

THE REACTIONS OF 7-syn-BENZENESULFONAMIDO AND  
7-syn-CARBOMETHOXYAMINO-2-exo-BROMONORBORNANE  
WITH SODIUM METHOXIDE IN METHANOL

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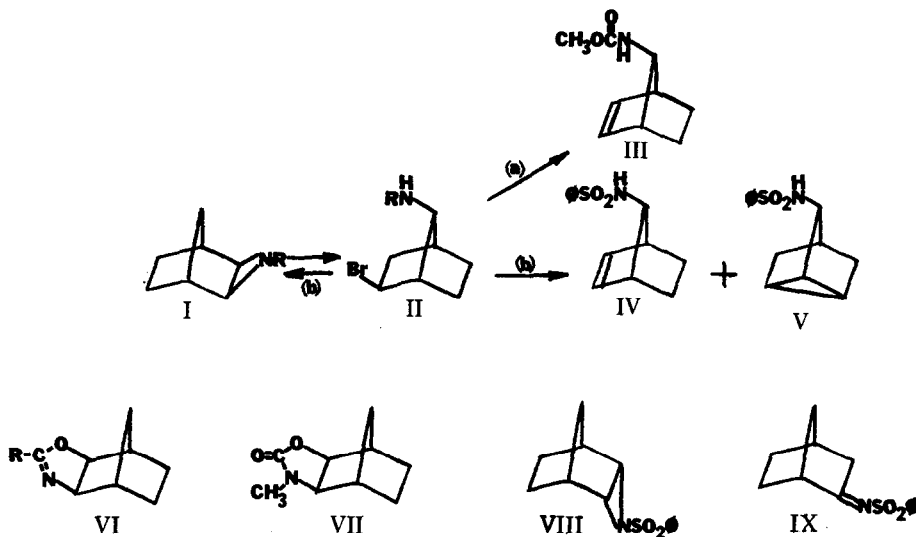
It has been known for sometime that exo aziridines such as I, on treatment with hydrogen halides, are readily converted into 2-exo-halo-syn-7-aminonorbornane derivatives (II)<sup>1,2</sup>. In fact, this has been the basis of an efficient synthesis of syn-7-norbornenylamines. Thus, Tanida et al<sup>2</sup> prepared syn-7-N-carbomethoxyaminonorbornene (III) in overall isolated yield of 62% by treating aziridine I (R = CO<sub>2</sub>Et) in pentane with hydrogen bromide and then subjecting the intermediate II (R = CO<sub>2</sub>Et) to treatment with sodium methoxide in refluxing methanol (path a).

In an attempt to prepare the analogous syn-7-benzenesulfonamidonorbornene (IV), we subjected II (R = SO<sub>2</sub>φ. δ<sup>DCCl<sub>3</sub></sup> 3.54, d, J = 8; 3.95, m; 5.65, d, J = 8. δ<sup>DCCl<sub>3</sub> + D<sub>2</sub>O</sup> 3.54, s; 3.95, m)<sup>3</sup> to similar conditions to those described above and were surprised to find that the major product was aziridine I (R = SO<sub>2</sub>φ) from which the starting bromoamide II had been made! In addition to the aziridine I, there were obtained as minor products syn-7-benzenesulfonamidonorbornene (IV), 3-benzenesulfonamidonortricyclene (V) and some not well characterized methoxyl containing materials, presumably solvolysis products (path b). The product composition varied somewhat with concentration of II. Thus a 0.061M solution of II gave 58% I, 8% IV, 10% V and 24% solvolysis products, whereas a 0.31M solution of II gave 41% I, 16% IV, 30% V and 13% solvolysis products. In each case a ten fold molar excess of sodium methoxide was used and the starting material II was completely converted into the indicated products.

The products I, IV and V ( $R = SO_2\phi$ ) were obtained in pure form by chromatography on silica gel coated with 25% silver nitrate. Aziridine I was found to be identical with an authentic sample<sup>1</sup> by melting point, glc, NMR and IR. 3-Benzenesulfonamidonortricyclene (V. m.p. 92-93°.  $\nu^{KBr} 3250\text{cm}^{-1}$ .  $\delta^{DCCl_3}$  3.27, d, J = 7; 5.43, d, J = 7.  $\delta^{DCCl_3 + D_2O}$  5.43, s) was identical to an authentic sample prepared from the known<sup>4</sup> 3-carboethoxyaminonortricyclene by saponification ( $NaOH, H_2O-HOCH_2CH_2OH$ ) followed by acylation with benzenesulfonyl chloride. The final compound eluted off the column was identified as syn-7-benzenesulfonamidonorbornene (IV. m.p. 71-72°.  $\nu^{KBr} 3248, 1625\text{cm}^{-1}$ .  $\delta^{DCCl_3}$  3.99, d, J = 10; 4.96, d, J = 10; 5.93, 2H, t, J = 2) by its IR and NMR spectra and by comparison of the latter with those of norbornene ( $\delta^{DCCl_3}$  6.0, 2H, t, J = 2) and the previously reported III<sup>2</sup>.

