

SYNTHESIS OF 1,3-BISHOMOADAMANTANE, 1,3-BISHOMO-
ADAMANT-4-ENE AND 1,3-BISHOMOADAMANTA-4,7-DIENE¹

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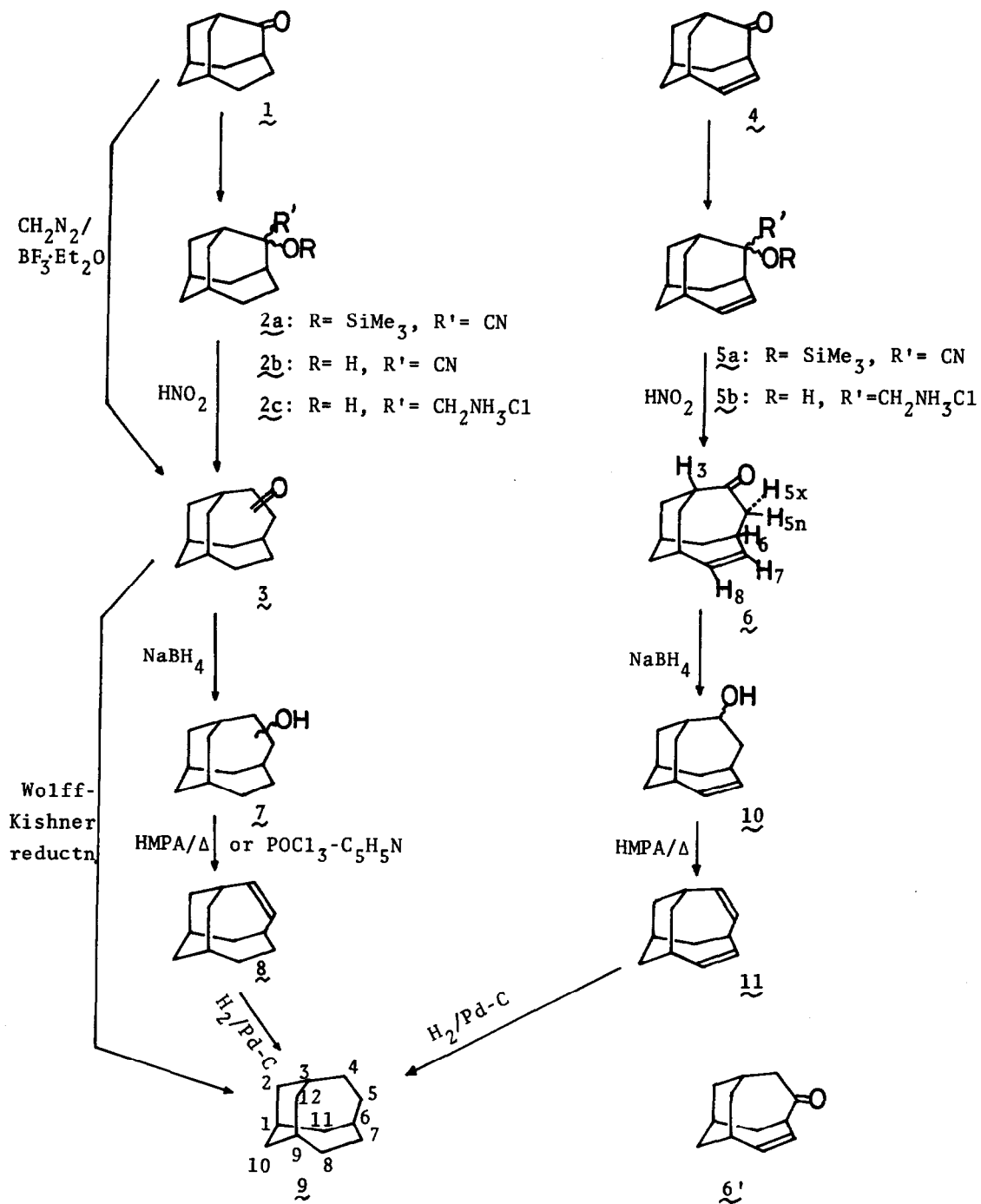
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Among three possible isomers of bishomoadamantane, 1,1-bishomoadamantane (tricyclo[5.3.1.1^{3,9}]dodecane)² and 1,5-bishomoadamantane (tricyclo[4.4.1.1^{3,8}]dodecane)³⁻⁵ are known heretofore, however, parent hydrocarbon of 1,3-bishomoadamantane (tricyclo[4.4.1.1^{3,9}]dodecane) (9) seems to be not recorded yet.⁶ We now wish to report the synthesis of 9 as well as its 4-ene (8) and 4,7-diene derivatives (11).

