1,3-Dipolar Cyclo-additions which yield *endo*-Adducts. The Reaction of Benzenesulphonyl Azide with *cis-endo*- and *cis-exo*-Norbornene-5,6-dicarboxylic Acid Anhydrides

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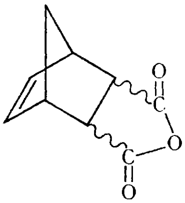
IN 1935 Alder and Stein showed that norbornene derivatives reacted with phenyl azide to give *exo*-triazolines.[1] On the basis of this work, these workers formulated[1,2] the "*exo*-addition rule" which has been widely applied.

We have investigated the reaction of *exo*-anhydride (III) and re-investigated[3] the reaction of (I) with benzenesulphonyl azide. Using improved isolation techniques it has been possible to show that (I) yields 60% *endo*-aziridine (II) and 19% *exo*-aziridine (V), while (III) gives 74% *endo*-aziridine (IV) and 22% *exo*-aziridine (VI).[4] In addition, benzenesulphonyl azide was found not to evolve nitrogen on heating under the reaction conditions in carbon tetrachloride alone or in the presence of dihydro-(I) or dihydro-(III). Thus, mechanisms involving intermediate nitrenes[3] or induced decomposition of the azide by the anhydride functions could be discounted.

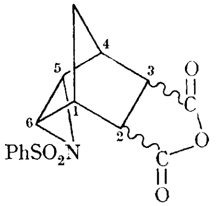
Hydrolysis of (IV) followed by oxidative bisdecarboxylation with lead tetra-acetate in pyridine gave (VII), which on catalytic hydrogenation gave *endo*-aziridine (VIII). Treatment of (VIII) with potassium thiophenoxide, followed by catalytic hydrogenolysis gave the known[5] sulphonamide (IX). Additional support for structure (VII) was provided by its n.m.r. spectrum and by comparison with the isomeric *exo*-aziridine (X).[6] *Endo*-$[2,3\text{-}^2H_{1\cdot4}]$-(IV) was oxidatively decarboxylated to yield $[2,3\text{-}^2H_{1\cdot4}]$-(VII) thus eliminating the possibility of rearrangement during decarboxylation. The structure of (II) has been previously established.[3]

The structures of the *exo*-aziridines (V) and (VI) were apparent from examination of the n.m.r. spectra of their dimethyl esters and comparison of these with the spectrum of the known *exo*-aziridine (XI).[7] In each of these spectra, H-5 and H-6 were identical and gave a single sharp signal as compared to the triplets observed for these protons in the *endo*-aziridines.

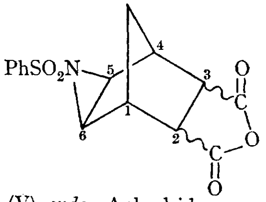
Support for a mechanism involving an intermediate triazoline has been obtained by observing that the entropy of activation of this reaction ($\Delta S^{\ddagger}$ — 29 cal/degree) compares favourably with that reported for the reaction of norbornene with phenyl azides ($\Delta S^{\ddagger}$ — 30 cal/degree).[8,9] Additional support for the formation of these aziridines by way of a "1,3-dipolar cyclo-addition" intermediate was found in the comparative insensitivity of the rate of the reaction to solvent polarity.[8,9] Thus, norbornene reacts about ten times more rapidly than (III), which in turn reacts about ten times more rapidly than (I) with benzenesulphonyl azide.



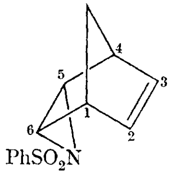
(I) *endo*-Anhydride
(III) *exo*-Anhydride



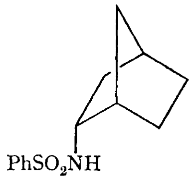
(II) *endo*-Anhydride
(IV) *exo*-Anhydride



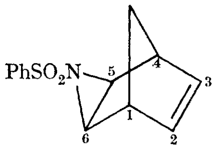
(V) *endo*-Anhydride
(VI) *exo*-Anhydride



(VII)
(VIII) [2,3-Dihydro-]



(IX)



(X)
(XI) [2,3-Dihydro-]

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The predominant formation of *endo*-aziridines (II) and (VI) is particularly striking when one recollects that bicyclopentadienyl reacts with benzenesulphonyl azide to give an *exo*-aziridine[7] and (I) and (III) have been reported[1,10] to react with phenyl azide to give *exo*-triazolines. It is, however, clear that the "*exo*-addition rule" must be used with caution.

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[2] K. Alder and G. Stein, *Annalen*, 1936, **525**, 183.

[3] L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, 1963, **28**, 3309.

[4] The structure of (IV) had previously been assumed to be (VI) on the basis of the "*exo*-addition rule." (Ref. 3.)

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