# Diels–Alder Cycloadditions using Alkenyl Sulphoxides

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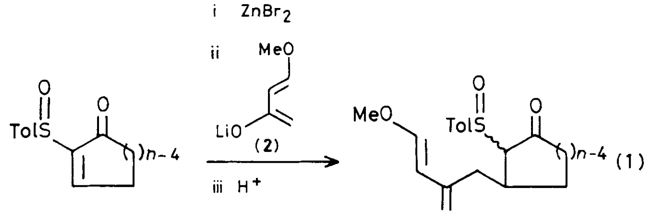
The first example is presented of a highly diastereoselective Diels–Alder cycloaddition using an electrophilic sulphinyldiene as a chiral enophile.

Control of stereochemistry is one of the most important aspects of Diels–Alder cycloadditions. Because of our interest in controlling the stereochemistry of carbon–carbon bond formation using chiral alkenyl sulphoxides,[1] we have combined these two areas by examining Diels–Alder cycloadditions using a sulphinylalkene as a dienophile[2] and, as reported in this communication, in a complementary fashion using a sulphinyldiene as an enophile.

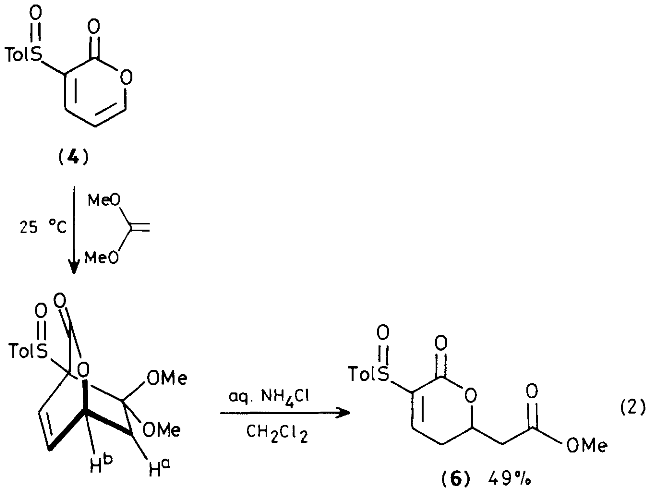
The unsaturated sulphoxides such as (**1a**) are poor dienophiles and do not undergo typical Diels–Alder reaction even in the presence of a Lewis acid. Compounds (**1a**,**b**)[3] do undergo Michael addition with the enolate (**2**) to give the adduct (**3**) which is stable with respect to intramolecular cyclisation under a variety of conditions, equation (1).

Sulphinyldiene (**4**), prepared easily from 3-bromo-2-pyrone,[4] is a strongly electrophilic enophile which undergoes an extraordinarily mild (25 °C) inverse electron demand Diels–Alder cycloaddition with 1,1-dimethoxyethylene[5] to give bridged bicyclic adduct (**5**) in nearly quantitative fashion (equation 2). Extrusion of carbon dioxide does *not* occur under the reaction conditions. The olefinic protons of this adduct appear at δ 5.56—5.65 (m, 1H) and at δ 5.83—5.93 (m, 1H) in its $^1$H n.m.r. spectrum. The chiral sulphinyl group in racemic pyrone sulphoxide (**4**) influences the stereochemical course of this cycloaddition so that adduct (**5**) was formed as a mixture of two diastereoisomers. The diastereoisomeric ratio was determined conveniently by 400 MHz $^1$H n.m.r. spectroscopy, integrating the characterisic and well-separated peaks for H$^a$ at δ 2.07 and 1.98 (both dd, *J* 13.4, 1.46 Hz) and for H$^b$ at δ 5.12—5.17 and 5.20—5.26 (both multiplets). These peak assignments are made by very good analogy to literature data[6] reported for bridged lactones structurally very similar to lactone (**5**). The best diastereoselectivity of 76% (*i.e.*, 88 : 12 ratio of diastereoisomers) is achieved using toluene or hexanes as solvent with 40—50 equivalents of 1,1-dimethoxyethylene per equivalent of sulphinyldiene in a 0.1—0.2 M solution with a reaction time of 48 h at 25 °C. This is the first example of an asymmetric Diels–Alder cycloaddition using a sulphinyldiene as an enophile.[7] Acid treatment of adduct (**5**) led mainly to ring-opened, double bond-isomerized product (**6**).†



(**1a**) *n* = 5
(**1b**) *n* = 6

(**3a**) 88 %
(**3b**) 55 %



(**4**)

(**5**) > 95 %

(**6**) 49 %

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† This new compound was fully characterized spectroscopically and by high resolution mass spectrometry.

The high diastereoselectivity in formation of adduct (**5**) encourages us to continue studying asymmetric inverse electron demand Diels–Alder cycloadditions using sulphur-substituted pyrones as enophiles.

We thank the National Science Foundation for financial assistance in the form of a research grant and a grant towards purchase of a departmental 400 MHz n.m.r. spectrometer. We also thank the NIH for contributing toward purchase of the n.m.r. spectrometer.

*Received, 14th August 1985; Com. 1220*

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