Convenient Syntheses of Hydroindans and Hydronaphthalenes

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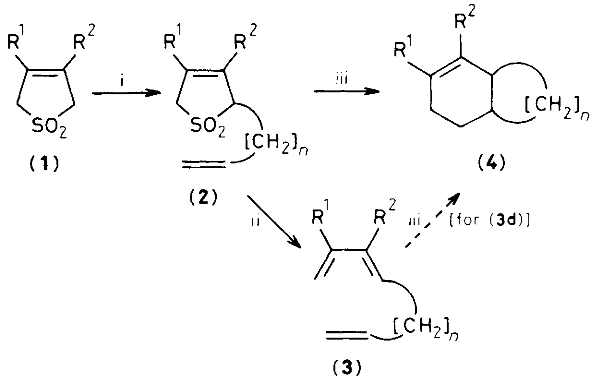
Thermolysis of several new 2-(ω-alkenyl)-3-sulpholenes, prepared by direct deprotonation and alkylation of 3-sulpholenes, led to cheletropic extrusion of SO_2 followed by intramolecular Diels–Alder reaction to yield the corresponding hydroindans and hydronaphthalenes.

There has been increasing interest recently in intramolecular Diels–Alder reactions, particularly for the synthesis of natural products containing the hydroindan or hydronaphthalene skeletons,[1] because of the simplicity of this approach to multicyclic molecules. However, the appropriate triene precursors may be difficult to prepare and handle, and a general and facile route to 1,3,8- and 1,3,9-trienes, which are ideal precursors for hydroindans and hydronaphthalenes, would be valuable. We have already reported the direct alkylation of 3-sulpholenes giving 2-alkyl-3-sulpholenes followed by cheletropic extrusion of SO_2 giving the 1-alkylbuta-1,3-dienes, and the application of this route for the syntheses of ocimene and farnesene.[2] If the 1-alkyl group contained another double bond suitably located for intramolecular Diels–Alder reaction, 1,3,8- or 1,3,9-trienes should be easily prepared (Scheme 1).

Thus, 5-iodopent-1-ene and 6-iodohex-1-ene were prepared; they reacted smoothly with the 3-sulpholenes (**1a**—**c**),



Scheme 1. *Reagents and conditions:* i, $LiN(SiMe_3)_2$, tetrahydrofuran, then $CH_2{=}CH[CH_2]_nI$; ii, 240 °C; iii, 580 °C.

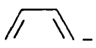
Table 1. Preparation of the hydroindans and hydronaphthalenes (**4a**—**f**).

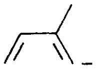
R^1	R^2	*n*	Sulpholene	Cycloadduct, % yield
H	H	3	(**1a**)	(**4a**),[a] 67
H	H	4	(**1a**)	(**4b**),[b] 73
H	Me	3	(**1b**)	(**4c**),[c] 75
H	Me	4	(**1b**)	(**4d**),[d] 76
Me	Me	3	(**1c**)	(**4e**),[c] 58
Me	Me	4	(**1c**)	(**4f**),[c] 51

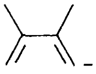
[a] 3 : 1 Mixture of *cis*- and *trans*-isomers; both isomers were isolated and identified by spectroscopic comparison with literature data.[4]
[b] 1 : 1 Mixture of *cis*- and *trans*-isomers; both isomers were isolated.[5]
[c] Only one major product (>95%) was isolated; its stereochemistry was not determined.
[d] *trans*-Isomer was isolated as the major product (>95%).[6]

either commercially available or easily prepared by the reaction of the appropriate 1,3-diene and SO_2 in a pressure bottle, to give the expected 2-(ω-alkenyl)-3-sulpholenes (**2a**—**f**) in good yields.[†] The substituted sulpholenes (**2a**—**f**) were then thermolysed by passing dilute solutions in n-hexane through a tube in a furnace under N_2 at 580 °C; the substituted hydroindans and hydronaphthalenes (**4a**—**f**) were obtained, presumably *via* the intramolecular Diels–Alder reaction of the triene intermediates (**3a**—**f**). If desired, the pure 1,3,8- and 1,3,9-trienes (**3a**—**f**) could be isolated from the sulpholenes (**2a**—**f**) by the cheletropic extrusion of SO_2 on preparative g.l.c. (SE-30 column; injection temp. 240 °C; oven temp. 150 °C). In each case, only a single product was isolated. According to the literature,[3] the C(3)–C(4) double bond should have the *trans*-configuration for compounds (**3a**—**f**). When compound (**3d**) was thermolysed at 580 °C, the product was identical to that isolated from the thermolysis of (**2d**), confirming that the trienes were indeed the intermediates of the high-temperature thermolysis.

Since the starting materials (**1a**—**c**) are readily available and easily alkylated regiospecifically [as for the alkylation of (**1b**)], they serve as the 1-carbanion equivalents of the unsubstituted and substituted buta-1,3-dienes (**5a**—**c**). The cheletropic extrusion of SO_2 is also highly stereospecific so that compounds (**3a**—**f**) are produced exclusively with the C(3)–C(4) double bond *trans*. Finally, since compounds (**2a**—**f**) are the protected equivalents of the trienes (**3a**—**f**) and can be thermolysed directly to give the cycloadducts (**4a**—**f**), the isolation and handling of the air- and acid-sensitive trienes (**3a**—**f**) can thus be avoided.


(**5a**)


(**5b**)


(**5c**)

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[†] All new compounds gave satisfactory spectroscopic (n.m.r., i.r., and mass) and analytical data. Reactions were carried out on a 20 mmol scale.