for the thermal dimerization). Freshly distilled dimers were separated into two fractions at 90° by preparative v.p.c. on a Megachrom apparatus, equipped with eight 6 ft. × 5/8 in. columns packed with 35% Apiezon J. The two separated fractions consisted of a mixture of two stereoisomers, *exo*-dicyclopentadiene (**13**) and *endo*-dicyclopentadiene (**12**), and pure *trans*-tricyclo[5.3.0.0^{2,6}]-3,9-decadiene (**14**). The two stereoisomers were separated by preparative v.p.c. employing a single 6 ft. × $^5/_8$ in. β,β'-oxydipropionitrile column in the Megachrom. The *endo*-dicyclopentadiene produced in the photodimerization had b.p. 170–172°, n^{25}D 1.5080, and infrared and n.m.r. spectra identical with those of an authentic sample prepared by the method of Bartlett and Goldstein.[15] *trans*-Tricyclo[5.3.0.0^{2,6}]-3,9-decadiene had b.p. 170–172°, n^{25}D 1.5080.

Hydrogenation of *trans*-Tricyclo[5.3.0.0^{2,6}]-3,9-decadiene 14.—A 0.5-g. sample of the dimer, **14**, contaminated with about 20% of *endo*-dicyclopentadiene was dissolved in 5 ml. of 95% ethanol and then placed in a 25-ml. hydrogenation flask. Platinum dioxide (50 mg.) was added and the mixture was treated with hydrogen gas (uptake 170 ml.). The mixture was then filtered and concentrated. Analysis by v.p.c. on a β,β'-oxydipropionitrile column at 80° showed that the diene had been completely converted and a compound of considerably shorter retention time was detected. This compound was obtained pure by preparative v.p.c. The material did not decolorize a solution of bromine in carbon tetrachloride or an aqueous solution of potassium permanganate. The infrared and n.m.r. spectra of the saturated material were identical with those of the hydrocarbon produced by Wolff–Kischner reduction of *trans*-tricyclo[5.3.0.0^{2,6}]-3,8-decanedione.[16]

***trans*-Ditosyloxytricyclo[5.3.0.0^{2,6}]-3,8-decane.**—Tricyclo-[5.3.0.0^{2,6}]-3,8-decanedione was prepared by the method of Eaton.[16] A 10.0-g. sample was dissolved in 250 ml. of 95% ethanol and cooled in an ice bath. A solution of 5.0 g. of sodium borohydride in 20 ml. of 0.1 *N* aqueous sodium hydroxide was then added slowly. An exothermic reaction occurred and the mixture became cloudy. After 2 hr. of stirring with cooling, the mixture was concentrated to 50 ml. and diluted with 20 ml. of cold water. The alcohol was exhaustively extracted with ether and methylene chloride. The extracts were combined, dried, and concentrated until crystals appeared. The crystals were filtered and dried; m.p. 193–194°; yield, 8.0 g.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.50; H, 9.54. Found: C, 71.88; H, 9.66.

The spectrum of a potassium bromide pellet showed a broad alcohol band at 3200 cm.$^{-1}$. The diol (1.0 g.) was dissolved in pyridine (15 ml.) and cooled in an ice bath. A solution of 3.0 g. of tosyl chloride dissolved in 15 ml. of pyridine was added to the stirred solution. After 5 hr. of stirring the mixture was left overnight in the refrigerator. The mixture was then poured into cold 1 *N* sulfuric acid and crystals appeared. The crystals were washed with pentane and then recrystallized from hexane; m.p. 158–159° dec.; yield, 1.8 g.

Anal. Calcd. for $C_{24}H_{28}S_2O_6$: C, 60.50; H, 5.92; S, 13.43. Found: C, 59.44; H, 5.88; S, 13.54.

***trans*-Tricyclo[5.3.0.0^{2,6}]-3,8-decadiene (15).**—Potassium was dissolved in freshly distilled *t*-butyl alcohol (20 ml.) under nitrogen. A 1.5-g. sample of the tosylate was added slowly to the solution and the mixture was heated under reflux overnight. Cold water (100 ml.) was added to the cooled solution. The mixture was filtered and the aqueous filtrate was extracted three times with pentane. The extract was dried and concentrated to yield 80 mg. of product. The product was obtained pure by preparative vapor chromatography on a β,β'-oxydipropionitrile column. The pure material had a retention time longer than that of the tricyclodiene produced in the photoreaction and could be separated from the latter.

***trans*-Ditosyloxytricyclo[5,3,0,0^{2,6}]-3,9-decane.**—Tricyclo-[5.3.0.0^{2,6}]-3,9-decanedione was separated from the mixture of cyclopentenone photodimers according to the method of Eaton[16] and reduced with sodium borohydride by the procedure described previously for the preparation of the isomeric diol. The diol was purified by continuous extraction with ether in a Soxhlet apparatus; m.p. 168–170°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 71.50; H, 9.54. Found: C, 71.16; H, 9.68.

The tosylate of this diol was prepared as described previously. The crude tosylate was extracted three times with benzene and then recrystallized from hexane; m.p. 119–120°.

Anal. Calcd. for $C_{24}H_{28}S_2O_6$: C, 60.50; H, 5.88; S, 13.43. Found: C, 60.58; H, 6.12; S, 12.60.

***trans*-Tricyclo[5.3.0.0^{2,6}]-3,9-decadiene (14).**—Four grams of the tosylate was added to a refluxing solution of 4 g. of potassium in 35 ml. of *t*-butyl alcohol (under nitrogen). The mixture was analyzed after 5 hr. by v.p.c. on a β,β'-oxydipropionitrile column and a product was found with retention time identical with that of the tricyclodecadiene produced in the photodimerization of cyclopentadiene. The yield calculated from the v.p.c. data was 0.6 g. The material was obtained pure by preparative chromatography on a β,β'-oxydipropionitrile column. It possessed infrared and n.m.r. spectra identical with those of the tricyclic dimer.

The Reaction of Benzenesulfonyl Azide with Bicyclo[2.2.1]-2-heptene

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Benzenesulfonyl azide has been found to react with bicyclo[2.2.1]-2-heptene at room temperature in an inert solvent to give a product II, in excellent yield, arising from the addition of the azide to the alkene followed by loss of molecular nitrogen. The nitrogen-containing ring of II was readily opened with hydrogen bromide, hydrogen chloride, acetic acid, and neutral, acidic, and alkaline aqueous solutions to give 7-benzenesulfonamidobicyclo[2.2.1]heptane derivatives. N-Acetyl, chloroacetyl, and benzenesulfonyl derivatives of 7-aminobicyclo-[2.2.1]heptane prepared from II were shown not to be identical with similar derivatives of 2-*exo*- and 2-*endo*-aminobicyclo[2.2.1]heptane by melting point, infrared spectra, and thin layer and gas chromatography. Two possible structures, the aziridine A and the azetidine C, are consistent with the chemical data. The azetidine structure C is suggested for the product on the basis of n.m.r. comparisons and base-catalyzed opening of the nitrogen-containing ring ultimately to yield 7-aminobicyclo[2.2.1]heptane.

