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RING STRAIN AND THE COPE REARRANGEMENT.
THE SYNTHESIS OF TRICYCLO[7.3.0.$0^{4,12}$]DODECA-2,5,7,10-TETRAENE.[1a,b]

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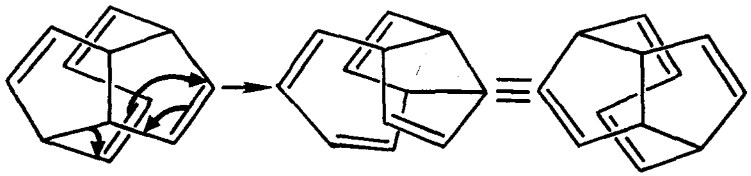
The title $(CH)_{12}$ hydrocarbon 1 has the potential to undergo a series of structurally degenerate Cope rearrangements[2], one of which is illustrated below. The complete cycle leads to the scrambling pattern shown in 2: eight positions (marked ●) form one equivalent set, while the remaining four comprise another. As shown, each Cope rearrangement also interchanges enantiomers. Thus, rapid rearrangement would be evidenced in a temperature dependent nmr spectrum; slower reaction might be followed by the racemization of (partially) resolved 1. We now report the synthesis of racemic 1, and some preliminary thermal studies.



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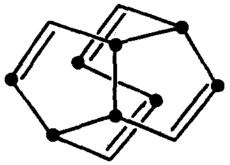

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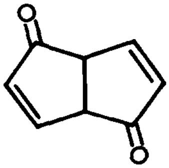
The synthesis begins with bicyclo[3.3.0]octa-3,7-diene-2,6-dione 3.[3] Reduction of 3 with diisobutylaluminum hydride[4] in toluene at -40° gave a mixture of epimeric dienediols (89% yield); low temperature recrystallization from acetone afforded the major isomer, cis, endo-diol 4[5] (m.p. 93-93.7°). Orthoester Claisen rearrangement[6] of 4 required drastic conditions (e.g., several days in boiling triethylorthoacetate with continuous distillation and frequent addition of pivalic acid catalyst), reflecting the congestion beneath the bicyclic nucleus and presumably the enforced boat-like transition state. The oily diester 5[5] was obtained in 52% yield after distillation, removal of lactone 6[5] (m.p. 84.8-85.2°) by precipitation with hexane, and chromatography on acidic alumina to remove the mixed ester 7.[5]



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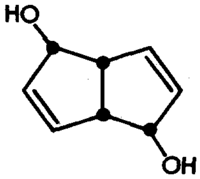

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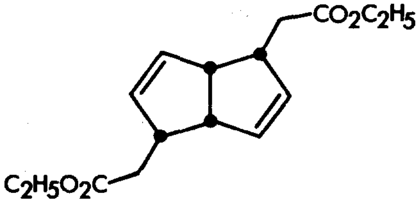

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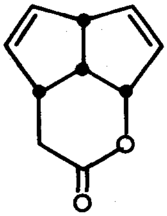

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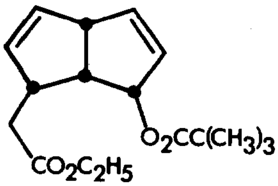

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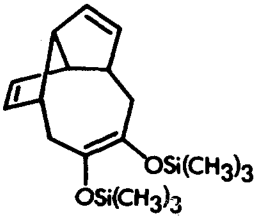

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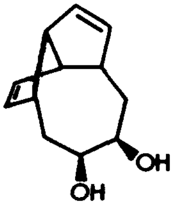

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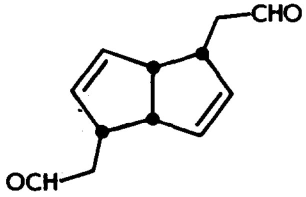

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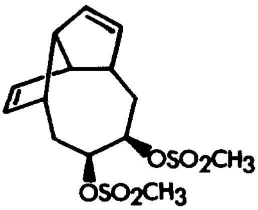

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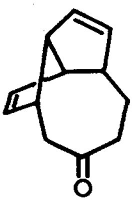

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Acyloin condensation of 5 proceeded satisfactorily in the presence of chlorotrimethylsilane[7] in hot toluene, affording the desired tricyclic product 8 in 40-55% yield. Removal of the trimethylsilyl groups was complicated by reactions involving the other (cyclopentene) double bonds, giving tetracyclic products, and by polymerization. However, treatment of 8 with an enormous (40-60 fold) excess of sodium borohydride in weakly basic aqueous ethanol[8] afforded the waxy diol 9[5] (dec. without melting above 100°) in 70-80% yield after chromatography. The gross structure of the diol was confirmed by periodic acid oxidation to dialdehyde 10, also obtained from diester 5 by reduction with lithium aluminum hydride followed by oxidation with chromium trioxide in pyridine. The *cis*-disposition of the hydroxyls was assigned on the basis of nonequivalence of the methyl groups of the dimesylate 11 (m.p. 99.5-101.5° decomp.). Finally, treatment of 11 with excess potassium *t*-butoxide in dimethylsulfoxide at 60-70° gave a mixture containing modest amounts (*ca.* 30%) of hydrocarbon 1[5], isolable by chromatography on alumina, together with ketone 12[5] and other products which were not identified.

Tetraene 1 is a soft, volatile, white solid with a pronounced oelfinic odor. The proton nmr spectrum is in agreement with the *static* structure 1, showing a complex pattern in the olefinic region (δ5.1-6.0, 8 protons) and a broad singlet for the bridgehead hydrogens (δ3.21, 4 protons). *This spectrum is unchanged up to 141°*, the highest temperature we have yet investigated. Furthermore, there is no change in the relative intensities of the signals in the olefinic region upon saturation of the δ3.21 signal at 100°. Thus, Cope rearrangement of 1 is slow on the nmr time scale. As the geometry appears ideal for a Cope rearrangement[2], this slow rate is probably due to the absence of a small ring and its accompanying strain. Recent MO calculations[9] support the intuitively reasonable idea that release of strain is a major factor in lowering the transition state for rearrangement of molecules such as bullvalene, and our results support this conclusion. We are continuing our studies on this new $(CH)_{12}$ isomer, and are attempting its resolution, so that the kinetics of the Cope may be determined and a more quantitative assessment of the importance of strain in such molecules may be made.

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