

AN UNUSUAL REARRANGEMENT OF THE 4-HOMOADAMANTYL CATION

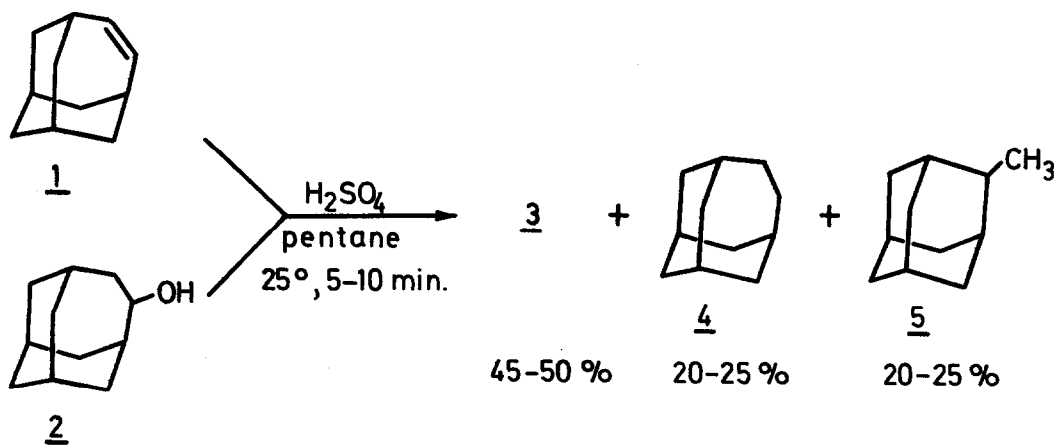
ONE-STEP PREPARATION OF 2,6-TRIMETHYLENEBICYCLO/2.2.2/OCTANE

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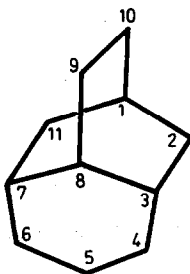
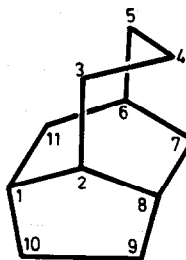
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Homoadamantene is readily converted by Lewis-acid catalysts into a single major product 2-methyladamantane.¹ However, the behaviour of the 4-homoadamantyl cation generated from homoadamantene¹ (1) and 4-homoadamantanol² (2) by concentrated sulphuric acid in the presence of pentane was quite different! Instead of one, three major products (90-95% by glc) were formed in the ratio 2:1:1. Almost identical products distribution was obtained from both 1 and 2.³ Two minor components were identified as homoadamantane (4) and 2-methyladamantane (5) by ¹H nmr, ir, and mass spectra, and glc comparison with authentic samples.



The major product (3) had a melting point 56-58⁰ (Kofler), considerably lower than in most adamantoid hydrocarbons. The spectra, ¹H nmr (CDCl₃; δ 1.0-2.0 ppm (m, maximum at 1.42 ppm)), ir (CCl₄; 2920, 2864, 1471, 1460, 1446, 1438 cm⁻¹), and ms (m/e: 150 (100%), 135 (14%), 122 and 121 (38%), 107 (21%), 93 (33%), 80 and 79 (48%)), indicated the absence of unsatu-

ration and alkyl groups. The ^{13}C nmr spectrum showed eight signals at 33.01, 32.20, 31.83, 30.75, 26.97, 26.22, 24.65, and 15.16 ppm downfield from TMS. Each of the signals at 32.20, 31.83, and 30.75 ppm corresponds to two equivalent carbon atoms. The proton off resonance decoupled spectrum indicated the presence of three different CH groups (the signals at 33.01, 30.75, and 24.65 ppm) and five different CH_2 groups. Such a ^{13}C nmr spectrum can correspond only to the structures 3a and 3b among all possible eleven-carbon tricyclic hydrocarbons possessing all carbons in rings and having no three- and four-membered rings.⁴

