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PHOTOCHEMICAL SYNTHESIS OF A TRICYCLO[3.2.1.$0^{3,6}$]OCTANE[1]

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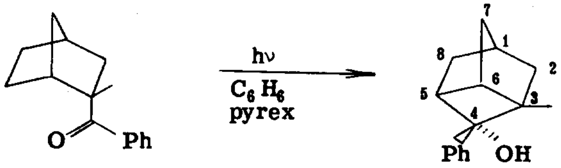
The photochemical synthesis of novel bridged polycyclic cyclobutanols has been the subject of recent attention.[3] We wish to report the quantitative and stereospecific conversion of endo-2-benzoyl-2-methylnorbornane (1) to the tricyclo[3.2.1.$0^{3,6}$]octane 2. This reaction



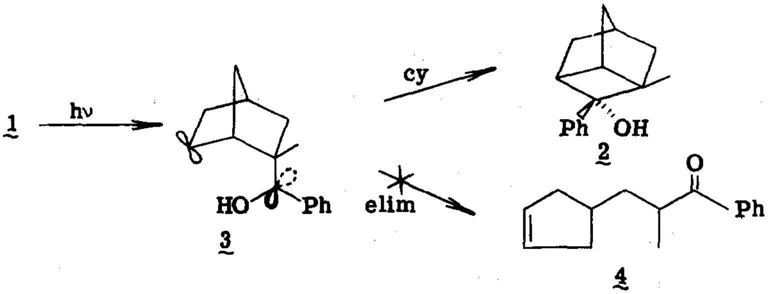
1 2

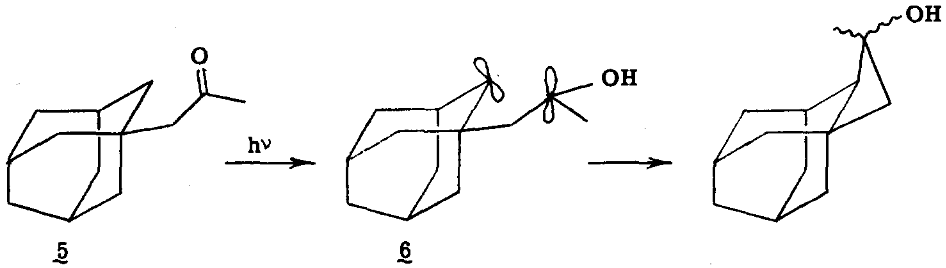
is of considerable interest both in providing a simple, high yield synthesis of a tricyclo[3.2.1.$0^{3,6}$]octane system[4] and in providing further information about the nature of 1,4-biradical intermediates.[5]

The phenyl ketone 1 was synthesized in good yield from 5-methylnorborene-5-carboxylic acid[6] by reaction with phenyl lithium followed by hydrogenation over palladium on carbon. Irradiation of dilute solutions of 1 in degassed or non-degassed benzene resulted in complete conversion to 2 (>95%). No other products could be detected by analytical gas chromatography or by nmr analysis. The assignment of structure 2 to the photo product follows mainly from its spectral characteristics. The mass spectrum of 2 is similar to that of 1, having peaks at m/e 214 (M^+), 196, 109 (base peak), 105 and 94. The nmr spectrum (CCl_4, δ units) of 2 is composed of a sharp aromatic region at 7.1, three bridgehead multiplets at 2.15, 2.45 and 2.65, a broad six proton methylene region, a methyl singlet at 1.24, and a sharp hydroxyl singlet at 1.65. The hydroxyl proton chemical shift and its lack of significant concentration or solvent dependence are indicative of a hindered hydroxyl group. The ir of **2** (0.13 M in CCl_4) exhibits a free O-H stretch at 3610 cm^{-1} and a weak hydrogen-bonded O-H stretch at 3460 cm^{-1} with $\epsilon(OH)^b/\epsilon(OH)^f = 0.09$. Only the sharp free O-H stretch is observed for 0.018 M **2**. Thus the ir spectra also indicate a very hindered hydroxyl group, as expected for **2**, but not for its C_4 epimer.

