

THE REACTION OF N,N-DIBROMCBENZENESULFONAMIDE WITH  
NORBORNYLENE. THE OCCURRENCE OF A HYDRIDE SHIFT  
DURING AN TONIC ADDITION TO NORBORNYLENE

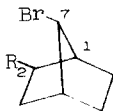
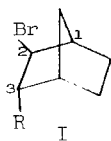
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The addition of N,N-dibromobenzenesulfonamide to norbornylene has been found to lead to an extremely rapid exothermic reaction with concomitant precipitation of benzenesulfonamide (27%). The benzene soluble portion of the reaction mixture yielded, after chromatography on alumina, three major fractions. The first fraction (65% based on norbornylene consumed), eluted in petroleum ether, was comprised of 3-bromonorbornene (85%) and norbornane dibromides (15%), the second fraction, eluted in benzene-chloroform, yielded A (20%),  $C_{13}H_{16}BrNO_2S$ , m.p. 93-94°, and the third fraction, eluted with chloroform, gave B (9%), isomeric with A.

The analogous additions of bromine<sup>3</sup> and hypobromous acid<sup>4</sup> to norbornylene have been shown to yield the trans-2,3 products I (R = Br or OH) and the 2-exo-7-syn products II and III



II R = Br

III R = OH

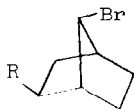
IV R =  $NHSO_2C_6H_5$

respectively. The n.m.r. spectrum of A showed the proton on the carbon bearing the benzenesulfonamido group as a multiplet ( $\delta$  3.47) which sharpened to a triplet upon the addition of trifluoroacetic acid, and the proton attached to the bromine-bearing carbon appeared as an unresolved signal ( $\delta$  3.79) of half-height-width ( $W_{1/2h}$ ) <sup>4</sup> c.p.s. The n.m.r. spectra of II and III were similar to that of A, each showing H<sub>2</sub> as a triplet and H<sub>7</sub> as a broad signal ( $W_{1/2h} = 4$  c.p.s.). Thus, structure IV was suggested for A and that this was indeed correct was shown as follows. Reduction of A with sodium in sec-butyl alcohol gave the known 2-exo-norbornyl amine identified by conversion to the corresponding acetate and comparison of the latter with an authentic sample by I.R., m.p. and g.l.c.<sup>5</sup> That epimerization of the sulfonamido group had not occurred in the above transformation was shown by reduction of 2-endo-norbornyl amine benzenesulfonate to the 2-endo-amine under the same conditions. Heating A with aqueous hydrochloric acid in a sealed tube at 175° followed by oxidization<sup>6</sup> of the resulting bromo amine gave the known syn-7-bromonorbornanone.<sup>4</sup>

The n.m.r. spectrum of B was very similar to that of A, showing the proton on the nitrogen-bearing carbon as a multiplet centered at  $\delta$  3.20 which sharpened to a quartet on the addition of trifluoroacetic acid, and the proton on the bromine-bearing carbon as a broad ( $W_{1/2h} = 4$  c.p.s.) signal centered at  $\delta$  4.15. Thus B could not be represented by structure I (R = NHSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) since in that case H<sub>3</sub> would be coupled to H<sub>2</sub> and to H<sub>1</sub> and the observed signal for the proton on the carbon bearing bromine in B is too narrow ( $W_{1/2h} = 4$  c.p.s.) to accommodate such coupling.

Thus, the n.m.r. spectrum of B suggested that the bromine atom was also attached to C<sub>7</sub> just as in IV.

Reduction of B with sodium in sec-butyl alcohol also gave 2-exo-norbornyl amine and it therefore appeared that B possessed



