Bridged Ring Compounds. X.[1,2] The Reaction of Benzenesulfonyl Azide with Norbornadiene, Dicyclopentadiene, and Bicyclo[2.2.2]-2-octene

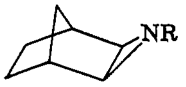
A. C. OEHLSCHLAGER[3] AND L. H. ZALKOW[4]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

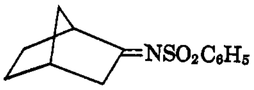
Received June 23, 1965

Benzenesulfonyl azide reacts rapidly at room temperature with norbornadiene to give initially the *exo*-aziridine XI which rearranges spontaneously to give N-benzenesulfonyl-2-azabicyclo[3.2.1]-3,6-octadiene (V). With dicyclopentadiene the same reagent was found to yield exclusively the *exo*-aziridine XIV. Benzenesulfonyl azide reacts only slowly with bicyclo[2.2.2]octene to give the *exo*-aziridine XVII and the sulfonimido derivative XVI. The latter compound hydrolyzes on standing in moist air to give bicyclo[2.2.2]octanone and benzenesulfonamide. The mechanism of the reaction of benzenesulfonyl azide with strained olefins is discussed and arguments are presented in support of a reactive triazoline intermediate which decomposes *via* a diazonium ion type intermediate to give aziridines and/or sulfonimide derivatives.

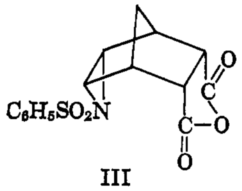
In previous reports we have described the reaction of benzenesulfonyl azide with norbornylene[1d,h] and with 2,3-*endo*-*cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride.[1g] In the former case, it has been shown that the sole product at room temperature or below is the *exo*-aziridine Ia,[1d,5] whereas at higher temperatures small amounts of the sulfonimide II are produced.[1d] On the other hand, 2,3-*endo*-*cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride reacts much more slowly with benzenesulfonyl azide and the major product is the *endo*-aziridine III.[1g] Benzoyl azide likewise reacts with norbornylene, but more slowly than benzenesulfonyl azide, to yield the aziridine Ib and, in addition, the oxazoline IV.[1d,6] We now wish to describe the reaction of benzenesulfonyl azide with norbornadiene, dicyclopentadiene, and bicyclo[2.2.2]-2-octene and to discuss the mechanism of the reaction.



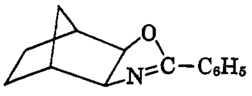
Ia, R = $SO_2C_6H_5$
b, R = COC_6H_5
c, R = $CH_2C_6H_5$



II

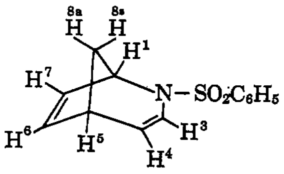


III

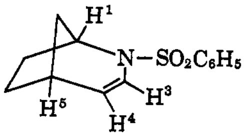


IV

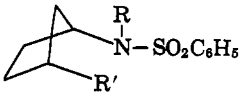
When benzenesulfonyl azide and norbornadiene were mixed together in an inert solvent, there was an immediate evolution of nitrogen. The initially formed major product was found to be unstable and to change spontaneously to a stable product. The stable product, isolated by chromatography on alumina, has been found to be N-benzenesulfonyl-2-azabicyclo[3.2.1]-3,6-octadiene (V) as follows. The n.m.r. spectrum of V (Figure 1) shows two high-field protons as an AB quartet; one of these protons appears as a simple doublet (J^{8s-8a} = 10 c.p.s.) centered at δ 1.23 while the other proton appears as a pair (J^{8s-8a} = 10 c.p.s.) of triplets ($J^{1,5-8a}$ = 4 c.p.s.) centered at δ 1.70. An examination of a Dreiding model of V indicates that the dihedral angle between H-8s and H-1 and H-5 is close to 90°, whereas the dihedral angle between H-8a and H-1 and H-5 is approximately 55–60°; thus, the doublet centered at δ 1.23 can be assigned to H-8s while the multiplet centered at δ 1.70 can be assigned to H-8a. The n.m.r. spectrum also showed the following signals which can be assigned as indicated on the basis of evidence presented below for structure V: δ 2.65 (H-5, quintet), 4.80 (H-1), 5.1–5.5 (H-4, H-6), 6.15 (H-7, quartet, J^{7-1} = 2.9 c.p.s., J^{7-6} = 5.7 c.p.s.), 6.35 (H-3, quartet, J^{3-4} = 7.5 c.p.s., J^{3-5} = 1.5 c.p.s.), 7.46–8.03 (five aromatic protons).



V



VI



VII, R = R' = CHO
VIII, R = H, R' = CO_2H
IX, R = H, R' = CH_3

Hydrogenation of V at atmospheric pressure gave the dihydro derivative VI. The infrared spectrum of VI indicated an enamine-type structure by the presence of a band at 1625 cm.$^{-1}$, while the n.m.r. spectrum (Figure 2) showed two nonequivalent olefinic protons centered at δ 5.25 (H-4, sextet, J^{4-3} = J^{4-5} = 7.5 c.p.s.) and 6.47 (H-3, quartet, J^{3-4} = 7.2 c.p.s., J^{3-5} = 1.5 c.p.s.). Chemical evidence to support structure VI and therefore *ipso facto* structure V was provided by the degradation of VI to 3-methylcyclopentanone. Ozonolysis of VI gave VII on reductive work-up of the product and VIII on oxidative work-up. Wolff–Kishner reduction of VII gave IX as a *cis–trans* mixture.

---

[1] Previous papers in this series: (a) A. C. Oehlschlager and L. H. Zalkow, *Chem. Commun.* (London), 70 (1965); (b) *J. Am. Chem. Soc.*, **86**, 4208 (1964); (c) *Tetrahedron Letters*, 2663 (1964); (d) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. Ind.* (London), 1556 (1964); (e) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **29**, 1625 (1964); (f) L. H. Zalkow and C. D. Kennedy, *ibid.*, **29**, 1290 (1964); (g) *ibid.*, **28**, 3309 (1963); (h) L. H. Zalkow and A. C. Oehlschlager, *ibid.*, **28**, 3303 (1963); (i) L. H. Zalkow and C. D. Kennedy, *ibid.*, **28**, 852 (1963).

[2] For a preliminary account of a part of this work, see ref. 1a and 1d.

[3] National Defense Education Act Fellow, 1962–1965. Taken from the Ph.D. Thesis of A. C. Oehlschlager, submitted April 1965, Oklahoma State University.

[4] To whom inquiries should be addressed: School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.

[5] (a) J. E. Franz and C. Osuch, *Tetrahedron Letters*, 837 (1963); (b) J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964).