Because of the striking differences in behavior of II depending on the nature of R (path (a) vs path (b)), we prepared II ( $R = CO_2Me$ )<sup>5</sup> from I ( $R = CO_2Me$ ) in the usual manner and it indeed gave only III and no aziridine under the previously reported conditions<sup>2</sup>. Since I ( $R = CO\phi$ ) is known to lead to oxazoline VI ( $R = \phi$ ) on heating<sup>6</sup>, we attempted to prepare oxazoline VI ( $R = OCH_3$ ) in a similar manner to investigate the possibility of it being an intermediate in the formation of III. Under conditions where aziridine I ( $R = CO\phi$ ) is transformed into oxazoline VI ( $R = \phi$ ), aziridine I ( $R = CO_2Me$ ) remains unchanged and on more extended heating it gives the oxazolidone VII ( $\nu^{film} 1740, 1030\text{cm}^{-1}$ .  $\delta^{DCCl_3}$  2.83, 3H, s; 3.52, 1H, d, J = 7; 4.37, 1H, d, J = 7)<sup>7</sup>. Therefore, oxazoline VI ( $R = \phi$ ) was subjected to the reaction conditions which lead to the formation of III and it remained unchanged!

We then turned our attention to the conditions under which II ( $R = SO_2\phi$ ) led to I ( $R = SO_2\phi$ ). Thus, II ( $R = SO_2\phi$ ) remains unchanged in refluxing methanol in the absence of methoxide ion while in refluxing pyridine II ( $R = SO_2\phi$ ) yields predominantly IV and some V (ratio 6:1) but no aziridine. In the presence of sodium hydride in benzene I was produced almost quantitatively. It was desired to determine the necessity of the N-H bond in the above reaction but all attempts to prepare the N-methyl derivative of II ( $R = SO_2\phi$ ) under alkaline conditions (dimethyl sulfate and sodium hydroxide or methyl iodide and sodium hydride in benzene) led directly to I<sup>8</sup>. Treatment of II ( $R = SO_2\phi$ ) with silver nitrate in methanol led to a mixture comprising approximately 30% V and 60% of two methyl ethers but no aziridine, while refluxing II in a methanol solution containing an excess of sodium azide gave only



recovered starting material indicating that under these conditions a carbonium ion was not formed. The conversion of II ( $R = \text{SO}_2\phi$ ) into I, under alkaline conditions, thus appears to be an example of neighboring anion induced solvolysis. The difference in behavior between II ( $R = \text{CO}_2\text{Me}$ ) and II ( $R = \text{SO}_2\phi$ ), on treatment with base, is apparently related to their intrinsic differences as ambident anions.

Finally, pyrolysis of II ( $R = \text{SO}_2\phi$ ) in the inlet port of the gas chromatograph ( $210^\circ$ ) gave mostly unchanged starting material (80%), no aziridine I, 11% IV and 4% V. Under these gas chromatograph conditions aziridine I was found not to rearrange, but on prolonged refluxing (>72 hrs) in mesitylene under nitrogen there was obtained a mixture comprising 63% unreacted I, 14% V and 18% IV. By comparison, heating the isomeric *endo* aziridine VIII<sup>9</sup> neat at  $150\text{--}165^\circ$  lead to its conversion in >90% yield to the imine IX.

#### REFERENCES

- (1) (a) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).
- (b) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabot and R. L. Hale, *Chem. & Ind.*, 1556 (1964).
- (2) H. Tanida, T. Tsuji and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966).

- (3) This compound was previously reported <sup>1a</sup> but was assumed to arise from an azetidine rather than the aziridine and the stereochemistry of the bromine atom in II was not clearly defined. That the starting compound was an aziridine was later clarified<sup>1b</sup>.
- (4) G. Miller and R. Merten, Chem. Ber., 98, 1107 (1965).
- (5) Tanida et al<sup>2</sup> reported that II (R = CO<sub>2</sub>Et) was unstable and did not characterize it. We found that II (R = CO<sub>2</sub>Me) is a relatively stable crystalline compound (m.p. 89.5-93<sup>o</sup>).
- (6) R. Huisgen, et al., Chem. Ber. 98, 3992 (1965).
- (7) In spite of numerous attempts, including the use of KI with 18-crown-6 ether, we have been unable to convert I (R = CO<sub>2</sub>Me) into VI (R = OMe).
- (8) Thus far attempts to methylate II (R = SO<sub>2</sub>θ) under nonalkaline conditions (e.g., with methyl fluorosulfonate) have been unsuccessful.
- (9) The endo aziridine VIII was obtained, as a minor product, in the reaction of norbornene with benzenesulfonyl azide. The ratio of endo to exo aziridines in this reaction is particularly sensitive to reaction conditions. Details will be published at a later date.
- (10) We thank Professor Charles Liotta for helpful discussions.