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AN ADAMANTANE --> PROTOADAMANTANE REARRANGEMENT AND ATROPISOMERISM ABOUT A *TERT.*-BUTYL-TO-PROTOADAMANTYL BOND

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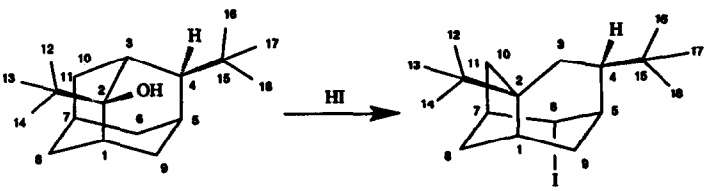
Summary: The hydriodic-acid-catalyzed rearrangement of di-*tert.*-butyladamantanol (1) afforded iodo-di-*tert.*-butyl protoadamantane (2). A three-step rearrangement sequence is proposed. The ^{1}H and ^{13}C NMR signals of the *tert.*-butyl groups in 2 show coalescence effects at different temperatures indicating atropisomerism.

It is widely accepted that protoadamantanes are intermediates in acid-catalyzed multiple rearrangements of diamondoid hydrocarbons[1]; the last step in such rearrangement cascades is a 1,2-bond shift which converts the protoadamantane skeleton into an adamantane[1,2]. In the course of our investigation of highly congested adamantanes[3] we found that this reaction can be reversed and a protoadamantane be synthesized from an adamantane under conditions of acid catalysis.

Scheme 1:

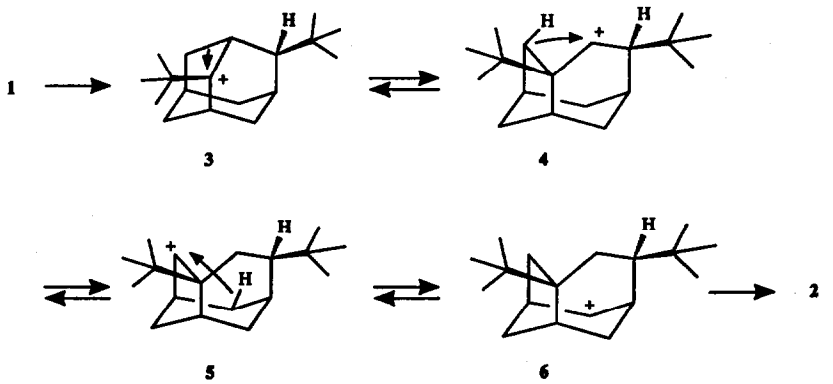


1 2

2[a]-Hydroxy-2[e],4[a]-di-*tert.*-butyladamantane (1)[4], obtained from 4-bromoadamantanone[5] and *tert.*-butyllithium[3], was dissolved in CCl_4. Gaseous HI was added at room temperature and the solution stirred overnight at 20°C. After purification of the crude product and separation by column chromatography, the protoadamantane 2[6] (scheme 1) was obtained in 28% yield along with 26% of 2[a]-iodo-2[e],4[a]-di-*tert.*-butyladamantane[3]. The structural and stereochemical elucidation of the starting alcohol and two products is based on extensive one- and two-dimensional NMR experiments including NOE-difference spectra which are described elsewhere[3]. These experiments enabled us even to assign unambiguously the ^{1}H and ^{13}C signals within the two *tert.*-butyl groups. The structure of 2 has been confirmed by X-ray analysis[7].

The mechanism of rearrangement 1 --> 2 is clearly complex. We propose a pathway which involves one carbon and two hydride shifts (scheme 2). Firstly, following protonation a water molecule is eliminated to afford cation 3[8]. By a 1,2-bond shift (3 --> 4) the protoadamantane framework is reached, and a sequence of two 1,3-hydride shifts leads to ion 6 *via* 5. Due to steric reasons the iodine atom can approach C-6 in 6 only from the *exo*-side. Cations 3 - 6 may be in equilibrium, with attack of the nucleophile prohibited in 3, 4 and 5 by the *tert.*-butyl groups.

