formation of the rearranged product XVII suggests the presence of the carbon-bridged cation intermediate XXII; this is analogous to the formation of IV *via* intermediate VI in the norbornylene reaction. The formation of XVI in the reaction of bicyclo[2.2.2]-octene corresponds to the formation of nortricyclene bromide in the norbornylene reaction. It sould be noted that *no* product arising by a hydride shift,

(16) N. A. LeBel, J. E. Huber, and L. H. Zalkow, *J. Am. Chem. Soc.*, **84**, 2226 (1962).

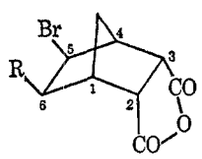
(17) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, **83**, 988 (1961).

(18) Part X: A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965).

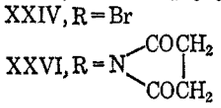
(19) W. R. Moore, W. R. Moser, and J. E. LaPrade, *ibid.*, **28**, 2200 (1963).

as in the formation of V, was detected in the bicyclo[2.2.2]octene reaction, but, owing to the difficulty in isolating the adducts in this case, it cannot be stated categorically that none of such a product was produced. It is not clear whether intermediates XXI and XXII are in equilibrium.

endo-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride was found to react with NNDBS to give the *cis-exo* product XXIII analogous to its reaction with bromine to give XXIV.[20] The yield of XXIII decreased when the molar ratio of alkene to NNDBS was less than 2:1[6] and the reaction was unaffected by free-radical retarders or light.

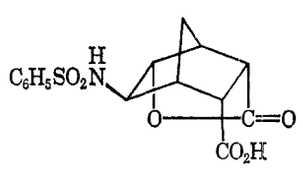


XXIII, R = $NHSO_2C_6H_5$
XXIV, R = Br

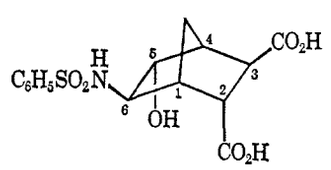


XXVI, R = N(COCH$_2$)(COCH$_2$)

Treatment of XXIII with aqueous sodium carbonate gave the known[20] lactone XXV. The dimethyl ester from XXIII was unaffected under these conditions, indicating that XXV was not formed *via* an intermediate aziridine as might be expected if the bromine atom were *trans* to the sulfonamido group in XXIII.



XXV



XXVII

The formation of XXV firmly established the stereochemistry of the sulfonamido group and strongly suggested that the bromine atom in XXIII was *exo* also. The nmr spectrum of the dimethyl ester from XXIII, obtained by hydrolysis in acetone–water followed by treatment with ethereal diazomethane, provided conclusive evidence for the 5,6-*cis-exo* arrangement. The *endo* C-5 proton appeared as a doublet ($J_{5,6}$ = 7 cps) centered at δ 4.75,[21] and the *endo* C-6 proton appeared as a triplet[21] ($J_{5,6}$ = 7 cps, $J_{6\text{-NH}}$ = 7 cps) centered δ 3.88. In trifluoroacetic acid the C-5 and C-6 protons showed an AB quartet with J = 7 cps. The closely analogous compound XXVI[20] shows a similar AB quartet with J = 7 cps and such couplings are characteristic of *cis-endo* protons in the norbornyl ring system.

When XXIII was refluxed in 20% sodium hydroxide, a hydroxybenzenesulfonamide was obtained which failed to yield a lactone on pyrolysis.[20] The nmr spectrum of the dimethyl ester acetate of this product (the compound itself was insoluble in all common nmr solvents) revealed the proton at C-5 (XXVII acetate dimethyl ester) as a triplet with J = 3.6 cps. Such coupling is characteristic of an *exo* proton and therefore XXVII is tentatively assigned to the product obtained on strong alkaline treatment of XXIII.

(20) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **29**, 1290 (1964).

(21) Each of these signals showed small coupling (J = 2 cps) which presumably arises from coupling with the *anti* C-7 proton.

Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded with a Beckman IR-5 spectrophotometer; nmr spectra were obtained with a Varian A-60 nmr spectrometer, using tetramethylsilane as an internal standard (δ = 0). Carbon and hydrogen analyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind. All gas chromatographs were obtained using an Aerograph Auto-Prep with a thermoconductivity detector.

