Stereoselective Synthesis of Substituted Functionalized Butadienes

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Summary The synthesis and pyrolysis of tricyclo[4,2,1,0²,5]nonene derivatives provides a stereoselective route to functionalized butadienes.

Since compound (8; \( R = \text{Me} \)) was required for a natural product synthesis, and existing methods for the preparation of 1,4-diacetoxybuta-1,3-dienes\(^1\) 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 \((1; \ R = \text{Me})\) was converted into the diester \((3)\)\(^3\) in 87% yield by the addition of \(\text{NaOMe} \) (1 mol. equiv.) followed by \(\text{Me}_2\text{SO}_4\). The acyloin reaction\(^4\) of \((3; \ R = \text{Me})\) furnished (90% yield) after acidic hydrolysis, the ketol \((4; \ R = \text{Me})\); \([\alpha]_D^2 = 4.51 \ (1H, d, J \ 9 \text{ Hz}, \text{CHOH}) \) and \(1.40 \ (3H, s, \text{Me})\); i.r. \(2.97 \text{ and } 5.64 \text{ pm}\). Reduction with \(\text{NaBH}_4\) gave the trans-diol \((5; \ R = \text{Me})\) which on treatment with \(\text{Ac}_2\text{O}\) yielded the trans-diacetate \((6; \ R = \text{Me})\); \([\alpha]_D^2 = -5.13 \ (1H, \text{ dd, } J 8 \text{ and } 8 \text{ Hz}, \text{HA})\), 4.72 (1H, dd, \( J 8 \text{ and } 2 \text{ Hz}, \text{HB})\) and 1.42 (3H, s, Me); i.r. 5.72 \text{ pm}\). 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 be separated by column chromatography on silica gel. The structure of (8; R = Me) was inferred from its n.m.r. \( \gamma: 7.30 (1H, d, J 13 Hz, H_a) 6.97 br (1H, s, H_b) 6.42 (1H, d, J 13 Hz, H_c) 2.12 (6H, s, OAc) \) and 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.

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2. O. Diels and K. Alder, Annalen, 1928, 460, 98.
5. The preparation of substituted maleic anhydrides \( \text{[e.g. (6)] from alkyl halides (W. R. Vaughn and K. S. Anderson, J. Amer. Chem. Soc., 1955, 77, 6702), should allow for the preparation of a large number of butadienes.} \)