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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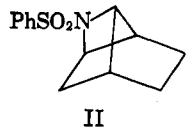
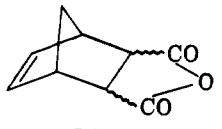
Benzenesulfonyl azide has been found to react with 2,3-*endo-cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride in refluxing carbon tetrachloride to give the aziridine 8-aza-N-benzenesulfonamidotricyclo[2.2.1.1$^{2,3\text{-}endo}$] octane-5,6-*endo*-dicarboxy anhydride (VII). The structure and sterochemistry 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.

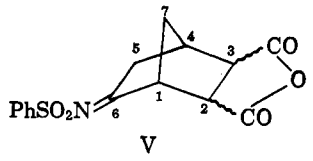
Recent work from this laboratory has shown that benzenesulfonyl azide reacts with bicyclo[2.2.1]-2-heptene (I) at room temperature to give the azetidine II in quantitative yield.[2] In an attempt to investigate the scope of this reaction, the isomeric alkenes 2,3-*endo*-III and 2,3-*exo-cis*-dicarboxybicyclo[2.2.1]-5-heptene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



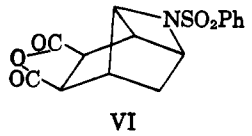
II



III *endo*
IV *exo*



V



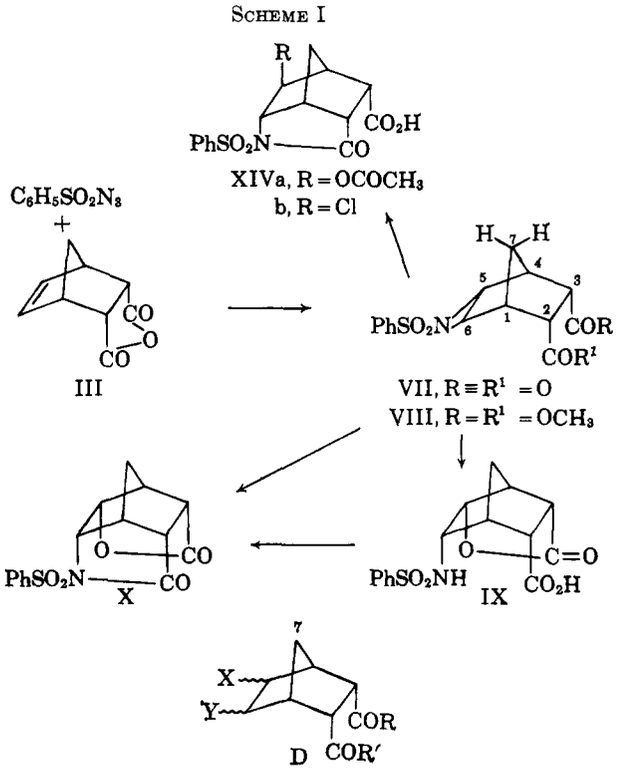
VI

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

(1) National Defense Education Act Fellow, 1959–1962.
(2) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).
(3) L. Bruner, Ph.D. dissertation, University of Michigan, 1958.

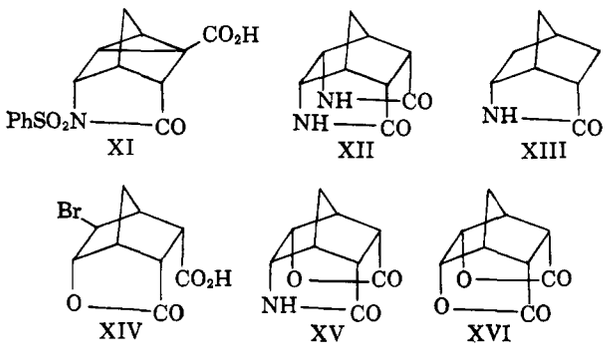
SCHEME I



benzenesulfonyl azide, since lactam formation is clearly not possible in this case. Structure VI was to be expected if the reaction had proceeded in an analogous manner to that observed in the reaction of norbornylene to yield II.