Over fifty years ago phenyl azide was reported to react with acetylene to give 1-phenyltriazole, on heating the reactants in an acetone solution in a sealed tube at 100° for 20 hr.[3] Later it was found that bicyclo-[2.2.1]-2-heptene and its derivatives react with phenyl azide in the cold to form triazolines which usually crystallized from the solution after only a few minutes.[4] Since only strained alkenes were found to react readily with phenyl azide, the reaction soon became a diagnostic test for angular strain in double bonds. Recently, Huisgen and his associates[5] have found that this reac-

(1) National Science Foundation Undergraduate Research Participant, Oklahoma State University, summer, 1962.

(2) National Defense Education Act Fellow, 1962–1965.

(3) O. Dimroth and F. Fester, *Ber.*, **43**, 2219 (1910).

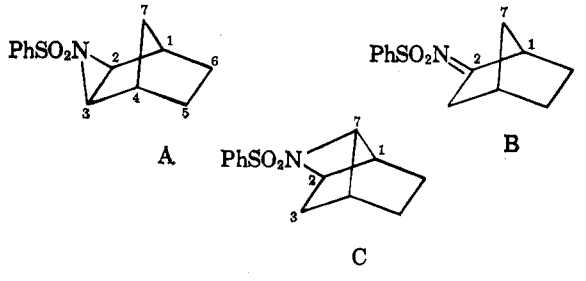
(4) K. Alder and G. Stein, *Ann.*, **485**, 211 (1931); **501**, 1 (1933).

(5) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).

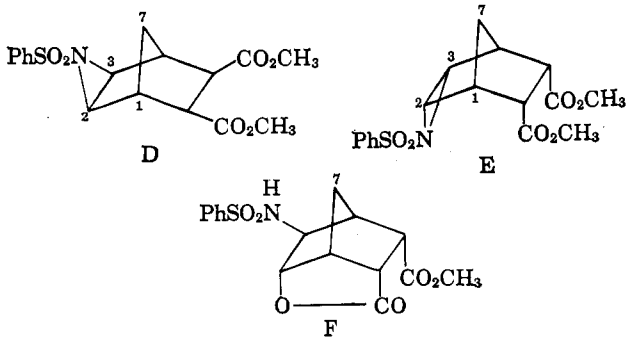
tion is only one member of a large group of reactions which they refer to as "1,3-dipolar cycloadditions."

Bruner[6] recently found that *p*-toluenesulfonyl azide also reacts with strained alkenes such as dicyclopentadiene, bicyclo[2.2.1]-2-heptene, and *endo*- and *exo*-bicyclo[2.2.1]-2-heptene-5,6-dicarboxylic anhydride to give products having analyses corresponding to the addition of a mole of the azide to one mole of the alkene followed by the loss of a mole of nitrogen from the adduct. He, however, provided no chemical evidence to support structures for any of the aforementioned products, but suggested that the dicyclopentadiene derivative possessed the sulfonimide ($C_6H_5SO_2N{=}C<$) structure.

We have investigated the reaction of benzenesulfonyl azide with bicyclo[2.2.1]-2-heptene at room temperature. When benzenesulfonyl azide was added to bicyclo[2.2.1]-2-heptene in benzene or petroleum ether at room temperature, an exothermic reaction occurred with evolution of nitrogen, and the product, which could be isolated in quantitative yield, began to crystallize from the solution almost immediately. The infrared and n.m.r. spectra of the product of the reaction, II, showed that it contained the benzenesulfonamido group, but no N–H band appeared to be present. The three structures, A, B, and C are consistent with the elemental and spectral data and may be expected on mechanistic and steric grounds. Structure B could be



eliminated by examination of the n.m.r. spectrum of II which showed two protons on carbon attached to the nitrogen atom of the benzenesulfonamido group. The two bicyclic aziridines D and E[7] showed signals for the protons at C-2 and C-3 as triplets (J = 2 c.p.s.) centered at δ 3.50 and δ 3.63, respectively, whereas in II the corresponding signal appeared as a sharp singlet much further upfield (δ 2.84). If the correct structure



of II is C, then it is surprising that the C-2 and C-7 protons appear equivalent and that the *endo* C-2 proton is not split by the C-3 *endo* proton. In D and E the C-7 protons appeared as a pair of doublets (J = 10–11 c.p.s.) centered at δ 1.92, 2.32 and δ 1.53, 2.00, respectively. An examination of the n.m.r. spectrum of II reveals only one possibility of a similar AB type splitting to that observed above for the C-7 protons and this is the following: a doublet (J = 10 c.p.s.) centered at δ 0.70 could be assumed to arise from one of the protons at C-7 of A, and the second doublet arising from the other C-7 proton, since it is not obvious, could be assumed to be hidden in the complex group of peaks at δ 1.2–1.6. The signal at δ 0.70 seems to appear at too high field to arise from one of the C-7 protons of A. An examination in our laboratory of a large number of norbornane derivatives containing the sulfonamido and related groups, such as D, E, and F, failed to show any compounds in which the C-7 protons appeared at such a high field.[7] For example, in F, the C-7 proton at highest field showed a doublet (J = 12 c.p.s.) centered at δ 1.84.[7] The signal centered at δ 0.70 in the spectrum of II may arise from one of the C-3 protons of structure C. Although the n.m.r. spectrum of II does not allow an unambiguous decision between structures A and C, we feel the total weight of evidence favors structure C.[8]

In order to distinguish chemically between structures A and C, cleavage of the nitrogen-containing ring to give a benzenesulfonamido derivative seemed appropriate. Structure A would lead to a 2-amido derivative, whereas the 7-amido derivative would be expected from C, since displacement should occur at C-2 rather than at C-7.[9] Bruner[6] reported that the adduct formed between dicyclopentadiene and *p*-toluenesulfonyl azide was unchanged with alcoholic potassium hydroxide and hot glacial acetic acid, whereas strong mineral acids gave unidenitfiable products. We have found that the nitrogen-containing ring of II was readily opened with hydrogen bromide and hydrogen chloride in carbon tetrachloride, with acetic acid and with neutral, acidic and alkaline aqueous solutions as shown in Scheme I. Opening of the nitrogen-containing ring of II under acidic conditions does not provide suitable evidence for use in distinguishing between structures A and C, since under carbonium ion conditions both structures could lead to the same 7-amido derivatives as shown on p. 3305, col. 1, top.