[6] R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

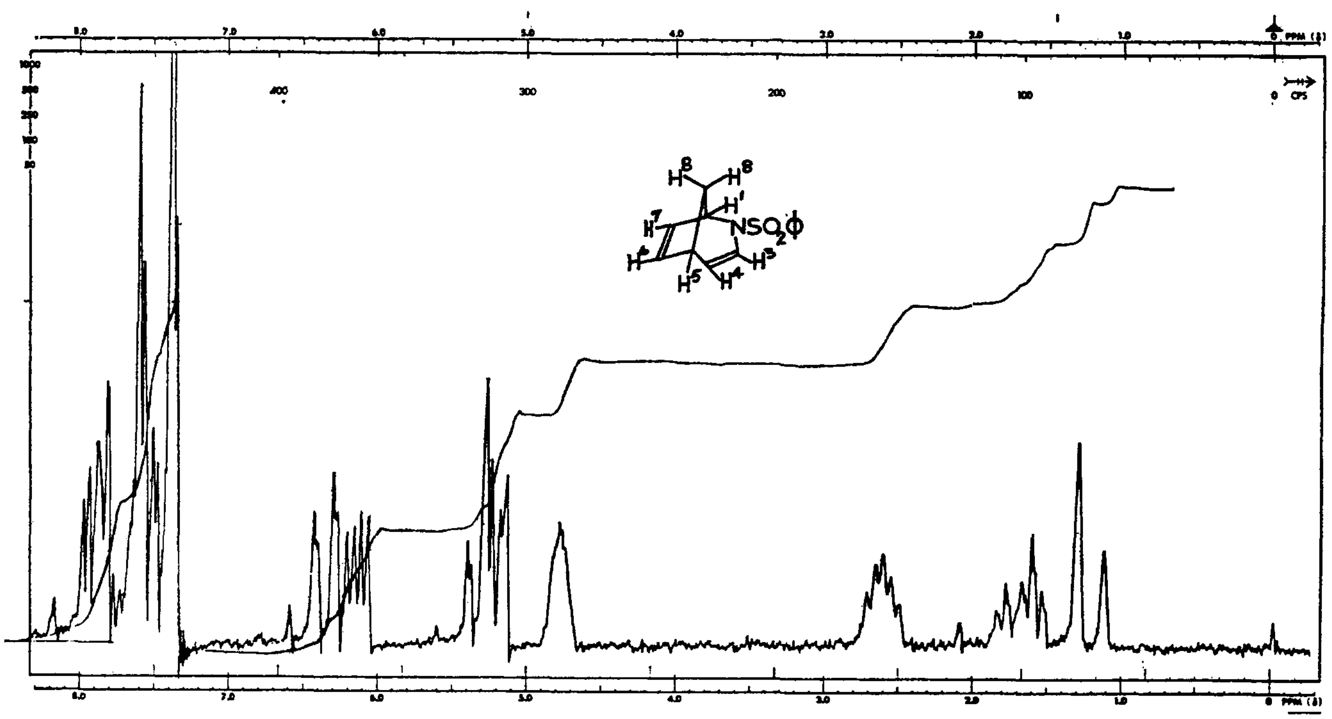


Figure 1.—The n.m.r. spectrum of N-benzenesulfonyl-2-azabicyclo[3.2.1]-3,6-octadiene.

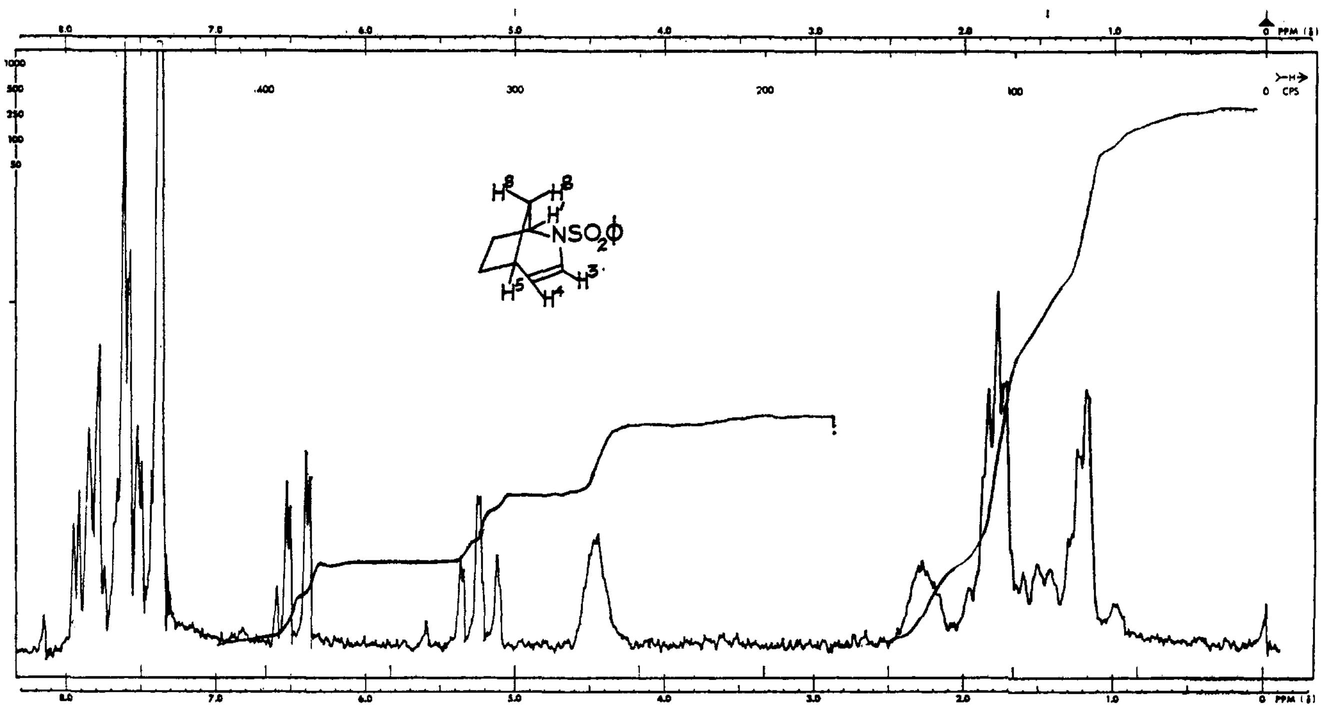
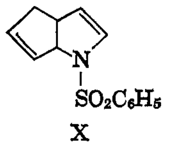
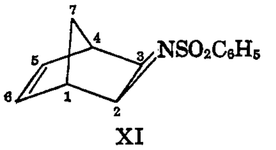


Figure 2.—The n.m.r. spectrum of N-benzenesulfonyl-2-azabicyclo[3.2.1]-3-octene.

