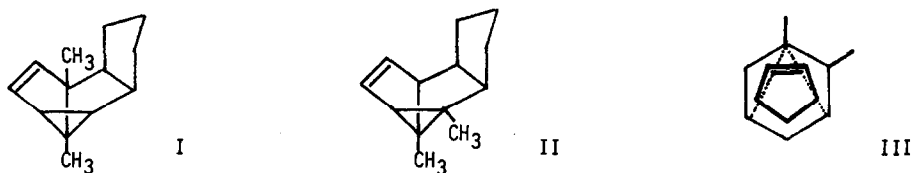


SYNTHESIS OF [4.3.3] PROPELLANES BY THE PHOTOCHEMICAL ADDITION OF TETRALIN TO OLEFINS

C. S. Angadiyavar, J. Cornelisse, V. Y. Merritt and R. Srinivasan
 IBM T. J. Watson Research Center
 Yorktown Heights, N. Y. 10598, U.S.A.

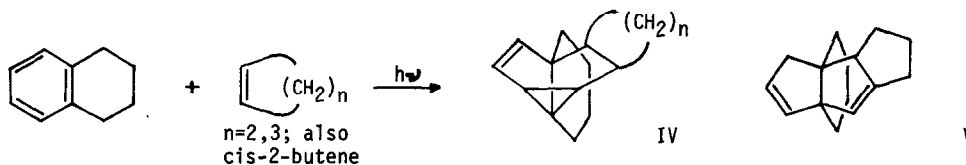
(Received in USA 24 August 1973; received in UK for publication 25 September 1973)

It has been pointed out^{1,2} that the photochemical 1,3-additions of alkylbenzenes to cyclic olefins show a high degree of orientational specificity. Thus, the addition of *o*-xylene to cyclopentene yields I and II in the ratio of 3:1 as the only products although six such adducts (with endo fusion of the cyclopentane ring) are theoretically possible.



This specificity is believed² to depend on the formation of a complex between the aromatic hydrocarbon in its singlet excited state and the olefin with a structure represented by III, the closure of the cyclopropane ring along the dotted lines giving rise to I and II.

In the course of a study of the scope of these additions, it has been found that the 1,3-addition of tetralin to several olefins leads to derivatives of



the ring system IV which incorporates a [4,3,3] propellane in it. Although propellanes, in general^{3,4}, and [4.3.3] propellanes in particular have been studied before, the ease with which the present reaction can be carried out makes it a useful synthetic route. Typically, a solu-

tion of tetralin (10%) and cyclobutene (10%) in cyclohexane was irradiated for 36 hours at Experimental: Typically, 30 ml of a solution of tetralin (10%) and cyclobutene (10%) in cyclohexane was irradiated for 36 hours at 254 nm (four Rayonet type RS modules from The Southern N. E. Ultraviolet Co. were used). The unreacted material and solvent were removed by distillation at room temperature in a good vacuum and reirradiated. The residues from four such passes of 36 hours each were distilled first at 1 atm. at 125° and then distilled bulb-to-bulb at 5 torr at 125° when the crude adduct of tetralin to cyclobutene (25%) was collected. The material was purified by vapor phase chromatography (UCON-550X, 12', 150°; R.T. 52 min.) although considerable loss of material due to thermal decomposition was evident.

Procedures using other olefins were identical. The use of dihydroindene instead of tetralin did not lead to any adduct.

In common with other 1,3-photoadducts of benzene to olefins⁵, the propellane adducts (IV)⁶

maxima (pentane) at 220 nm ($\epsilon \sim 2000$) due to the presence of a vinylcyclopropane chromophore^{5a}. Their nmr spectra (220 MHz, CCl_4 solution, TMS as internal reference) indicated the presence of two vinyl protons (ca. 5.5 δ), one proton in midfield (ca. 3.1 δ) and the remaining protons between 0.9 and 2.3 δ . The nmr spectrum of the adduct of tetralin to cyclobutene- d_6 indicated two olefinic protons in the molecule which in turn showed that they originated in the tetralin.

All of the adducts underwent pyrolysis readily even at temperatures below 150° to yield tetralin and the corresponding olefin. Therefore the carbon skeleton of the tetralin had evidently not undergone a rearrangement during the photoreaction. The presence of two olefinic protons in the adducts requires that (with a cyclic olefin) they should be pentacyclic. The points of attachment of the cyclohexane ring in tetralin to the benzene moiety in the adduct became evident when the nmr spectrum of the olefinic protons was examined in detail. In the 1,3-adducts of benzene to cis-2-butene^{5a} or cyclobutene^{5c}, these two proton absorptions appear as doublet of doublets, the strong coupling (~ 6 Hz) being to each other and the weak component (~ 2 Hz) being to the (respective) adjacent allytic proton. In the major adduct of o-xylene to an olefin (I) as well as in the propellane adducts (IV), the olefin absorption at high field occurred as a doublet ($J = 5.5$ Hz) while the olefinic absorption at lower field was a doublet of doublets ($J = 5.5$ and 2.0 Hz). This confirmed that the cyclohexane ring in the adduct must be as in IV. The endo orientation of the olefinic ring follows by analogy from the structures of all of the adducts of alkylbenzenes to olefins² which were endo oriented without exception.

The quantum yield at 253.7 nm for the addition of tetralin (1.1 M) to cyclopentene (1 M) in cyclohexane was measured to be 0.011. This may be compared to the value of 0.08 for the 1,3-adducts of o-xylene to the same olefin under identical conditions.² The considerably greater strain in the propellane may account for its poor quantum yield.

The adduct of tetralin to cyclopentene can be cleaved readily with a catalytic amount of HCl to the diolefin V. Details of these investigations will be published elsewhere.

Acknowledgment: The authors wish to thank the Air Force Office of Scientific Research (AFSC), U. S. Air Force for Contract No. F44620-72-C-0024 under which this work was carried out

References:

1. R. Srinivasan, J. Am. Chem. Soc. **93**, 3555 (1971).
2. J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *ibid*, **95**, in press (1973).
3. D. Ginsburg, Accounts Chem. Res. **2**, 121 (1969).
4. P. E. Eaton and K. Nyi, J. Am. Chem. Soc. **93**, 2786 (1971).
5. (a) K. E. Wilzbach and L. Kaplan, *ibid*, **88**, 2066 (1966). (b) D. Bryce-Smith, A. Gilbert, and B. H. Orger, Chem. Comm. 512 (1966). (c) R. Srinivasan, IBM J. Res. Dev. **15**, 34 (1971). (d) H. Morrison and W. I. Ferree, Jr., Chem. Comm. 268 (1969).
6. All new compounds gave satisfactory elemental and/or mass spectral analyses.