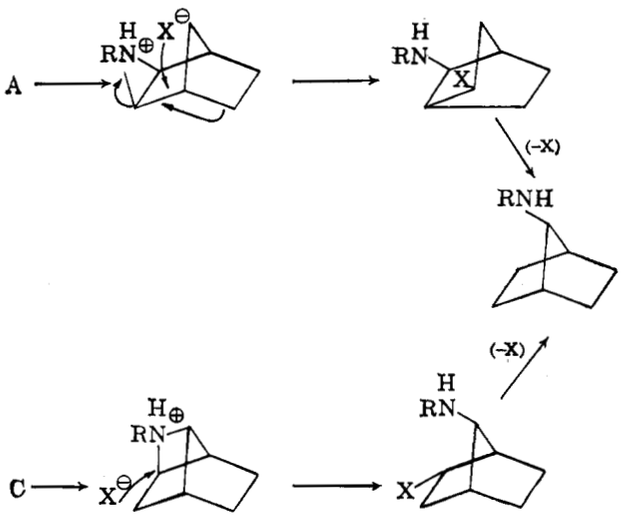
When the nitrogen-containing ring of II was opened by neutral and alkaline aqueous solution, the major product was the same alcohol (IIIα, m.p. 142–144°) as isolated in the acid-catalyzed ring opening. This alcohol also was obtained by treating II with acetic acid followed by saponification. In addition, a second alcohol (IIIβ) was obtained in the neutral, acid, and alkaline hydrolysis but only to a minor extent, except in the acidic hydrolysis. Both N–H and O–H bands were clearly visible in the infrared spectrum of IIIα. Oxidation of IIIα with chromic anhydride in acetic acid gave ketone IV. The latter ketone was also obtained from the bromide VII, itself obtained by treating II with hy-

(6) L. Bruner, *Dissertation Abstr.*, **19**, 438 (1958).

(7) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **28**, 3309 (1963).

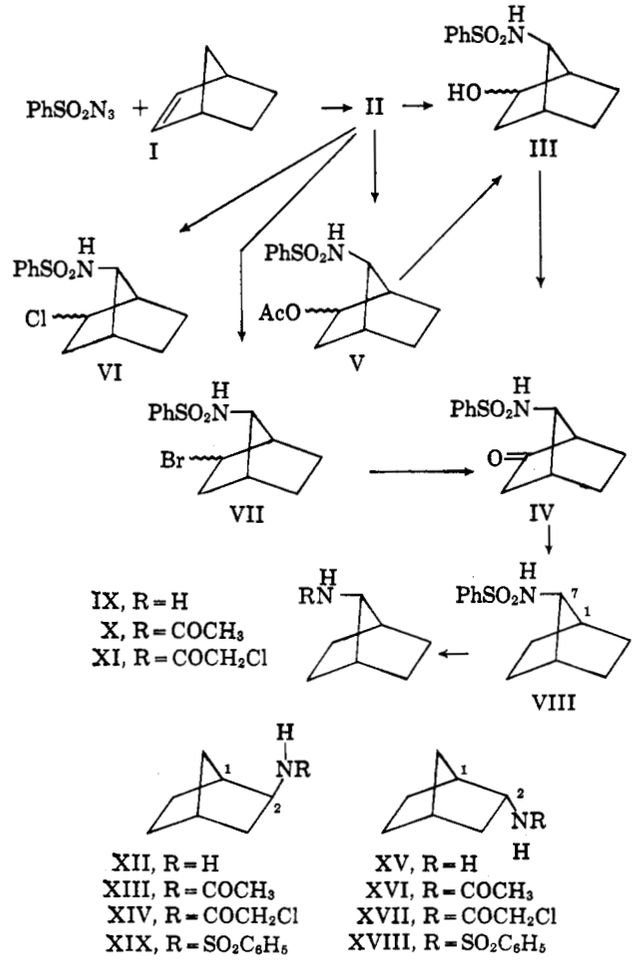
(8) After the submission of this paper, Franz and Osuch [*Tetrahedron Letters*, No. **13**, 837 (1963)] reported the preparation of II, under different conditions, and assigned structure A to the adduct because of the correspondence of the n.m.r. spectrum of *exo*-2,3-epoxynorbornane with that of II. These authors pointed out that identical chemical shifts were observed, except for the aromatic protons, in the two cases. In view of our n.m.r. studies,[7] we suggest that this identity is purely fortuitous.

(9) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, pp. 334–336.



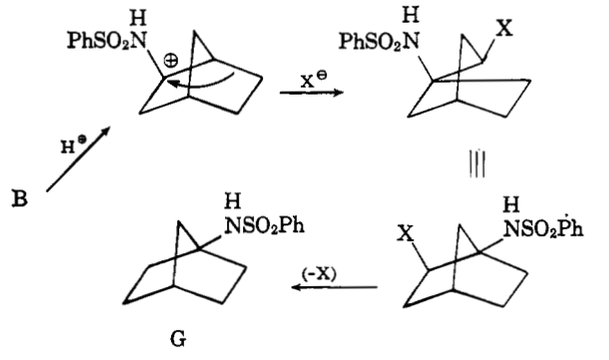
drogen bromide, by hydrolysis with aqueous lithium carbonate solution followed by oxidation with chromic anhydride. Compound IV showed an N–H band at 3130 cm.$^{-1}$ and a carbonyl band at 1725 cm.$^{-1}$ in its infrared spectrum, indicating that the carbonyl function was in a six-membered ring. Wolff–Kishner reduction of ketone IV gave 7-benzenesulfonamidobicyclo[2.2.1]-heptane (VIII). That the benzenesulfonamido group was attached at C-7 was shown as follows. Both 2-*exo*- and 2-*endo*-aminobicyclo[2.2.1]heptane were prepared by known procedures and converted into their N-benzenesulfonyl derivatives. Melting point comparisons

SCHEME I



of the N-benzenesulfonyl derivatives were not found useful. However, thin layer chromatography showed that VIII was not identical with either 2-*endo*-benzenesulfonamidobicyclo[2.2.1]heptane (XVIII) or 2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane (XIX) and was less polar than either of these two isomers. Sulfonamide VIII was hydrolyzed with aqueous hydrochloric acid by heating at 150–175° in a sealed tube for 12 hr. The amine IX thus obtained was converted into its N-acetyl derivative X, which was compared with 2-*exo*-acetamidobicyclo[2.2.1]heptane (XIII) and 2-*endo*-acetamidobicyclo[2.2.1]heptane (XVI) by melting point and gas chromatography. Again melting point comparisons were not conclusive, but gas chromatographic analysis showed that X was less polar than either the 2-*exo* or 2-*endo* isomer.