Sodium–alcohol reduction of IX gave a mixture of *cis*- and *trans*-3-methylcyclopentylamine, which on nitrous acid deamination gave a mixture of 3-methylcyclopentanol (62%) and olefins (29%). Chromic acid oxidation of the deamination mixture gave as the only ketonic product 3-methylcyclopentanone, which was identified by gas chromatography and mixture melting point of its dibenzylidene derivative with an authentic sample. The possibility of rearrangement in the deamination reaction to yield 3-methylcyclopentanol can be eliminated since both *cis*- and *trans*-2-methylcyclopentylamine are known not to yield 3-methylcyclopentanol on deamination under identical conditions.[7] The nitrogen-containing moiety in VII must therefore be γ to the aldehyde group as required by structure VI. These results are clearly not compatible with X, suggested by others[8] as a possible



X



XI

---

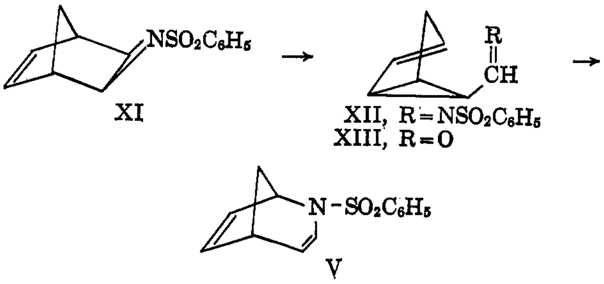
[7] W. Hueckel and K. D. Thomas, *Chem. Ber.*, **96**, 2514 (1963).

[8] J. E. Franz and C. Osuch, *Chem. Ind.* (London), 2058 (1964).

structure for the stable product of the reaction of benzenesulfonyl azide with norbornadiene.

A periodic n.m.r. analysis of a solution of benzenesulfonyl azide and norbornadiene in deuteriochloroform showed that the initially formed major product was XI, which spontaneously rearranged to V. The n.m.r. spectrum initially showed the following signals arising from XI: an AB quartet ($J = 8.5$ c.p.s.) arising from H-7a and H-7s centered at δ 1.07 and 1.66, a broad multiplet centered at δ 2.96 owing to H-1 and H-4, a singlet at δ 3.18 owing to H-2 and H-3, and a triplet ($J = 1.5$ c.p.s.) centered at δ 6.35 which could be assigned to H-5 and H-6. After 3 days, rearrangement to V was complete. Hydrogenation of the reaction product after the rearrangement was approximately 50% complete afforded a 1:1 mixture of VI and Ia which were separated by chromatography on alumina. The *exo*-aziridine Ia, thus obtained, was identical in all respects with Ia obtained in the reaction of norbornylene with benzenesulfonyl azide.

The rearrangement of XI to V can be visualized as occurring *via* the intermediate XII and is analogous to the formation of bicyclo[3.2.1]-2,6-octadiene during the Wittig reaction on XIII.[9] The latter aldehyde is formed by attempted epoxidation of norbornadiene.[10]

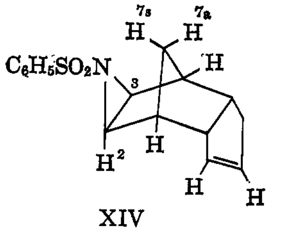


XI

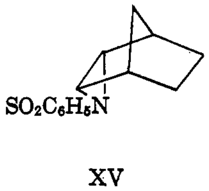
XII, R=NSO₂C₆H₅
XIII, R=O

V

Dicyclopentadiene reacted smoothly with benzenesulfonyl azide in an inert solvent at room temperature to give a product which has been assigned structure XIV. The infrared and n.m.r. spectra of XIV showed the presence of a double bond and a benzenesulfon-



XIV



XV

amido group, but the absence of N–H absorption. A sulfonimide-type structure ($C_6H_5SO_2N{=}C{<}$), previously suggested for the product of the reaction of dicyclopentadiene and *p*-toluenesulfonyl azide,[11] could be eliminated by the appearance of an AB quartet ($J^{2-3} = 5.5$ c.p.s.) in the n.m.r. centered at δ 2.62 (H-2) and 2.88 (H-3), arising from two protons attached to carbons bearing the benzenesulfonamido group. Catalytic hydrogenation of XIV gave the dihydro derivative, the n.m.r. spectrum of which showed a singlet (δ 2.90) for these two protons, indicating they were now equivalent. This observation eliminates an azetidine-type structure for XIV.[5] Alder, *et al.*,[12] showed that phenyl azide reacts with dicyclopentadiene, to give a triazoline instead of an aziridine, only at the C-2 double bond. This was also indicated in XIV by the complexity of the olefinic protons in the n.m.r. spectrum. Hence, it could be assumed, from the evidence presented above, that the product of the reaction of dicyclopentadiene and benzenesulfonyl azide was either XIV or the isomer of XIV possessing an *endo*-aziridine ring.

That the correct structure was XIV was evident from careful examination of the n.m.r. spectra of the addition product and its dihydro derivative. The spectrum of the addition product showed an AB quartet ($J^{7s-7a} = 9.5$ c.p.s.) centered at δ 0.88 (H-7a) and 1.55 (H-7s), while in the dihydro derivative a doublet ($J^{7s-7a} = 9.5$ c.p.s.) appeared at δ 0.92 (H-7a) and the other doublet was buried in the methylene envelope. Tori, *et al.*,[13] have shown that *exo* three-membered rings (cyclopropanes, epoxides, and aziridines) exhibit an anisotropic long-range shielding effect on the *anti* protons in norbornyl and bicyclo[2.2.2]-octyl derivatives. This shielding effect is obvious in the spectra of *exo*-aziridines Ia, b, and c (H-7a, δ <1),[1d] while it is absent in the spectra of III and its derivatives. The protons at C-7 in XV, the synthesis of which will be described in a forthcoming communication, were found to be equivalent and to appear at δ 1.25. Thus it is clear that the adduct possesses structure XIV and the nonequivalence of H-2 and H-3 arises from the shielding of *endo* H-2 by the double bond.

Alder and co-workers[6,12] showed that bicyclo[2.2.2]-octene reacted much slower than norbornene with phenyl azide but each gave a triazoline product. We, therefore, were interested in comparing the reaction of bicyclo[2.2.2]-2-octene with benzenesulfonyl azide with that observed with norbornene. In particular, we wondered if the less strained olefin would yield a triazoline product rather than an aziridine as obtained with norbornene, norbornadiene, and dicyclopentadiene. Under conditions where the last three olefins reacted in a vigorous exothermic reaction, no detectable reaction or evolution of nitrogen could be observed. However, in refluxing benzene two products, XVI and XVII, were obtained. By following the reaction with infrared spectroscopy it was observed that, as the azide absorption (2108 cm.$^{-1}$) disappeared, a new band appeared at 1612 cm.$^{-1}$ ($>$C=N–) and no N–H absorption was observed. If the crude product was allowed to stand in moist air overnight, the band at 1612 cm.$^{-1}$ disappeared and new bands at 3300 (N–H) and 1730 cm.$^{-1}$ ($>$C=O) were observed. By chromatography of the hydrolyzed product, bicyclo[2.2.2]-2-octanone, isolated as its 2,4-dinitrophenylhydrazone, and benzenesulfonamide were isolated, and thus XVI was found to comprise about 30% of the reaction product. The n.m.r. spectrum of the second product showed two protons on carbon attached to the nitrogen of the benzenesulfonamido group by the presence of a multiplet centered at δ 2.88. The two structures

---

[9] C. Cupas, W. E. Watts, and P. v. R. Schleyer, *Tetrahedron Letters*, 2503 (1964).

