

Reactions of Cyclohexadienes. Part XIII.¹ Catalytic Conversion of 1-Methoxycyclohexa-1,4-dienes into 1-Methoxycyclohexa-1,3-dienes

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Dichloromaleic anhydride, aluminium chloride, and toluene-*p*-sulphonic acid, are active catalysts in promoting conjugation of 1-methoxycyclohexa-1,4-dienes to the 1,3-isomers. Experimental procedures involved are simple, and since the 1,4-dienes are conjugated *in situ* they are directly capable of Diels–Alder reactions with suitable dienophiles under mild conditions. Examples are given.

THE equilibration of the 1-methoxycyclohexa-1,4-dienes (obtained by metal–ammonia reductions of anisole derivatives) with the more stable 1,3-dienes has been accomplished by using potassamide in liquid ammonia,² through salt formation involving the 6-position. Recently³ it has been shown that conjugation is also brought about by electron-accepting substances such as dienophiles; in particular dichloromaleic anhydride (DCMA) is an effective catalyst.⁴ Some experimental details are now reported. The Lewis acid aluminium chloride and the protic acid toluene-*p*-sulphonic acid (PTS) are also observed to be active in the same manner. The yield of equilibrated product is high (Table 1).

TABLE 1
Conjugations

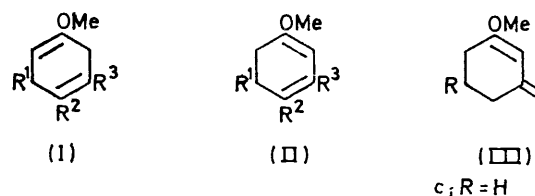
1,4-Diene	1,3-Diene	1,3-Diene in product (%)	Catalyst	Total yield (%)
(Ia)	(IIa)	84	DCMA	76
(Ib)	(IIb)	73	PTS	86
(Ic)	(IIc)*	35	AlCl ₃	84
(Ie)	(IIe)	70	DCMA	84
(If)	(III _f)		AlCl ₃	90

* Some exocyclic diene [type (III)] was also formed.

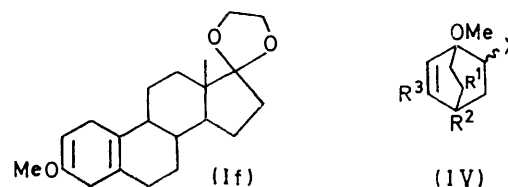
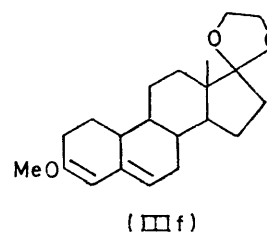
The proportions of 1,3- and 1,4-dienes are the same as in the base-catalysed procedure, but the process is experimentally more convenient. The proportions must represent equilibrium values.

The present procedure has the much greater advantage that it permits *in situ* conjugation in Diels–Alder reactions, so that the initial 1,4-diene can be used directly with a dienophile and the total diene, rather than the equilibrium proportion, is potentially capable of reaction. Also, although normal dienophiles can themselves act as

conjugation catalysts³ the conditions required are frequently drastic, and with added small proportions of an appropriate catalyst the reactions using such dieno-



- a; R¹ = R² = R³ = H
 b; R¹ = R³ = H, R² = Me
 c; R¹ = R² = H, R³ = Me
 d; R¹ = R³ = Me, R² = H
 e; R¹ = H, R² = R³ = Me



- a; R¹ = R² = R³ = H, X = CN
 b; R¹ = R² = R³ = H, X = CO₂Me
 c; R¹ = R³ = H, R² = Me, X = CO₂Me
 d; R¹ = R³ = Me, R² = H, X = CO₂Me
 e; R¹ = H, R² = R³ = Me, X = CN

¹ Part XII, A. J. Birch and E. G. Hutchinson, *J. Chem. Soc. (C)*, 1972, 3671.

² A. J. Birch and G. Subba Rao, *Adv. Org. Chem.*, 1972, 8, 1.