Reaction of N,N-Dibromobenzenesulfonamide (NNDBS) with Bicyclo[2.2.1]heptene.—To a solution of 20 g of bicyclo[2.2.1]-heptene in 80 ml of dry benzene was slowly added 39.2 g of NNDBS.[22] The addition of NNDBS was continued until aliquots withdrawn from the solution did not decolorize bromine in carbon tetrachloride. After the exothermic reaction subsided (15 min), the benzenesulfonamide which had precipitated was removed by filtration and washed with benzene (9.1 g, mp 151–152°). The combined benzene filtrate and wash was removed through a Vigreux column and the residue was chromatographed on 500 g of Merck acid-washed alumina.

Elution with 700 ml of petroleum ether (bp 50–70°) gave 25 g of bromobicyclo[2.2.1]heptanes. The mixtures of bromides was analyzed by gas chromatography using a 0.25 in. × 9 ft column containing 10% Silicone 550 on acid-washed firebrick at 150°, a helium flow rate of 63 cc/min. The mixture contained 86 ± 3% 3-bromotricyclo[2.2.1.$0^{2,6}$]heptane identified by mixed injection, and 15 ± 3% dibromides of bicyclo[2.2.1]heptane. The benzene removed from the reaction contained another 1–2 g of 3-bromotricyclo[2.2.1.$0^{2,6}$]heptane as detected by gas chromatography.

Elution with 2 l. of benzene and 0.3 (19:1), 0.9 (9:1), and 0.6 l (1:1) of benzene–chloroform gave 13.4 g of IV which crystallized from ethanol and had mp 92–93°; ν_{max}^{KBr} 3225, 1315, 1160, and 1090 cm^{-1}; nmr ($CDCl_3$) δ 1.0–2.0 (4 protons), 2.11 (H^4), 2.30 (H^1), 3.42 (H^2, multiplet; sharpened to a triplet, J = 6.7 cps, upon addition of CF_3COOH), 3.80 (H^7), 5.38 (N–H, doublet, J = 10.5 cps; vanished upon addition of CF_3COOH), and 7.6–8.1 (5 aromatic protons).

Anal. Calcd for $C_{13}H_{16}BrNO_2S$: C, 47.28; H, 4.88. Found: C, 47.33; H, 5.24.

Elution with 0.6 l. of chloroform gave 2.29 g of an oil which thin layer chromatography (10 cm on silica gel G in chloroform) showed to be a mixture of IV and V. Continued elution with 0.4 l. of chloroform gave 6.1 g of V as an oil which crystallized from aqueous methanol and had mp 90–91°; ν_{max}^{KBr} 3300, 1332, 1160, and 1090 cm^{-1}; nmr (in $CHCl_3$) δ 1.0–2.5 (6 protons), 3.22 (H^2, multiplet; sharpened to a quartet, $J_{2,3\text{-}cis}$ = 8.1 cps, $J_{2,3\text{-}trans}$ = 3.9 cps), 4.16 (H^7), and 5.96 (NH, doublet, J = 7 cps; vanished upon addition of CF_3COOH).

Anal. Calcd for $C_{13}H_{16}BrNO_2S$: C, 47.28; H, 4.88. Found: C, 47.52; H, 5.02.

The mixture melting point of IV (mp 92–93°) and V (mp 90–91°) was 75–80°.

Conversion of IV to 2-*exo*-Acetamidobicyclo[2.2.1]heptane.—A solution of 1.38 g of IV in 25 ml of dry *sec*-butyl alcohol was treated with small pieces of metallic sodium (2 g) over a period of 15 min. The reaction mixture was heated to 110° over a period of 2 hr and then stirred at 110° for 6 hr. The solution was then cooled, acidified with 10% hydrochloric acid, and washed with ether. The acidic aqueous solution was then rendered basic by addition of sodium hydroxide solution and extracted with ether. The ether extent, after drying over anhydrous magnesium sulfate, was evaporated to give 0.21 g of 2-*exo*-aminobicyclo[2.2.1]heptane. The N-acetyl derivative was prepared by treatment of the amine with acetyl chloride in pyridine and had mp 138–140° after crystallization from hexane.

Analysis of the acetyl derivative by gas chromatography was performed on a 0.25 in. × 10 ft Craig polyester column at 200° using a helium flow rate of 56 cc/min. The mixed injection of 2-*exo*-acetamidobicyclo[2.2.1]heptane obtained from IV and an authentic sample[11] gave a single peak. Mixed injection of the 2-*endo*-amine acetate[11] and the 2-*exo*-amine acetate gave two peaks at 18.0 and 18.8 min, respectively.

