The Diels–Alder Reaction of Furan and Phenylsulphonylpropadiene. The Simple Base Induced Rearrangement of 3-Methylene-2-*endo*-phenylsulphonyl-7-oxabicyclo[2.2.1]hept-5-ene†

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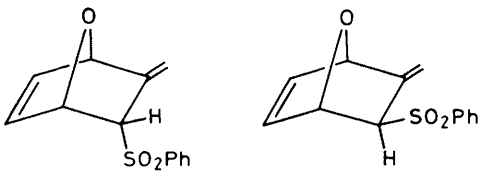
The Diels–Alder reaction of furan and phenylsulphonylpropadiene gives predominantly the 7-oxabicyclo[2.2.1]heptene (**1**), whose hydrogenation products (**3**) and (**4**) provide a simple entry to the synthesis of substituted cyclohexenols.

Cycloaddition reactions of furan with mono-activated olefins have been shown to proceed extremely slowly to give mixtures of *endo*- and *exo*-7-oxabicyclo[2.2.1]hept-5-enes in low yield.[1,2] These Diels–Alder addition reactions can be accelerated utilising high pressure[3] or in certain cases by the addition of catalytic amounts of copper salts.[4] In contrast to these extensive studies, the reactions of furan with mono-activated allenes[5] have received little attention despite a report[6] of the simple cycloaddition of furan with allenic ketones. Such cycloadditions would provide a good synthetic route to a variety of 7-oxabicyclo[2.2.1]hept-5-enes and 7-oxabicyclo-[2.2.1]heptanes. In this communication we report the cycloaddition of furan and phenylsulphonylpropadiene and a simple base induced rearrangement of 3-methylene-2-*endo*-phenylsulphonyl-7-oxabicyclo[2.2.1]hept-5-ene and its hydrogenation products.

Phenylsulphonylpropadiene[7] was conveniently prepared by treating a toluene solution of 3-phenylsulphonylpropyne[8] with triethylamine and was found to react very slowly with furan in toluene solution at 45 °C. However, under more vigorous conditions (sealed tube, 100 °C, 24 h), a toluene solution of

† The terms *endo* and *exo* refer to the positions of substituents (*e.g.* SO_2Ph) relative to the C(5)–C(6) bond.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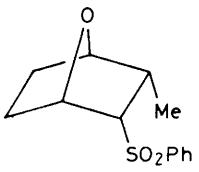
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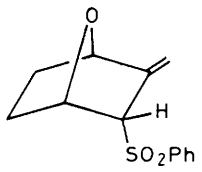
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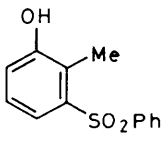
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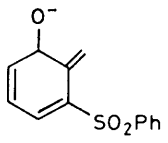
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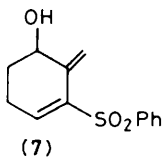
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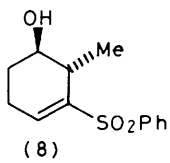
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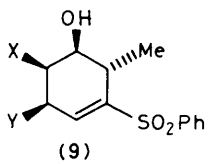
(9)

the allene (10 mmol), furan (40 mmol), and hydroquinone (0.1 mmol) gave after flash chromatography‡ [eluted with toluene–EtOAc (19 : 1)] a 58% yield of the *endo*-isomer (**1**), m.p. 91—92 °C (hexane–toluene) and a 3% yield of the *exo*-isomer (**2**), m.p. 89—91 °C (hexane–diethyl ether). A study of the ^{1}H n.m.r. spectra ($CDCl_3$) of the two cycloaddition products was instrumental in their structure assignments. The C(2)-*exo* ring proton of the major *endo*-isomer appeared as a multiplet centred at δ 4.3 whereas the C(2)-*endo* ring proton of the minor *exo*-isomer was found as a singlet at δ 3.68. This predictable zero coupling between the C(2)-*endo* proton and the C(1) proton and the large difference in chemical shifts between the C(2)-*exo* and -*endo* ring protons have been observed in ^{1}H n.m.r. studies on other substituted 7-oxabicyclo[2.2.1]hept-5-enes.[9]