³ I. Alfaro, W. Ashton, L. D. McManus, R. C. Newstead, K. L. Rabone, N. A. J. Rogers, and W. Kernick, *Tetrahedron*, 1970, 26, 201.

⁴ A. J. Birch and K. P. Dastur, *Tetrahedron Letters*, 1972, 41, 4195.

philes with the available 1,4-dienes may be much faster and feasible at lower temperatures without the use of pressure equipment. The Diels–Alder reaction of 1-methoxycyclohexa-1,4-diene (Ia) with acrylonitrile in the presence of DCMA gave the adduct (IVa) in good yield (Table 2). However, under similar conditions but with exclusion of DCMA, only starting materials were recovered. This exemplifies the role played by the catalyst. Some results of *in situ* Diels–Alder reactions are shown in Table 2. The regioselectivity of such additions in the sense shown has already been established.⁵

TABLE 2
Catalysed Diels–Alder reactions

1,4-Diene	Catalyst	Dienophile	Product	Reaction time (h)	Yield* (%)
(Ia)	DCMA	CH ₂ =CH·CN	(IVa)	15	75
(Ia)	DCMA	CH ₂ =CH·CO ₂ Me	(IVb)	20	63
(Ib)	PTS	CH ₂ =CH·CO ₂ Me	(IVc)	44	82
(Id)	AlCl ₃	CH ₂ =CH·CO ₂ Me	(IVd)	20	74
(Ie)	AlCl ₃	CH ₂ =CH·CN	(IVe)	25	74

* Based on recovered starting material.

When the initial 1-methoxycyclohexa-1,4-diene has a 3-alkyl substituent, conjugation by use of any catalyst at present available can give rise to the exocyclic rather than the endocyclic 1,3-diene. Thus 17,17-ethylenedioxy-3-methoxyoestra-2,5(10)-diene (If) yields predominantly the exocyclic 3,5(6)-diene (IIIIf), as judged from spectral data and the product's inability to form a Diels–Alder adduct with dimethyl acetylenedicarboxylate.

The exact mechanism of the conjugation process is not yet established; however it is clear that charge transfer involves the donor properties of the enol ether group in the 1-methoxycyclohexa-1,4-diene. This supposition is supported by the yellow-to-orange colouration produced on addition of catalyst and by the fact that when no enol ether group is present, as in cyclohexa-1,4-diene and 1-methylcyclohexa-1,4-diene, conjugation does not occur. Complexing presumably labilises the same proton as that removed in the base-catalysed procedure, since the products are the same.

EXPERIMENTAL

I.r. spectra were run for liquid films with a Perkin-Elmer 257 spectrometer; u.v. spectra were obtained with a Unicam SP 800 instrument, and n.m.r. spectra with a Minimar 100 spectrometer. G.l.c. measurements were recorded with a Varian Aerograph 1700 machine.

Isomerisation of 1-Methoxycyclohexa-1,4-dienes to the 1,3-Isomers.—(a) 1-Methoxycyclohexa-1,3-diene (IIa). 1-Methoxycyclohexa-1,4-diene (Ia) (5 g), prepared by Birch reduction of anisole,² was heated under reflux with DCMA (5 mg) for 2 h. Ether (50 ml) was added and the organic phase was washed with 5*N*-sodium hydroxide (5 ml), then dried (K₂CO₃). Removal of ether followed by distillation afforded a liquid (3.8 g, 76%) shown by g.l.c. to comprise the 1,3-diene (IIa) (84%) (2 m 3% SE30; 70°; *t*_R 2.2 min) and un-

changed (Ia) (16%) (*t*_R 2.6 min). Comparisons were made with products obtained by base-catalysed isomerisation of the parent 1,4-diene with potassiumamide in liquid ammonia.² Spectral characteristics of the product mixture were identical with those reported.⁶ Comparable g.l.c. patterns were obtained when the isomerisation was effected with PTS or AlCl₃ in similar proportion to DCMA under the same conditions.