The N-chloroacetyl derivatives of 2-*exo*-, 2-*endo*-, and 7-aminobicyclo[2.2.1]heptane were reported to have significantly different melting points, and, therefore, this derivative was also prepared in each case. The melting point of the N-chloroacetyl derivative of IX (XI) checked closely for that reported for the 7-amino derivative. Mixture melting points with the 2-*exo* and 2-*endo* isomers again, although slightly depressed, were not conclusive. Thin layer chromatography showed that XI was not identical with *exo*- (XIV) or *endo*-N-2-chloroacetylamidobicyclo[2.2.1]heptane (XVII). This evidence conclusively established that the nitrogen-containing moiety of VIII and its derivatives was not attached at positions 2, 3, 5, or 6 of the bicyclo[2.2.1]heptane nucleus; this leaves only position 7 and the bridgehead positions as possibilities. Mechanistically, attachment at the bridgehead position seems unlikely although one can visualize a 1-aminobicyclo[2.2.1]heptane derivative arising from structure B as follows.

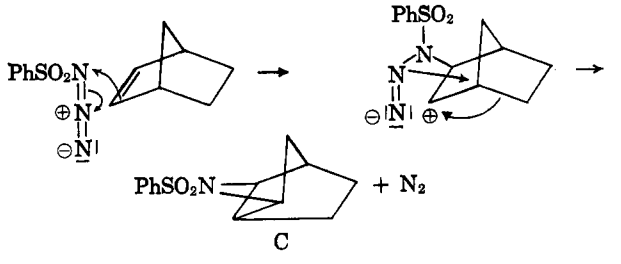


That VIII was not represented by structure G was shown by its n.m.r. spectrum which clearly indicated that the nitrogen-containing moiety was attached to a carbon containing one proton. This proton appeared as a doublet (J = 5 c.p.s.) centered at δ 3.01, splitting arising from the hydrogen attached to nitrogen which itself appeared at δ 5.93 (doublet, J = 5 c.p.s.).

These data can be interpreted in two ways. First, one can assume that the correct structure of II is A and that in neutral and even in alkaline solution the aziridine ring slowly opens in an SN1 reaction with skeletal rearrangement to give III. In such a case the hydroxyl group of III may be either *exo* or *endo*. If the correct structure of II is A, the ring opening to yield III should not be base catalyzed (SN2) since this would lead not to III, but to 2-*exo*-benzenesulfonamido-3-*endo*-hy-

droxybicyclo[2.2.1]heptane. The second interpretation is that the correct structure of II is C, and the azetidine ring is opened either by SN1 or SN2 solvolysis to yield III. In an SN1 solvolysis the hydroxyl group in III might be either *exo* or *endo*, but in an SN2 solvolysis it would be *endo*. In this case the ring opening to yield III (with *endo* hydroxyl group) would be base catalyzed.

In order to test these two possibilities it was necessary first to examine carefully product III obtained in the hydrolytic ring opening of II. The alcoholic products obtained in the neutral, acidic, and alkaline hydrolyses were compared by thin layer chromatography. In each case mixtures were obtained, but in neutral and alkaline solutions one product, IIIα, was by far predominant. As mentioned earlier, oxidation of IIIα, gave IV, which contains the benzenesulfonamido group at C-7. A second isomeric alcohol, IIIβ, obtained to only a minor extent in the neutral and alkaline solvolyses, was present to a very large extent in the acid hydrolysis product. Oxidation of IIIβ likewise gave IV. The structures of IIIα and IIIβ must, therefore, be 2-*endo*- and 2-*exo*-hydroxy-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane, respectively. Base catalysis (we thank the referee for suggesting that we demonstrate this) was demonstrated in the ring-opening reaction by measuring the extinction of the N–H peak in product III by infrared spectroscopy, using various base concentrations and water. Demonstration of base catalysis with concomitant formation of increasing amounts of IIIα strongly suggests that the correct structure of II is the azetidine C. Further kinetic studies are underway.



By a study of kinetic solvent effects, Huisgen[5] concluded that phenyl azide adds to bicyclo[2.2.1]-2-heptene by a polycenter mechanism, that is, both ends of the 1,3-dipole become attached to the double bond at the same time. The polycenter mechanism would not satisfactorily account for the carbon skeleton rearrangement observed here. The benzenesulfonyl nitrene intermediate ($C_6H_5SO_2N$) would not be expected to be involved in the formation of II since such intermediates are usually produced only at much higher temperatures than used here or by photolysis.[10] The observed carbon skeleton rearrangement is likewise not consistent with the formation of an intermediate free radical.[11] Azetidine II is probably formed by an ionic mechanism in which the nitrogen attached to sulfur becomes attached at C-2 from the less hindered *exo* side of the bicyclic ring with simultaneous skeletal rearrangement and loss of nitrogen as pictured. The reaction is analogous to the formation of 2-*exo*-7-*syn*-dibromobicyclo[2.2.1]heptane in the bromination of bicyclo[2.2.1]-2-heptene.[12] Walker and Waters,[13] on the basis of kinetic evidence, concluded that *p*-methoxyphenyl azide reacted with indene by a similar mechanism involving a concerted elimination of nitrogen leading to an aziridine intermediate which was not isolated.

(10) (a) O. C. Dermer and M. T Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955); (b) J. F. Heacock and M. T. Edmison, *ibid.*, **82**, 3460 (1960); (c) G. Smolinsky, *ibid.*, **84**, 3220 (1962).

(11) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).

Experimental

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded with a Beckman IR-5 spectrophotometer; n.m.r. spectra were obtained with the Varian A-60 n.m.r. spectrometer, using tetramethylsilane (TMS) as an internal standard (δ 0). Carbon and hydrogen analyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind., and nitrogen analyses were performed by a previously described procedure.[14]

Preparation of N-Benzenesulfonyl-8-azatricyclo[2.2.1.1^{2,7}]octane (II).—Benzenesulfonyl azide was prepared as previously described, but with the modification that the liquid benzenesulfonyl chloride was added directly to the ethanolic sodium azide solution. When the benzenesulfonyl chloride was dissolved in ethanol before addition to the ethanolic sodium azide solution, as done by previous workers,[10a,b] appreciable amounts (up to 25%) of ethyl benzenesulfonate were formed as shown by the presence of the characteristic ethyl group signals in the n.m.r.

