Syntheses and NMR Spectra of Substituted 2-*tert*-Butyladamantan-2-ols

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The synthesis of a number of substituted 2-*tert*-butyladamantan-2-ols from the corresponding ketones is described. In addition to these addition reactions, some unexpected rearrangements were observed. Reaction mechanisms are proposed to rationalize the experimental results. ^{13}C NMR spectra of some adamantanes are discussed in terms of substituent interaction effects.

Introduction

Due to their unique structural properties adamantanes play a significant role in organic chemistry as model compounds for studying reaction mechanisms, for problems in stereochemistry, and for spectroscopic investigations.[1,2] In the past few years, we investigated some acid-catalyzed rearrangement reactions involving substituted adamantanes.[3-6] From the reaction products we were able to obtain subtle information about the respective mechanisms and their stereochemical implications.

Our spectroscopic interest in this class of compounds stems from the fact that in the adamantane framework substituents can be arranged in various mutual orientations with fixed geometries so that their interaction can be studied by monitoring ^{13}C chemical shifts.[7] Torsional angles are nearly exactly 60° and 180°, and these values remain more or less unchanged provided the substituents are not too bulky and their steric interference not too severe. For example, the geometry of 2-iodoadamantane is practically undistorted as compared with adamantane itself.[8] Only in compounds with severe through-space interference of big substituents, like bromine atoms in the 1,3-diaxial configuration, can a divergence from normal torsional angles be assumed from nonadditivities of substituent effects on certain ^{13}C chemical shifts.[9] MM2 calculations show that a *tert*-butyl substituent at a nonbridgehead position is bulky enough to produce significant deviations from the usual adamantane geometry. This is due to its steric congestion since, necessarily, there is a six-membered ring to which the *tert*-butyl group is fixed in an axial position.

Accordingly, we became interested in synthesizing highly congested *tert*-butyl-substituted adamantanes and investigating their reactions and the effects of their internal strain on ^1H and ^{13}C NMR parameters. During this work we were confronted with a number of surprising results which are reported.

Results

In order to introduce a *tert*-butyl group into the adamantane framework we used the addition of *tert*-butyllithium to ketones under argon, producing *tert*-butyl-substituted carbinols.[10] The starting materials, namely the adamantanones **1–18**, and the reaction products **19–53** are collected in Chart I, , and all results from these reactions are listed in Table I. As can be seen from the structures in the chart, not only were *tert*-butyl-substituted adamantanes obtained, but fragmentation and rearrangement products could be isolated as well.

In general, the overall yields of our reactions including recovered material were between 75 and 88%. These values refer to isolated compounds after chromatographic separation and/or purifcation. This procedure, which included reduced pressure distillation of the solvent on a rotary evaporator, frequently caused losses of material due to the volatility of many of the adamantanes, particularly those not containing polar groups.

A reliable structural elucidation of the products was a crucial factor in this work and is the basis of all discussions of reaction mechanisms. The principal method was ^1H and ^{13}C NMR spectroscopy. By two-dimensional homo- and heteronuclear correlated spectra (HH and HC COSY)[11] the connectivities of protons and carbons were established. If necessary, correlation spectra indicating long-range proton–carbon couplings (COLOC) were recorded to confirm these connectivities.[12] In one instance (**43**) it was necessary to record a two-dimensional INAEDQUATE spectrum which indicates carbon–carbon connectivities.[13] The stereochemical assignments of the nuclei and the structures were assisted by one-dimensional NOE difference spectroscopy.[14] The way in which we elucidated molecular structures by a combined evaluation of these various spectra has been described by us earlier.[5,15]

NMR data are collected in the Tables III (^{13}C) and IV (^1H), available as supplementary materials.

Discussion

Syntheses. Equations 1–7 compile all products which could be identified from the reaction of the adamantanones