Preparation of 2-*endo*-Acetamidobicyclo[2.2.1]heptane from 2-*endo*-Benzenesulfonamidobicyclo[2.2.1]heptane.—The 2-*endo*-sulfonamide[11] (500 mg) was refluxed for 6 hr in 25 ml of dry *sec*-butyl alcohol containing 1.4 g of metallic sodium. The amine

(22) S. Akiyoski and K. Okuno, *J. Am. Chem. Soc.*, **76**, 693 (1954).

was isolated by the procedure described above and the N-acetyl derivative was prepared with acetic anhydride. The crude acetamide thus prepared was shown to be the 2-*endo* isomer and to be free of the 2-*exo* isomer by gas chromatography.[11] Crystallization from hexane gave a product of mp 129–130°, lit.[11] mp 128–129°.

Conversion of IV to 7-*syn*-Bromo-2-*exo*-aminobicyclo[2.2.1]heptane.—A suspension of 2.01 g of IV in 15 ml of 10% hydrochloric acid was heated in a sealed tube at 175° for 24 hr. The reaction mixture was cooled and washed with ether. The ether extract was decolorized with charcoal, dried over anhydrous magnesium sulfate, and evaporated to give 1.13 g of IV. Evaporation of the acidic aqueous solution gave an oil which crystallized in methanol–ether to give a 46% yield of the hydrochloride of 7-*syn*-bromo-2-*exo*-aminobicyclo[2.2.1]heptane. The amine was liberated by addition of dilute aqueous sodium hydroxide to an aqueous solution of the hydrochloride. The basic solution was extracted with ether which, after drying over anhydrous magnesium sulfate, was evaporated to give the amine as an oil.

Preparation of 7-*syn*-Bromobicyclo[2.2.1]heptanone.—To 215 mg of the amine and 11 mg of $Na_2MoO_4 \cdot 2H_2O$ in 1 ml of water and 1 ml of 30% hydrogen peroxide was added enough methanol to make the mixture homogeneous.[23] The solution was stirred overnight, acidified, diluted with 15 ml of water, and extracted with ether. Addition of acidic, methanolic, 2,4-dinitrophenylhydrazine solution to the ether extract gave a fine crystalline precipitate upon standing, which after three recrystallizations from petroleum ether gave mp 203–203.5°. Mixture melting point with the 2,4-dinitrophenylhydrazone of authentic[9,24] 7-*syn*-bromobicyclo[2.2.1]heptanone was undepressed and the two derivatives gave identical infrared spectra. The two ketones were also identical by gas chromatography.

Conversion of V to 2-*exo*-Acetamidobicyclo[2.2.1]heptanone.—The reduction of V with sodium in alcohol was carried out in 50% yield in the manner described above for the reduction of IV. The amine prepared in this manner gave an N-acetyl derivative (mp 138–140°) which was shown by gas chromatography, as described above, to be identical with authentic[11] 2-*exo*-amino derivative and different from the 2-*endo* isomer.

Conversion of V to 7-*anti*-Bromobicyclo[2.2.1]heptanone.—A suspension of 2.01 g of V in 15 ml of 10% hydrochloric acid was heated at 175° for 48 hr in a sealed tube. The reaction was worked up by the procedure described above for the hydrolysis of IV. No V was recovered and the yield of the 2-*exo*-amine hydrochloride was 12.6% after recrystallization from aqueous methanol, 235–245° dec. The free amine was liberated by addition of the dilute aqueous base to an aqueous solution of the hydrochloride. The aqueous basic solution was extracted with ether which, after drying over anhydrous magnesium sulfate, was evaporated to give 2-*exo*-amino-7-*anti*-bromobicyclo[2.2.1]-heptane as an oil which was directly oxidized without further purification.

Oxidation of 745 mg of the 2-*exo*-amine by the procedure described above gave about 50 mg of crude bromo ketone. A portion of the crude product was treated with excess acidic methanolic 2,4-dinitrophenylhydrazine solution. The 2,4-dinitrophenylhydrazone prepared in this manner was purified by chromatography on Merck acid-washed alumina using benzene as the eluent followed by preparative thin layer chromatography on silica gel G (19 cm) in benzene. Finally, the derivative was crystallized from petroleum ether to give a solid which melted at 116.5–117.5° and then resolidified and remelted at 151.5–152.5°. Mixture melting point with the 2,4-dinitrophenylhydrazone of authentic 7-*anti*-bromobicyclo[2.2.1] heptanone, prepared as described below, was 151.5–152.5°. The two ketones were also shown to be identical by gas chromatography.

