

Reaction of 2-Diazopropane with an Arylsulphonyl-trimethylsilyl Substituted Alkene. Steric Control of Regiochemistry by the Trimethylsilyl Group

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The 1,3-dipolar cycloaddition of 2-diazopropane with trimethyl[3-(*p*-tolylsulphonyl-2,5-norbornadiene-2-yl)]silane occurs across the unsubstituted double bond; regiochemical control can be attributed to steric rather than to stereoelectronic factors.

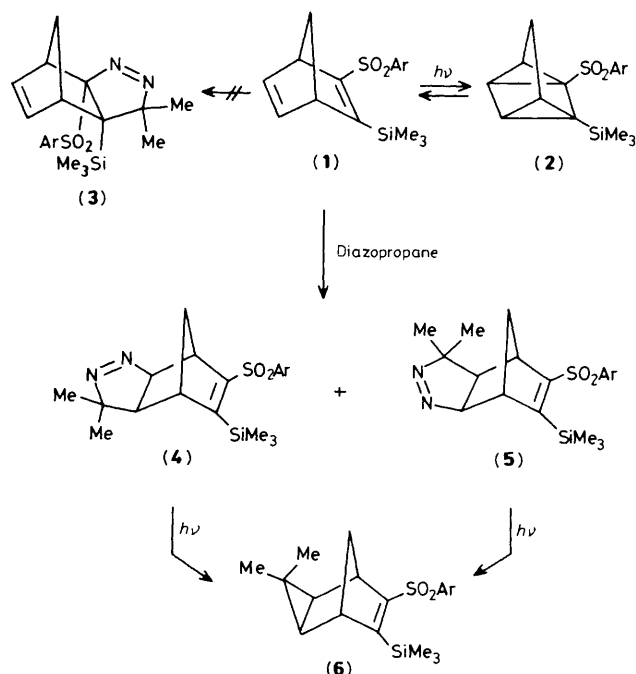
Chemical reactivity and regioselectivity in cycloaddition processes can be significantly modified by the appropriate choice of substituent groups.¹ Frontier MO theory predicts that attachment of a sulphonyl group to ethylene will significantly lower the energy of the LUMO and thereby enhance the cycloaddition rate.² An interesting application of such an effect has been provided by the Paquette³ and DeLucchi⁴ groups in their use of bis(phenylsulphonyl)-ethylene as an acetylene equivalent in Diels–Alder chemistry. Very recently, Williams and Sung have reported on the unexpected regioselectivity in the Diels–Alder reaction of 1-phenylsulphonyl-2-trimethylsilylacetylene with excess cyclopentadiene.⁵ We report here the results of our related cycloaddition studies with bicycloheptadiene (1) (Ar = *p*-MeC₆H₄) which show that diazoalkanes cycloadd preferentially across the unsubstituted π -bond.

As part of a study concerned with the synthesis of highly strained ring systems,⁶ we examined the photochemistry of the bicycloheptadiene (1). Our hope was that the resulting quadricyclane (2) would undergo a fluoride-induced elimination of the trimethylsilyl-*p*-tolylsulphonyl groups to produce a highly strained quadricyclene by analogy with related literature reports.⁷ Although we did not find a way to trap the quadricyclene, we have observed that the quadricyclane (2) was readily formed on u.v. excitation of (1) (m.p.

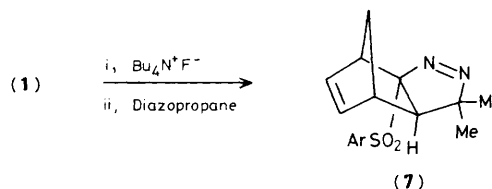
85–86 °C).^{8†} This material could readily be converted back to (1) either by thermolysis (190 °C) or by reaction with silver perchlorate.⁹

We have also studied the 1,3-dipolar cycloaddition behaviour of (1) with 2-diazopropane.¹⁰ We originally anticipated that addition would occur at the electronically activated double bond with the well precedented *exo* attack¹¹ leading to cycloadduct (3). Although the cycloaddition reaction did proceed readily at 25 °C, the only products formed corresponded to the alternative set of regioisomers (4) and (5) in a 2.5 : 1 ratio. The structures of cycloadducts (4) and (5) rest largely upon the interpretation of the ¹³C and ¹H n.m.r. spectra‡ and the photolytic conversion of both compounds into the cyclopropane (6).§

