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TRICYCLO[3.1.1.0^{3,6}]HEPTANES: SYNTHESIS FROM A BICYCLO[2.2.0]HEXANE

J. Meinwald* and J. Mioduski
Spencer T. Olin Laboratory, Department of Chemistry
Cornell University, Ithaca, New York 14850

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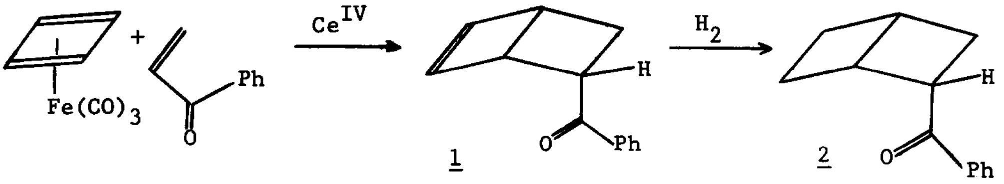
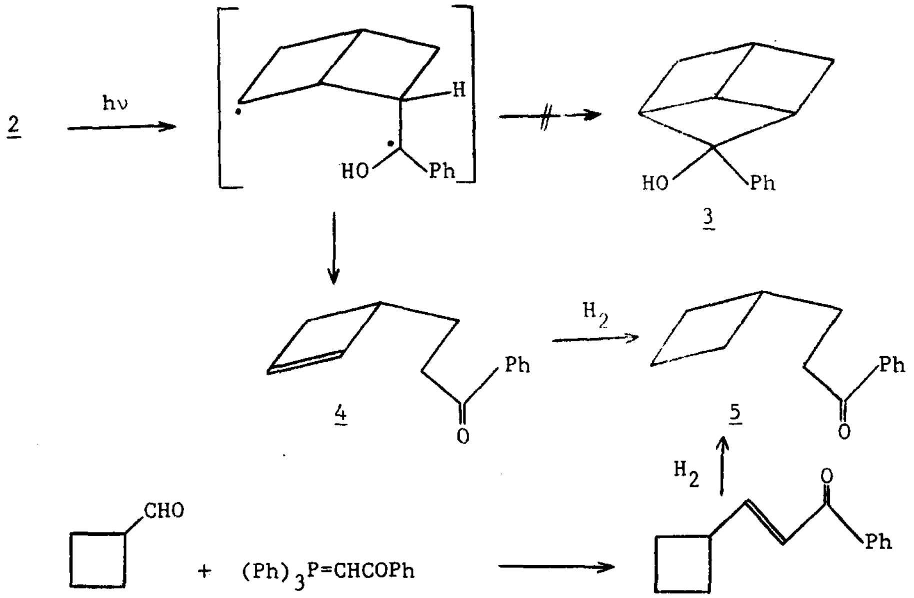
In recent years there has been considerable interest in the synthesis of highly strained cyclobutanols by photocyclization of aryl alkyl ketones which have an accessible γ-hydrogen.[1-6] We wish to report a synthesis of the previously unknown tricyclo[3.1.1.0^{3,6}]heptane ring system using this process.

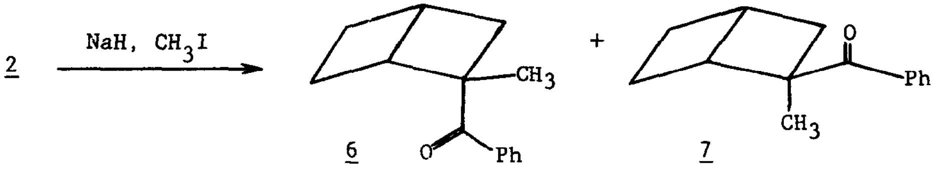
It was first reported by Pettit and co-workers that the oxidation of cyclobutadieneiron tricarbonyl at 0° in the presence of certain olefins yields derivatives of bicyclo[2.2.0]hexane.[7] We have found that when acrylophenone is used as the olefin, endo-2-benzoylbicyclo[2.2.0]hex-5-ene (1) (mp 50-51°)[8] is obtained in 80% yield.[9] Hydrogenation of this adduct at atmospheric pressure over 5% palladium on charcoal afforded the bicyclo[2.2.0]hexane 2 (mp 55-56°).