Synthesis of Authentic 7-*anti*-Bromobicyclo[2.2.1]heptanone.—The reaction of 2,4-dinitrobenzenesulfenyl bromide with bicyclo-[2.2.1]heptene to give *endo*-3-bromo-*exo*-2-2′,4′-dinitrophenylsulfidobicyclo[2.2.1]heptane (mp 171–173°, lit.[12] mp 173.8–174.8°) was carried out in 87% yield according to the procedure of Kwart and Miller.[12] The nmr spectrum of the product in nitrobenzene showed the proton on carbon bearing the bromine at δ 4.14 as a triplet (J = 4.1 cps) and the proton on carbon bearing the sulfur at δ 3.42 as a quartet ($J_{2,3\text{-}trans}$ = 4.1 cps, $J_{2\text{-}endo\text{-}7\text{-}anti}$ = 2.0 cps).

(23) K. Kohr and C. Berther, *Chem. Ber.*, **93**, 132 (1960).

(24) R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 210 (1964).

Chlorine gas was passed through a slurry of 80 g of the bromodinitrophenyl sulfide in 261 ml of 96% acetic acid for 1 hr.[12] The mixture was stirred overnight and unreacted bromodinitrophenyl sulfide (about 15 g) was removed by filtration. The filtrate was diluted with 250 ml of ice–water and extracted with petroleum ether. The petroleum ether extract was washed with aqueous sodium carbonate solution, dried over anhydrous magnesium sulfate, and evaporated. The residue was fractionally distilled under vacuum to give 2.1 g nortricyclene bromide [bp 35–40° (0.7–0.6 mm)], 10.5 g of 2-*exo*-chloro-7-*anti*-bromobicyclo[2.2.1]heptane [bp 50–52° (0.7 mm), lit.[12] bp 40–52° (0.55 mm)], 10.2 g of a mixture of 2-*exo*-chloro-7-*anti*-bromo- and 2-*exo*-acetoxy-7-*anti*-bromobicyclo[2.2.1]heptane [bp 52–70° (0.7 mm)], and 4.8 g of the latter compound [bp 70–72° (0.7 mm), lit.[12] bp 61–67° (0.6 mm)]. The nmr spectrum of the 2-*exo*-chloro-7-*anti*-bromo derivative in CS_2 showed the signal for the 2-*endo* proton at 3.86 as a quartet ($J_{2,3\text{-}trans}$ = 4.3 cps, $J_{2,3\text{-}cis}$ = 7.5 cps) and the 7-*syn* proton appeare as a tall narrow multiplet. The nmr spectrum of the 2-*exo*-acetoxy-7-*anti*-bromo derivative in CS_2 showed the signal for 2-*endo* proton at δ 4.15 as a quartet ($J_{2,3\text{-}trans}$ = 3.0 cps, $J_{2,3\text{-}cis}$ = 7.5 cps) and the 7-*syn* proton appeared as a tall narrow multiplet.

A solution of 1.5 g of the acetoxy bromide and 0.15 g of lithium aluminum hydride in 25 ml of dry ether was refluxed for 4 hr. The solution was diluted with wet ether, acidified with aqueous 10% hydrochloric acid, and finally extracted with ether. The ether extract, after drying over anhydrous magnesium sulfite, was evaporated to give an oil. The oil was distilled under vacuum to give 1.1 g of 2-*exo*-hydroxy-7-*anti*-bromobicyclo[2.2.1]heptane: bp 75–80° (0.7 mm); nmr (in CS_2) δ 3.68 (H^1, quartet, $J_{2,3\text{-}trans}$ = 2.9 cps, $J_{2,3\text{-}cis}$ = 7.1 cps), 3.76 (O–H, vanished upon addition of D_2O), and 4.14 (H^1, triplet, $J_{7,1\text{-}4}$ = 1.4 cps).

A solution of 806 mg of the 2-*exo*-hydroxy-7-*anti*-bromo derivative in 8 ml of dry acetone was treated with a 0.5 molar excess of Jones reagent.[25] The solution was stirred for 4 hr after which time it was diluted with 40 ml of water and extracted several times with petroleum ether. The petroleum ether extract, after drying over anhydrous magnesium sulfate, was evaporated to give 450 mg of 7-*anti*-bromobicyclo[2.2.1]heptanone: nmr (in CS_2) δ 4.19 (H^7, triplet, $J_{7,1\text{-}4}$ = 1.4 cps). The 2,4-dinitrophenylhydrazone was prepared by addition of excess acidic, methanolic 2,4-dinitrophenylhydrazine solution to the ketone. The derivative was purified by chromatography on Merck acid-washed alumina using benzene as the eluent, followed by preparative thin layer chromatography (19 cm on silica gel G in benzene). The 2,4-dinitrophenylhydrazone crystallized from petroleum ether and had mp 116.5–117.5° (see above for double melting point). The analytical sample was prepared by crystallization from ether and had mp 152–153°.