We reasoned that the observed regioselectivity with the bicycloheptadiene (1) was most likely a consequence of steric hindrance by the trimethylsilyl group. In order to test this hypothesis we carried out the desilylation of (1) with tetrabutylammonium fluoride and treated the resulting norbornadiene with 2-diazopropane (1 equiv.). The exclusive product formed (7), corresponded to cycloaddition across the more activated vinylsulphonyl group (m.p. 154–155 °C)



Scheme 1



Scheme 2

† *N.m.r. data* for (1): ¹H n.m.r. (CDCl₃, 360 MHz) δ -0.07 (s, 9H), 1.57 (dd, 1H, *J* 4.3 and 1.4 Hz), 1.74 (dd, 1H, *J* 4.3 and 2.5 Hz), 2.09 (dt, 1H, *J* 11.8 and 1.4 Hz), 2.17 (dt, 1H, *J* 11.8 and 1.4 Hz), 2.30 (ddd, 1H, *J* 5.4, 2.5 and 1.4 Hz), 2.45 (s, 3H), 2.86 (dd, 1H, *J* 5.4 and 2.5 Hz), 7.32 (d, 2H, *J* 8.3 Hz), and 7.71 (d, 2H, *J* 8.3 Hz).

‡ *N.m.r. data* for (4): ¹H n.m.r. (CDCl₃, 360 MHz) δ 0.41 (s, 9H), 0.73 (bd, 1H, *J* 10.1 Hz), 1.07 (s, 3H), 1.31 (bd, 1H, *J* 10.1 Hz), 1.35 (s, 3H), 1.68 (dd, 1H, *J* 6.5 and 1.4 Hz), 2.46 (s, 3H), 2.69 (bs, 1H), 3.81 (bs, 1H), 4.89 (d, 1H, *J* 6.5 Hz), 7.34 (d, 2H, *J* 8.3 Hz), and 7.73 (d, 2H, *J* 8.3 Hz); ¹³C n.m.r. (20 MHz) δ -0.16, 19.4, 21.4, 28.4, 42.4, 46.9, 47.9, 50.9, 84.8, 97.1, 127.7, 129.8, 137.0, 144.4, 159.0, and 161.0.

For (5): ¹H n.m.r. (CDCl₃, 360 MHz) δ 0.33 (s, 9H), 0.73 (bd, 1H, *J* 8.8 Hz), 1.16 (s, 3H), 1.31 (bd, 1H, *J* 8.8 Hz), 1.41 (s, 3H), 1.51 (dd, 1H, *J* 6.5 and 1.8 Hz), 2.46 (s, 3H), 2.99 (bs, 1H), 3.50 (bs, 1H), 4.89 (d, 1H, *J* 6.5 Hz), 7.38 (d, 2H, *J* 8.3 Hz) and 7.82 (d, 2H, *J* 8.3 Hz); ¹³C n.m.r. (20 MHz) δ -0.23, 19.5, 21.5, 28.6, 42.2, 46.9, 48.2, 50.2, 84.8, 96.4, 122.3, 127.8, 129.9, 136.7, 144.4, 154.5, and 165.5.

§ *N.m.r. data* for (6): ¹H n.m.r. (CDCl₃, 360 MHz) δ 0.33 (s, 9H), 0.72 (d, 1H, *J* 7.6 Hz), 0.76 (d, 1H, *J* 7.6 Hz), 0.88 (d, 1H, *J* 9.0 Hz), 0.93 (s, 3H), 1.31 (s, 3H), 1.52 (d, 1H, *J* 9.0 Hz), 2.43 (s, 3H), 3.04 (bs, 1H), 3.23 (bs, 1H), 7.33 (d, 2H, *J* 9.0 Hz), and 7.79 (d, 2H, *J* 9.0 Hz).

(Scheme 2).[¶] Thus, regiochemical control in the cycloaddition of 4 π -components to this bicycloheptadiene (**1**) appears to be steric rather than stereo-electronic in origin.

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[¶] *N.m.r. data* for (**7**): ¹H n.m.r. (CDCl₃, 360 MHz) δ 0.76 (bd, 1H, *J* 9.7 Hz), 1.38 (dq, 1H, *J* 9.7 and 1.7 Hz), 2.29 (*d*, 1H), *J* 1.7 Hz), 1.48 (s, 3H), 1.52 (s, 3H), 2.49 (s, 3H), 2.87 (bs, 1H), 2.96 (bs, 1H), 6.29 (m, 1H), 6.33 (m, 1H), 7.42 (d, 2H, *J* 8.2 Hz), and 7.92 (d, 2H, *J* 8.2 Hz).