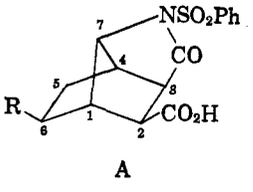
Structure VII (Scheme I) is suggested for the product of the reaction of III with benzenesulfonyl azide and, *ipso facto*, the structures IX and X are assigned to A and B, respectively. The n.m.r. spectrum of VIII (in deuteriochloroform, δ 0 for tetramethylsilane), the dimethyl ester from VII, supports the assigned structures. The two C-7 protons appeared as a pair of doublets (J = 10 c.p.s.) centered at δ 1.53 and δ 2.00; the two protons at C-2 and C-3 were located at δ 2.82, and the two protons on the bridgeheads C-1 and C-4, showed a doublet (J = 1.5 c.p.s.) centered at δ 2.92. The two protons at C-5 and C-6 gave an ill-defined multiplet centered at δ 3.63. The six protons of the methyl ester groups appeared as a single sharp signal at δ 3.53, and the five aromatic protons gave multiplets in the region δ 7.3–8.0 downfield from tetramethylsilane N.m.r. spectra of IX and X (in CF_3CO_2H) showed the C-7 protons as singlets centered at δ 1.80 and δ 2.00, respectively. An extensive study, in this laboratory,[4] of compounds possessing structure D, where x and y are nitrogen, oxygen, or halogen has shown that only when both x and y (but not x ≡ y), are *endo* do the C-7 protons appear as a singlet. When x or y or both x and y are *exo*, then the two C-7 protons appear nonequivalent and show a pair of doublets with J = 11 to 13 c.p.s.

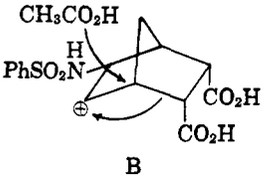
The carbonyl bands in the infrared spectrum of X are of particular interest. Momose, *et al.*,[5] found that the amide-I band of N-acetylsulfonamides was shifted to higher frequencies as compared to unsulfonated amides. We likewise have observed that the amide-I



band of XI, prepared as described in the Experimental, appears at 1753 cm.$^{-1}$, whereas the amide-I band of XII[6] and XIII[7] appear at 1675 and 1690 cm.$^{-1}$, respectively. The infrared spectrum of XIV[8] shows the lactone carbonyl band at 1764 cm.$^{-1}$ and the lactone–lactam XV[6] shows carbonyl bands at 1660 and 1761 cm.$^{-1}$. The lower frequency band (1660 cm.$^{-1}$) in XV, by analogy, can be assigned to the lactam carbonyl and the higher frequency band (1761 cm.$^{-1}$) can be assigned to the lactone carbonyl. It is interesting that in the dilactone XVI[9] two distinct and separate bands appear at 1795 and 1770 cm.$^{-1}$. We, therefore, assign the 1790-cm.$^{-1}$ band in X to the lactone carbonyl, and the 1748-cm.$^{-1}$ band to the lactam carbonyl group.

When VII was refluxed in glacial acetic acid, X was again obtained and, in addition, a second product was isolated for which structure XIVa has been assigned. The elemental analysis, neutralization equivalent and infrared and n.m.r. spectra were consistent with structure XIVa. Structure A (R = OAc) also must be con-





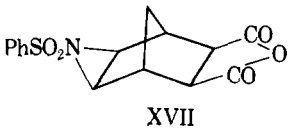
sidered on mechanistic grounds for the product of the reaction of VII with acetic acid. Structure A could arise by protonation of the nitrogen atom in VII to give the carbonium ion B which then rearranges to yield the product. The n.m.r. spectrum of the product, however, is not in agreement with structure A. The spectrum showed two protons as doublets at high field (δ 1.78 and δ 2.25) each with a coupling constant of 13 c.p.s. analogous to that observed in compounds of type D. Thus, the high field protons behave as a typical AB case, and the observed signals can be assigned to the C-7 protons of XIVa. If structure A had been correct, an ABX type spectrum containing more lines would be expected. In addition, the proton on the carbon carrying the acetoxy group (C-5 in XIVa, C-6 in A) appeared as a sharp singlet at δ 5.35. This again is more consistent with structure XIVa (J_{45} = 0, J_{56} = 0) than with structure A [$J_{5\text{-}endo\text{-}6} \gtrsim 0$].[10]

In a similar manner treatment of VII with concentrated hydrochloric acid in acetone gave XIVb. Struc-