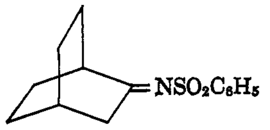
[10] J. T. Lumb and G. H. Whitham, *J. Chem. Soc.*, 1189 (1964); J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1964).

[11] L. Bruner, *Dissertation Abstr.*, **19**, 438 (1958).

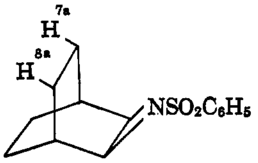
[12] K. Alder, G. Stein, and S. Schneider, *Ann.*, **485**, 211, 223 (1931); **515**, 165 (1935).

[13] K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 869 (1965), and references therein.

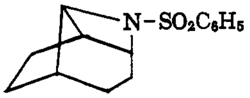
XVII and XVIII are consistent with the infrared and n.m.r. observations and are to be expected on mechanistic grounds. That structure XVII was correct was shown by cleavage of the aziridine ring of XVII by thiophenoxide ion in an SN2 reaction to give XIX which was reduced to 2-benzenesulfonamidobicyclo[2.2.2]octane (XX). The latter compound was synthesized by reduction of bicyclo[2.2.2]-2-octanone oxime and treatment of the resulting amine with benzenesulfonyl chloride. In XVII, H-7a and H-8a are deshielded by the aziridine ring and appear in the n.m.r. spectrum as a doublet (J = 9.5 c.p.s.) centered at δ 1.13, as expected for such a structure.[13] Evidence to support the *trans* stereochemistry depicted in XIX and expected in an SN2 reaction, was provided by examination of the n.m.r. spectrum of XIX in the presence of a small amount of trifluoroacetic acid. Under these conditions (coupling of N–H with H-2 removed), H-2 and H-3 were coupled to give a quartet with J = 6.5 c.p.s. The size of this coupling is consistent with a *trans* arrangement of the groups in XIX; *cis* protons would be expected to show a coupling of approximately 10 c.p.s.[14,15]



XVI

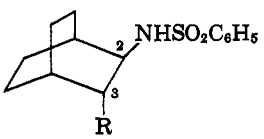


XVII

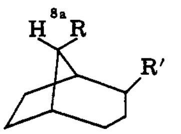


XVIII

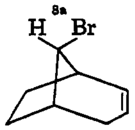
Cleavage of the aziridine ring of XVII with hydrogen bromide in carbon tetrachloride gave a separable mixture of XXI and XXII. The n.m.r. spectrum of XXI was, as expected, similar to that of XIX with $J^{2,3}$ = 5 c.p.s. We have observed that disubstituted bicyclo[2.2.2]octyl and bicyclo[3.2.1]octyl derivatives can be distinguished by comparison of the methylene envelope region of their spectra. The bicyclo[2.2.2]-octyl derivatives show a much narrower methylene envelope region. The n.m.r. spectrum of the second bromide, XXII, in the presence of trifluoroacetic acid, showed the proton on carbon bearing the benzenesulfonamido group as a triplet (J = 4 c.p.s.) centered at δ 3.49 and the proton on the carbon bearing the bromine atom appeared as a multiplet centered at δ 4.28. In the isomeric compound XXIII, the synthesis of which is described in a forthcoming publication, and in XXIV[16] the H-8a protons appear as triplets with J = 4 c.p.s. centered at δ 4.08 and 4.13, respectively. The skeletally rearranged product XXII undoubtedly arises by protonation of the nitrogen atom in XVII to yield a C-2 carbonium ion which undergoes a Wagner–Meerwein shift of the C-1–C-6 bond and a concerted attack by bromine on the developing positive charge at C-1. Such rearrangements are well known in this series.[17]



XIX, R = SC_6H_5
XX, R = H
XIX, R = Br

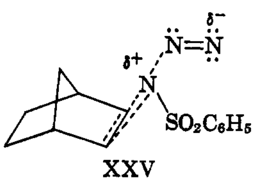


XXII, R = $NHSO_2C_6H_5$, R' = Br
XXIII, R = Br, R' = $NHSO_2C_6H_5$

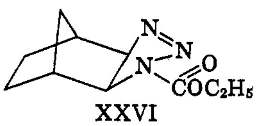


XXIV

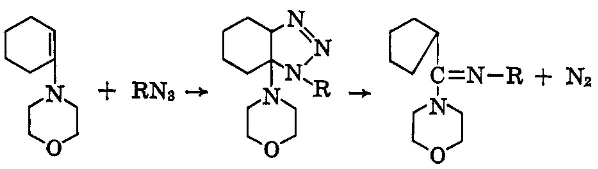
One is immediately struck by the observation that phenyl azide and related azides add to strained olefins to give 1,3-dipolar cycloaddition products, the triazolines, whereas benzenesulfonyl azide gives an aziridine, and no triazolines have thus far been isolated with this reagent. It has been suggested that benzenesulfonyl azide reacts *via* an epoxide-type transition state such as XXV.[5b] However, it appears that the evidence available in the literature supports a triazoline intermediate in this case also. Electron-withdrawing groups attached to the triazoline ring apparently destabilize the ring by facilitating the loss of molecular nitrogen. For example, triazoline XXVI decomposes at 70°, whereas aryl-substituted triazolines decompose only in excess of 150°.[18] Likewise it has been reported that aziridine Ib is formed from the corresponding triazoline at 40°. However, it is not clear from the literature that XXVI and the triazoline from benzoyl azide have actually been isolated as discrete intermediates. Further evidence which supports the conclusion that electron-withdrawing groups destabilize triazoline rings is provided by the reported reaction of aryl azides with enamines.[19] Thus *p*-nitrophenyl azide adds to XXVII to give the triazoline XXVIII which decomposes to yield XXIX on heating at 150°, whereas 2,4-dinitrophenyl azide and *p*-toluenesulfonyl azide give XXIX (R = 2,4-dinitrophenyl and *p*-tosyl, respectively) directly.[19] Recently, it has been reported that cyanogen azide reacts rapidly, even with



XXV



XXVI



XXVII XXVIII XXIX

---

[14] T. G. Taylor, *J. Am. Chem. Soc.*, **86**, 244 (1964).