Norbornylene was prepared by a well established procedure.[15]

Benzenesulfonyl azide (4.7 g.) was added to a solution of 5 g. of norbornylene in benzene or petroleum ether at room temperature with stirring. The evolution of nitrogen, which began immediately, ceased after 1.5 hr. The crystalline product which precipitated in quantitative yield as the exothermic reaction proceeded, was filtered out and recrystallized three times from 95% ethanol to give 5.3 g. (79%) of II, m.p. 105°; ν_{max}^{KBr} 1310, 1155, 1090, 975, 910, 720, and 690 cm.$^{-1}$; n.m.r. (in CCl_4), δ 2.42 (2 protons), 2.84 (2), 7.3–8.0 (5).

Anal. Calcd. for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.96; H, 6.05; N, 5.41.

Preparation of 2-Hydroxy-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane (III). A. Acid-Catalyzed Hydrolysis of II.—A solution prepared by adding 0.92 g. of II to 10 cc. of water containing 10 drops of concentrated hydrochloric acid was refluxed for 15 min. The solution was evaporated to yield an oil which was taken up in ether. After drying over anhydrous magnesium sulfate, the ether was evaporated to yield 0.92 g. of oil (III) which partially crystallized after two distillations (b.p. 160° at 0.07 mm.) and standing in the refrigerator for 2 weeks. Three recrystallizations from ethanol gave IIIα, m.p. 142–144°; ν_{max}^{KBr} 3450 (OH), 3116 (NH), 1310, 1163, 767, 721, and 691 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{17}NO_3S$: N, 5.24. Found: N, 5.22.

The hydroxyl group in IIIα is assigned the *endo* (α) configuration since it is the major product in the base-catalyzed (SN2) hydrolysis of II. When the oily product from the acid-catalyzed hydrolysis of II was chromatographed on alumina and the chromatography followed by thin layer chromatography a second alcohol, IIIβ, was detected in the oil. Both IIIα and IIIβ gave the same ketone IV on oxidation (see below); therefore, IIIβ must be the isomer of IIIα with an *exo* (β) hydroxyl group.

Preparative thin layer chromatography on Silica Gel-G, using chloroform–ethyl acetate (3:1) as the solvent system, was used to separate a small amount of the oily acid-catalyzed hydrolysis product into alcohols IIIα and IIIβ. Oxidation of these alcohols with chromic anhydride in acetic acid gave the same ketone IV as detected by thin layer chromatography (detection by 2,4-dinitrophenylhydrazone).

B. Hydration of II.—A suspension of 3 g. of II in 25 cc. of water was refluxed for 24 hr., then the solution was extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, decolorized with Norit and evaporated to give 2.8 g. of an oil, identical in infrared spectrum with the product obtained by the acid-catalyzed hydrolysis of II. This sample of alcohol, on oxidation, gave the same crystalline ketone IV as obtained by the oxidation of alcohol prepared by procedure A.

(12) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954).

(13) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(14) L. Miller and J. A. Houghton, *J. Biol. Chem.*, **159**, 373 (1945).

(15) J. Meinwald and N. J. Hudak, *Org. Syn.*, **37**, 65 (1957).

C. Alkaline Hydrolysis of II.—II (3.94 g.) was added to a solution prepared by the addition of 10 g. of potassium hydroxide to 10 cc. of water and 10 cc. of ethanol and the entire solution refluxed for 2 days. After extraction with ether, the remaining aqueous solution was acidified with dilute hydrochloric acid, then extracted again with ether. This latter ether extract was washed with an aqueous sodium carbonate solution, dried over magnesium sulfate, and evaporated to yield 0.81 g. of an oil which gave crystalline ketone IV identical in all respects with ketone IV prepared from the alcohol as obtained by procedure A. On evaporation, the ether extract of the alkaline solution gave 2.35 g. of unchanged II. In strong base such as this, where III exists in an ionic form, it is possible that product III is reconverted to II.

Basic catalysis in the conversion of II to III was demonstrated as follows. Four 20-cc. ethanolic solutions each containing 0.8132 g. of II were prepared. To one was added 10 cc. of 1.0 *N* sodium hydroxide, to a second was added 10 cc. of 0.10 *N* sodium hydroxide, to a third was added 10 cc. of 0.01 *N* sodium hydroxide, and to the fourth 10 cc. of water was added. The four solutions were refluxed under identical conditions for 4 days and at intervals of 6–12 hr., 1-cc. aliquots were removed from each solution, diluted to 4 cc. with water, and carefully neutralized, in the cold, with dilute hydrochloric acid. The aqueous solutions were extracted twice with 5-cc. portions of benzene; the benzene solutions were dried over anhydrous magnesium sulfate and evaporated *in vacuo* to yield an oily residue of 25 ± 5 mg. in each case. After drying overnight under reduced pressure, each sample was weighed and diluted to 0.20 cc. with dry chloroform. The infrared spectrum was then obtained in a 00.96-cm. cell in the region 2.5–3.5 μ. Using weighed reference samples of II and IIIα, the extinction of the N–H absorption in the various samples was determined, and the per cent conversion in each sample was determined. A plot of concentration in moles/liter of II *vs.* hours of reaction time gave the following times for 50% conversion of II: 0.3 *N* sodium hydroxide, disregarded because of precipitate formation during reaction; 0.03 *N* sodium hydroxide, 27 hr.; 0.003 *N* sodium hydroxide, 32 hr.; water, 45 hr.

The various samples from the kinetic runs were compared by thin layer chromatography, and all showed the same spots but increasing amounts of IIIα were present with increasing reflux time and with increasing basic strength. The unused solutions from the kinetic runs were combined and after working up as described previously, the residues were chromatographed on Merck acid-washed alumina. Crystalline IIIα (m.p. 143–144°) was obtained from the eluent.

Thin layer chromatographic comparisons of the acid, alkaline, and neutral hydrolysis products gave the comparisons shown in Table I.

TABLE I

Products	R_f[a]	Relative intensities and conditions A[b]	B[b]	C[b]
Benzenesulfonamide	0.10			1
Unknown	.20	1	1	1
Unknown	.22	1	1	1
IIIα	.40	4	4	4
IIIβ	.57	1	1	3
II	.63	2	1	3

[a] All thin layer chromatograms were run on Silica Gel-G using 3:1 chloroform–ethyl acetate, allowing the solvent front to advance 15 cm., and detecting with iodine vapor. [b] A, 96 hr. refluxing water; B, 96 hr. refluxing 0.03 *N* sodium hydroxide; C, 30 min. refluxing dilute hydrochloric acid. Intensities were determined by visually estimating the darkness of the iodine detected spots: darkest spot, 4; lightest, 1.