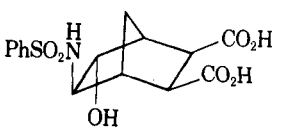
(4) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, submitted.
(5) T. Momose, Y. Ueda, T. Shoji, and H. Yano, *Chem. Pharm. Bull.* (Tokyo), **6**, 659 (1958).
(6) W. S. Worrall, *J. Am. Chem. Soc.*, **82**, 5707 (1960).
(7) R. W. Iles and W. S. Worral, *J. Org. Chem.*, **26**, 5233 (1961).
(8) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4078 (1954).
(9) A. Winston and P. Wilder, *ibid.*, **76**, 3045 (1954).
(10) F. A. C. Anet, *Can. J. Chem.*, **39**, 789 (1961).

ture XIVb is again consistent with the observed n.m.r. spectrum. The C-7 protons appeared as a pair of doublets centered at δ 1.81 and δ 2.47, with a coupling constant of 13 c.p.s. The C-5 proton appeared as a sharp singlet at δ 4.27.

Structure XVII is suggested for the product of the reaction of 2,3-*exo-cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride (IV) with benzenesulfonyl azide. The aziridine structure XVII rather than an azetidine type



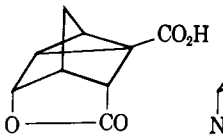
XVII



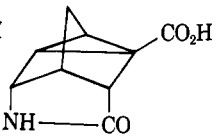
XVIII

structure such as II is suggested for this product because of the similarity of the n.m.r. spectrum of the dimethyl ester from XVII with that of VIII. The *exo* configuration is assigned to the aziridine ring of XVII since the reactive benzenesulfonamido intermediate would be expected to react with the alkene IV from the less hindered *exo* side in the absence of electronic effects. When XVII was refluxed in water, a hydroxy dicarboxylic acid was obtained. Structure XVIII is suggested for this product.

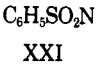
All attempts to synthesize X from the previously reported lactone–lactam XV were unsuccessful. When XV was treated with aqueous sodium hydroxide and benzenesulfonyl chloride under various conditions the benzenesulfonyl group did not become attached to the nitrogen atom presumably because of interference by the opened lactone group. During the work-up of the above reaction, the alkaline solution was acidified with hydrochloric acid at room temperature, and this resulted in the formation of the known nortricyclene derivative XIX.[11] N-Alkyl cleavage in acid hydrol-



XIX



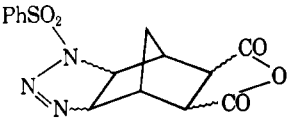
XX



XXI

ysis of norbornane γ-lactams has been previously reported under more drastic conditions.[11] Another example of this type of hydrolysis was observed when the dilactam XII was refluxed with 5% hydrochloric acid. The product of this reaction, XX, although not directly isolated, was converted into the known lactone XIX with nitrous acid, and treatment of XX with benzenesulfonyl chloride and sodium hydroxide gave XI. The lactam carbonyl bands of XI, XIVa, and XIVb all appeared at approximately 1750 cm.$^{-1}$. This observation provides additional support for the assigned infrared carbonyl band absorptions in the spectrum of X. It is interesting that only one of the lactam bonds of XII underwent N-alkyl acid hydrolysis.

The mechanism involved in the formation of VII is of interest since the benzenesulfonamido group becomes attached to alkene III from the more hindered *endo* side. The sluggishness of the reaction of III and IV as compared to norbornylene[2] with benzenesulfonyl azide and the formation of aziridines in the former case as compared to an azetidine in the latter case suggests that different mechanisms are involved in the two cases. Under the conditions in which VII and XVII were formed, benzenesulfonyl azide most probably decomposes slowly to yield the benzenesulfonyl nitrene XXI which then adds to the double bond. The nitrene XXI is known to be strongly electrophilic,[12] and it is, therefore, probably attracted to the *endo* side of III by the electron-rich oxygen atoms of the anhydride group. (The referee has suggested the possibility that the double bonds of III and IV also induce decomposition of the azide, but to a lesser degree than observed with norbornylene[2] and the C_1–C_2 bond migration does not occur with III and IV since these bonds are less electron rich because of the inductive effect of the carbonyl groups.) In the formation of XVII only steric factors would be involved, and thus the *exo* aziridine is to be expected. However, the evidence available does not premit conclusive elimination of a triazoline type intermediate such as XXII in the formation of aziridines VII and XVII. The opening of the aziridine ring of VII to yield lactone IX under alkaline conditions is unusual since a front side displacement is involved.



