

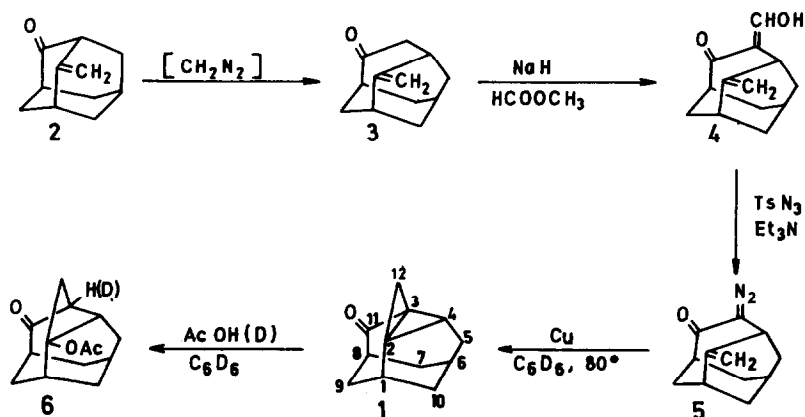
2,3-METHANO-2,4-DIDEHYDRO-11-HOMOADAMANTANONE¹:
A [4.1.1]PROPELLANONE.

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Summary: A new [4.1.1]propellane, 2,3-methano-2,4-didehydro-11-homoadamantanone (1), has been prepared quantitatively by an intramolecular cycloaddition of 2-methylene-5-oxo-4-homoadamantylidene, and its reactivity toward electrophiles and free radicals has been investigated. This is the smallest carbocyclic propellane that has been prepared².

As a part of our extensive interest in the synthesis and chemistry of small-ring propellanes³, we have prepared a [4.1.1]propellane 1 and investigated the effect of electro-negative substituents, such as the carbonyl group, on the reactivity and nature of the adjacent bond between inverted carbon atoms. The synthesis of 1 started with 4-methylene-2-



-adamantanone (2)^{3b} which was converted into the corresponding methylene ketone 3 in 36% yield⁴ with diazomethane.⁵ Treatment of 3 with sodium hydride followed by methyl formate gave a 78% yield of α -formyl ketone 4 which was treated with tosyl azide⁶ to give, after purification by chromatography on alumina, 44% of 5.⁴ Propellane 1 was prepared by the intramolecular cycloaddition of 2-methylene-5-oxo-4-homoadamantylidene which was generated by catalytic decomposition of 5 in the presence of copper in benzene- d_6 at 80°C. It was more than 95% pure by ¹³C NMR. The structure proof of 1 is based on spectral data.⁷ The IR spectrum^{7b} exhibited characteristic bicyclobutane C-H vibrational band at 3080 and 3030 cm⁻¹,

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carbonyl absorption frequency at 1695 cm^{-1} , as well as, the frequencies at 575 and 410 cm^{-1} characteristic for strained ring propellanes.⁸ The ^1H NMR displayed three multiplets at 2.4 – 2.2 (1H), 2.2 – 2.0 (1H) and 1.8 – 0.9 (12H), with two distinctive doublets at 1.72 and 1.14 ($J=2.3$ Hz). The ^{13}C NMR spectrum unambiguously established the structure of **1**: (C_6D_6) δ 207.1 (s, C_{11}), 49.1 (d, $J=172$ Hz, C_4) 44.7 (d, $J=133$ Hz, C_8), 35.7 (dd, $J=152$ and 172 Hz, C_{12}), 35.0, 32.5, 30.4 (2C) (t, $J=128$, 129 and 128 Hz, respectively, C_5 , C_7 , C_9 or C_{10}), 26.5 (d, $J=134$ Hz, C_6 or C_1), 22.7 (d, $J=137$ Hz, C_1 or C_6), 19.6 (s, C_3), 14.0 (s, C_2). Contrary to all other small-ring propellanes studied by us³, the [4.4.1]propellanone **1** is completely inert toward carbon tetrachloride and dimethyl disulfide. On the other hand, it reacts readily with acetic acid, which adds preferentially across the propellane central bond to give 2-acetoxy-2,4-methano-5-homoadamantanone (**6**) as the major product (80% of volatile product). The structure of **6** was based on spectral data¹⁰ and by comparison of its spectral data with the spectral data of the product obtained with deuterated acetic acid. The carbonyl group appears to decrease the reactivity of the adjacent bond between the inverted carbon atoms. This is consistent with the electron-withdrawing effect of the carbonyl group, which should decrease both the electron density in the region of the propellane central bond and the energy of the HOMO of **1**. The study of the chemistry of **1** is in progress.

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References and Notes

1. Pentacyclo [6.3.1.0^{3,5}.0^{3,6}.0^{5,10}]dodecan-2-one.
2. A [3.3.1]propellane-2,8-dione has been synthesized recently: Reingold, I.D.; Drake, J. *Tetrahedron Lett.* **1989**, 30, 1921.
3. (a) Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1980**, 102, 1418. (b) Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1983**, 105, 7389. (c) Vinković, V.; Majerski, Z. *J. Am. Chem. Soc.* **1983**, 104, 4027. (d) Majerski, Z.; Žuanić, M.; *J. Am. Chem. Soc.* **1987**, 109, 3496. (e) Majerski, Z.; Veljković, J.; Kaselj, M. *J. Org. Chem.* **1988**, 53, 2662. (f) Mlinarić-Majerski, K.; Majerski, Z.; Rakvin, B.; Vekšli, Z. *J. Org. Chem.* **1989**, 54, 545.
4. Satisfactory analytical and spectral data were obtained for all new compounds.
5. According to the procedure of: Schleyer, P.v.R.; Funke, E.; Liggero, S.H. *J. Am. Chem. Soc.* **1969**, 91, 3965. Three products were obtained: 2-methylene-5-homoadamantanone (**3**), 2-methylene-4-homoadamantanone and 2-methylenadamantane-4-spirooxirane, respectively in a 5:3:1 ratio.
6. Regitz, M.; Rüter, J.; Liedhener, A. *Org. Synth. Coll. Vol.* **6**, **1988**, 389.
7. (a) Mass spectrum: m/e 174 (M^+ , 41), 131 (51), 105 (88), 91 (100), 79 (65), 77 (67%). (b) IR (KBr) ν 3080, 3030, 2930, 2860, 1695, 1450, 1045, 825, 575 and 410 cm^{-1} .
8. Wiberg, K.B.; Walker, F.H.; Pratt, W.E. Michl, J. *J. Am. Chem. Soc.* **1983**, 105, 3638.
9. After heating of **1** at 80° for a 24 h in C_6D_6 solution no decomposition was detected.
10. Spectral data of **6**: MS m/e 234 (M^+ , 19), 206 (19), 174 (72), 146 (19), 91 (13), 79 (14), 43 (100); IR (KBr) ν 3005, 2900, 2840, 1725, 1685, 1460, 1450, 1360, 1250, 1090, 1010, 710 cm^{-1} ; ^1H NMR (C_6D_6) δ 3.1–2.8 (m, 3H), 2.8–1.8 (m, 3H), 1.7–0.8 (m, 12H), 1.64 (s, CH₃); ^{13}C NMR (C_6D_6) δ 212.2 (s), 168.7 (s), 80.5 (s), 48.0 (d), 47.5 (d), 39.8 (d), 34.9 (dd), 33.7 (t), 32.7 (d), 29.7 (t, 2C), 29.1 (t), 26.4 (d), 21.3 (q).