Scheme 2:



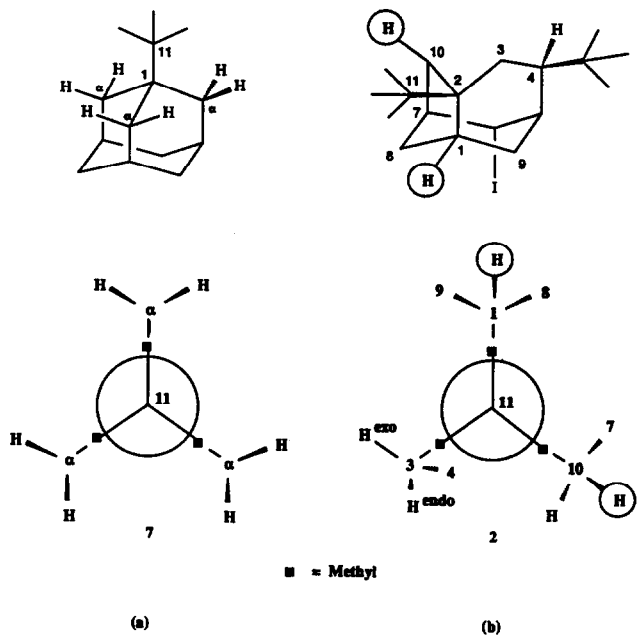
Under normal conditions a protoadamantane --> adamantane rearrangement takes place only to a very limited extent[2a] because of the higher strain energy in protoadamantane; according to calculated[9a] and experimental[8b] heats of formation adamantane is ca 48 kJ/mol more stable than protoadamantane. In our reaction, however, the adamantane derivative 1 suffers from severe steric interference of the *syn*-diaxial hydroxyl and 4[a]-*tert.*-butyl groups. Moreover, the hydroxyl group in 1 is geminal to the other *tert.*-butyl group and, in addition, this second *tert.*-butyl group is in axial position with respect to the six-membered ring C-1/C-2/C-3/C-10/C-7/C-8. The adamantane --> protoadamantane rearrangement relieves strain by placing one *tert.*-butyl group at a bridgehead position; the ring bearing the secondary *tert.*-butyl group is forced into a boat conformation and the substituent assumes a pseudo-equatorial position. Thus, the driving force of the 1 --> 2 rearrangement is steric relief.

Interestingly, 2 displays atropisomerism about two sp^3-sp^3 bonds. The ^1H and ^{13}C NMR spectra show separate coalescence effects for the two *tert.*-butyl group at C-2 (coalescence at ca 0°C) and at C-4 (at ca -50°C). Such restricted *tert.*-butyl rotations are rather rare in literature and have been observed only in specially designed, highly crowded compounds like 9,9'-bifluorenyls and 9-alkyltriptycenes[10,11]. Our findings are corroborated by MM2 calculations which afford barriers of ca 39 kJ/mol for the rotation around the C-2/C-11 bond and ca 26 kJ/mol for the C-4/C-1

bond. For comparison: the corresponding calculated rotation barrier in 1-*tert.*-butyladamantane (7) is ca 22 kJ/mol and low-temperature NMR spectra do not display any signal broadening down to -90°C. The value of 39 kJ/mol corresponds rather well to values published by Oki et al. for restricted *tert.*-butyl group rotations in trypticenes[12,13].

The reason for the remarkable increase of the rotation barrier of the *tert.*-butyl group at C-2 (bridgehead) can be rationalized as follows (Scheme 3).

