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A CATALYTIC CONVERSION OF 1-METHOXYCYCLOHEXA-1,4-DIENES INTO 1-METHOXYCYCLOHEXA-1,3-DIENES

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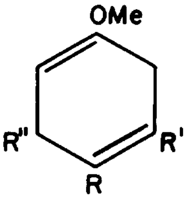
The first equilibration of 1-methoxycyclohexa-1,4-dienes, readily available from metal-ammonia reduction of anisoles,[1] with the more stable cyclohexa-1,3-dienes, was with potassamide in ammonia.[1] This, and other basic reagents in DMSO, have experimental disadvantages.

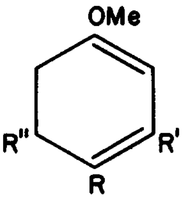
The observation[2,3] that dienophiles react directly with the 1,4-dienes to give Diels-Alder adducts of the 1,3-dienes was interpreted in terms of equilibration through charge-transfer complexes. The conditions vary with the dienophile (e.g. room temperature with maleic anhydride to 150-200° with vinyl ketones and related substances[3]) and we have investigated to see whether a dienophile could be found to act as a catalyst at lower temperatures, without itself removing a high proportion of the product.

Dichloromaleic anhydride, although clearly not unique, is such a catalyst. The unconjugated diene was refluxed gently with DCMA (0.1%) for 2-3 hr, extracted with alkali to remove anhydride, and distilled. The recovery was 75-85%, with some polymer. The relative proportions of 1,3- to 1,4-diene were determined by n.m.r. and g.l.c. examination. The ratios agree reasonably with those obtained on base-catalysed isomerisation, when this has been examined, usually with a higher proportion of the desired 1,3-diene. I(a)/II(a) 17:83; I(b)/II(b) 27:73; I(c)/II(c)/III 40:30:30.

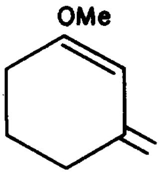
Further treatment produced polymerisation. Somewhat disappointingly, the process does not stop at the endocyclic diene in the case of I(c) but, as in the base-catalysed process, goes on to form (III). The formation of a charge-transfer complex is supported by the initial yellow to green colour, not shown by cyclohexa-1,4-diene, which does not undergo conjugation. DCMA was used as an *in situ* catalyst to induce Diels-Alder reactions between several of the 1,4-dienes and some dienophiles, at 80-90° under atmospheric pressure for 14-18 hr, instead of the 150° for 30-60 hr previously found necessary. Examples are summarised below. The products were identified by spectra, and IV(a) and IV(b) are known compounds.



(I)



(II)



(III)

(a) R,R',R'' = H

(b) R = Me; R',R'' = H

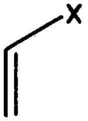
(c) R,R'' = H; R' = Me

(d) R,R',R'' = Me

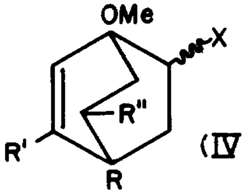
(a) R,R',R'' = H

(b) R = Me; R',R'' = H

(c) R,R'' = H; R' = Me



(V)



(IV)

(a) R,R',R'' = H; X = CN from I(a) and V, X = CN (75%)

(b) R,R',R'' = H; X = CO_2Me from I(a) and V, X = CO_2Me (65%)

(c) R,R',R'' = Me; X = CN from I(d) and V, X = CN (63%)

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