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THE THERMAL ELECTROCYCLIC OPENING OF CYCLOBUT-2-ENOLS. DIRECTED CONROTATIONS AND STABLE DIENOLS.

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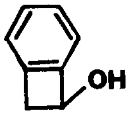
The heat-induced isomerization of cyclobutene to butadiene is a familiar example of a conrotatory electrocyclic process[1]. However, it is less well-known that substituents can dramatically influence the direction of conrotation[2]. A notable illustration is provided by benzcyclobutenol (1). Heating at 110° results in its smooth conversion to o-tolualdehyde (4). Although conrotatory rupture of the cyclobutene fragment can occur in both directions, evidence was only forthcoming for the E-dienol (3). Oxygen, as a substituent, displays a net refusal to adopt the Z configuration, at least when it is attached to the 1,2-dimethylene-1,2-dihydrobenzene structure (2)[3].



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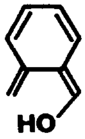

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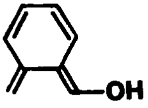

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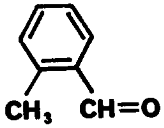

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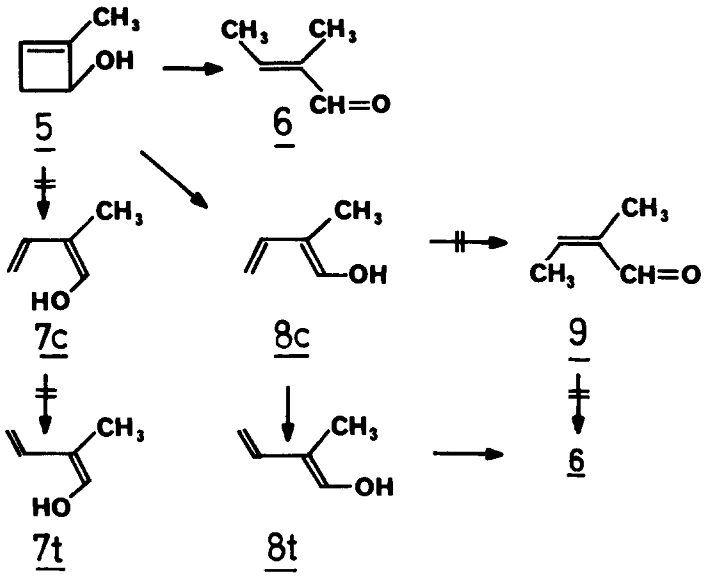
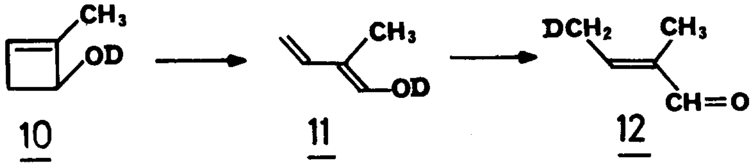
We now report on the behaviour of 2-methylcyclobut-2-enol (5)[4]. Here the stability of the hypothetical intermediate dienols will not be compromised by the demands of aromatisation, moreover the conformational restraints should be less severe and the ketonization step might be amenable to study.

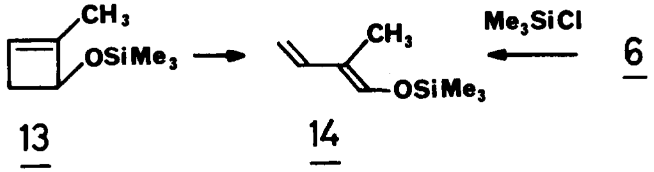
Heating 5 in deuteriochloroform at 100° for 5 minutes gave tiglic aldehyde 6 in quantitative yield. Clearly the first step requires electrocyclic ring cleavage to give one or both of the cisoid dienols of Z and E configuration (7c and 8c). Subsequent hydrogen transfer intra or intermolecularly in 7c and 8c respectively will give angelic aldehyde (9). In view of the known instability of cis aldehydes of this general type, it was initially thought that conversion of angelic to tiglic aldehyde (6) would be rapid[5]. A search, even at low temperatures (∿50°), uncovered no trace of 9. Moreover, heating a mixture of an authentic sample of angelic aldehyde and 5, under conditions which gave tiglic aldehyde, left its angelic isomer unchanged[6]. Therefore 7c is an unlikely intermediate since its ketonization to 9 should be instantaneous on account of the ideal arrangement for a [1,5] hydride shift. Similarly, conversion to conformation 7t will have small chances of success. Instead, it is concluded that E-dienol 8c is formed, but that it immediately adopts the transoid conformation 8t and then tautomerizes to tiglic aldehyde 6.

These conclusions are confirmed by the pyrolytic behaviour of the deuteriated cyclobutenol 10 and the silyl ether 13. In each case, single products were observed, which, as their nmr spectra were essentially identical, were assigned structures 11 and 14. Further warming of 11 gave only monodeuteriotiglic aldehyde (12).

These results are important for their pertinence to the ketonization-enolization problem and for their synthetic potential. Firstly, the stability of such dienols (11 and 8t) is rare[7], yet nevertheless understandable as the electronic criterion of intramolecular ketonization, although satisfied, is thwarted by the impossibility of the actual manoeuvre required for a 1,5 shift. Intermolecular ketonization, however, is possible, but slower and involves transfer of protons (or deuterons) between the ends of the dienols disposed in the transoid conformation. Interestingly, the enolization process of tiglic aldehyde with chlorotrimethylsilane and triethylamine (used for preparing 14) requires a similar transoid conformation of the developing dienol.







A second noteworthy feature is that electrocyclic opening of substituted cyclobut-2-enols affords in principle a novel approach for the synthesis of the aldehydic isoprene synthon.

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(4) 2-Substituted cyclobut-2-enols are conveniently prepared from the 1-substituted cyclobutenes on reaction with singlet oxygen. The resulting secondary hydroperoxides are reduced to the alcohols by triphenylphosphine in ether. (C.W. Jefford & C.G. Rimbault, Helv. to appear)

(5) Cis-2-methylpropenals are less stable than the trans isomers, and it now appears that isomerization rates are not so fast as was originally thought. (A.F. Thomas & M. Ozainne, J.C.S. Chem. Comm. 46 (1969)).

(6) Angelic aldehyde was readily synthesized by oxidation of the alcohol with manganese dioxide in methylene chloride. (cf. K.C. Chan, R.A. Jewell, W.H. Nutting & H. Rapoport, J. Org. Chem. 33, 3382 (1968)).

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