Preparation of 2-Keto-7-*syn*-benzenesulfonamidobicyclo[2.2.1]-heptane (IV).—To a solution containing 0.63 g. of oily III in 31 cc. of glacial acetic acid was added a mixture of 0.17 g. of chromic anhydride, 5 cc. of acetic acid, and 2 cc. of water. After stirring at room temperature for 48 hr., methanol was added to destroy excess chromic anhydride, and the solution was diluted with 200 cc. of water. The aqueous solution was extracted with ether, and the extract was washed with sodium carbonate solution, dried over anhydrous magnesium sulfate, and evaporated to yield 0.54 g. of ketone IV as an oil which could be crystallized from ether to give m.p. 147–148°; ν_{max}^{KBr} 3130 (N—H), 1725 (C=O), 1335, 1163, 1090, 887, 773, 761, 719, and 691 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{17}NO_3S$: C, 58.85; H, 5.70. Found: C, 53.30; H, 5.62.

The 2,4-dinitrophenylhydrazone was readily formed by the addition of an acidified, methanolic 2,4-dinitrophenylhydrazine solution to the ketone. Recrystallization from 95% ethanol gave m.p. 240–242°.

Anal. Calcd. for $C_{19}H_{19}N_5O_6S$: C, 51.25; H, 4.27. Found: C, 51.12; H, 4.73.

Alcoholic mixture III was also oxidized as follows. To a solution containing 0.36 g. of III in 10 cc. of acetone was added 2 cc. of Jones reagent[16] (1 cc. ≡ 0.004 mole of alcohol). After standing at room temperature for 1 hr., the solution was diluted with excess 10% sodium carbonate solution and extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to yield 0.34 g. of oil, which after crystalzation from ether gave 0.19 g. of IV, m.p. 146–147°; 2,4-dinitrophenylhydrazone, m.p. 242°; identical in all respects with IV prepared as described previously.

Preparation of 2-Acetoxy-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane (V).—A solution containing 2.16 g. of II in 10 cc. of acetic acid was heated on the steam bath for 0.5 hr. The solution was then poured on ice and extracted with ether. The ether extract was washed with aqueous sodium carbonate solution, dried over anhydrous magnesium sulfate, and evaporated to give 2.37 g. of an oil which distilled at 134–135° at 0.07 mm. The distilled oil was crystallized from ethanol–water to give V (59%), m.p. 134–135°. The analytical sample was obtained by three recrystallizations from ethanol–water and had m.p. 135–136°; ν_{max}^{KBr} 3200 (N–H), 1700 (C=O), 1260, 1160, 1088, 1052, 900, 853, 760, 723, and 689 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{19}O_4NS$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.15; H, 6.30; N, 4.56.

Hydrolysis of V.—Acetate V, 4.42 g., in 30 cc. of ethanol and 10 cc. of 20% aqueous potassium hydroxide was heated on the steam bath for 2 hr. After cooling to room temperature, the solution was diluted with 50 cc. of water and carefully neutralized with 5% hydrochloric acid. The neutral aqueous solution was extracted with ether, which after drying over anhydrous magnesium sulfate, was evaporated to yield 3.42 g. of crude alcohol from which crystalline III (m.p. 142–143°) was obtained as previously described.

Preparation of 2-Chloro-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane (VI).—Dry hydrogen chloride gas was passed through a refluxing solution containing 0.46 g. of II dissolved in 25 cc. of dry carbon tetrachloride for 1.5 hr. The solvent was removed under reduced pressure and the residue distilled to give 0.48 g. of oil, b.p. 160° at 0.07 mm. Crystallization of the oil from ethanol at 0° gave 0.37 g. (70%) of VI, m.p. 114–115°; ν_{max}^{film} 3300 (N–H), 1450, 1320, 1162, 890, 758, 720, 690, and 1092 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{16}ClNO_2S$: C, 54.63; H, 5.64; N, 4.90. Found: C, 54.45; H, 5.83; N, 4.96.

Preparation of 2-Bromo-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane (VII).—Dry hydrogen bromide was passed through a solution of 2.2 g. of II dissolved in 15 cc. of carbon tetrachloride at room temperature for 1.5 hr. The solution was then swept with nitrogen and the solvent evaporated to yield 2.3 g. of oil from which 1.2 g. of crystalline material precipitated after standing at 0° for 1 week. The analytical sample of VII was prepared by recrystallization from ethanol, m.p. 99–100°; ν_{max}^{KBr} 3200 (N–H), 1485, 1445, 1325, 1160, 1100, 918, 760, 720, and 691 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{16}BrNO_2S$: C, 47.28; H, 4.88. Found: C, 47.50; H, 4.82.

Conversion of VII to IV.—A solution prepared by adding 2.3 g. of VII and 1 g. of lithium carbonate to 5 cc. of methanol and 25 cc. of water was refluxed for 3 days. The aqueous solution was extracted with ether; the ether extract was dried over anhydrous magnesium sulfate and evaporated to yield an oily re idue. Distillation of the residue gave 0.98 g. of a liquid, b.p. 160° at 0.05 mm., whose infrared spectrum showed the presence of N–H (3300 cm.$^{-1}$) and O–H (3520 cm.$^{-1}$).

Jones oxidation of 371 mg. of this alcohol gave 220 mg. of IV, m.p. 146–147°, identical in all respects with ketone IV prepared as previously described.

(16) K. Bowden, I. M. Heilborn, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, **39**, (1946).

Attempted Reconversion of VII to II.—A solution containing 0.18 g. of VII in 2 cc. of dry pyridine was refluxed for 48 hr. After the pyridine was removed *in vacuo* the residue was analyzed by thin layer chromatography (Silica Gel-G, chloroform) and found to contain starting material (R_f 0.50), benzenesulfonamide (R_f 0.06), and a new product (R_f 0.43). Chromatography on alumina gave the new product as an oil whose n.m.r. spectrum showed it not to be the desired II but an alkene, presumably 7-benzenesulfonamidobicyclo[2.2.1]-2-heptene; n.m.r. (in carbon disulfide), δ 5.85, triplet with J = 2 c.p.s., two protons. Under similar conditions the olefinic protons of norbornylene appeared at δ 5.85, triplet with J = 2 c.p.s.

Preparation of 7-Benzenesulfonamidobicyclo[2.2.1]heptane (VIII).—Ketone IV (1.77 g.) was added to a solution of 3.5 g. of potassium hydroxide in 2.6 g. of 95+% hydrazine and 15 cc. of ethylene glycol, and the reaction mixture was refluxed for 3 hr. The excess hydrazine and water were removed by distillation until the pot temperature reached 185°, and the solution was then refluxed an additional 17 hr. After cooling to room temperature, 50 cc. of water was added and the solution neutralized with 5% hydrochloric acid. The neutral solution was extracted with ether, and the extract was dried over anhydrous magnesium sulfate and evaporated to yield 1.16 g. of VIII, which, after recrystallization from ethanol–water, gave m.p. 104–105°; ν_{max}^{KBr} 3028 (N–H), 1450, 1438, 1341, 1325, 1160, 1095, 905, 751, 719, 688; n.m.r. (in CS_2), δ 0.8–1.8 (10 protons), 3.01 (1 proton, doublet at 5 c.p.s.), 5.93 (1 proton, doublet at 5 c.p.s.), 7.2–8.0 (5 protons).