(1) (a) Fort, R. C., Jr *Adamantane. The Chemistry of Diamond Molecules*; Marcel Dekker: New York, 1976. (b) *Caged Hydrocarbons*; Olah, G., Ed.; John Wiley and Sons: New York, 1990.
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(4) Duddeck, H.; Brosch, D. *J. Org. Chem.* **1983**, *48*, 3569.
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(6) Duddeck, H.; Brosch, D. *Tetrahedron* **1985**, *41*, 3753.
(7) (a) Duddeck, H.; Feuerhelm, H.-T. *Tetrahedron* **1980**, *36*, 3009. (b) Duddeck, H. *Top. Stereochem.* Eliel, E. L., Wilen, S. H., Allinger, N. L., Eds.; Wiley: New York, 1986; Vol. 16, p 219.
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(9) Duddeck, H. *Tetrahedron* **1978**, *34*, 247.
(10) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628.
(11) (a) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University Press: Reidel, Dordrecht, 1982. (b) Benn, R.; Günther, H. *Angew. Chem.* **1983**, *95*, 381; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350. (c) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: Oxford, 1986; 2nd ed., 1987. (e) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy, a Guide for Chemists*; Oxford University Press: Oxford, 1987. (e) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987. (f) Croasmun, W. R.; Carlson, R. M. K. *Two-Dimensional NMR Spectroscopy, Applications for Chemists and Biochemists*; VCH Publishers: New York, 1987. (g) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem.* **1988**, *100*, 507; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490. (h) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH: Weinheim, 1988.
(12) Martin, G. E.; Zektzer, A. S. *Magn. Reson. Chem.* **1988**, *26*, 631.
(13) Buddrus, J.; Bauer, H. *Angew. Chem.* **1987**, *99*, 642; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 62.
(14) Neuhaus, E.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989.
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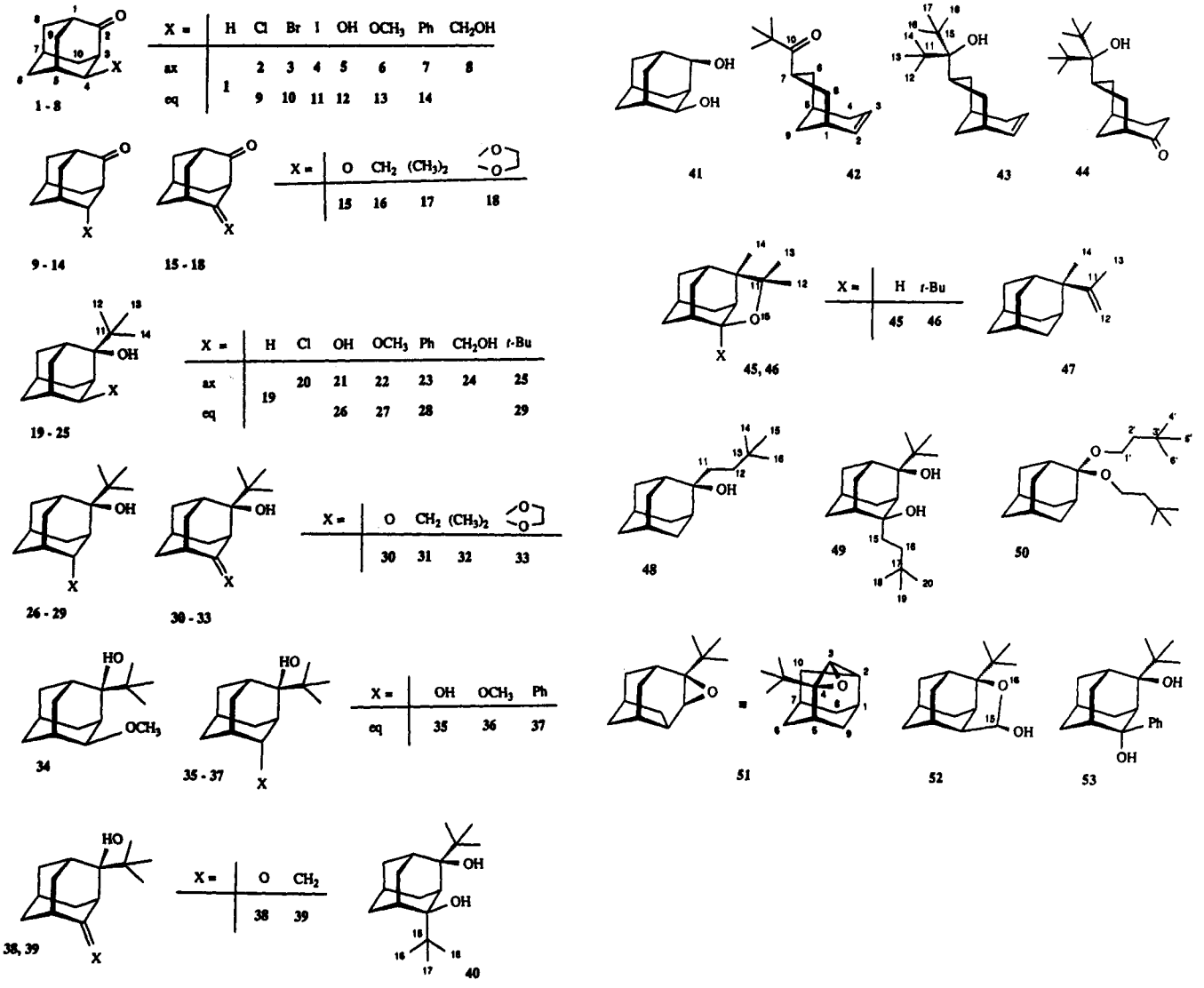
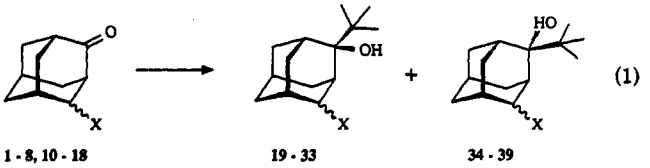
Chart I[a]