[15] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

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

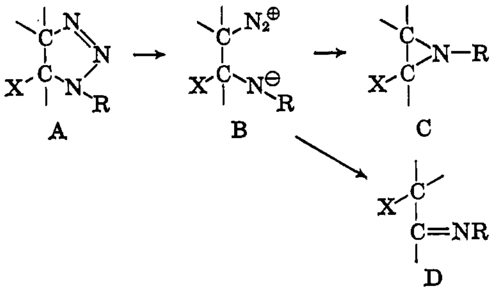
[17] J. A. Berson in "Molecular Rearrangements," part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

[18] P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).

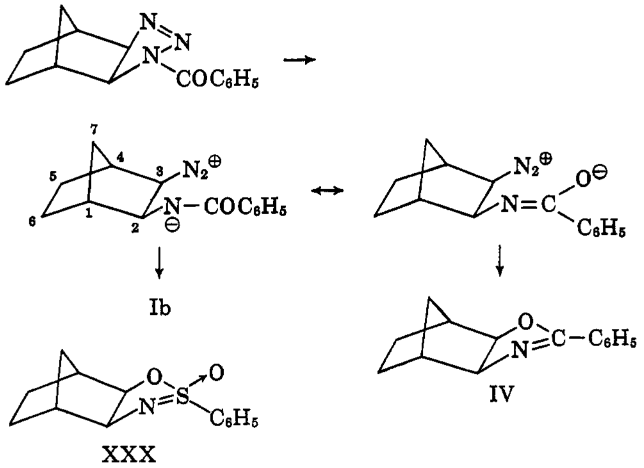
[19] (a) R. Fusco, G. Bianchetti, and S. Rossi, *Gazz. chim. ital.*, **91**, 933 (1961); (b) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Ber.*, **96**, 802 (1963); (c) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).

unstrained olefins, at low temperatures to give alkylidene cyanamides (>C=N—CN) and N-cyanoaziridines.[20] The latter workers[20] also state that they have evidence which indicates that the rate-determining step is the concerted addition of the azide to give an unstable triazoline. Thus it appears likely that the reaction of strained olefins with benzenesulfonyl azides proceeds by way of an unstable triazoline intermediate. We now wish to discuss the reasons for the instability of triazoline rings possessing electron-withdrawing groups.

It has recently been shown that, even in the addition of phenyl azides to norbornene, considerable negative charge resides on the α-azido nitrogen in the transition state and *p*-nitrophenyl azide reacts faster than expected from a simple Hammett treatment, suggesting that this substituent stabilizes the transition state in an exceptional manner.[21] The direction of addition of azides to enamines also indicates a negative charge on the α-azido nitrogen in the transition state.[19] The decomposition of triazoline XXVIII has been postulated as proceeding through an intermediate diazonium betaine,[19] and similarly the intramolecular reaction of azides with double bonds has been shown to proceed *via* isolable triazolines which are postulated as opening in a rate-determining step to give diazonium ion type intermediates.[22] The formation of N-cyanoaziridines are likewise postulated as proceeding *via* these ionic intermediates[20] and apparently picryl azide behaves similarly.[23] Thus all of these ring contractions appear to proceed by a similar mechanism which involves collapse of the triazoline A to give the diazonium ion intermediate B which then loses nitrogen to give as



products aziridine C and/or the Schiff base D (X = C of H). The ring contraction is facilitated by R substituents which are able to stabilize the negative charge on nitrogen in intermediate B. The relative amounts of aziridine C and Schiff base D appear to depend on the nature of the olefin used, the substituent R, and the reaction conditions. The formation of the oxazoline IV in the reaction of benzoyl azide with norbornylene is also consistent with the intermediacy of a diazonium ion intermediate as shown below. The analogous compound from the reaction of benzenesulfonyl azide with norbornylene (XXX) has not yet been detected.



It is interesting that *no* azetidines have been observed in the reaction of norbornylene and related compounds with any of the azides which readily yield aziridines. Thus, if intermediates such as B are involved, there must be little participation of the C-4–C-5 bond of the norbornane skeleton during the loss of nitrogen, and the resulting carbonium ion must react with the adjacent negatively charged nitrogen moiety before rearranging. Other interesting questions which remain to be answered are (a) an explanation for the decreased reactivity of the double bond in norbornylene when an anhydride moiety is added (*exo* or *endo*) to the ring as in 2,3-*cis*-dicarboxybicyclo[2.2.1]-5-heptene anhydride and (b) the reason for the formation of the *endo* aziridine III rather than the less hindered *exo* isomer. We have recently obtained evidence[24] which shows that III is not formed by reaction of the benzenesulfonyl nitrene with the olefin as previously suggested,[1g] and even the isomeric *exo*-anhydride gives predominantly the *endo*-aziridine rather than the previously assumed less hindered *exo*-aziridine.[1g] It is hoped that kinetic studies presently underway in our laboratory will soon provide firm evidence for the mechanism of the reaction of benzenesulfonyl azide with strained olefins and answers will be found to the stereochemical anomalies mentioned above.[25]

Experimental Section

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) and using deuteriochloroform, carbon tetrachloride, or carbon disulfide as a solvent. Carbon and hydrogen analyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind., and nitrogen analyses were performed by a previously described procedure.[26] All thin

---

[20] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

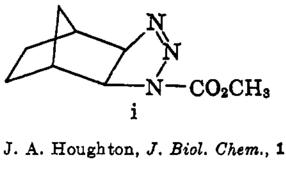
[21] P. Scheiner, J. H. Shomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *ibid.*, **87**, 306 (1965).

[22] A. L. Logothetis, *ibid.*, **87**, 749 (1965).

[23] A. S. Bailey, J. J. Merer, and J. E. White, *Chem. Commun.* (London), 4 (1965).

[24] Unpublished results, L. H. Zalkow, A. C. Oehlschlager, and P. Tillman.

[25] Since the submission of this paper, we have obtained kinetic evidence[24] which supports the conclusion that benzenesulfonyl azide reacts with norbornyl-type olefins, under the conditions described in this paper, to give initially an unstable triazoline, which decomposes *via* a diazonium betaine to give aziridines. Thus, the entropy of activation for the reaction of norbornylene with benzenesulfonyl azide has been found to be $\Delta S^* -28$ cal./deg., which is in good agreement with that reported[21] for the reaction of norbornylene with phenyl azides to give triazolines. The relative rates of decomposition of triazoline i at 71.4° in 1,1-diphenylethane, triglyme, and dimethyl sulfoxide were found[24] to be 1:3:20 as expected[22] for a diazonium betaine intermediate.



i

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

layer chromatograms were developed in iodine vapor unless otherwise stated.