XXII

Experimental

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded with a Beckman IR-5 spectrophotometer, and 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 Microlab, Inc., Indianapolis, Ind., and nitrogen analyses were performed by a previously described procedure.[13]

Preparation of 8-Aza-N-benzenesulfonamidotricyclo[2.2.1.1$^{2,3\text{-}endo}$]octane-5,6-*endo*-dicarboxy Anhydride (VII).—A solution of 16.4 g. of *endo-cis*-2,3-dicarboxybicyclo[2.2.1]-5-heptene anhydride (both III and IV were shown to be homogeneous and uncontaminated with each other by gas chromatographic analysis using a 0.25-in. diameter × 10-ft. long column of 5% SE-30 on acid-washed Chromosorb W and a helium flow rate of 80 cc./min.; under these conditions, the retention times were III, 6.42 min.; IV, 5.25 min.), III, and 18.3 g. of benzenesulfonyl azide[2] in 125 cc. of carbon tetrachloride was refluxed for 34 hr. during which time a gummy solid precipitated. The precipitate was collected by filtration, washed thoroughly with chloroform, and dried to give 13.4 g. of aziridine VII, m.p. 207–210°. The analytical sample was obtained after recrystallization from acetone and gave m.p. 215–216.5°; ν_{max}^{KBr} 1865, 1822, 1780, 1327, and 1163 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{13}O_5NS$: C, 56.43; H, 4.08; N, 4.39. Found: C, 56.85; H, 4.34; N, 4.38.

The dimethyl ester of VII was prepared by adding an excess of diazomethane in a 1:1 absolute methanol–ether solution to the solid anhydride VII. Recrystallization of the dimethyl ester VIII from methanol–ether gave a sample of m.p. 130–131°; ν_{max}^{KBr} 1733, 1333, and 1143 cm.$^{-1}$; n.m.r. (in deuteriochloroform), δ 1.53 (J = 10 c.p.s., one proton at C-7), δ 2.00 (J = 10 c.p.s., one proton at C-4), δ 2.82 and 2.92 (4 protons at C-1, C-4, C-2, and C-3), δ 3.53 (6 protons of methyl ester), δ 3.63 (2 protons at C-2 and C-5), and δ 7.3–8.0 (5 aromatic protons).

(11) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **28**, 852 (1963).

(12) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955); J. F. Heacock and M. T. Edmison, *ibid.*, **82**, 3460 (1960).

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

Preparation of *endo*-5-Hydroxy-*endo*-6-benzenesulfonamido-*endo-cis*-2,3-dicarboxybicyclo[2.2.1]heptane γ-Lactone (IX).—A mixture of 0.50 g. of aziridine VII and 25 cc. of 10% sodium carbonate solution was refluxed for 12 hr. Cooling and acidification of the solution with concentrated hydrochloric acid gave lactone IX (0.26 g.), m.p. 228–234°. Recrystallization from acetone–water and drying at 144° and 1 mm. gave the analytical sample, m.p. 242–245°; ν_{max}^{KBr} 3250, 3200–2800 (broad), 1755, 1727, 1360, 1340, and 1170 cm.$^{-1}$; n.m.r. (CF_3CO_2H), δ 1.80 (2 protons at C-7).

Anal. Calcd. for $C_{15}H_{15}O_8NS$: C, 53.41; H, 4.41. Found: C, 53.17; H, 4.31.

Lactone IX also was prepared by heating aziridine VII with 10% aqueous sodium hydroxide on the steam bath for 4 hr.

Preparation of *endo*-5-Hydroxy-*endo*-6-benzenesulfonamido-*endo-cis*-2,3-dicarboxybicyclo[2.2.1]heptane γ-Lactone–γ-Lactam (X).—Lactone IX (0.050 g., m.p. 242–245°) was heated at 260° and 35 mm. in a sublimation apparatus. The product X (0.042 g.) was collected as a sublimate and gave m.p. 244.5–245°. The analytical sample was obtained by resublimation and gave m.p. 248–248.5°; ν_{max}^{KBr} 1790, 1748, 1355, 1347, and 1155 cm.$^{-1}$; n.m.r. (CF_3CO_2H), δ 2.05 (2 C-7 protons).