(b) 1-Methoxy-4-methylcyclohexa-1,3-diene (IIb). 1-Methoxy-4-methylcyclohexa-1,4-diene (Ib) (5 g) was heated to 80 °C, after which PTS (5 mg) was added. Gentle refluxing (1 h) followed by direct distillation afforded a liquid (4.3 g, 86%) which contained as its major component the 1,3-diene (IIb) (73%) (2 m 3% SE30; 100°; *t*_R 2.5 min), in admixture with unchanged (Ib) (27%) (2 m 3% SE30; 110°; *t*_R 3.0 min). Spectral characteristics of the product mixture were identical with those reported.⁶ Conjugation with DCMA or AlCl₃ gave identical g.l.c. patterns.

(c) 1-Methoxy-3-methylcyclohexa-1,3-diene (IIc). 1-Methoxy-5-methylcyclohexa-1,4-diene (Ic) (5 g) was refluxed gently for 30 min with powdered AlCl₃ (5 mg). Prolonged refluxing caused conversion of the 1,3-diene (IIc) into the exocyclic isomer (IIIc). Direct distillation gave a product (4.2 g, 84%) shown by g.l.c. to comprise the 1,3-diene (IIc) (35%) (2 m 3% SE30; 80°; *t*_R 1.8 min), the 1,4-diene (Ic) (40%) (2 m 3% SE30; 80°; *t*_R 2.2 min), and the exocyclic isomer (IIIc) (25%) (2 m 3% SE30; 80°; *t*_R 2.15 min). (Comparisons were made with products obtained by base-catalysed isomerisation of the parent 1,4-diene with potassiumamide in liquid ammonia.²) Spectral characteristics of (IIc) in the product mixture agreed well with those reported.⁵

(d) 1-Methoxy-3,4-dimethylcyclohexa-1,3-diene (IIe). 1-Methoxy-4,5-dimethylcyclohexa-1,4-diene (Ie) (5 g) was refluxed gently with DCMA (5 mg) for 1 h; the mixture was then distilled to yield a liquid (4.2 g, 84%) shown by g.l.c. to contain the 1,3-diene (IIe) (70%) (2 m 3% SE30; 100°; *t*_R 1.6 min) and some unchanged starting material (Ie) (30%) (*t*_R 2.0 min). The mixture had ν_{\max} 1665 and 1610 cm⁻¹ [conjugated dienol ether type (II)] and showed resonances due to (IIe) at τ (CDCl₃) 5.25 (1H, s, olefinic H), 6.45 (3H, s, MeO), 7.8 (4H, s, 2 × CH₂), and 8.3 (6H, s, 2 × Me).

(e) 17,17-Ethylenedioxy-3-methoxyoestra-3,5(6)-diene (IIIIf). 17,17-Ethylenedioxy-3-methoxyoestra-2,5(10)-diene (If) (1 g) was dissolved in freshly distilled 1,2-dimethoxyethane (15 ml) together with powdered AlCl₃ (2 mg). After 2 h heating under reflux the solvent was removed; the residue was dissolved in ether (30 ml) and shaken with 5*N*-sodium hydroxide (5 ml). Drying (Na₂SO₄) and removal of ether gave a pale yellow semi-crystalline solid (0.9 g, 90%) consisting predominantly of the 3,5(6)-diene (IIIIf). The product had λ_{\max} (hexane) 238 nm [characteristic of diene type (III)],⁷ and showed resonances due to (IIIIf) at τ (CDCl₃) 4.7 (1H, d, *J* 4 Hz, olefinic H), 4.8 (1H, s, olefinic H), 6.1 (4H, s, 2 × CH₂O), and 6.4 (3H, s, MeO). Little starting material (If) remained [only a faint n.m.r. signal was observed at τ 5.3, corresponding to the olefinic H of (If)], and no appreciable amount of endocyclic 3,5(10)-diene was detected (lack of absorption at λ_{\max} 270 nm).⁷ When the 2,5(10)-diene (If) was fused with DCMA for 5 min, in the absence of solvent, identical spectral data were obtained from the product.

Diels–Alder Reactions.—(a) 1-Methoxybicyclo[2.2.2]oct-5-ene-2-carbonitrile (IVa). 1-Methoxycyclohexa-1,4-diene (Ia)

⁷ A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 1961, 5376.