Exhaustive hydrogenation (5% Pd/C catalyst–ethyl acetate) of the *endo*-isomer (**1**) gave 3-*endo*-methyl-2-*endo*-phenylsulphonyl-7-oxabicyclo[2.2.1]heptane (**3**), m.p. 124 °C (hexane–absolute ethanol) in 92% yield. The ^{1}H n.m.r. spectrum ($CDCl_3$) of (**3**) showed a coupling constant $J_{2H,3H}$ 11 Hz, consistent with di-*endo* structure assignment.[9,10] Partial hydrogenation of (**1**) selectively reduced the ring double bond to produce the *exo*-methylene compound (**4**), m.p. 79—81 °C (toluene–hexane) in 77% yield.

‡ All flash chromatography was done using Merck Kieselgel 60 (9385).

Treatment of a tetrahydrofuran solution of the sulphone (**1**) at −70 °C with n-butyl-lithium furnished a yellow anion, which on quenching with water at −70 °C gave after acidification and flash chromatography [eluted with toluene–EtOAc (5 : 1)] the phenol (**5**), m.p. 166—168 °C (diethyl ether) in 40% yield. The production of the phenol (**5**) is thought to involve α-sulphonylcarbanion formation followed by carbon–oxygen bond cleavage to give the oxyanion (**6**). The related base induced rearrangement of β-epoxy-sulphones into γ-hydroxy-sulphones has been reported recently[11] and Kozikowski[12] has described an analogous reorganisation of the carbanion derived from a 2-ethoxycarbonyl-7-oxabicyclo[2.2.1]hept-5-ene. When the hydrogenation products (**3**) and (**4**) were treated in an identical fashion with n-butyl-lithium analogous ring opening reactions occurred. The *exo*-methylene compound (**4**) gave, after purification of the crude product by flash chromatography [eluted with toluene–EtOAc (10 : 3)], a 50% yield of the sulphone (**7**), m.p. 101—103 °C (toluene), ^{1}H n.m.r., δ ($CDCl_3$) 7.8 (m, 2H, aromatic protons), 7.5 (m, 3H, aromatic protons), 7.3 (m, 1H, ring=CH), 5.75 (s, 1H, *exo*=CH), 5.25 (s, 1H, *exo* =CH), 4.2 (t, 1H, O–CH), 2.55 (t, 2H, CH_2), and 1.85 (m, 3H, CH_2 and OH). Similarly the fully hydrogenated product (**3**) furnished a 68% yield of the sulphone (**8**), m.p. 118 °C (diethyl ether), ^{1}H n.m.r., δ ($CDCl_3$) 7.85 (m, 2H, aromatic protons), 7.55 (m, 3H, aromatic protons), 7.15 (m, 1H, =CH), 3.85 (m, 1H, O–CH), 2.4 (m, 3H, CH_2 and CH), 1.8 (m, 2H, CH_2), 1.5 (s, 1H, OH), and 1.1 (d, 3H, Me). All attempts to trap the α-sulphonylcarbanions generated from (**1**), (**3**), and (**4**) with electrophiles failed.

The stereoselective functionalisation[13,14] of the ring double bond of the cycloaddition product, (**1**) should enable the synthesis of highly substituted cyclohexenols of type (**9**) to be carried out using the methods described in this communication. Brion has just reported[15] an analogous synthesis of cyclohexenols utilising the base promoted ring opening of various 2-methoxycarbonyl-7-oxabicyclo[2.2.1]heptanes. Substituted cyclohexenols related to (**7**) and (**8**) should prove more versatile synthons than these cyclohexenols functionalised with methoxycarbonyl groups.

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