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SPIRO[ADAMANTANE-2,2'-ADAMANTANE]

E. Boelema, J. Strating and Hans Wynberg
Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

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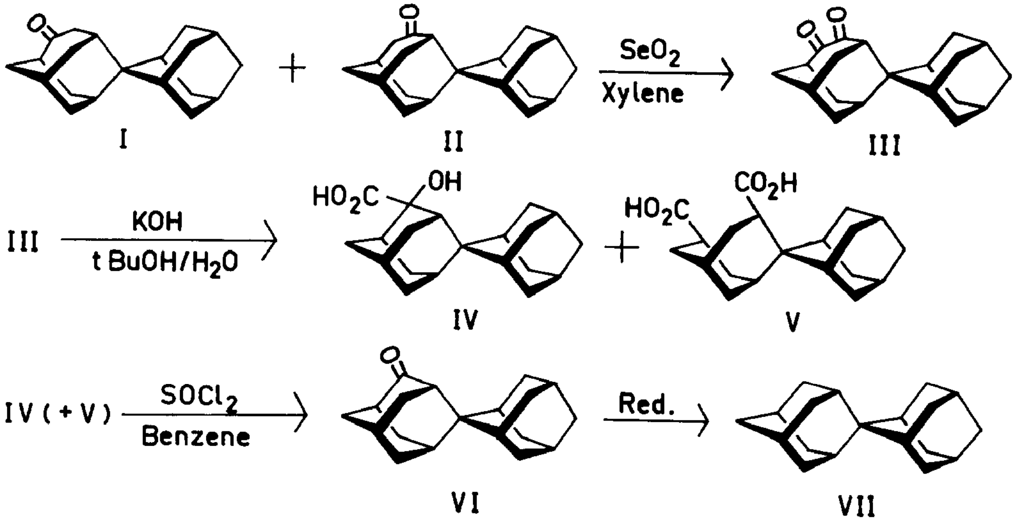
We wish to report the synthesis of spiro[adamantane-2,2'-adamantane], VII. Although a few spiroadamantane derivatives have been reported[1], it was not until the spiro[adamantane-homoadamantane] system became accessible[2] that a rational route to VII presented itself.

Starting material for the synthesis of this highly symmetrical $C_{19}H_{28}$ hydrocarbon VII[3] was a mixture of the isomeric spiroketones I and II[4]



Selenium dioxide oxidation[5] of a mixture of I and II in refluxing xylene gave in a yield of 88% the α-diketone III [m.p. 166-168°; i.r. (KBr): $\nu_{C=O}$ at 1694 and 1712 cm^{-1}; u.v. (C_2H_5OH): λ_{max} at 429 mμ, ε = 47; m.s.: M^+ at m/e = 298, m/e 270 ($C_{19}H_{26}O^+$), 100%; n.m.r. ($CDCl_3$): τ = 6.42 (broad doublet, 1H), complex multiplet at τ = 6.83-8.80 (25H)]. Treatment of this diketone III with KOH in t-butanol/water yielded the benzilic acid rearrangement[6] product IV (a sharp absorption at 3550 cm^{-1}). In addition to IV the diacid V[7] was formed. Thusfar we have not been able to separate IV from V. However, on treatment of this mixture (IV and V) with thionylchloride in benzene[8], IV was transformed into the ketone VI [melting range 243.4-246.7° (corrected)[10], dec.; i.r. (KBr): $\nu_{C=O}$ at 1708 cm^{-1}; m.s.: M^+ at m/e = 270 ($C_{19}H_{26}O^+$), 100%, m/e = 135 ($C_{10}H_{15}^+$); n.m.r. ($CDCl_3$): τ = 6.97 (broad singlet, 1H), complex multiplet at τ = 7.43-8.83 (25H)], which could be isolated readily in about 50% yield by column chromatography over alumina (neutral, activity I) with benzene/ether (4:1) as eluent.

Wolff-Kishner—Huang-Minlon reduction[9] of spiroketone VI gave the desired spiro[adamantane-2,2'-adamantane] (VII), melting from 252.3-255.1° (corrected)[10], dec., in a yield of 84%.

Barring unusual rearrangements during the benzilic acid transformation and/or during the degradation of IV to the ketone VI we feel justified in proposing the spiro[adamantane-2,2'-adamantane]structure VII, based on the following facts:

a. the synthetic route.

b. the high temperature at which the compound melts. We have noted melting points below 200° for all of our spiro[adamantane-homoadamantane]compounds.

c. the mass spectrum, which gives the parent peak at m/e = 256 ($C_{19}H_{28}^+$). This peak is also the base peak of the spectrum. A second intense peak occurs at m/e = 135 ($C_{10}H_{15}^+$).

d. the infrared spectrum is very similar to that of adamantane and distinctly different from that of spiro[adamantane-2,2'-homoadamantane]. For comparison the values of adamantane are placed between brackets. Intense absorptions are found at 1090 (1098, s), 1337, 1350 (1350, s), 1450 (1448, s), 1470, 2860 (2845, s), 2900 (2900, s), 2940 (2927, s) cm^{-1}, medium intense absorptions occur at 802 (769, s), 828, 925, 985 (965, m), 1198, 1310 and 1372 cm^{-1}.

e. the n.m.r. spectrum ($CDCl_3$), consisting of a multiplet between τ = 7.1 and τ = 8.8, shows no unusual features. Examination of a model suggests the occurrence of a number of inequivalent protons in VII.

Compound VII is completely odourless and sparingly soluble in solvents like hexane benzene and chloroform.

REFERENCES AND NOTES

1. H. Wynberg, S. Reiffers and J. Strating, *Rec. Trav. Chim.*, **89**, 982 (1970) and references cited therein.
2. a. H. Wynberg, E. Boelema, J.H. Wieringa and J. Strating, *Tetrahedron Letters*, **1970**, 3613;
   b. G.B. Gill and D. Hands, *ibid.*, **1971**, 181;
   c. E. Boelema, H. Wynberg and J. Strating, *ibid.*, **1971**, 4029.
3. All new compounds gave satisfactory elemental analyses.
4. For the preparation of I and II see ref. 2c. The yield of I and II could be raised considerably by the observation that spiro[adamantane-2,5'-(2',4'-dehydrohomoadamantane)] was isomerised almost quantitatively to spiro[adamantane-2,5'-homoadamantan-2'-ene] (m.p. 171-173°) on a column of alumina (neutral, activity I).
5. N. Rabjohn in "Organic Reactions", Vol. V, Wiley, New York, N.Y., 1949, chapter 8.
6. S. Selman and J.F. Eastham, *Quart. Rev. (London)*, **14**, 221-235 (1960).
7. Diacid V [dec. 223°; i.r. (KBr): $\nu_{C=O}$ at 1700 cm^{-1} (broad); m.s.: M^+ at m/e = 332 ($C_{20}H_{28}O_4^+$), m/e = 314 (M^+-H_2O), m/e = 296 (M^+-2H_2O), m/e = 135 ($C_{10}H_{15}^+$), 100%] was the only product isolated (yield 70%) from the reaction of III with periodic acid in dioxan/water at 70° during 65 hrs.
8. Ae. de Groot, J.A. Boerma and H. Wynberg, *J. Org. Chem.*, **33**, 4025 (1968).
9. Huang-Minlon, *J. Amer. Chem. Soc.*, **68** 2487 (1946).
10. These rather large melting ranges have been observed for compounds VI and VII which are homogeneous and pure by the techniques at our disposal (C and H analysis, G.L.C., T.L.C., spectroscopic methods).