Reaction of Benzenesulfonyl Azide with Norbornadiene. Preparation of N-Benzenesulfonyl-2-azabicyclo[3.2.1]-3,6-octadiene (V).—A solution of 22 g. of benzenesulfonyl azide and 32 g. of norbornadiene in 200 ml. of benzene was stirred overnight at room temperature. The benzene was removed *in vacuo* and the residue was chromatographed on 750 g. of Merck acid-washed alumina. Elution with 2 l. of benzene gave 18.3 g. of V as an oil which decomposed on standing. Elution with 2 l. of ethyl ether gave 5.7 g. of a mixture of several unidentified polar components which showed N-H, O-H, and carbonyl absorption in the infrared spectrum. An analytical sample of V was prepared by distillation at 100° and 0.03 mm.

Anal. Calcd. for $C_{12}H_{13}NO_2S$: C, 63.13; H, 5.30. Found: C, 63.64; H, 5.53 (sample decomposed on standing).

N.m.r. Study of the Reaction of Benzenesulfonyl Azide with Norbornadiene.—A solution of 0.244 g. of norbornadiene and 0.240 g. of benzenesulfonyl azide in 1 ml. of deuteriochloroform (1% tetramethylsilane) was placed in an n.m.r. tube at 26° and the spectrum was recorded periodically. Based on the integration of total aromatic protons in the mixture and selected nonaromatic protons in XI and V, the percentage (±2%) of each component at a given time after mixing is shown in Table I.

TABLE I

REARRANGEMENT OF XI TO V

Time, hr.	XI, %	V, %
2	53	13
4.5	50	25
8.5	54	31
19	43	45
48	21	60
72	<1	81

The following signals in the n.m.r. spectrum at 2 hr. were attributed to XI: an AB quartet (J = 8.5 c.p.s.) at δ 1.07 and 1.66 arising from H-7a and H-7s, a broad multiplet centered at δ 2.96 owing to the bridgehead protons, a sharp singlet at δ 3.18 for H-2 and H-3, and a triplet (J = 1.5 c.p.s.) centered at δ 6.35 arising from H-5 and H-6.

Preparation of N-Benzenesulfonyl-8-azatricyclo[3.2.1.1$^{2,3\text{-}exo}$]-octane Ia from XI.—A solution of 32 g. of norbornadiene and 21.4 g. of benzenesulfonyl azide in 300 ml. of benzene was stirred overnight. Removal of the benzene *in vacuo* left 28.7 g. of an oil the n.m.r. analysis of which showed 33 ± 2% XI and 40 ± 2% V. A solution of 5.8 g. of this mixture in 50 ml. of ethyl acetate was hydrogenated in the presence of 0.7 g. of platinum oxide. After the uptake of hydrogen ceased, the catalyst was removed by filtration and the solvent was evaporated to give 5.9 g. of an oil. Analysis of the hydrogenated mixture by n.m.r. showed the presence of 33 ± 2% Ia and 42 ± 2% VI. The hydrogenated mixture was chromatographed directly on 700 g. of Merck acid-washed alumina. Elution with 1 l. of benzene gave 1.232 g. of VI, m.p. 47–51°. Further elution with 1 l. of benzene, 2 l. of benzene–chloroform (9:1), and 1 l. of benzene–chloroform (7:3) gave 3.75 g. of a mixture of Ia and VI from which 0.99 g. of Ia crystallized from ether–petroleum ether (b.p. 30–60°), m.p. 104–105°. A mixture melting point with an authentic sample of Ia (m.p. 104–105°) was undepressed.

Preparation of N-Benzenesulfonyl-2-azabicyclo[3.2.1]-3-octene (VI) from V.—A solution of 18 g. of V in 250 ml. of methanol was stirred for 24 hr. under hydrogen at atmospheric pressure in the presence of 2 g. of 5% palladium on charcoal. After hydrogen uptake ceased, the reaction mixture was filtered and the methanol was removed *in vacuo*. The hydrogenated product was chromatographed on 750 g. of Merck acid-washed alumina. Elution with 2 l. of benzene gave 15.3 g. of VI which crystallized and had m.p. 47–51°. This material showed only one spot (R_f 0.45) upon thin layer chromatography (silica gel G, 20 cm., chloroform as mobile phase). The analytical sample was prepared by sublimation three times at 50° and 0.03 mm. and had m.p. 51–52° (lit.[8] m.p. 50–53°); $\nu_{\max}^{\text{melt}}$ 1625, 1318, 1165, 1100, 968, and 726 cm.$^{-1}$.

Ozonolysis of VI.—A stream of oxygen containing ozone (~4%) was passed through a solution of 15 g. of VI in 50 ml. of methylene chloride maintained at −70°. After the uptake of ozone ceased (*ca.* 2 hr.), the solution was poured into 50 ml. of 50% acetic acid containing approximately 2 g. of zinc dust and the slurry was stirred overnight. The acidic aqueous layer was neutralized with sodium carbonate and the organic layer was decanted. The aqueous layer was extracted with additional methylene chloride. The methylene chloride extracts were combined, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. Chromatography of the concentrate on 500 g. of Merck acid-washed alumina yielded 7.1 g. of VII as an oil eluted with benzene–ether (9:1): $\nu_{\max}^{\text{film}}$ 2775, 1725, 1365, 1230, 1177, and 1100 cm.$^{-1}$; n.m.r. (in $CDCl_3$) δ 1.40–2.74 (seven protons) 4.34 (H-3), 7.59–8.09 (five aromatic protons), 9.22 (N-formyl proton), and 9.71 (aldehydic proton, doublet, J = 1.5 c.p.s.).

Preparation of 3-Benzenesulfonamidocyclopentanecarboxylic Acid (VIII) and Its Methyl Ester.—A stream of oxygen containing ozone was passed through a solution of 9.7 g. of VI in 20 ml. of methylene chloride maintained at −70°. After the uptake of ozone ceased (*ca.* 1 hr.), the solution was treated with 25 ml. of 30% hydrogen peroxide and stirred for 4 hr. The excess peroxide was then destroyed by the addition of platinum oxide and the methylene chloride solution was treated directly with excess Tollens reagent (16 g. of $AgNO_3$ in 320 ml. of water mixed with 160 ml. of 10% NaOH and 160 ml. of dilute NH_4OH just before use). After 24 hr. the excess Tollens reagent was destroyed by addition of formaldehyde. The aqueous basic solution was washed with ether and acidified. The acidic aqueous solution was extracted with ether which, after drying over anhydrous magnesium sulfate, was evaporated to give 8.2 g. of VIII as an oil. Crystallization of VIII from ether in the cold gave m.p. 117–119°, $\nu_{\max}^{\text{KBr}}$ 3280 (N-H) and 1715 (C=O) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{15}NO_4S$: C, 53.31; H, 5.97. Found: C, 53.20; H, 5.56.