Anal. Calcd for $C_{13}H_{13}BrN_4O_4$: C, 42.29; H, 3.55. Found: C, 42.60; H, 3.72.

Preparation of 3-*exo*-Bromo- and 3-*endo*-Bromobicyclo[2.2.1]heptanone.—Bicyclo[2.2.1]-2-heptanone was brominated according to the procedure of Woods and Roberts.[26] The bromo ketones obtained were fractionally distilled under vacuum using a 0.25 × 10 in. tantalum spiral column to give the pure 3-*exo*-bromo ketone, mp 25°, bp 80–82° (1 mm) [lit.[26] mp 30°, bp 126.5–128.5° (23 mm)], nmr[27] (neat) δ 3.86 (H^3, doublet, $J_{3,7\text{-}anti}$ = 3 cps).

Heating the 3-*exo*-bromo ketone with 10 g of glacial acetic acid containing 10 g of potassium acetate for 24 hr according to the procedure of Krieger[28] gave a 1:1 mixture of the 3-*exo*-bromo and 3-*endo*-bromo ketones.

Gas Chromatographic Comparisons of Bromobicyclo[2.2.1]heptanones.—All gas chromatographic analyses were performed on a 0.25 in. × 10 ft silicone 550 column at 165° using a helium flow rate of 120 cc/min. The following retention times were observed for the bromobicyclo[2.2.1]heptanones: 7-*anti*-bromo, 15.0 min; 7-*syn*-bromo and 3-*endo*-bromo, 20.8 min; and 3-*exo*-bromo, 18.5 min.

Solvolysis of 7-*anti*-Bromo-2-*exo*-benzenesulfonamidobicyclo-[2.2.1]heptane.—A solution of 603 mg of the bromosulfonamide in 12 ml of aqueous 80% methanol, containing an excess of sodium

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(27) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1963).

(28) H. Krieger, *Suomen Kemistilehti*, **31B**, 175 (1958); *Chem. Abstr.*, **54**, 7769 (1960).

carbonate, was refluxed for 25 hr. The solution was diluted with 15 ml of water and extracted with chloroform. The chloroform extract was evaporated under vacuum into a Dry Ice trap to which acidic, methanolic 2,4-dinitrophenylhydrazine solution was added.

The residue left by evaporation of the chloroform contained a precipitate of 24 mg of benzenesulfonamide (mp 151–152°), which was collected by filtration. The benzenesulfonamide was washed with benzene and the wash was returned to the residue. The combined residues were concentrated and analyzed by thin layer chromatography on silica gel G (15 cm) in chloroform. Major spots were found at R_f values of 0.053 (benzenesulfonamide), 0.30, 0.53, and 0.60. The above mixture was oxidized by the Jones procedure[25] without further purification. The oxidized mixture was chromatographed by preparative thin layer chromatography on silica gel G (15 cm) in 3:1 chloroform–ethyl acetate. Spots were evident at R_f values 0.10, 0.30, and 0.60.

The silica gel containing the major spot (R_f 0.30) was removed and eluted with chloroform. Evaporation of the chloroform eluent and recrystallization of the eluate from ether gave 51 mg of 7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptanone (XIII), mp 146–147°, identical in all respects with an authentic sample.[11]

The contents of the Dry Ice trap were evaporated and the concentrate chromatographed directly on Merck acid-washed alumina. Elution with benzene gave the 2,4-dinitrophenylhydrazone of 3-cyclopentenylacetaldehyde (XI). Crystallization of the eluate from hexane gave 215 mg of the 2,4-DNP: mp 100–101° (lit.[29] mp 98–99°); nmr (in CS_2) δ 1.17–2.13 (2 protons), 2.13–2.58 (4-protons), 2.83–3.22 (1 proton), 4.05 (2 protons), 7.42–8.33 (3 protons), 8.88 (1 proton, doublet, J = 2 cps), and 10.97 (1 proton).

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.97; H, 4.86. Found: C, 53.86; H, 5.14.

Attempted Alkaline Hydrolysis of 7-*syn*-Bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane.—A solution of 2.10 g of the bromosulfonamide in 20 ml of 5% NaOH and 5 ml of 95% ethanol was refluxed for 60 hr. The reaction mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to give back 2.01 g of starting material (mp 90–91°).

