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anti-BISHOMOCYCLOPENTADIENONE AND SOLVOLYSIS OF *anti*-BISHOMOCYCLOPENTADIENYL *p*-NITROBENZOATE

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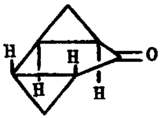
Cyclopentadienones are exceedingly unstable species[1] and therefore invite studies of the mono- and bishomo materials. We wish to report the synthesis and properties of *anti*-tricyclo-[4.1.0.0^{2,4}]heptan-5-one, **1**, a parent bishomocyclopentadienone[2] and solvolysis of *anti*-tricyclo[4.1.0.0^{2,4}]heptan-5-yl *p*-nitrobenzoate, **2**-OpNB, which could give rise to a bishomo antiaromatic cation. This cation is of further interest because it could potentially undergo a series of coupled degenerate cyclopropylcarbinyl-cyclopropylcarbinyl[3] cationic rearrangements.[4]



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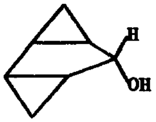

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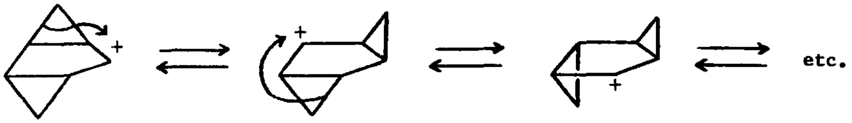
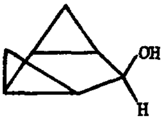


trans-Cyclopentanone-3,4-dicarboxylic acid,[5] **3**, was converted to the methyl ester, ketalized with ethylene glycol, reduced with lithium aluminum hydride, converted to the ditosylate, and deketalized to give *trans*-3,4-bistosyloxymethylcyclopentanone, **4**. Addition of **4** to molten potassium hydroxide in a stream of helium at 200° and sublimation of the volatile liquid product gave crystalline **1** (mp 44° in a sealed tube) in 15% yield. Pmr of **1** (100 MHz in CCl_4): unsymmetrical quartet, J = 3.5 Hz, at δ 0.75 (2 H); complex multiplet at δ 1.15 (2 H); complex multiplet at δ 1.43 (2 H); symmetrical multiplet at δ 1.95 (2 H). Ir of **1**

(CCl_4): 3090, 3050, 3010, 1795 sh, 1720; 1450, 1350, 1190, 1140 (w); 1050 sh, 1030, intense 955 and 935, and 855 cm^{-1}. λ_{max} (C_6H_{12}): 287 nm (ϵ = 30). λ_{max} (H_2O): 200 nm (ϵ = 6200).[6] *M/e* = 108.0574.

Confirmation of the stereochemistry was provided by hydride reduction to *anti*-tricyclo-[$4.1.0.0^{2,4}$]heptan-5-ol, 2, whose stereochemistry follows from its unsymmetrical pmr spectrum: quartet, J = 4 Hz, at δ -0.12 (1 H); triplet of doublets, J = 8 and 5 Hz, at δ 0.39 (1 H); multiplet at δ 0.53 (2 H); unsymmetrical five line pattern with each line separated by 4 Hz at δ 0.84 (1 H); complex multiplet at δ 1.25 (1 H); complex multiplet at δ 1.45 (2 H); broad singlet at δ 1.75 (1 H); doublet, J = 5.5 Hz, at δ 4.38 (1 H). This spectrum is inconsistent with that expected for either of the *syn* alcohols 5 or 6.



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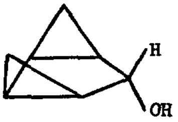

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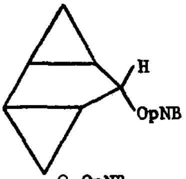
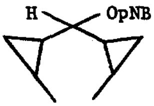
The *p*-nitrobenzoate of 2 was prepared (mp 59-60°) and subjected to solvolysis in 90% acetone-d_6 and 10% deuterium oxide at 25°. The rate constant for this solvolysis as determined by nmr analyses was 1.5 x 10^{-7}/sec, a factor of 125 *less* than that for bis(2-methylcyclopropylcarbinyl) *p*-nitrobenzoate, 7, and that for *cis,syn*-tricyclo[$5.1.0.0^{3,5}$]octan-2-yl *p*-nitrobenzoate, 8.[7] Thus 2-OpNB is substantially less reactive than model compounds. Whether this is due to bishomo antiaromaticity or to poor overlap of the developing *p*-orbital and the cyclopropyl groups due to the geometry is not clear. However, preparation and solvolysis of 5 and 6 would assist in making a decision. The sole product from solvolysis of 2-OpNB was starting alcohol.



2-OpNB



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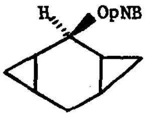

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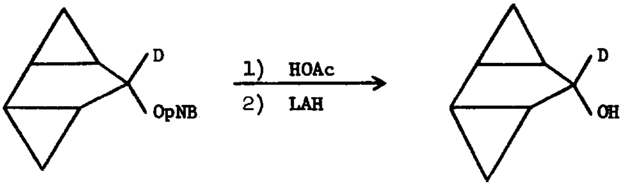
Hydrolysis (90% acetone)

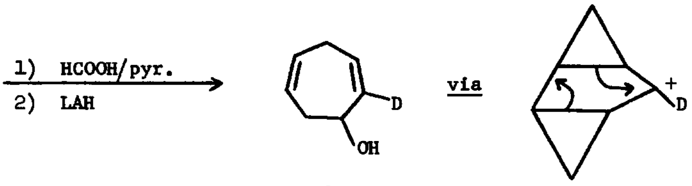
k_{rel} : 1 125 125

In an effort to uncover the hypothesized degenerate rearrangement, 2-αD was prepared and its p-nitrobenzoate subjected to buffered acetolysis at 50°. The acetate product was cleaved with lithium aluminum hydride and distilled giving only starting alcohol. Recovered 2 had most if not all of the deuterium on the α carbon indicating little if any rearrangement.

In an attempt to extend the lifetime of the carbonium ion, 2-αd OpNB was subjected to formolysis in ca. 10:1 formic acid - pyridine solution for a day at room temperature. A single product was formed which upon hydride cleavage and distillation gave a material whose spectroscopic properties were consistent with cyclohepta-2,5-dien-ol, 9, with a vinyl bound deuterium. This material, which conceptually is easily derivable from 2, further indicates that the hypothesized degenerate rearrangement is not very favorable here because 20% of the deuterium should have appeared at the carbinol carbon in 9 if scrambling were complete.



2-OpNB



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