

Stereoselective Synthesis of Substituted Functionalized Butadienes

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Summary The synthesis and pyrolysis of tricyclo[4,2,1,0^{2,5}]-nonene derivatives provides a stereoselective route to functionalized butadienes.

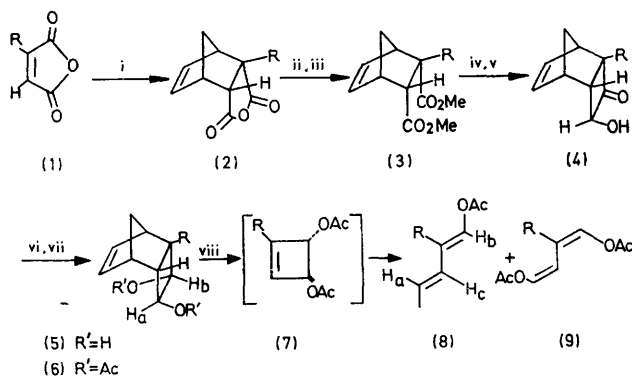
SINCE compound (**8**; R = Me) was required for a natural product synthesis, and existing methods for the preparation of 1,4-diacetoxybuta-1,3-dienes¹ could not be applied to compounds with a 2-alkyl group, an alternative general method was developed, based on the thermal conrotatory electrocyclic isomerization of *trans*-3,4-diacetoxy-1-methylcyclobutene (**7**), which was synthesised as outlined in the Scheme.

The known *endo*-adduct (**2**),² prepared in 95% yield *via* the Diels-Alder reaction between cyclopentadiene and the anhydride (**1**; R = Me) was converted into the diester (**3**)³ in 87% yield by the addition of NaOMe (1 mol. equiv.) followed by Me₂SO₄. The acyloin reaction⁴ of (**3**; R = Me) furnished (90% yield) after acidic hydrolysis, the ketol (**4**; R = Me)† [δ : 4.51 (1H, d, *J* 9 Hz, CHOH) and 1.40 (3H, s, Me); i.r. 2.97 and 5.64 μ m]. Reduction with NaBH₄ gave the *trans*-diol (**5**; R = Me) which on treatment with Ac₂O yielded the *trans*-diacetate (**6**; R = Me) [δ : 5.13 (1H, dd, *J* 8 and 8 Hz, H_a), 4.72 (1H, dd, *J* 8 and 2 Hz, H_b) and 1.42 (3H, s, Me); i.r. 5.72 μ m]. Pyrolysis of this

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‡ Satisfactory spectral data have been obtained for all new compounds reported.

compound (460° at 25 mmHg) with trapping at -80°C afforded in fair yield a 2.5:1 mixture of the *trans,trans*- (**8**; R = Me) and the *cis,cis*-isomers (**9**; R = Me), which could

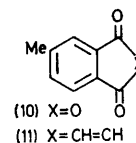


SCHEME. Reagents: i, C_6H_6 ; ii, NaOMe, MeOH; iii, Me_2SO_4 ; iv, Na, Me_3SiCl , PhMe; v, H_3O^+ ; vi, NaBH_4 , EtOH; vii, Ac_2O , $\text{C}_6\text{H}_5\text{N}$; viii, 460° , 25 mmHg.

be separated by column chromatography on silica gel. The structure of (**8**; R = Me) was inferred from its n.m.r. [δ :

7.30 (1H, d, J 13 Hz, H_a) 6.97 br (1H, s, H_b) 6.42 (1H, d, J 13 Hz, H_c), 2.12 (6H, s, OAc), and 1.77 (3H, J 1.5 Hz, Me], i.r. (5.68 and 6.14 μm), u.v. [λ_{max} 250 nm, (ϵ 20,000)] and mass spectra. The diene (**9**) exhibited a similar n.m.r. spectrum, except that the coupling constant of the olefinic protons was 7 Hz, indicating a *cis* double bond.

Compound (**8**; R = Me) is a mildly reactive diene in Diels-Alder reactions affording the adducts (**10** and **11**; R = Me) respectively with maleic anhydride and quinone. This method of diene synthesis should be generally applicable.⁵



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¹ C. F. Kohll and R. van Helden, *Rec. Trav. chim.*, 1967, **86**, 193; Shell International Research, Netherlands P. Appl., 6,509,342; H. H. Inhoffen, J. Heimann-Trosien, H. Muxfeldt, and H. Kramer, *Chem. Ber.*, 1957, **90**, 187; H. Schmid and E. Grob, *Helv. Chim. Acta*, 1949, **32**, 77; W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Annalen*, 1948, **560**, 1; R. Crigece, W. Horauf, and W. D. Schellenberg, *Chem. Ber.*, 1953, **86**, 126.

² O. Diels and K. Alder, *Annalen*, 1928, **460**, 98.

³ I. N. Nazarov, V. F. Kucherov, and V. G. Bukharov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, 1957, 91.

⁴ For reaction conditions, see J. J. Bloomfield, *Tetrahedron Letters*, 1968, 587.

⁵ The preparation of substituted maleic anhydrides [e.g. (**6**)] from alkyl halides (W. R. Vaughn and K. S. Anderson, *J. Amer. Chem. Soc.*, 1955, **77**, 6702), should allow for the preparation of a large number of butadienes.