Reaction of NNDBS with Bicyclo[2.2.2]octene.—To 30 g of XV in 300 ml of dry benzene were slowly added 44 g of NNDBS. The solution was stirred overnight and the benzene carefully removed through a Vigreux column. The reaction mixture was chromatographed directly on 750 g of Merck acid-washed alumina. Elution with benzene–petroleum ether (1:1) gave 21 g of *endo*-8-bromobicyclo[3.2.1]octene (XVI), bp 65–70° (5 mm) (95% pure by gas chromatography). Elution with benzene and benzene chloroform mixtures gave 4.7 g of a mixture of adducts. Thin layer chromatography of this mixture on silica gel G in chloroform showed spots at R_f 0.40, 0.30 0.27, and 0.17. Elution with 9:1 chloroform–methanol gave 7.1 g of benzenesulfonamide (mp 151–152°). The crude mixture of adducts obtained above was chromatographed repeatedly on alumina varying the polarity of the elutent from petroleum ether to benzene to chloroform. The benzene eluates were oils from which XVII (R_f 0.40) crystallized from cold ether and had mp 99–100°; ν_{max}^{KBr} 3230, 1325, 1160, 753, 721, and 792 cm^{-1}; nmr (in $CHCl_3$) δ 3.45 (H^2, multiplet), 4.08 (H^8, triplet J = 4 cps), and 6.32 (NH, doublet, J = 5.4 cps).

Anal. Calcd for $C_{14}H_{18}BrNO_2S$; C, 48.84; H, 5.27. Found: C, 49.14; H, 5.67.

Thin layer chromatography of the benzene-chloroform eluates on silica gel G in chloroform showed XVIII (R_f 0.30) and XX (R_f 0.27) poorly resolved. Fractions consisting mostly of XVIII were combined and upon standing in the cold XVIII crystallized from ethanol. After several recrystallizations it had mp 135–136° and was identical in all respects with an authentic sample.[18] The third adduct XX (R_f 0.27) crystallized from fractions rich in it upon standing in the cold in ethanol. Three recrystallization from ethanol gave XX: mp 189–190°; ν_{max}^{KBr} 3270, 1310, 1160, 1080, 970, 753, 725, and 688 cm^{-1}; nmr (in $CHCl_3$) δ 1.42–2.50 (10 protons), 3.25 (H^3, multiplet; sharpened to triplet, J = 6.5 cps, upon addition of CF_3COOH), 3.98 (H^2, multiplet), and 5.62 (NH, doublet, J = 5 cps, disappeared upon addition of CF_3COOH).

Anal. Calcd for $C_{14}H_{18}BrNO_2S$: C, 48.84; H, 5.27. Found: C, 49.29; H, 5.39.

The chloroform eluates gave mixtures of XVIII, XX, and a third minor component (R_f 0.17) which could not be separated by chromatography or crystallization.

Conversion of XVII to Axial 2-Acetamidobicyclo[3.2.1]octane.—A solution of 1.42 g of XVII in 30 ml of dry *sec*-butyl alcohol was treated with 3 g of metallic sodium over a period of 0.5 hr. The reaction mixture was refluxed for 4 hr and worked up in the usual manner to yield 452 mg of axial 2-aminobicyclo[3.2.1]octane as a waxy solid. The N-acetyl derivative was prepared with acetic anhydride and after crystallization from ether–petroleum ether had mp 122–123°. Repeated recrystallizations did not raise the melting point; ν_{max}^{KBr} 3280, 1645, 1565, 1195, and 1040 cm^{-1}.

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.24. Found: C, 71.64; H 10.43.

Preparation of Equatorial 2-Acetamidobicyclo[3.2.1]octane.—A suspension of 0.4 g of lithium aluminum hydride in 40 ml of ether containing 0.8 g of bicyclo[3.2.1]-2-octanone oxime, prepared by a known procedure,[30] was stirred overnight. After the excess hydride was destroyed, the solution was made acidic with dilute hydrochloric acid. The acidic aqueous solution was washed with ether, then made basic and extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to give 271 mg of equatorial 2-aminobicyclo-[3.2.1]octane as a waxy solid. The N-acetyl derivative, prepared with acetic anhydride, after crystallization from ether–hexane had mp 137–138°. Repeated recrystallizations did not raise the melting point; ν_{max}^{KBr} 3280, 1646, 1550, 1122, 1085, 944, and 910 cm^{-1}. The infrared spectra of the axial and equatorial isomers were different; the mixture melting point of the two was 128–131°.