Anal. Calcd. for $C_{15}H_{13}O_5NS$: C, 56.43; H, 4.08; N, 4.39. Found: C, 56.15; H, 4.04; N, 4.49.

The Reaction of Aziridine VII with Acetic Acid. Preparation of XIVa.—Aziridine VII (4.6 g., m.p. 215–216.5°) was dissolved in 30 cc. of hot glacial acetic acid and the solution refluxed for 6 hr. The solution was then allowed to stand at room temperature, and the lactone–lactam X crystallized as needles after several hours. Filtration, washing with glacial acetic acid, and drying gave 1.32 g. of X, m.p. 245–247°, identical in all respects with X prepared as described in the preceding experiment. Thin layer chromatography of X on silica gel using 8:1 ethanol–acetic acid gave only one spot R_f 0.5 (detection by iodine vapor).

The filtrate remaining after the removal of X was concentrated to approximately 20 cc. after which acetate lactam XIVa crystallized slowly from the solution as plates. Filtration and drying at 144° and 1 mm. gave 1.52 g. of XIVa, m.p. 209–211°. The mother liquor deposited an additional 0.90 g. of XIVa, m.p. 209–212° after several days. The analytical sample was prepared by recrystallization from 1:1 ethanol–water and gave, after drying at 144° and 1 mm., m.p. 214–215°; ν_{max}^{KBr} 3100–2800 (broad), 1745, 1700, 1362, and 1140 cm.$^{-1}$; n.m.r. (CF_3CO_2H), δ 1.78 (doublet, J = 13 c.p.s., one C-7 proton), δ 2.25 (doublet, J = 13 c.p.s., one C-7 proton; the lower field signal of this doublet is buried under the strong signal of the methyl ketone protons), δ 4.69 (doublet, J = 5 c.p.s., C-6 proton), and δ 5.35 (C-5 proton).

Anal. Calcd. for $C_{17}H_{17}O_7NS$: C, 53.81; H, 4.51; neut. equiv., 379.4. Found: C, 53.90; H, 4.38; neut. equiv., 370.

Thin layer chromatography of XIVa on silica gel as described gave one spot R_f 0.63. When X and XIVa were mixed together and the mixture thin layer chromatographed two distinct spots appeared (R_f 0.50 and 0.63).

The Reaction of VII with Hydrochloric Acid. Preparation of XIVb.—A mixture of 0.50 g. VII (m.p. 213–216°), 10 cc. of concentrated hydrochloric acid, and 10 cc. of acetone was heated on the steam bath for 15 min. After standing at room temperature for 12 hr., XIVb crystallized as needles. Filtration, washing with ethanol, and drying at 144° and 1 mm. gave 0.3 g. of XIVb, m.p. 214–215°; ν_{max}^{KBr} 3050–2800 (broad), 1747, 1717, 1370, 1340, 1175, and 1129 cm.$^{-1}$; n.m.r. (CF_3CO_2H), δ 1.81 (doublet, J = 13 c.p.s., one C-7 proton), δ 2.47 (doublet, J = 13 c.p.s., one C-7 proton), and δ 4.27 (doublet, J = 5 c.p.s., C-6 proton).

Anal. Calcd. for $C_{15}H_{14}O_5NSCl$: C, 50.63; H, 3.94; N, 3.94. Found: C, 50.76; H, 4.15; N, 3.92.

Preparation of XVII.—A gummy solid precipitated after refluxing a solution of 6.4 g. of IV (m.p. 141–142°) prepared as previously described,[14] and 6 g. of benzenesulfonyl azide in 63 cc. of carbon tetrachloride for 24 hr. The gummy precipitate was washed with benzene, whereupon it gave a crystalline solid. Pure aziridine XVII (3.6 g.) was obtained after recrystallization of the solid product from benzene and gave m.p. 168–168.5°; ν_{max}^{KBr} 1863, 1830, 1775, 1345, 1320, and 1163 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{13}O_6NS$: C, 56.43; H, 4.08; N, 4.39. Found: C, 56.59; H, 4.13; N, 4.40.