The methyl ester was prepared by treatment of VIII with excess ethereal diazomethane and was obtained as a viscous oil on evaporation of the ether: thin layer chromatography of the methyl ester on silica gel G (15 cm.) with a mobile phase of chloroform–acetone (9:1) gave R_f 0.45; $\nu_{\max}^{\text{KBr}}$ 3250, 1730, 1320, and 1160 cm.$^{-1}$; n.m.r. (in $CHCl_3$) δ 1.47–2.15 (six protons), 2.45–3.12 (H-1), 3.65 (four protons, methyl ester protons superimposed on H-3, 5.95 (N-H, doublet, J = 8 c.p.s.), and 7.55–8.10 (five aromatic protons).

Conversion of VII to N-3-(Methylcyclopentyl)benzenesulfonamide (IX).—To a solution of 3.9 g. of VII in 45 ml. of ethylene glycol were added 10.5 g. of potassium hydroxide and 5 ml. of 95+% hydrazine. The reaction mixture was refluxed for 4 hr., then the temperature was raised to 210° by distillation of water and excess hydrazine. More hydrazine (5 ml.) was added and the solution was refluxed at 190° for an additional 18 hr. The reaction mixture was cooled, poured onto 100 ml. of water, neutralized with dilute sulfuric acid, and extracted with ether. The ether extract was washed twice with 100-ml. portions of water and then dried over anhydrous magnesium sulfate. Evaporation of the ether gave an oil which was chromatographed on 250 g. of Merck acid-washed alumina. Elution with 1 l. of benzene–ether (9:1) gave 2.0 g. of IX as an oil. Thin layer chromatography of the eluate on silica gel G (15 cm.) (chloroform) showed that successive chromatograhic fractions contained two poorly resolved components (R_f 0.40, 0.42). An analytical sample of IX was prepared by distillation of the eluate at 150–160° and 0.05 mm.: n.m.r. (in $CDCl_3$) δ 0.78–1.0 (three protons, methyl protons as two overlapping doublets), 1.0–2.0 (seven protons), 3.64 (H-1, sextet), 6.01 (N-H, doublet, J = 7.5 c.p.s.), and 7.44–8.17 (five aromatic protons.)

Anal. Calcd. for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16. Found: C, 60.31; H, 7.13.

Conversion of IX to 3-Methylcyclopentylamine.—To a solution of 1.5 g. of IX in 20 ml. of *sec*-butyl alcohol was added 2 g. of metallic sodium over a period of 15 min. The solution was refluxed overnight, cooled, diluted with water, and acidified with dilute hydrochloric acid. The reaction mixture was then concentrated *in vacuo* and then extracted several times with chloroform. The aqueous portion was rendered basic and extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, was slowly evaporated through a Vigreux column to give 450 mg. of the amine as a foul-smelling oil. The amine was converted into its HCl salt by the addition of excess dilute hydrochloric acid followed by evaporation *in vacuo* of the excess hydrogen chloride and water. The HCl salt thus prepared was used without further purification.

Nitrous Acid Deamination of 3-Methylcyclopentylamine.—A solution of 405 mg. of the HCl salt of the amine prepared above in 2 ml. of water was heated at 60° for 4 hr. with 0.32 g. of sodium nitrite and 7 drops of glacial acetic acid. After this time, the solution was neutralized with aqueous sodium carbonate solution and steam distilled. The steam distillate was extracted with ether which, after drying over anhydrous magnesium sulfate, was slowly evaporated through a Vigreux column leaving 200 mg. of a mixture of 3-methylcyclopentanol and olefins. Gas chromatography of the mixture on a 0.25 in. × 10 ft. DEGS column at 120° using a helium flow rate of 115 cc./min. showed the following peaks: 0.5 (29%, olefins), 1.75 (6%), 4 (3%), and 6.5 min. (62%, 3-methylcyclopentanol). Cyclopentanol had a retention time of 5.5 min. under these conditions.

Preparation of 3-Methylcyclopentanone.—A portion (160 mg.) of the deamination mixture from above was stirred for 24 hr. with 300 mg. of chromic anhydride in 3 ml. of 90% acetic acid. The reaction mixture was diluted with 5 ml. of water and neutralized with sodium carbonate. The neutral solution was extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and evaporated slowly through a Vigreux column to give 102 mg. of 3-methylcyclopentanone. Gas chromatography of the oxidation mixture using the same conditions described above except for a flow rate of 86 cc./min. showed 3-methylcyclopentanone as the major component (retention time 6.5 min.), identical with an authentic sample upon mixed injection and different from 2-methylcyclopentanone, which under these conditions had a retention time of 5.5 min. The dibenzylidene derivative had m.p. 156–157°, after recrystallization from methanol; mixture melting point with an authentic sample showed no depression.

Reaction of Benzenesulfonyl Azide with Dicyclopentadiene.—A solution of 4.3 g. of dicyclopentadiene and 7.0 g. of benzenesulfonyl azide in 10 ml. of chloroform was stirred at room temperature for 3 hr. During this time nitrogen was smoothly evolved and a white solid precipitated from the reaction solution. The solid was recrystallized from benzene–petroleum ether (1:1) to give 9.49 g. of XIV: m.p. 138°; $\nu_{\max}^{\mathrm{KBr}}$ 1310, 1160, 1090, 885, and 750 cm.$^{-1}$; n.m.r. (in CCl_4) δ 0.88 (H-7a, J^{7a-7s} = 9.5 c.p.s.), 1.55 (H-7s, J^{7a-7s} = 9.5 c.p.s.), 2.62 (H-2, J^{2-3} = 5.5 c.p.s.), 2.88 (H-3, J^{2-3} = 5.5 c.p.s.), 2.2–3.2 (six protons, broad multiplet), 5.4–5.9 (two vinylic protons), and 7.4–7.9 (five aromatic protons).

Anal. Calcd. for $C_{16}H_{17}NO_2S$: C, 67.37; H, 5.96; N, 4.91. Found: C, 67.27; H, 5.92; N, 4.68.

Hydrogenation of XIV.—A solution of 0.560 g. of XIV in 20 ml. of 95% ethanol was hydrogenated in a Parr hydrogenation apparatus with 0.5 g. of Raney nickel (wet weight) under an initial pressure of 40 p.s.i.g. After 48 hr. the solution was filtered and the hydrogenated product was precipitated (0.526 g.) from the alcoholic filtrate by addition of water. The dihydro product had m.p. 144–145°; $\nu_{\max}^{\mathrm{KBr}}$ 1310, 1160, and 878 cm.$^{-1}$; n.m.r. (in CS_2) δ 0.92 (H-7a, J^{7a-7s} = 9.5 c.p.s.), 1.35–1.72 (nine protons), 2.21–2.40 ((H-1, H-4, H-5, H-6), 2.90 (H-2, H-3), and 7.23–7.82 (five aromatic protons).

Anal. Calcd. for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62. Found: C, 66.54; H, 6.66.