Preparation of Bicyclo[3.2.1]-2-octanone from XVII.—Oxidation of 104 mg of the amine obtained by reduction of XVII as described above by the procedure described earlier gave a low yield of crude ketone. A portion of the crude product was treated with excess acidic, methanolic 2,4-dinitrophenylhydrazine solution. The derivative was purified by chromatography on Merck acid-washed alumina using benzene as the eluent. The hydrazone crystallized from ether and had mp 137–138°. The 2,4-dinitrophenylhydrazone thus obtained was identical with an authentic sample.[31]

Degradation of XVII to *endo*-8-Bromobicyclo[3.2.1]-2-octene (XVI).—A suspension of 2.05 g of XVII in 15 ml of 10% hydrochloric acid was heated at 175° in a sealed tube for 24 hr. The reaction mixture was cooled and the acidic solution was washed twice with chloroform. Evaporation of the acidic aqueous solution gave 125 mg of bromoamine hydrochloride. The bromoamine was isolated by treatment of the hydrochloride salt with dilute aqueous base followed by ether extraction of the basic aqueous solution. The ether extract, after drying over anhydrous magnesium sulfate, was carefully evaporated to give 105 mg of bromoamine which was used without further purification. The bromoamine (105 mg) was stirred with 120 mg of 90% formic acid and 90 mg of 40% formaldehyde for 24 hr at room temperature and then for 2 hr on a steam bath.[32] Dilute hydrochloric acid was added to the solution and the excess formic acid and formaldehyde were removed by distillation. The concentrate was diluted with 5 ml of water and washed with several portions of chloroform. The acidic aqueous solution was made basic and the aqueous sodium hydroxide solution was extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to give 53 mg of bromo-N,N-dimethylamine as a light brown oil. The crude bromo-N,N-dimethylamine was treated with 1 ml of 30% hydrogen peroxide in 1 ml of methanol for 12 hr at room temperature. The excess peroxide was destroyed by treatment of the alcoholic solution with a small amount of 5% platinum on charcoal. The catalyst was removed by filtration and evaporation of the filtrate *in vacuo* gave 39 mg of bromo-N,N-dimethylamine oxide as a viscous oil.

The N,N-dimethylamine oxide (39 mg) was heated over a period of 0.75 hr to 135° and maintained at that temperature for 0.5 hr under 30–40 mm, during which time 12 mg of an oil distilled. Gas chromatographic analysis of the distillate on a 0.25 in. × 10 ft Craig polyester column at 135° using a helium

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flow rate of 74 cc/min showed *endo*-8-bromobicyclo[3.2.1]-2-octene (XVI) as the major component (95%), identified by mixed injection with an authentic sample.[9] Analysis on a 0.125 in. × 10 ft silicone rubber column at 80° using a nitrogen flow rate of 40 cc/min also showed XVI as the major component by mixed injection.

Reduction of XVIII with Sodium in Alcohol.—A solution of 2.1 g of XVIII in 42 ml dry *sec*-butyl alcohol was slowly treated with 3.4 g of metallic sodium. The reaction mixture was heated to 110° and refluxed for 6 hr. After cooling, the reaction mixture was acidified with 10% hydrochloric acid and washed with ether. The acidic aqueous solution was made basic and the product extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to give a mixture of amines. The amine mixture was treated with acetic anhydride and the amine acetates (mixture) isolated in the usual manner. The nmr spectrum of the crude acetylated mixture showed that >90% of the acetylated product possessed a secondary halogen function. Gas chromatography of the crude acetylated mixture on a 0.25 in. × 10 ft silicone nitrile column at 220° using a helium flow rate of 100 cc/min showed only a single peak with a retention time less than 25 min. Under these conditions 2-acetamidobicyclo[2.2.2]octane prepared from the corresponding amine[18] by the usual method had a retention time identical with the amine acetate derived from XVIII.

Conversion of XX to Bicyclo[3.2.1]-3-octanone.—Reduction of 430 mg of XX with sodium in alcohol by the usual procedure gave 102 mg of amine as a waxy solid. The amine thus obtained was oxidized with 30% hydrogen peroxide in the presence of $Na_2MoO_4 \cdot 2H_2O$ in aqueous methanol. After acidification of the oxidation reaction solution with dilute hydrochloric acid, the aqueous solution was extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to give 15 mg of bicyclo[3.2.1]-3-octanone. Gas chromatographic analysis of the crude ketone on a 0.02 in. × 150 ft ECNSS-S column showed one major component (about 95%). Mixed injection of a mixture of bicyclo[3.2.1]-2-octanone and bicyclo[3.2.1]-3-octanone prepared by hydroboration of bicyclo[3.2.1]-2-octene[33] showed the ketone derived from XX to be identical with bicyclo[3.2.1]-3-octanone and different from bicyclo[3.2.1]-2-octanone. The ketone derived from XX was also shown to be identical with bicyclo[3.2.1]-3-octanone and different from bicyclo[2.2.2]-2-octanone by mixed injection on a 0.25 in. × 10 ft silicone nitrile column at 220° using a helium flow rate of 115 cc/min. The 2,4-dinitrophenylhydrazone of bicyclo[3.2.1]-3-octanone derived from XX had mp 163–164° (lit.[19] mp 165–166.2°).