Anal. Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82. Found: C, 62.53; H, 7.13.

Preparation of 7-Aminobicyclo[2.2.1]heptane and Derivatives.—A suspension of VIII (0.59 g.) in 2 cc. of 10% hydrochloric acid was heated in a sealed tube at 150–175° for 12 hr. Concentrated hydrochloric acid (10 cc.) was added to the solution after the tube was opened, and the solution was extracted with ether. The remaining aqueous solution was made basic with 20% sodium hydroxide and extracted with ether. After drying and evaporation, the ether yielded 0.12 g. of 7-aminobicyclo[2.2.1]-heptane which was converted into the N-acetyl derivative by heating a few minutes with excess acetic anhydride. The excess acetic anhydride and acetic acid were removed by distillation under reduced pressure. The residue was crystallized from hexane three times to give 7-acetamidobicyclo[2.2.1]heptane, m.p. 130–131°; ν_{max}^{KBr} 3280, 2925, 1620, 1540, 1315, 1300, 1290 cm.$^{-1}$. The crystalline derivative and the hexane-free mother liquor from which it was obtained were found to be identical and to differ from the corresponding 2-*endo* and 2-*exo* isomers by gas chromatography.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.55; H, 9.87. Found: C, 70.49; H, 9.98.

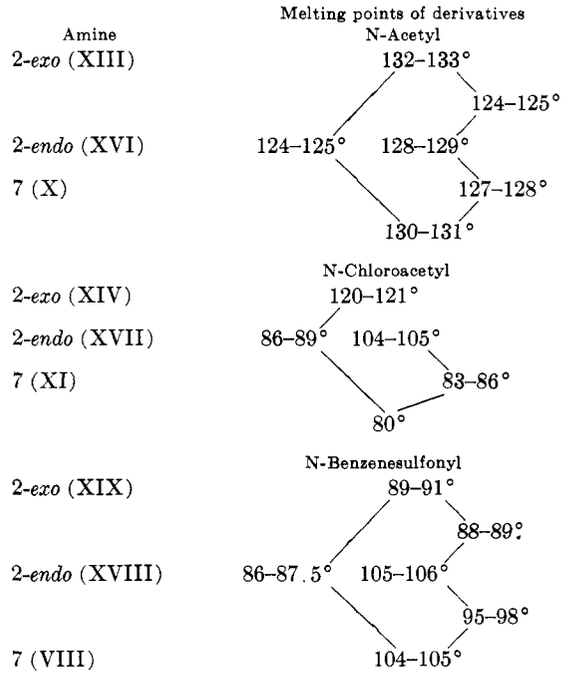
The N-chloroacetyl derivative was prepared by heating the amine with chloroacetyl chloride in pyridine–benzene and had m.p. 80° after recrystallization from petroleum ether (lit.[17] m.p. 84–85°).

Preparation of 2-*endo*-Aminobicyclo[2.2.1]heptane.—A suspension of 30 g. of norbornylene in 75 cc. of cold 60% sulfuric acid was shaken with occasional cooling until the solution became homogeneous. After neutralization, the aqueous solution was extracted with ether which in turn was dried and evaporated to yield 18 g. of norborneol.[18]

The norborneol was oxidized to give norcamphor as previously described.[19] Norcamphor was converted into 2-*endo*-aminobicyclo[2.2.1]heptane by preparation of the oxime and subsequent catalytic reduction as described by Alder and Stein.[20] The N-acetyl derivative (m.p. 130–132°, lit.[21] m.p. 131–132°) was prepared by the usual method and was found by gas chromatography (see later section) to be uncontaminated by the *exo* isomer.

When norcamphor oxime was reduced with sodium in ethanol, the resulting amine was shown to be the *endo* amine contaminated with *exo* isomer by gas chromatographic analysis of the acetylated amine.

SCHEME II



The benzenesulfonyl derivative of 2-*endo*-aminobicyclo[2.2.1]-heptane was prepared using benzenesulfonyl chloride in pyridine and the analytical sample was obtained by three recrystallizations from methanol; m.p. 105–106°.

Anal. Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82. Found: C, 62.63; H, 6.76.

The chloroacetyl derivative was prepared as previously described and had m.p. 104–105° (lit.[17] m.p. 105–106°).

Preparation of 2-*exo*-Aminobicyclo[2.2.1]heptane.—A mixture of *endo*- and *exo*-2-cyanobicyclo[2.2.1]-5-heptene was prepared by the Diels–Alder reaction of acrylonitrile and cyclopentadiene as previously described.[22] *exo*-2-Carbamylbicyclo[2.2.1]-5-heptene was prepared from the mixture of cyanides by the action of sodium amide in liquid ammonia as described by Boehme, *et al.*[23] Hydrogenation of the unsaturated amide with platinum oxide catalyst in ethanol gave the previously reported[23] saturated amide (m.p. 192°, lit.[23] m.p. 192.5–193.5°), which was converted into 2-*exo*-aminobicyclo[2.2.1]heptane by the Hofmann reaction according to the procedure of Berson and Ben-Efriam.[21] The N-acetyl derivative, prepared with acetic anhydride, gave m.p. 132–133°, lit.[21] m.p. 140–143°. The gas chromatogram of this derivative indicated a slight contamination with the *endo* isomer.

The benzenesulfonyl derivative of the *exo* amine was prepared by treating the amine in pyridine with benzenesulfonyl chloride. The analytical sample was obtained by four recrystallizations from aqueous methanol; m.p. 89–91°.

Anal. Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82. Found: C, 62.54; H, 7.20.

The N-chloroacetyl derivative, prepared as described previously, had m.p. 120–121°, lit.[17] m.p. 126–127°.

Gas Chromatographic Comparisons of Acetylated Amines, X, XIII, and XVI.—All gas chromatographic analyses were performed on a 0.25-in. diameter × 10-ft. Craig polyester column at 210° using a helium flow rate of 59 cc. per min. The following retention times were observed: 7-acetamidobicyclo[2.2.1]heptane (X), 12 min.; 2-*endo*-acetamidobicyclo[2.2.1]heptane (XVI), 13.3 min.; 2-*exo*-acetamidobicyclo[2.2.1]heptane (XIII), 14.0 min.