2-Aminomethylhomoadamantan-2-ol (2c) was obtained in 70-80% yield as hydrochloride, mp 269-272°⁷ on treatment of homoadamantan-2-one (1)^{8,9} with Me₃SiCN-ZnI₂¹⁰ or KCN-(NH₄)₂CO₃,¹¹ followed by LiAlH₄- or catalytic (PtO₂) reductions of, thus, produced cyanohydrin derivatives 2a, mp 244-247° or 2b, mp 238-241° (dec.). Nitrous acid deamination of 2c in aqueous acetic acid-sodium acetate afforded a ring-expanded ketone 3 (85-95% yield): mp >300°; ir (KBr) 1680 cm⁻¹; nmr(CDCl₃) δ 3.1-2.47 (m, 3H) and 2.47-0.8 (m, 15H). The structural assignment of 3 as the ring-expanded ketones rests on the spectral data and the following facts. The similar ring-expansion of homoadamant-4-en-2-one (4)^{8,9} via 5a, n_D²⁵ 1.4934, and 5b, mp 289-292° afforded 1,3-bishomoadamant-7-en-4-one (6) as a major product (41% overall yield from 4):¹² mp 293-295°; uv λ_{max}(MeOH) 225.0 (ε= 265) and 296.0 nm (44.5); ir(KBr)

Scheme



1680 and 1650 (shoulder) cm^{-1} ; $\text{nmr}(\text{CDCl}_3)$ δ 6.15-5.45 (m, 2H), 3.4-2.25 (m, 6H) and 2.25-1.2 (m, 8H). The nmr spectrum of 6 was better resolved with the aid of a shift reagent, tris(dipivalomethanato)europium(III) and the shift gradient G values¹³ were calculated for H_3 (16.8), H_{5n} (13.5), H_{5x} (12.2), H_7 and H_8 (4.2 and 4.3). On the basis of the obtained similar G values for H_7 and H_8 as well as the coupling constants for H_{5x} and H_{5n} ($J_{5x,5n}=14$ Hz, $J_{5x,6}=6$ Hz, $J_{5n,6}=1.5$ Hz), the 4-one structure of 6 was assigned. Catalytic hydrogenation (Pd-C) of 6 gave the corresponding saturated ketone which was practically identical with 3 obtained from 2c by comparison of ir spectra and glc retention times (Tenax GC, Silicone SE-30, and Apiezone grease L columns). However, the 4-one structure of 3 could not be concluded because 5-one isomer is assumed to have very similar glc retention times and spectral data.

Direct ring-expansion of 1 with diazomethane (ca. 10-fold excess) catalyzed with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ yielded also 3 in 50% yield but the use of a large excess amount of diazomethane (ca. 90-fold excess) afforded many side products.

Reductions of 3 and 6 with NaBH_4 gave the corresponding alcohols 7, mp $>300^\circ$ and 10, mp $>300^\circ$ in high yields. On heating in hexamethylphosphoramide (HMPA) or on treatment with POCl_3 in pyridine, 7 was converted to 1,3-bishomoadamant-4-ene (8) (74-83%): mp $265-268^\circ$; ir(KBr) 3010 and 1650 cm^{-1} ; $\text{nmr}(\text{CDCl}_3)$ δ 6.2-5.35 (m, 2H) and 3.0-1.1 (m, 16H). The similar dehydration of 10 gave 1,3-bishomoadamanta-4,7-diene (11) as very sublimable crystals (83%): mp $220-223^\circ$; ir(KBr) 3010, 1650 and 690 cm^{-1} ; $\text{nmr}(\text{CDCl}_3)$ δ 6.3-5.4 (m, 4H), 3.15-2.2 (m, 4H) and 2.2-1.1 (m, 8H). Catalytic hydrogenation (Pd-C) of 8 and 11 afforded 1,3-bishomoadamantane (9) in high yields as colorless crystals after sublimation: mp $292-295^\circ$; ir(KBr) 2900, 2700, 1455, 1170, 1110 and 808 cm^{-1} ; $\text{nmr}(\text{CDCl}_3)$ δ 2.6-0.8 (m). The Wolff-Kishner reduction of 3 gave also 9. All of these results are summarized in Scheme.

Further studies on the chemistry of 9 are in progress.¹⁴

REFERENCES AND FOOTNOTES

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6. After submission of this paper, the synthesis of 9 has been appeared: J. S. Polley and R. K. Murray, Jr., J. Org. Chem., 41, 3294 (1976).
7. All mps were measured in sealed capillary tubes and all new compounds reported here had correct mass spectral molecular weight and satisfactory analyses.
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11. This is our modified procedure for preparation of cyanohydrin. For example, treatment of adamantanone with KCN-(NH₄)₂CO₃ in 50% aqueous ethanol gave 2-hydroxy-2-cyanoadamantane in 98% yield ((cf. H. Stetter and V. Tillmanns, Chem. Ber., 105, 735 (1972)).
12. An endo-stereochemistry of C₂-OH and hence, an exo-CH₂NH₃Cl in 5b was suggested by the similar chemical shifts and signal pattern of vinyl proton nmr signals to those of 2-endo-hydroxyhomoadamant-4-ene (cf. ref. 8 and 9). Presumably isomeric ketone 6' was also produced in ca. 5% yield because of appearance of a minor peak on glc analysis of the crude ring-expanded ketone, which was purified on a silica gel column (n-hexane-CH₂Cl₂) to give pure 6.
13. A. F. Cockerill, G. L. O. Davies, R. C. Harden and D. M. Rackham, Chem. Rev., 73, 553 (1973).
14. Although the solvolysis product of 3-homoadamantylcarbinyl tosylate has been assigned tentatively as 1,3-bishomoadamantan-6-ol by us (ref. 2), its definitive skeletal structure remains unknown and hence, we are actively exploring the bridgehead functionalization of 9.