Scheme 3:



As expected, the MM2 calculations show that the transition state for this rotation is a conformation with ca 0° torsional angles around the C-2/C-11 bond, i.e. the eclipsed conformation. In 1-*tert.*-butyladamantane (7, scheme 3a) all torsional angles in moieties with the atoms C-11, C-1, one of the α carbons and any α hydrogen (attached to the respective α carbon) are very near to +60° or -60°, respectively. Thus, steric interference of those hydrogens with the *tert.*-butyl group is not so different in the ground and transition state of the rotation. In the protoadamantane 2 (scheme 3b), however, two of the corresponding torsional angles, namely C-11/C-2/C-1/H-1 and C-11/C-2/C-10/H-10*exo* (in scheme 3b the two hydrogens are encircled), are very near to 0° so that these hydrogens are protruding strongly into the space needed for the methyl groups of the *tert.*-butyl

substituent. This double congestion occurs mainly in the transition state (eclipsed conformation) whereas it is much weaker in the ground state (staggered conformation) so that a rotation barrier results which is larger than that of **7**.

Acknowledgements. The authors gratefully acknowledge financial support from the Fonds der Chemischen Industrie.

References and Notes

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3. H. Duddeck and D. Rosenbaum, in preparation.
4. The indices "a" and "e" denote the stereochemical position of the substituent with respect to the six-membered ring bearing the highest number of substituents; a: axial, e: equatorial.
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6. For consistency reason we adopt a carbon numbering equivalent to that of the adamantane skeleton. The correct name of **2** is: 8*exo*-iodo-6*exo*,7^a-bis[(1,1-dimethyl)ethyl]-2,3,3a,4,5,6,7,7a-octahydro-2,5-methano-1*H*-indene. NMR data (Bruker AM-400, ^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, $CDCl_3$, room temperature) are as follows. **1**: ^{1}H, δ = 1.90 (H-1), 2.34 (H-3), 1.61 (H-4e), 1.86 (H-5), 1.70 (H-6e), 1.68 (H-6a), 1.80 (H-7), 1.67 (H-8e), 2.15 (H-8a), 1.39 (H-9e), 2.34 (H-9a), 1.58 (H-10e), 2.26 (H-10a), 1.08 (H-12, H-13, H-14), 0.97 (H-16, H-17, H-18), 1.18 (OH); ^{13}C, δ = 34.9 (C-1), 77.0 (C-2), 38.2 (C-3), 59.3 (C-4), 28.7 (C-5), 43.0 (C-6), 27.5 (C-7), 35.3 (C-8), 33.7 (C-9), 38.2 (C-10), 40.0 (C-11), 28.7 (C-12, C-13, C-14), 34.1 (C-15), 30.4 (C-16, C-17, C-18). **2**: ^{1}H, δ = 2.00 (H-1), 1.46 (H-3), 1.27 (H-3'), 1.41 (H-4), 2.07 (H-5), 4.54 (H-6), 2.52 (H-7), 1.60 (H-8), 1.98 (H-8'), 1.42 (H-9), 1.83 (H-9'), 1.59 (H-10, H-10'), 0.84 (H-12, H-13, H-14), 0.81 (H-16, H-17, H-18); ^{13}C, δ = 35.8 (C-1), 47.5 (C-2), 26.5 (C-3), 50.0 (C-4), 41.6 (C-5), 49.6 (C-6), 46.0 (C-7), 39.0 (C-8), 28.4 (C-9), 37.2 (C-10), 36.3 (C-11), 25.8 (C-12, C-13, C-14), 33.7 (C-15), 27.1 (C-16, C-17, C-18); MS, 70 eV, (rel. int.), m/z = 359 (0.04, M^+-CH_3), 289 (0.18, M^+-C_6H_{13}), 247 (100, M^+-I), 191 (33, M^+-I-C_4H_9), 177 (83, M^+-I-C_5H_{10}), 57 (97, $C_4H_9^+$), 41 (32); high resolution MS, m/z = 247.2425, calculated for $C_{18}H_{31}$ 247.2426.
7. B. Kojić-Prodić, unpublished results.
8. In scheme 2 all secondary cation are defined as localized and not as bridged ions; see ref. 2 and: R. Dutler, A. Rauk, T.S. Sorensen and S.M. Whitworth, *J. Amer. Chem. Soc.* **111**, 9024 (1989). This, however, does not affect stereochemical implications of the reaction.
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