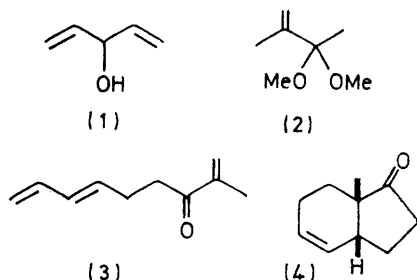


A *cis*-Perhydroindanone Synthesis utilising an Intramolecular Diels–Alder Reaction

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An intramolecular Diels–Alder reaction of 2-methylnona-1,6,8-trien-3-one yields *cis*-2,3,3a,6,7,7a-hexahydro-7a-methylhydrinden-1-one as the major product. The triene is readily synthesised from penta-1,4-dien-3-ol.

THE intramolecular variant of the Diels–Alder reaction has been used relatively infrequently in the past,¹ but the utility of the method is now becoming apparent.² We have applied it to a *cis*-perhydroindanone synthesis from the divinyl alcohol³ (1), which was treated with the acetal (2) by using Johnson's variant⁴ of the Claisen rearrangement (90 °C for 8 h in toluene containing



2,4-dinitrophenol) to give the trienone (3), λ_{\max} (EtOH) 235 nm (ϵ 19 000), ν_{\max} 1 670, 1 630, 1 600, and 990 cm^{-1} , τ (CCl_4) 3.5–4.3 (5H, m), 4.6–5.2 (2H, m), and 8.1 (3H, d, J 1.2 Hz). The trienone (3), which is expected to be of *E* stereochemistry, was characterised as its 2,4-dinitrophenylhydrazone and readily gave a Diels–Alder adduct with maleic anhydride. On heating in degassed benzene solution (190 °C; 13 h) the trienone (3) was converted into a mixture of three components in the ratio 30:4:3. The major component (4),[†] ν_{\max} 1 740 cm^{-1} , τ (CCl_4) 4.3 (2H, m) and 8.94 (3H, s), was isolated by preparative g.l.c. and on catalytic hydrogenation gave *cis*-7a-methylperhydroindan-1-one.⁶ Thus the major product is that predicted by the Alder *endo*-addition rule and the orientation rule. Under these stringent conditions for addition intermolecular processes might be expected to compete with the intramolecular addition. We have found no evidence for

these but the possible reversibility of the reactions may lead predominantly to one product if it is thermodynamically the more stable.

EXPERIMENTAL

2-Methylnona-1,6,8-trien-3-one (3).—3,3-Dimethoxy-2-methylbut-1-ene⁷ (1 g) was added to a stirred solution of penta-1,4-dien-3-ol³ (542 mg) and 2,4-dinitrophenol (647 mg) in toluene (10 ml). The mixture was heated at 90 °C for 8 h with further acetal being added after 3 h (1.2 g) and 5 h (800 mg). The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (120 g). Elution with 3% ether in light petroleum (b.p. 40–60°) gave the triene (3) (251 mg), b.p. 45–47° at 14 mmHg; 2,4-dinitrophenylhydrazone, m.p. 133–134° (from methanol) (Found: C, 58.1; H, 5.6; N, 17.0. $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_4$ requires C, 58.2; H, 5.5; N, 17.0%).

On heating the ketone in benzene with maleic anhydride an adduct was obtained, m.p. 117–119° (from benzene-pentane) (Found: C, 67.6; H, 6.4. $\text{C}_{14}\text{H}_{16}\text{O}_4$ requires C, 67.7; H, 6.5%), τ (CDCl_3) 8.13 (3H, d, J 1.2 Hz) and 4.3–3.9 (4H, m).

2,3,3a,6,7,7a-Hexahydro-7a-methylhydrinden-1-one (4).—The triene (3) (470 mg) and hydroquinone (10 mg) in degassed benzene solution (1.5 ml) were heated in an evacuated tube at 190 °C for 13 h. Removal of solvent left a dark liquid which was rapidly distilled; b.p. 75–100° (bath) at 0.1 mmHg. The distillate (402 mg) was shown to contain three components in the ratio 30:4:3. The major component was isolated by preparative g.l.c., and shown to be the ketone (4), ν_{\max} 1 740 cm^{-1} , τ (CCl_4) 8.94 (3H, s) and 4.3 (2H, m); 2,4-dinitrophenylhydrazone, m.p. 147–148° (from methanol) (Found: C, 58.3; H, 5.5; N, 16.9. $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_4$ requires C, 58.2; H, 5.5; N, 17.0%).

Hydrogenation of the ketone (4) (Pd–C; ethanol) gave *cis*-7a-methylperhydroindan-1-one; 2,4-dinitrophenylhydrazone, m.p. 140–142° (lit., 142–143°) (Found: M^+ , 332.1496. Calc. for $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_4$: M , 332.1485).

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[†] We thank a referee for pointing out that a bicyclo[5.4.0]-undecane synthesis utilising an intramolecular Diels–Alder reaction has been reported.⁵

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