Diels–Alder Cycloaddition Reactions of Methyl 2-Methylthiopenta-2,4-dienoate: a *gem*-Captodative Diene Reacting as Dienophile by its Terminal Double Bond

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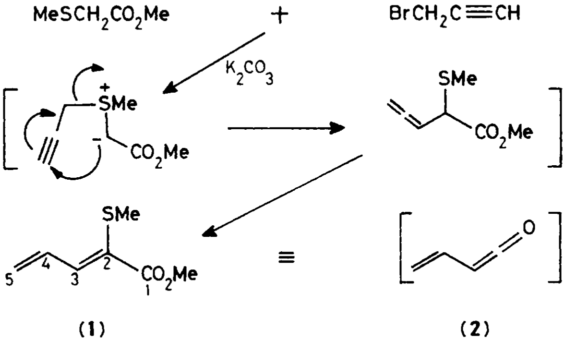
The captodative diene methyl 2-methylthiopenta-2,4-dienoate (**1**) reacts cleanly as a dienophile, at the less substituted double-bond, in Diels–Alder cycloaddition reactions with unactivated conjugated dienes.

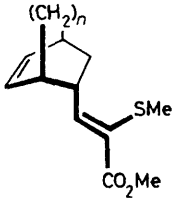
α-Alkylthio-acrylic esters are very useful captodative alkenes acting as Michael acceptors,[1] radicophiles[2] or π-2 partners in [4 + 2],[2] in [3 + 2],[3] and in [2 + 2][2] cycloaddition reactions but, in contrast, the corresponding α-alkylthio-diene-esters have not yet been investigated: with the exception of recent reports on synthesis[4] and cycloaddition reactions of α-amino-diene nitrile[5] or ester[6] to electrophilic dienophiles, little is known about the *gem*-captodative conjugated dienes.[2] We report our first results concerning the dienophilic reactivity of methyl 2-methylthiopenta-2,4-dienoate (**1**) which can be regarded as a vinyl ketene (**2**) equivalent.[7]

Following a procedure (Scheme 1) similar to that of Viehe,[4] the diene (**1**) is smoothly prepared by stirring a dimethylformamide (DMF) solution of methyl 2-methylthioacetate with 3-bromoprop-1-yne (2 equiv.) in the presence of potassium carbonate (2 equiv.) for 7 days at 20 °C [54% yield, b.p. 40—45 °C at 0.03 mmHg (1 mm Hg = 133.322 Pa)]. The only isomer obtained has the 2*Z* configuration as indicated in the n.m.r. spectra by the small value (4 Hz) observed for *J*(1-C,3-H). The unprecedented dienophilic Diels–Alder reactivity of the diene (**1**) was exemplified by its cycloaddition to cyclopentadiene, cyclohexa-1,3-diene and isoprene.

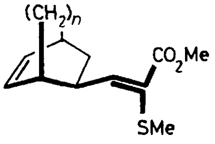
The reaction of diene (**1**) with cyclopentadiene (15 equiv.) occurs efficiently by refluxing the mixture (60 °C, 20 h, 72% yield) and occurs also, slowly, at room temperature (5 equiv., 48 h, 33% yield) to afford the same mixture of Diels–Alder adducts (**3a**) and (**3b**) (55 : 45), b.p. 70—72 °C at 0.02 mmHg, kugelrohr). Structures (**3a**) and (**3b**) were confirmed by



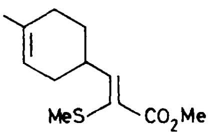
Scheme 1



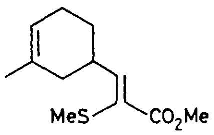
(3a); $n = 1$
(4a); $n = 2$



(3b); $n = 1$
(4b); $n = 2$



(5a)



(5b)

elemental analysis, mass spectroscopy ($M^{+\cdot}$, m/z 224), i.r., ^{1}H and ^{13}C n.m.r. spectroscopy. The cycloadducts (**4a**) + (**4b**) (55 : 45) and (**5a**) + (**5b**) (70 : 30) were similarly formed in 39 and 38% yields respectively, when the diene (**1**) was heated with cyclohexa-1,3-diene (3 equiv., 80 °C, 48 h) and with isoprene (3 equiv., 120 °C, 8 h).

A noteworthy aspect of the chemical behaviour of the diene (**1**) is its reaction as a dienophile by its terminal double bond and the retention of the *Z* configuration for its unreacted trisubstituted double bond. This is of both theoretical and preparative interest. The cycloaddition products are captodative alkenes and thus allow a variety of further transformations.[2] We are currently investigating reaction with other *gem*-captodative dienes and the transformations of the cycloadducts.

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