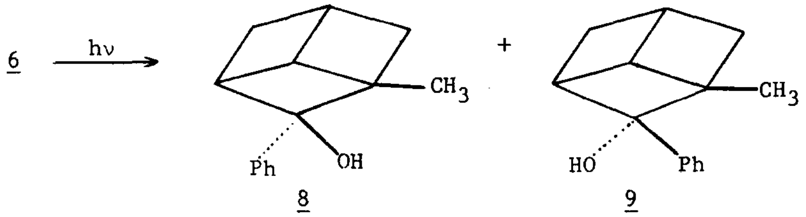
It was anticipated that irradiation of 2 would lead to a biradical intermediate which could then either cyclize to the desired tricycloheptanol 3, or undergo a Norrish type-II fragmentation to give the cyclobutene derivative 4. In fact, irradiation of 2 in benzene (Hanovia 450-W lamp, Pyrex filter, 30 min) yielded only the fragmentation product 4. Hydrogenation of 4 gave the corresponding cyclobutane 5, which was identical to a sample synthesized as shown below.



Treatment of 2 with sodium hydride and methyl iodide gave a 6:1 mixture of *endo*-2-benzoyl-2-methylbicyclo[2.2.0]hexane (6) (mp 55-56°) and its epimer, 7.

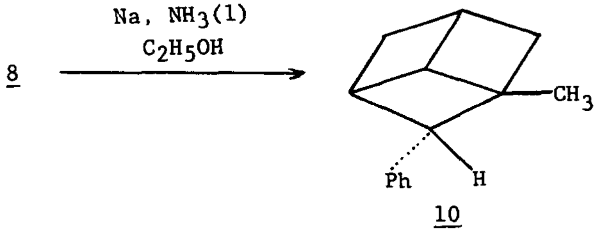


Upon irradiation (same conditions as for the irradiation of 2), 6 was converted quantitatively to a 1:1 mixture of epimeric tricyclo[3.1.1.0^{3,6}]heptanols, 8 (mp 61-62°) and 9. A similarly dramatic example of the ability of an α-methyl substituent to completely suppress Norrish type-II fragmentation in favor of cyclization was previously observed by Lewis and Ruden in the irradiation of *endo*-2-benzoylbicyclo[2.2.1]heptane.[5]

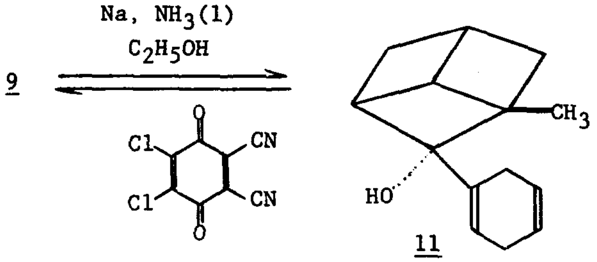


The nmr spectrum of 1-methyl-7-*exo*-phenyltricyclo[3.1.1.$0^{3,6}$]heptan-7-ol (9) shows the methyl resonance shifted upfield to τ 9.36, due to the shielding effect of the aromatic ring. In contrast, the methyl group of 1-methyl-7-*endo*-phenyltricyclo[3.1.1.$0^{3,6}$]heptan-7-ol (8) appears at τ 8.63.

The reaction of 8 with sodium in liquid ammonia resulted in reductive cleavage of the tertiary benzylic alcohol to afford a single hydrocarbon product, 10. The stereochemistry of 10 is assigned mainly on the basis of its nmr spectrum, which shows the methyl resonance at τ 8.59.



Surprisingly, an attempt to reduce 9 in a similar manner gave instead the dihydro compound 11, resulting from Birch reduction of the aromatic ring. Oxidation of 11 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone regenerated 9.



The efficient synthesis of bicyclo[2.2.0]hexenes from cyclobutadieneiron tricarbonyl provides a ready source of starting materials for the preparation of a variety of small ring compounds, and we hope to describe other, related synthetic efforts in the near future.

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References and Footnotes

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8. All new compounds gave satisfactory ir, nmr, and mass spectral data.
9. We wish to thank Professors R. Breslow and R. Pettit for their generosity in providing samples of cyclobutadieneiron tricarbonyl.