Thin Layer Chromatographic Comparisons of Amine Derivatives.—The thin layer chromatograms were obtained by ascending (15 cm.) chromatography on glass plates coated with a 50-μ thick layer of silica gel. Detection was by iodine vapor and the reported R_f values shown in Table II are for leading edges.

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(18) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5397 (1954).
(19) G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).
(20) K. Alder and G. Stein, *ibid.*, **525**, 183 (1936).
(21) J. A. Berson and D. A. Ben-Efriam, *J. Am. Chem. Soc.*, **81**, 4094 (1959).
(22) K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958).
(23) W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Am. Chem. Soc.*, **80**, 5488 (1958).

TABLE II

	R_f					
	N-Benzenesulfonamido			N-Chloroacetamido		
	2-*endo*	2-*exo*	7	2-*endo*	2-*exo*	7
Solvent	XVIII	XIX	VIII	XVII	XIV	XI
Chloroform	0.25	0.20	0.32	0.16	0.14	0.24
1:1 Chloroform–benzene	.29	.23	.32			

Melting Point Comparisons of Amine Derivatives.—All mixture melting points, indicated by numbers at points of lines joining two melting points, as shown in Scheme II, were determined after mixing, melting, and allowing the solid mixture to resolidify.

Infrared Spectral Comparisons of N-Chloroacetyl Derivatives of Isomeric Amines.—In the 1500–4000-cm.$^{-1}$ region of the infrared spectrum all three N-chloroacetyl derivatives (XI, XIV, and XVII) exhibited essentially identical bands at 3330, 2790, 1800, and 1600 cm.$^{-1}$.

The following differences were noticed in the infrared spectra of the three isomers. In the 900–1500-cm.$^{-1}$ region, the 2-*exo* isomer showed a moderately strong band at 1107 cm.$^{-1}$ which was missing in the 2-*endo* and 7-isomers; the 2-*exo* and 2-*endo* isomers contained bands at 1340 and 1250 cm.$^{-1}$ which were shifted to 1320 and 1235 cm.$^{-1}$ in the 7-isomer; a moderately intense band at 1200 cm.$^{-1}$ in the spectrum of the 7-isomer was not present in the spectra of th 2-*exo* and 2-*endo* isomers. In the 750–900-cm.$^{-1}$ region a moderately intense band at 878 cm.$^{-1}$ in the 2-*exo* isomer was shifted to 888 cm.$^{-1}$ in the 2-*endo* isomer, and the 7-isomer showed a weak doublet at 873 and 890 cm.$^{-1}$; the 7-isomer showed a moderately intense doublet at 805 and 788 cm.$^{-1}$, whereas in the 2-*exo* isomer, the doublet appeared at 813 and 885 cm.$^{-1}$ and in the 2-*endo* isomer, a single band appeared at 788 cm.$^{-1}$ with a very weak band at 813 cm.$^{-1}$.

Acknowledgment.—We thank Drs. O. C. Dermer and C. D. Kennedy for helpful discussion during the course of the work.

The Reaction of Benzenesulfonyl Azide with 2,3-*endo-cis*-Dicarboxybicyclo[2.2.1]-5-heptene Anhydride

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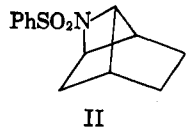
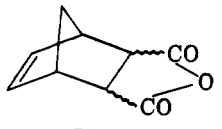
Benzenesulfonyl azide has been found to react with 2,3-*endo-cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride in refluxing carbon tetrachloride to give the aziridine 8-aza-N-benzenesulfonamidotricyclo[2.2.1.1$^{2,3\text{-}endo}$] octane-5,6-*endo*-dicarboxy anhydride (VII). The structure and sterochemistry of VII were established by its conversion to the lactone–lactam X under mild conditions. The corresponding 2,3-*exo*-anhydride (IV) reacts in a similar manner to give the *exo* aziridine XVII. 2,3-*endo-cis*-Dicarboxy-5,6-*endo-cis*-diaminobicyclo-[2.2.1]heptane dilactam (XII) was converted into the nortricyclene derivative XI.

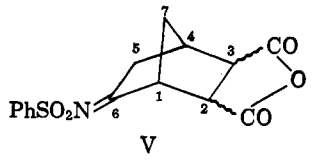
Recent work from this laboratory has shown that benzenesulfonyl azide reacts with bicyclo[2.2.1]-2-heptene (I) at room temperature to give the azetidine II in quantitative yield.[2] In an attempt to investigate the scope of this reaction, the isomeric alkenes 2,3-*endo*-III and 2,3-*exo-cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride (IV) have been treated with benzenesulfonyl azide.



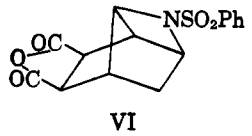
II



III *endo*
IV *exo*



V



VI

Under conditions where benzenesulfonyl azide reacts with I in a vigorous exothermic reaction with the evolution of nitrogen, no detectable evolution of nitrogen could be observed with alkenes III and IV. However, both III and IV reacted slowly with benzenesulfonyl azide in refluxing carbon tetrachloride to give products whose elemental analyses ($C_{15}H_{13}O_5NS$) indicated that the benzenesulfonamido group ($C_6H_5SO_2N$) had become attached to the alkene in each case. The infrared spectrum of each of these products showed the presence of anhydride and benzenesulfonamido groups but the absence of double bonds. Of particular interest was the absence of N–H absorption in the spectra of the products. Both products were readily converted into dimethyl esters with diazomethane in ether–methanol. The n.m.r. spectra of the two dimethyl esters were very similar and showed the presence of only one methylene group ($>CH_2$) in each compound, all other protons appearing further downfield. These data indicate that the products do not have the sulfonimide structure V. The sulfonimide structure had been suggested for the products of the reaction of III and IV with *p*-toluenesulfonyl azide by earlier workers.[3]

When the product from the reaction of III with benzenesulfonyl azide was refluxed in a 10% sodium carbonate solution and the solution then acidified, A ($C_{15}H_{15}O_6NS$) was obtained. The infrared spectrum of A showed the presence of an N–H band (3250 cm.$^{-1}$), a carboxyl group (3200–2800 and 1727 cm.$^{-1}$), and a γ-lactone (1755 cm.$^{-1}$). Heating of A at 260° and 35 mm. resulted in the loss of water and the formation of B ($C_{15}H_{13}O_5NS$). The infrared spectrum of B no longer showed the presence of an N–H band and the carboxyl group's characteristic absorptions were absent. In the carbonyl region, two sharp bands appeared at 1790 and 1748 cm.$^{-1}$. One of these bands (see later section) must arise from the carbonyl bond of the lactam group $C_6H_5SO_2N-\overset{|}{C}=\overset{|}{O}$. The formation of B eliminates structure VI for the product of the reaction of III with

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