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SYNTHESIS OF 9,10-DEHYDROHOMOADAMANTANE

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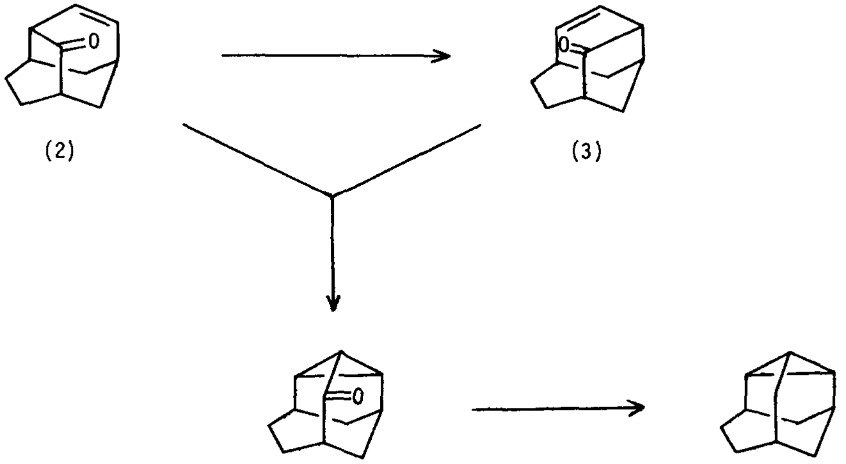
Of the five possible "non-bridgehead" dehydrohomoadamantanes,[1] only 2,4-dehydrohomoadamantane is known.[1-3] We now wish to report the synthesis of another member of this family of hydrocarbons, namely, 9,10-dehydrohomoadamantane (1).[4]

We anticipated that a suitable precursor for (1) would be 9,10-dehydrohomoadamantan-2-one (4). In principle, cyclopropylketone (4) might be realized by the oxa-di-π-methane photorearrangement[5] of either tricyclo[4.4.1.$0^{3,8}$]undec-4-en-2-one (2) or tricyclo[4.3.2.$0^{3,8}$]undec-4-en-2-one (3). The availability of (2)[6] led us to examine its photochemistry.



(2) (3)

(4) (1)

Irradiation of a 0.5% solution of (2) in acetone through a Corex filter with a Hanovia Type L 450-w lamp to complete conversion provides ketone (4)[7] [mp 211-213°; m/e 162 (P); ν_{max} (CCl_4) 1684 cm^{-1}; δ ($CDCl_3$) 0.9-3.1 (broad, complex multiplet)] in ca. 25% yield and enone (3) [mp 194-195°; m/e 162 (P); ν_{max} ($CHCl_3$) 1722 cm^{-1}; δ ($CDCl_3$) 1.2-3.2 (12H, broad, complex multiplet), multiplet centered at 5.90 (2H, olefinic protons)] in ca. 5% yield.[8,9]

In contrast, irradiation of an ether solution of (2) through a Pyrex filter leads exclusively to a formal 1,3-acyl migration and the formation of enone (3) in ca. 65% yield. Prolonged irradiation of (3) in acetone through a Pyrex filter also affords (4), but only in low yield (ca. 5%).

Treatment of (4) under the conditions of the normal Huang-Minlon modification of the Wolff-Kishner reduction gives 9,10-dehydrohomoadamantane (1) in ca. 60% yield. The structure of (1), mp 224-225°, follows from its mode of synthesis and spectroscopic properties [m/e (intensity relative to base peak) 148 (P, 68%), 133 (14), 120 (19), 119 (58), 106 (24), 105 (26), 93 (27), 92 (70), 91 (70), 79 (100); ir (CCl_4) 3025m, 2920s, 2860m, 1450m, 1190w, 1060w, 1037w, 1012w, and 908w cm^{-1}; δ ($CDCl_3$) 0.7-2.5 (broad, complex multiplet)].

Studies directed toward the synthesis of the remaining nonbridgehead dehydrohomoadamantanes are currently in progress.

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Footnotes and References

1. Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, Chem. Comm., 949 (1970).
2. R. Yamaguchi, T. Katsushima, T. Imagawa, and M. Kawanisi, Syn. Comm., 4, 83 (1974).
3. The synthesis of spiro[adamantane-2,5'-(2',4'-dehydrohomoadamantane)] has also been reported: E. Boelema, H. Wynberg, and J. Strating, Tetrahedron Lett., 4029 (1971).
4. Trivial nomenclature based on the conventional numbering of homoadamantane. By IUPAC nomenclature, (1) is tetracyclo[$4.4.1.0^{2,4}.0^{3,9}$]undecane.
5. For a review see: S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, Chem. Rev., 73, 531 (1973).
6. C. A. Cupas, W. E. Heyd, and M.-S. Kong, J. Amer. Chem. Soc., 93, 4623 (1971).
7. Satisfactory elemental analyses have been obtained for all new compounds.
8. Ketones (3) and (4) are readily separated by column chromatography on silica gel with benzene as eluent.
9. P. S. Engel and M. A. Schexnayder have previously reported [J. Amer. Chem. Soc., 94, 9252 (1972)] an "unprecedented triplet 1,3-acyl shift" in the photochemistry of a β,γ-unsaturated ketone. It is not clear if a similar isomerization is occurring in the present study or if the formation of (3) from (2) with triplet sensitization simply results from some "leakage" to the excited singlet of (2) under the photolysis conditions employed.