V R = NHSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

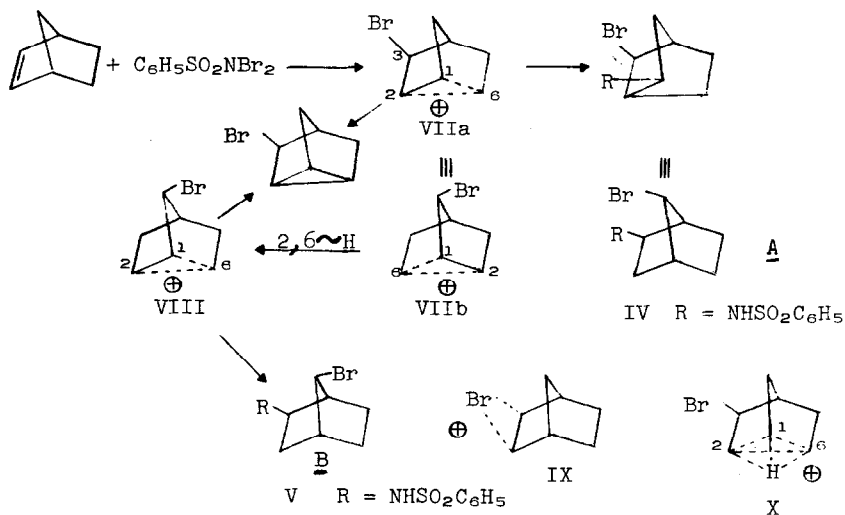
VI R = OCOCH<sub>3</sub>

structure V. Further evidence, which conclusively established structure V for B was obtained as follows. Hydrolysis of B with hydrochloric acid, as described above, and oxidation of the resulting amino bromide gave a bromonorbornanone (2,4-DNP m.p. 152-153°) found not to be identical with the 2-exo, 2-endo or 7-syn-bromonorbornanones by I.R., g.l.c., and by comparison of 2,4-DNP derivatives. This new compound was shown to be 7-anti-bromonorbornanone by synthesis of the latter. Kwart and Miller<sup>7</sup> have previously described the preparation of 2-exo-acetoxy-7-anti-bromonorbornane, VI, and this substance was treated with lithium aluminum hydride to give the bromo alcohol which was oxidized to give 7-anti-bromonorbornanone, identical in all respects with that obtained, as described above, from B (**V**).

The formation of **V** and the apparent absence of any appreciable amount of product (94% of the norbornylene consumed was accounted for) of structure III (R = NHSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) in the reaction of N,N-dibromobenzenesulfonamide with norbornylene is of particular interest. Mechanistically,<sup>9</sup> the formation of IV

and V can be visualized as occurring as outlined in Scheme I.

Scheme I



It is postulated that the carbon-bridged cation VII is the reactive intermediate formed rather than the halogen-bridged cation IX since the latter would be expected to lead to product I ( $\text{R} = \text{NHSO}_2\text{C}_6\text{H}_5$ ).<sup>8</sup> Attack of VIIa at  $\text{C}_1$  would lead to product IV (A) and 2,6-hydride shift of VIIb ( $\text{VIIa} \rightleftharpoons \text{VIIb}$ ) would lead to intermediate VIII which by attack at  $\text{C}_2$  would give V (B). The lack of reactivity of VIIa at  $\text{C}_2$  and VIII at  $\text{C}_1$  would arise from the unfavorable influence of the adjacent  $\text{C}_7$ -halogen dipole.<sup>10</sup> Intermediate X would likewise satisfactorily account for products IV and V, but if it were the sole reactive intermediate, it would be difficult to explain the almost 2:1 yield of IV compared to V.<sup>11</sup> Although 2,6-hydride shifts, as required in the formation of V, are well established in solvolysis reactions

they are virtually unknown during addition reactions of norbornylene, especially under the non-polar conditions used in this reaction. An explanation for the 2,6-hydride shift may be found in the relative sluggishness of the nucleophile  $\text{R}^{\ominus}$  ( $:\text{N}-\text{SO}_2\text{C}_6\text{H}_5$ ) involved which would allow the slow<sup>11</sup> hydride shift to occur before attack of the nucleophile.

The point at which the second bromine atom in N,N-dibromobenzenesulfonamide is lost is not clear at present. Kharasch and Priestley<sup>13</sup> first pointed out that N,N-dibromobenzenesulfonamide reacted with 2 moles of an alkene in an ionic manner to give the vicinal bromo-benzenesulfonamido derivative and a vinyl bromide. In the present case nortricyclene bromide is formed rather than an unsaturated bromide and its much larger yield as compared to that of IV + V indicates that it is formed, at least partly, independently of IV and V presumably via intermediates VII and VIII.

## REFERENCES

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- (2) To whom inquiries should be addressed.
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- (8) IX might well be an intermediate but if it is, it for some reason is not product producing. Berson (p. 163, ref. 9) has suggested that in the bromination of norbornylene, the carbon-bridged cation (VII) is readily converted into the halogen-bridged cation (IX). Perhaps VII and VIII are intimately associated with the negatively charged species in the present case, and this intimate ion pair is more stable than an intimate ion pair involving IX.
- (9) J. A. Berson, "Carbonium Ion Rearrangements in Bridged Bicyclic Systems," Chp. 3 in "Molecular Rearrangements," Part I, Edited by P. de Mayo, Interscience Publishers, New York, 1963.
- (10) pp. 150, 163, ref. 9.
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- (12) See however p. 165, ref. 9.
- (13) M. S. Kharasch and N. M. Priestley, J. Am. Chem. Soc., 61, 3425 (1939).