

SYNTHESIS OF 8,9-DEHYDRO-2-ADAMANTANONE BY THE
OXA-DI- π -METHANE PHOTOREARRANGEMENT OF 2-PROTOADAMANTENONE

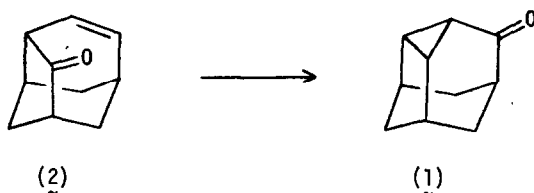
Roger K. Murray, Jr.* and Kevin A. Babiak

Department of Chemistry, University of Delaware, Newark, Delaware 19711

(Received in USA 21 November 1973; received in UK for publication 10 December 1973)

8,9-Dehydro-2-adamantanone (1) has been shown to be a useful precursor for the synthesis of adamantyl,^{1,2} protoadamantyl,^{3,4} and isotwistyl⁴ derivatives. However, it has not been convenient to employ (1) in synthesis, as the only reported preparation of (1) involves a multi-step reaction sequence which converts norbornadiene to (1) in an overall yield of 2%.¹ In view of several reports in the literature describing the triplet-sensitized photorearrangement of β,γ -unsaturated ketones to give isomeric cyclopropyl ketones (the oxa-di- π -methane photorearrangement),⁵ it appeared to us that (1) might be more expeditiously prepared by the photoisomerization of 2-protoadamantenone (2).

Irradiation of a 0.5% solution of (2)^{6,7} [λ_{\max} (EtOH) 296 nm, ϵ 230] in acetone through a Pyrex filter with a Hanovia L 450-W lamp proceeds smoothly to give (1).^{8,9} Under these conditions



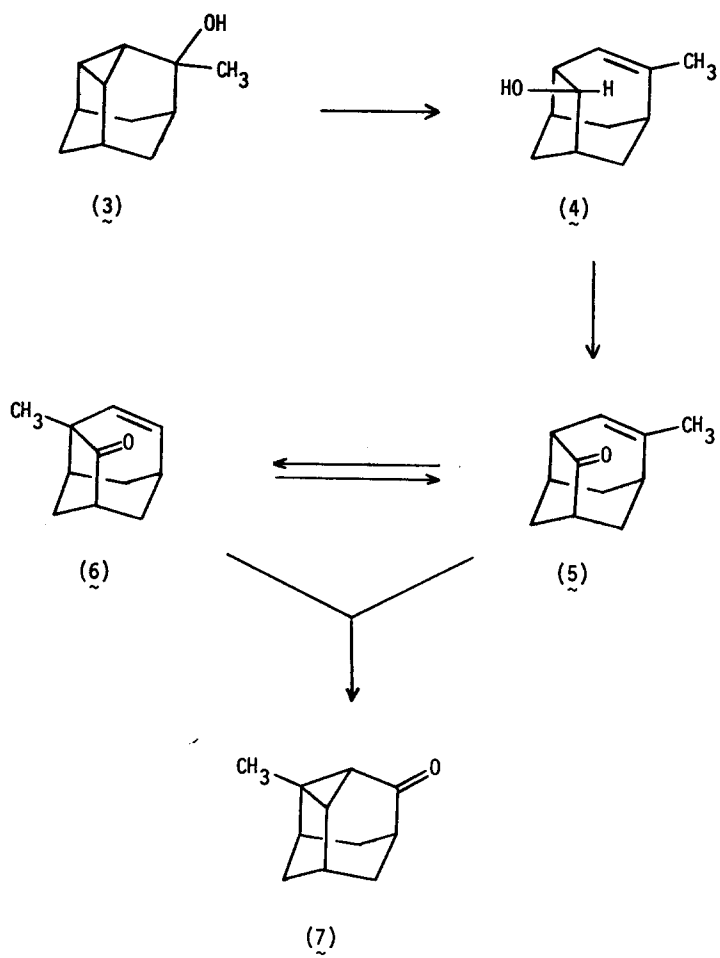
(1) [λ_{\max} (EtOH) 277 nm, ϵ 40] undergoes slow photodecomposition, but this reaction does not effectively compete with the photoisomerization of (2) to (1). Thus, irradiation of (2) to 80% conversion affords (1) in ca. 70% yield.