⁵ A. J. Birch and J. S. Hill, *J. Chem. Soc. (C)*, 1966, 419.

⁶ A. J. Birch and G. Subba Rao, *Austral. J. Chem.*, 1970, **23**, 1641.

(10 g) was refluxed with acrylonitrile (10 g) and DCMA (10 mg) for 15 h. Direct distillation gave some unchanged diene (Ia) (1.5 g) and a pale yellow oil (9.5 g, 75% based on recovered starting material), whose spectral properties coincided with those reported for (IVa).³

(b) *Methyl 1-Methoxybicyclo[2.2.2]oct-5-ene-2-carboxylate* (IVb). 1-Methoxycyclohexa-1,4-diene (Ia) (4 g) was refluxed with methyl acrylate (5 g) and DCMA (4 mg) for 20 h. Distillation afforded some unchanged diene (Ia) (0.5 g) and an oil (3.95 g, 63% based on recovered starting material), whose spectral properties were identical with those reported for (IVb).³

(c) *Methyl 1-Methoxy-4-methylbicyclo[2.2.2]oct-5-ene-2-carboxylate* (IVc). 1-Methoxy-4-methylcyclohexa-1,4-diene (Ib) (3 g) was refluxed with methyl acrylate (5 g) and PTS (3 mg) for 44 h. Distillation afforded a forerun of unchanged diene (Ib) (0.5 g), and the *bicyclo-ester* (IVc) as an oil (3.5 g, 82% based on recovered starting material), (2 m 3% SE30; 140°; t_R 2.5 min) (Found: C, 68.5; H, 8.6. $C_{12}H_{18}O_3$ requires C, 68.5; H, 8.6%), ν_{max} 1730 cm^{-1} (C=O), τ (CDCl₃) 3.8 (2H, m, olefinic), 6.45 (3H, s, CO₂Me), 6.65 (3H, s, MeO), and 9.0 (3H, s, Me).

(d) *Methyl 1-Methoxy-5,7-dimethylbicyclo[2.2.2]oct-5-ene-*

2-carboxylate (IVd). 1-Methoxy-3,5-dimethylcyclohexa-1,4-diene (Id) (10 g) was refluxed with methyl acrylate (12 g) and AlCl₃ (10 mg) for 20 h. Distillation afforded some unchanged diene (Id) (3.1 g) and the *bicyclo-ester* (IVd) as an oil (8 g, 74% based on recovered starting material) (2 m 3% SE30; 160°; t_R 1.3 min) (Found: C, 70.0; H, 9.1. $C_{13}H_{20}O_3$ requires C, 69.6; H, 9.0%), ν_{max} 1730 cm^{-1} (C=O), τ (CDCl₃) 4.2 (1H, m, olefinic H), 6.4 (3H, s, CO₂Me), 6.7 (3H, s, MeO), 8.2br (3H, s, vinylic Me), and 9.15 (3H, d, J 6 Hz, Me).

(e) *1-Methoxy-4,5-dimethylbicyclo[2.2.2]oct-5-ene-2-carbonitrile* (IVe). 1-Methoxy-4,5-dimethylcyclohexa-1,4-diene (Ie) (5 g) was refluxed with acrylonitrile (6 g) and AlCl₃ (5 mg) for 25 h. Distillation gave a forerun of unchanged diene (Ie) (0.8 g) and the *bicyclo-nitrile* (IVe) as a pale yellow oil (4.5 g, 74% based on recovered starting material) (2 m 3% SE30; 180°; t_R 1.7 min) (Found: C, 75.2; H, 9.2; N, 7.3. $C_{12}H_{17}NO$ requires C, 75.35; H, 9.05; N, 7.3%), ν_{max} 2240 cm^{-1} (C≡N), τ (CDCl₃) 4.05 (1H, s, olefinic H), 6.6 (3H, s, MeO), 8.25 (3H, d, J 2 Hz, vinylic Me), and 8.9 (3H, s, Me).

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