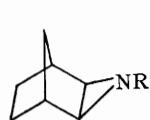


## The Structure and Rearrangement of the 1:1 Adduct of Benzenesulphonyl Azide and Norbornadiene

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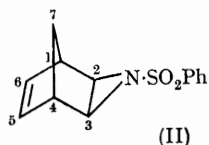
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BENZOYL AZIDE and benzenesulphonyl azide<sup>1,2</sup> react with norbornylene at room temperature to give (Ia) and (Ib), respectively. The recent communication of Franz and Osuch<sup>3</sup> on the "anomalous" reaction of benzenesulphonyl azide with norbornadiene prompts us to record our findings on the same reaction. We have found that

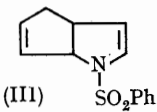


(Ia); R=PhCO

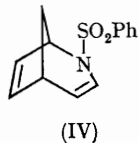
(Ib); R=PhSO<sub>2</sub>



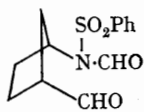
(II)



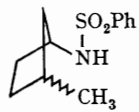
(III)



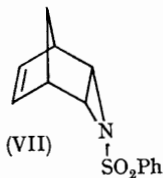
(IV)



(V)



(VI)



(VII)

benzenesulphonyl azide reacts with excess of norbornadiene to yield initially the expected aziridine (II). The nitrogen insertion product of

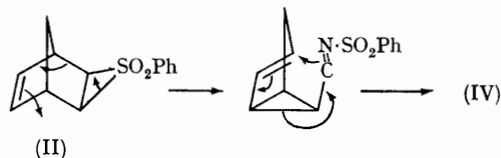
Franz and Osuch [formulated as either (III) or (IV)] has been shown to arise by rearrangement of (II) and to be correctly represented by structure (IV).

When a solution of benzenesulphonyl azide (1.36 mole) and norbornadiene (2.65 mole) in deuteriochloroform (1% tetramethylsilane) was kept at room temperature, nitrogen was immediately evolved. Periodic analysis of the reaction mixture by p.m.r. showed that (II) was formed initially and as time progressed increasing amounts of (IV) appeared as (II) decreased. The p.m.r. spectrum showed the following signals arising from (II): an AB quartet ( $J = 8.5$  c./sec.) at  $\delta 1.07$  and  $1.66$  arising from the C-7 protons,



(VIII)

(IX)



(II)

(IV)

a broad multiplet centred at  $\delta 2.96$  due to the bridgehead protons, a sharp singlet at  $\delta 3.18$  for the C-2 and C-3 protons, and a triplet ( $J = 1.5$  c./sec.) centred at  $\delta 6.35$  arising from the C-5 and C-6 protons. After three days, rearrangement to (IV) was complete and the i.r. and p.m.r. spectra were identical to those reported<sup>3</sup> for this product.

Hydrogenation of the reaction mixture after

<sup>1</sup> L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. and Ind.*, 1964, 1556.

<sup>2</sup> J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, 1964, 29, 2922.

<sup>3</sup> J. E. Franz and C. Osuch, *Chem. and Ind.*, 1964, 2058.

the rearrangement was approximately 50% complete afforded a 1:1 mixture of the known<sup>1,2</sup> aziridine (Ib) (m.p. 104–105°) and 6,7-dihydro-(IV), m.p. 51–52.5° (reported<sup>3</sup> m.p. 50–53°), which was separated by chromatography on alumina.

Ozonolysis of 6,7-dihydro-(IV) gave (V), which was both reduced and deformylated under Wolff-Kishner conditions to give *N*-(3-methylcyclopentyl)benzenesulphonamide<sup>4</sup> (VI). Reduction of (VI) with sodium in alcohol gave 3-methylcyclopentylamine<sup>4</sup> which on nitrous acid deamination gave a mixture of 3-methylcyclopentanol<sup>4</sup> (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 mixed melting point of its dibenzylidene derivative (m.p. 156–157°) with an authentic sample.<sup>5</sup> Rearrangement in the deamination to yield 3-methylcyclopentanol is ruled out since both *cis*- and *trans*-2-methylcyclopentylamine are known<sup>6</sup> not to yield 3-methyl

cyclopentanol on deamination under identical conditions. The nitrogen-containing moiety in (V) must therefore be  $\gamma$  to the aldehyde group, as required by structure (IV). These results are clearly not compatible with structure (III).

It has been suggested<sup>2</sup> that the mechanism of aziridine formation in the reaction of benzenesulphonyl azide with norbornylene parallels that of epoxidation. However, it is noteworthy that no detectable amount of (VII) was formed during the reaction, whereas the epoxidation of norbornadiene<sup>7</sup> gives an appreciable quantity of the corresponding *endo*-monoepoxide. It is also interesting to note that (VII) is quite stable<sup>8</sup> as is the corresponding *endo*-monoepoxide, suggesting that the rearrangement of (II) is facilitated by back-side participation of the 5,6-double bond as in the case of the recently reported<sup>7,9</sup> rearrangement of (VIII) to (IX) during the epoxidation of norbornadiene.

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<sup>4</sup> A mixture of *cis*- and *trans*-isomers.

<sup>5</sup> Kindly supplied by Dr. E. J. Eisenbraun.

<sup>6</sup> W. Hueckel and K. D. Thomas, *Chem. Ber.*, 1963, **96**, 2514.

<sup>7</sup> J. T. Lumb and G. H. Whitham, *J.*, 1964, 1189.

<sup>8</sup> Prepared by an independent route to be described.

<sup>9</sup> J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, 1964, **85**, 582.