The course of this photorearrangement is apparent from the photochemistry of 5-methyl-2-protoadamantenone (5). Enone (5)¹⁰ [$\nu_{C=O}$ (CCl₄) 1740 cm⁻¹; δ (CDCl₃) 1.77 (d, J 1.5 Hz, CH₃), 5.62 (br d, J 7 Hz, (CH₃)C=CH)] is prepared in an overall yield of ca. 70% from (1) by the following reaction sequence. Treatment of (1) with methyl lithium gives 8,9-dehydro-2-methyl-2-adamantanol (3) [δ (CDCl₃) 1.41 (s, CH₃)]. Isomerization of (3) with 0.005 M perchloric acid in refluxing 80% aqueous acetone affords 5-methyl-2-exo-protoadamantenol (4) [δ (CDCl₃) 1.68 (d, J 1.5 Hz, CH₃), 3.68 (br s, C(OH)H), 5.63 (br d, J 5 Hz, (CH₃)C=CH)] and Jones oxidation of (4) provides (5). Irradiation of an acetone solution of (5) through a Pyrex filter affords 8,9-dehydro-8-methyl-2-adamantanone (7) [$\nu_{C=O}$ (CCl₄) 1710 cm⁻¹; δ (CDCl₃) 1.33 (s, CH₃)] in ca. 65% yield. In the early stages of this photolysis another photoproduct is detected which disappears on continued irradiation. This photoproduct has been identified as 3-methyl-2-protoadamantenone (6), mp 117-119^o [$\nu_{C=O}$ (CCl₄) 1745 cm⁻¹; δ (CDCl₃) 1.27 (s, CH₃), 5.57 (d, J 8.8 Hz, (CH₃)C-CH=CH), 6.42 (dd, J 8.8 Hz and 8.5 Hz, (CH₃)C-CH=CH)]. Enone (6) can also be generated by irradiation of an ether solution of (5) through a Pyrex filter to give an approximately 1:1 photoequilibrium mixture of (5) and (6).¹¹ Irradiation of the photostationary mixture of (5) and (6) in acetone through a Pyrex filter gives only (7).

Ketone (7) is the first bridgehead substituted 2,4-dehydroadamantane which has been reported.¹² Since the organic lithium reagent that is employed in this synthesis can be varied considerably, the overall scheme offers a route for the preparation of a variety of 2-substituted 2,4-dehydroadamantanes.

We are currently exploring in detail the chemistry of the structurally rigid cyclopropyl ketone (1).

Acknowledgement. This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Delaware Research Foundation, and the Delaware Institute of Medical Education and Research.



Footnotes and References

1. J. E. Baldwin and W. D. Foglesong, J. Amer. Chem. Soc., 90, 4303 (1968).
2. R. K. Murray, Jr. and K. A. Babiak, J. Org. Chem., 38, 2556 (1973).
3. H. W. Whitlock, Jr. and M. W. Siefken, J. Amer. Chem. Soc., 90, 4929 (1968).
4. R. K. Murray, Jr. and T. K. Morgan, Jr., Tetrahedron Letters, 3299 (1973).
5. For a review see: S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, Chem. Rev., 73, 531 (1973).
6. C. A. Cupas, W. Schumann, and W. E. Heyd, J. Amer. Chem. Soc., 92, 3237 (1970).
7. Following the synthesis outlined in ref. 6, enone (2) could be prepared in two steps from tropylium tetrafluoroborate in an overall yield of ca. 35%.
8. The physical and spectral properties of the photoproduct are in complete agreement with those previously reported¹ for (1).
9. Direct irradiation of (2) does not afford (1).
10. Satisfactory elemental analyses and spectral data consistent with the structural assignments have been obtained for all new compounds.
11. Irradiation of an ether solution of (6) also affords a 1:1 mixture of (5) and (6).
12. Nonbridgehead substituted 2,4-dehydroadamantanes which have been reported are (1) and its derivatives¹ and 3,5-dehydrodiamantane.¹³
13. D. Farcasiu and P. v. R. Schleyer, Tetrahedron Letters, 3835 (1973).