The dimethyl ester of XVII was prepared in the same manner described for the preparation of VIII, and after recrystallization from cyclohexane gave m.p. 102–103°; ν_{max}^{KBr} 1740, 1327, and 1160 cm.$^{-1}$; n.m.r. ($DCCl_3$), δ 1.92 (J = 11 c.p.s., one proton at C-7), δ 2.32 (J = 11 c.p.s., one proton at C-7), δ 2.78 and δ 2.92 (4 protons at C-1, C-4, C-2, and C-3), δ 3.50 (2 protons at C-2 and C-5), δ 3.66 (6 protons of methyl ester), and δ 7.3–8.0 (5 aromatic protons).

Reaction of XVII with Water. Preparation of XVIII.—A solution of 1.0 g. of aziridine XVII (m.p. 168–168.5°) in 20 cc. of water was refluxed for 10 hr. Evaporation to dryness gave 1.1 g. of XVIII, m.p. 214–215°. The analytical sample was prepared by recrystallization from water, and after drying at 144° and 1 mm. gave m.p. 214–215°; ν_{max}^{KBr} 3400, 3260, 3000–2500 (broad), 1723, 1705, and 1155 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{17}O_7NS$: C, 50.69; H, 4.82. Found: C, 50.84; H, 5.02.

Treatment with ethereal diazomethane gave the dimethyl ester as a viscous oil which could not be crystallized; ν_{max}^{film} 3440, 3260, 1738, and 1160 cm.$^{-1}$.

Attempted Synthesis of X. Preparation of XIX.—The lactone–lactam XV (1 g.) prepared as previously described,[6] was refluxed in a 10% aqueous sodium hydroxide solution for 12 hr., then the solution was evaporated to dryness. The solid residue was dissolved in an aqueous solution prepared by the addition of 1 g. of benzenesulfonyl chloride to 20 cc. of water, and the entire mixture was stirred at room temperature for 4 hr. After acidification with concentrated hydrochloric acid, the aqueous solution was continuously extracted with ethyl ether for 72 hr. Evaporation of the ether yielded 0.90 g. of XIX, m.p. 202–204°, identical in mixture melting point and infrared spectrum with a sample of XIX prepared as previously described.[11] Other attempts to prepare X from XV using pyridine as a base and heating the reactants in a sealed tube were also unsuccessful.

Preparation of XI. Treatment of XII with Dilute Hydrochloric Acid.—Dilactam XII (0.150 g., m.p. 207–210°), prepared as previously described,[6] was refluxed in 15 cc. of 5% hydrochloric acid for 6.5 hr. After cooling, the aqueous solution was treated with sodium hydroxide (3 g.), and 1.5 g. of benzenesulfonyl chloride was added. After stirring at room temperature for 12 hr., the solution was acidified by the addition of 15 cc. of concentrated hydrochloric acid and then continuously extracted (12 hr.) with ether. Drying and evaporation of the ether gave 0.153 g. of XI, m.p. 233–236°. The analytical sample was obtained after recrystallization from absolute ethanol and gave m.p. 242–243°; ν_{max}^{KBr} 1753 and 1694 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{13}O_5NS$: C, 56.43; H, 4.08. Found: C, 56.54; H, 4.33.

Conversion of XII into XIX.—A solution of dilactam XII (0.10 g.) and 10 cc. of 5% hydrochloric acid was refluxed for 11 hr. after which 0.150 g. of sodium nitrite was added and the solution heated on the steam bath for 15 min. The solution was then taken to dryness and the residue was redissolved in 20 cc. of water, and the aqueous solution continuously extracted with ether. Drying, evaporation of the ether extract, and heating *in vacuo* at 70° for 30 min. gave 0.056 g. of XIX, m.p. 205–206°, identical in infrared spectrum and melting point with XIX prepared as previously described.[11]

When the hydrolysis solution, prior to the addition of sodium nitrite, was made basic, steam distilled, and the liberated ammonia collected and titrated as previously described,[13] it was found that 49% of the theoretical nitrogen content of XII was liberated as ammonia.

Infrared Spectra.—All of the infrared spectra of crystalline compounds mentioned in this paper with the exception of XIII were obtained as potassium bromide pellets on compounds prepared in this laboratory. Literature procedures were used in the synthesis of XII,[6] XIV,[8] XV,[6] and XVI.[9]

(14) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).