Tetrahedron Letters No.34, pp. 4089–4091, 1966. Pergamon Press Ltd.
Printed in Great Britain.

8,9-DEHYDROADAMANTANONE-2

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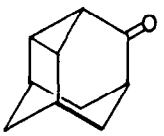
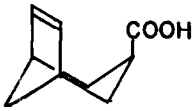
(Received 9 June 1966)

A rigid cyclopropyl ketone of potentially great versatility, 8,9-dehydroadamantanone-2 (I), has been synthesized.

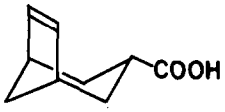


I

3-Bromobicyclo[3.2.1]octa-2,6-diene (1) was converted to the corresponding Grignard reagent with magnesium in tetrahydrofuran (2) and carbonated to give 3-bicyclo[3.2.1]octa-2,6-dienecarboxylic acid, m.p. 143-145° (3,4) in 44% yield after recrystallization from ethanol; the anilide had m.p. 192-193° (3). Selective reduction of this α,β-unsaturated acid with potassium in ammonia - isopropyl alcohol gave a mixture of epimeric 3-bicyclo[3.2.1]oct-6-enecarboxylic acids II and III, m.p. 41-55° (75-88% yield). Separation of this mixture through the usual iodolactone route (5) gave the endo-isomer II, m.p. 145-146° (3,4), from the zinc dust reduction of the iodolactone, m.p. 97-98.5° (3,4), and the exo-isomer III, m.p. 123.5-124.5° (3,4).



II



III

Direct treatment of the mixture of acids II and III with oxalyl chloride (6) gave the acid chlorides ($\bar{\nu}^{CCl_4}$ 1805 and 1775 cm.$^{-1}$; shoulder at 1745 cm.$^{-1}$) which were converted with diazomethane to the α-diazoketones ($\bar{\nu}$ 2100 and 1635 cm.$^{-1}$). Decomposition of the α-diazoketones in tetrahydrofuran at reflux in the presence of copper sulfate (7) gave, after chromatography on silica gel, sublimation, and recrystallization from pentane, the ketone I, m.p. 206.5-207.5° (3), in 15-20% yield from the mixture of II and III. The infrared spectrum of dehydroadamantanone showed prominent absorptions at 3040, 2940, 2864, 1702, 1343, 1053, 939, and 888 cm.$^{-1}$ in CCl_4. The n.m.r. spectrum of the ketone dissolved in CCl_4 showed complex absorption at 7.4-8.6 τ; no absorptions were present at lower fields. The molecular weight for $C_{10}H_{12}O$, 148, was confirmed by mass spectrometry. The 2,4-dinitrophenylhydrazone of I had m.p. 215-217° (3) and $\lambda_{max}^{CHCl_3}$ 376 mμ.

Improvements in the synthesis of dehydroadamantanone are being sought; intensive investigations of the chemistry of dehydroadamantanone (8), dehydroadamantane (9), and dehydroadamantanyl ions are in progress.

Support of this work by the National Science Foundation (Grant No. GP-5226) and a du Pont Grant-in-Aid to the Department of Chemistry and Chemical Engineering of the University of Illinois are acknowledged.

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3. Elemental analysis gave carbon, hydrogen, and nitrogen (if present) percentages within 0.3% of the calculated values.

4. Infrared and n.m.r. spectra for this compound were in full accord with expectations.

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