3a3b

Isomer 3a (2,6-trimethylenebicyclo/2.2.2/octane, tricyclo/5.3.1.0^{3,8}/undecane or 4-homoisotwistane⁶) appeared to be considerably more stable than 3b. (Empirical force field (strain) calculations using two different force fields⁷ predicted heats of formation for 3a and 3b to be (in kcal/mole) E = -28.60, A = -30.32 and E = -19.82, A = -20.29, respectively).⁵ Recently Krantz et al.⁸ reported a preparation of 3a. Our product 3 had identical ^1H nmr and ir spectra and mp with an authentic sample⁸ of isomer 3a.

The overall yield of glc purified 4-homoisotwistane (3a) was about 15%.⁹ However, since 4-homoadamantanol (2) is readily available², the described simple reaction provides an attractive method for the preparation of 3a.

Pure 3a, 4, and 5 were proved to be stable in H_2SO_4 /pentane mixtures during 24 hrs at 25°. However, the products distribution in the reaction mixtures of 1 and 2 was continuously changing with time, presumably due to the presence of carbonium ion promoters. Approximately

0.5 hr after the beginning of the reaction, in the reaction mixture was detected 1-methyladamantane (6) (identified by glc comparison with an authentic sample). The amounts of 5 and particularly 6 were increasing with time at the expense of 3a and 4 leading toward a thermodynamically controlled equilibrium.¹⁰ This is in accord with the calculated values of heats of formation (in kcal/mole) for 3a (see above), 4 (E = -29.84, A = -27.77), 5 (E = -37.94, A = -39.04), and 6 (E = -41.92, A = -42.89).^{5,7}

The initial products distribution should be kinetically controlled by the rate of hydride abstraction and the rearrangement rates of the 4-homoadamantyl cation into 5⁺ (probably via the bridged 4-homoadamantyl cation¹) and 3a⁺. Several mechanisms of the latter rearrangement can be proposed and are currently being tested by ¹³C labelling and ¹³C nmr in our laboratory.

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References and Notes

1. Z. Majerski and K. Mlinarić, Chem. Comm., 1030 (1972).
2. P. v. R. Schleyer, E. Funke, and S. H. Liggero, J. Amer. Chem. Soc., 91, 3965 (1969).
3. The yield of the crude products mixture (3, 4 and 5) was about 20% from 1 and 40% from 2 (1 mmole of 1 or 2, 1.5 ml of pentane, 0.8 ml of 98% H₂SO₄; 5-10 min, 25°). The reaction rate considerably decreased by a decrease of the starting material concentration. The glc analyses were performed on both SE-30 and FFAP columns at 80°.
4. Such a set of eleven-carbon tricyclic structures was also independently constructed by E. M. Engler and E. Osawa.⁵
5. P. v. R. Schleyer, private communication.
6. 4-Homoisotwistane seems to be a convenient simple trivial name for tricyclo/5.3.1.0^{3,8}/undecane (3a). Isotwistane has been suggested as the trivial name for the lower homolog, tricyclo/4.3.1.0^{3,7}/decane (L. A. Spurlock and K. P. Clark, J. Amer. Chem. Soc., 94, 5349 (1972)).

7. (E) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, J. Amer. Chem. Soc., in press;
(A) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, J. Amer. Chem. Soc., 93, 1637 (1971).
8. A. Krantz and C. Y. Lin, Chem. Comm., 1287 (1971). We are grateful to Professor A. Krantz for supplying us with a copy of the ^1H nmr and ir spectra, and mp data ($57-59^\circ$) of 4-homoisotwistane (3a).
9. Column $3/8'' \times 25'$, 12% SE-30 on Chromosorb P 45/60, 110° .
10. E.g. after 24 hrs the products distribution was found to be: 3a 16%, 4 26%, 5 29%, and 6 23%.