The quantum yields for disappearance of **1** and formation of **2** in degassed benzene solution using 3130 Å irradiation are both 0.49 ± 0.03.[7] Addition of increasing amounts of t-butyl alcohol to the solvent leads to an increase in the quantum yield to a value of 0.63 ± 0.03 observed in 67% t-butyl alcohol-benzene.[8] Addition of 0.5 M piperylene quenched over 95% of the formation of **2**. A linear Stern-Volmer plot (φ_0/φ vs [piperylene]) with a slope of 60 ± 2 M^{-1} was obtained.

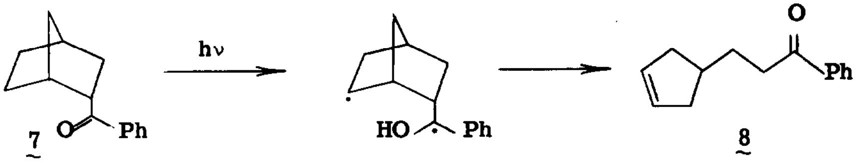
The formation of **2** most likely occurs via cyclization of a 1,4-biradical intermediate (**3**) which is formed upon γ-hydrogen abstraction by the carbonyl n,π* triplet excited state. The total absence of type II elimination product **4**[9] from the 1,4-biradical intermediate and the high quantum yield for cyclization are most unusual. We have previously observed high cyclization/elimination ratios for α,α-disubstituted aryl alkyl ketones;[10] however, the only previous example of a saturated alkanone in which γ-hydrogen abstraction results exclusively in cyclobutanol formation is that of adamantyl acetone (**5**).[3b] In the case of **5** elimination would produce



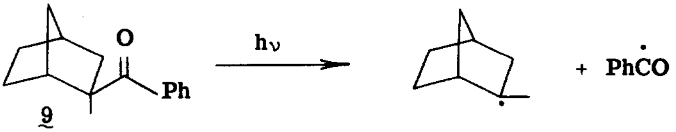


the highly strained olefin adamantene. Furthermore the most favorable transition state for elimination, which requires overlap of both radical orbitals with the bond undergoing cleavage, cannot be attained in the 1,4 biradical 6. In contrast, such a transition state can be attained by the biradical 3. Furthermore, the elimination product 4 would be expected to be *more* stable than the cyclobutanol 2. The absence of 4 can be explained by considering the transition state for elimination in which the phenyl and α-methyl groups must be eclipsed. No such eclipsing is present in the transition state for cyclization. This conclusion is in accord with our previous observation that cyclization/elimination ratios for 1,4-biradical intermediates are better explained by transition state considerations than by product stabilities.[5,10] The formation of the more thermodynamically stable of the two possible cyclobutanols is indicative of a small activation energy for cyclization of 3, in agreement with previous results.[11]

Evidence for the importance of the α-methyl-phenyl eclipsing interaction is provided by the observation that photolysis of the ketone 7 results primarily in the formation of the elimination product 8.[12]



The absence of products resulting from α-cleavage of 1 is of interest since other *t*-alkyl phenyl ketones having γ-hydrogens undergo α-cleavage in competition with γ-hydrogen abstraction.[10] The *exo* ketone 9 which has no geometrically accessable γ-hydrogens undergoes



α-cleavage with a rate constant of 1.7×10^7 sec^{-1}. Since the rate constant of γ-hydrogen abstraction of 1 obtained from the Stern-Volmer plot is 8.3×10^7 sec^{-1}, the total absence of α-cleavage from 1 indicates a considerably slower rate constant for α-cleavage from 1 than observed for 9. This result is in accord with Bartlett's observation that 2-methylnorbornyl radical is formed more rapidly upon decomposition of *exo*- than *endo*-2-methyl-2-carbo-*t*-butylperoxynorbornanes.[15]

REFERENCES

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9. The expected secondary photoelimination product from 4, propiophenone, could not be detected after prolonged photolysis either.

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12. In analogy to the result for 1 and 7, 2-benzoylbicyclo[2.2.2]octane undergoes photoelimination[13] whereas 2-methyl-2-benzoylbicyclo[2.2.2]octane undergoes photocyclization.[14]

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