Reaction of Benzenesulfonyl Azide with Bicyclo[2.2.2]-2-octene.—A solution of 12.4 g. of benzenesulfonyl azide and 7.3 g. of bicyclo[2.2.2]-2-octene in 30 ml. of benzene was heated on a steam bath for 3 days. Analysis of the reaction mixture by infrared spectroscopy at 24-hr. intervals showed an increase in absorption at 1612 cm.$^{-1}$ as the azide absorption and 2108 cm.$^{-1}$ decreased in intensity (no absorption for N–H was observed). Removal of the benzene under vacuum left 18.5 g. of semisolid residue.

The infrared spectrum of a portion of the reaction residue exposed to moist air overnight showed N–H absorption in the 3300-cm.$^{-1}$ region and a carbonyl absorption at 1730 cm.$^{-1}$ but no absorption at 1612 cm.$^{-1}$.

A 2.05-g. portion of the reaction mixture was finely ground and exposed to moist air overnight. Chromatography of this portion on 100 g. of silica gel gave 1.41 g. of solid upon elution with 0.8 l. of benzene–petroleum ether (1:1). Thin layer chromatography of the solid on silica gel G (10 cm.) with benzene–petroleum ether (1:1) showed this eluate to be a mixture of XVII and bicyclo[2.2.2]-2-octanone. These two components were separated by addition of excess acidic, ethanolic 2,4-dinitrophenylhydrazine followed by fractional recrystallization. The 2,4-dinitrophenylhydrazone derivative and XVII were separated by repeatedly adding water to ethanolic solutions of the mixture; the hydrazone precipitated immediately and the aziridine only upon standing. In this manner 0.685 g. of bicyclo[2.2.2]-2-octanone 2,4-dinitrophenylhydrazone, m.p. 165–166° (lit.[16] m.p. 165–166°), and 1.102 g. (54%) of XVII, m.p. 88–90°, were obtained. The analytical sample of XVII gave $\nu_{\max}^{\mathrm{KBr}}$ 1308, 1160, 1092, and 990 cm.$^{-1}$; n.m.r. (in CS_2) δ 1.13 (H-7a, H-8a, $J^{7a,8a-7s,8s}$ = 9.5 c.p.s.), 1.53 (six protons as broad multiplet), 1.82–2.05 (H-1, H-4), 2.88 (H-2, H-3, multiplet), and 7.47–7.84 (five aromatic protons).

Anal. Calcd. for $C_{14}H_{17}NO_2S$: C, 63.89; H, 6.51. Found: C, 63.95; H, 6.90.

Elution of the silica gel column with 150 ml. of 95% ethanol gave 0.8 g. of brown solid from which 0.4 g. (33%) of benzenesulfonamide, m.p. 150–152°, was sublimed; mixture melting point with an authentic sample was undepressed.

Preparation of *trans*-2-Thiophenoxy-3-benzenesulfonamidobicyclo[2.2.2]octane (XIX).—A solution of 1.7 g. of XVII and 1.3 g. of thiophenol in 13 g. of *t*-butyl alcohol, 0.1 *N* in potassium *t*-butoxide, was refluxed for 12 hr. The reaction mixture was diluted with water and carefully neutralized with dilute hydrochloric acid. The mixture was extracted with ether which was then dried over anhydrous magnesium sulfate and evaporated to give 2.17 g. (89%) of XIX: m.p. 135–136°; n.m.r. (in $CHCl_3$) δ 1.29–1.82 (ten protons), 3.10 (two protons, multiplet; sharpened to AB quartet upon addition of CF_3COOH with doublets centered at δ 2.82 and 3.02, $J^{2,3}$ = 6.5 c.p.s.), and 6.08 (N–H, doublet, J = 5.5 c.p.s.; disappears upon addition of CF_3COOH). An analytical sample was prepared by recrystallization from ether and had m.p. 135–136°.

Anal. Calcd. for $C_{20}H_{23}NO_2S_2$: C, 64.31; H, 6.21. Found: C, 64.11; H, 6.35.

Conversion of XIX to 2-Benzenesulfonamidobicyclo[2.2.2]octane.—A suspension of 12 g. of Raney nickel in 25 ml. of isopropyl alcohol containing 1.7 g. of XIX was refluxed for 12 hr.[5b] The reaction mixture was then filtered and the nickel was washed several times with isopropyl alcohol. Evaporation of the filtrate gave 1 g. of 2-benzenesulfonamidobicyclo[2.2.2]octane, m.p. 95–96°. An analytical sample was prepared by recrystallization from ether and had m.p. 97–98°; $\nu_{\max}^{\mathrm{KBr}}$ 3282, 1330, and 1165 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22. Found: C, 63.72; H, 7.37.

An authentic sample of 2-benzenesulfonamidobicyclo[2.2.2]octane was prepared from bicyclo[2.2.2]-2-octanone oxime, m.p. 113–116° (lit.[27] m.p. 114–118°), by catalytic reduction with Raney nickel in methanol to the amine and subsequent treatment of the amine with benzenesulfonyl chloride. The sample prepared in this manner had m.p. of 96–97°, and the mixture melting point with that prepared from XIX was undepressed.

Treatment of XVII with Hydrogen Bromide.—Dry hydrogen bromide was passed through a solution of 4.7 g. of XVII dissolved in 25 ml. of carbon tetrachloride at room temperature for 1 hr. The solution was allowed to stir overnight and then swept with nitrogen and washed with aqueous sodium carbonate solution. The carbon tetrachloride solution was dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed directly on 300 g. of Merck acid-washed alumina. Elution with benzene–chloroform mixtures gave an initial eluate (1.6 g.) containing two components (thin layer chromatography) from which XXII crystallized from petroleum ether–ether solution: m.p. 129–130°; $\nu_{\max}^{\mathrm{KBr}}$ 3300, 1318, 1170, and 1097 cm.$^{-1}$; n.m.r. (in $CHCl_3$) δ 1.10–2.31 (ten protons), 3.49 (H-8 multiplet; sharpened to a triplet, J = 4 c.p.s., upon addition of CF_3COOH), 4.28 (H-2, multiplet), and 6.09 (N–H, doublet, J = 9 c.p.s.; disappeared upon addition of CF_3COOH).

Continued elution with benzene–chloroform mixtures of increasing polarity gave 2.3 g. of XXI: m.p. 136–137°; $\nu_{\max}^{\mathrm{KBr}}$ 3230, 1310, 1160, and 1080 cm.$^{-1}$; n.m.r. (in $CHCl_3$–CF_3COOH) δ 1.27–2.0 (ten protons), 3.70 (H-2, doublet, J = 5 c.p.s.), 3.96 (H-3, doublet, J = 5 c.p.s.), and 7.50–8.15 (five aromatic protons).

Anal. Calcd. for $C_{14}H_{18}BrNO_2S$: C, 48.84; H, 5.27. Found: C, 49.18; H, 5.35.

---

[27] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).