The Reaction of NNDBS with *endo*-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic Anhydride.—A mixture of NNDBS (4.53 g), the unsaturated anhydride (5.86 g), and carbon tetrachloride (100 ml) were stirred together at room temperature for 5 min, then heated, with stirring, to reflux; the reaction mixture continued to reflux, after removal of external heat, for several minutes. As the reaction proceeded during the reflux period a light tan viscous oil precipitated. The mixture was then concentrated with a rotary evaporator. Chloroform (50 ml) was added to the residue and the solution was again concentrated until the residue began to foam; this procedure was repeated twice more to remove as much of the carbon tetrachloride as possible and finally the residue was dissolved in 50 ml of chloroform and allowed to stand at room temperature, open to the atmosphere, for 12–18 hr. The product XXIII crystallized during this period (1.59 g, mp 228–230°). Recrystallization from acetyl chloride and drying at 144° and 1 mm gave the analytical sample: mp 230–233°; ν_{max}^{KBr} 3250, 1760, and 1778 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}BrNO_5S$: C, 45.01; H, 3.53; Br, 19.97. Found: C, 45.16; H, 3.66; Br, 20.42.

When the above procedure was repeated using as free-radical traps anthracene (0.25 g), *p*-dinitrobenzene (0.25 g), chloranil (0.75 g), or oxygen (bubbled through the reaction mixture) there was no significant change in yield of product. Likewise, running the reaction in the dark produced the same product in essentially identical yield. The same product was also produced on stirring the reactants together in carbon tetrachloride at room temperature for 7 days.

The diacid was prepared by heating anhydride XXIII (0.50 g) with water (10 ml) and acetone (10 ml) until the compound dissolved. On cooling, the diacid precipitated, 0.33 g, mp 198–200°, ν_{max}^{KBr} 3250 and 1720 cm^{-1}. The diacid gave a positive Beilstein test for halogen.

Anal. Calcd for $C_{15}H_{16}BrNO_6S$: N, 3.14. Found: N, 3.05.

The corresponding dimethyl ester was prepared by treating the diacid with excess ethereal diazomethane. By allowing the ether solution to slowly evaporate in air, the dimethyl ester crystallized from solution, mp 130–130.5°. Recrystallization from ether did not raise the melting point. An analytical sample was prepared by drying the dimethyl ester for 5 hr at 100° and 1 mm: ν_{max}^{KBr} 3220, 1738, and 1723 (sh) $cm.^{-1}$

Anal. Calcd for $C_{17}H_{20}BrNO_6S$: C, 45.74; H, 4.51; N, 3.13. Found: C, 45.97; H, 4.94; N, 3.05.

The Conversion of XXIII to XXV.—Anhydride XXIII (0.5 g) and aqueous 5% sodium carbonate (20 ml) were refluxed for 45 min. The hydrolysis solution was then made acidic with excess concentrated hydrochloric acid (approximately 5 ml) and continuously extracted with ether for 12 hr. Concentration of the ether extract to a small volume (~5 ml) yielded XXV (0.27 g): mp 188–190°); ν_{max}^{KBr} 3240, 1780, and 1703 cm^{-1}. The melting point was raised to 193.5–194.5° by washing the crystals with a small amount of ether. The lactone thus obtained was identical in all respects with an authentic sample.[20]

The Reaction of XXIII with Strong Base.—Anhydride XXIII (0.50 g) and aqueous 20% sodium hydroxide (25 ml) were refluxed for 2 hr. The hydrolysis solution was acidified with excess concentrated hydrochloric acid. Continuous extraction of the acidic solution with ether for 12 hr followed by evaporation of the ether yielded XXVII as white platelike crystals (0.31 g): mp 235–235.5°; ν_{max}^{KBr} 3380, 3220, 2500–3000, and 1700 cm^{-1}. Diacid XXVII gave a negative Beilstein test and a neutralization equivalent of 179.6 (calcd for two carboxyls and $C_{15}H_{17}NO_7S$. 177.7).

Anal. Calcd for $C_{15}H_{17}NO_7S$: C, 50.70; H, 4.68; N, 9.01. Found: C, 50.71; H, 4.68; N, 9.05.

The dimethyl ester was prepared by treatment with ethereal diazomethane and this was transformed into the corresponding acetate, mp 142–144° from ether–petroleum ether, by heating with acetic anhydride and pyridine at 110° for 12 hr.

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