[a] The numbering of the adamantane carbons is not necessarily in accordance with the IUPAC nomenclature. For better comparison, however, we employed a numbering which is consistent throughout irregardless of the substituents. The term "axial" (a) and "equatorial" (e) denote the stereochemical position of the substituent with respect to the six-membered ring bearing the highest number of substituents.

1–18 with *tert*-butyllithium in ether/pentane. The equation numbers refer to different reactions pathways and corresponding entries in Table I. Compound numbers in brackets indicate that these compounds have not been isolated or are assumed intermediates.

It can be seen from eq 1 (addition reaction) that, indeed, *tert*-butyl-substituted adamantanols could be obtained in all cases apart from **9**, but often other products were formed (see below) and considerable amounts of starting material could be recovered. The *tert*-butyl group ap-



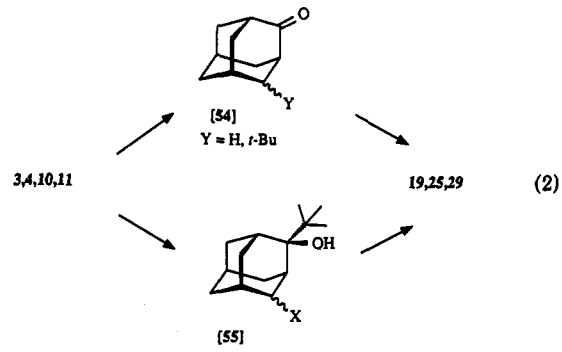
(1)

proaches the carbonyl group of the 4-axially substituted adamantanones **2**, **5**, **7**, and **8**[16] exclusively from the back-side producing alcohols **20**, **21**, **23**, and **24**, respectively. Only the methoxy derivative **6** afforded both isomers **22** and **34**, though **22** predominated strongly. In the series of equatorially substituted adamantanones **12**–**14**[16] the corresponding isomeric *tert*-butyladamantanols **26**/**35**, **27**/**36**, and **28**/**37**, respectively, were obtained in similar quantities. This indicates that in the axially substituted compounds **2**, **5**, **7**, and **8** steric hindrance is the dominating factor in the stereoselectivity. The exception, **34**, may be explained by a temporary complexation of the approaching *tert*-butyllithium to the methoxy group, enabling its front-side attack. The diketone **15** and the keto olefin **16** gave rise to the carbinols **30**/**38** and **31**/**39**, respectively, as expected, without significant stereoselection. A double reduction of **15** to form the symmetrical diol **40** took place only to a limited extent. From the compounds **17** and **18** carrying two geminal substituents at C-4 the carbinols **32** and **33**, respectively, were produced, again stereoselectively.

Except for **15**, considerable amounts of unreacted starting material could be recovered in the above reactions.

In contrast to all other compounds the bromides **3** and **10** as well as the iodides **4** and **11**, were reduced to 2-*tert*-butyladamantan-2-ol (**19**). We assume a halogen–lithium exchange, either prior to *tert*-butyllithium addition (via [**54**], Y = H) or after (via [**55**]), and a replacement of lithium by hydrogen during workup (eq 2). This inter-

(16) Duddeck, H.; Feuerhelm, H.-T.; Snatzke, G. *Tetrahedron Lett.* **1979**, 829.

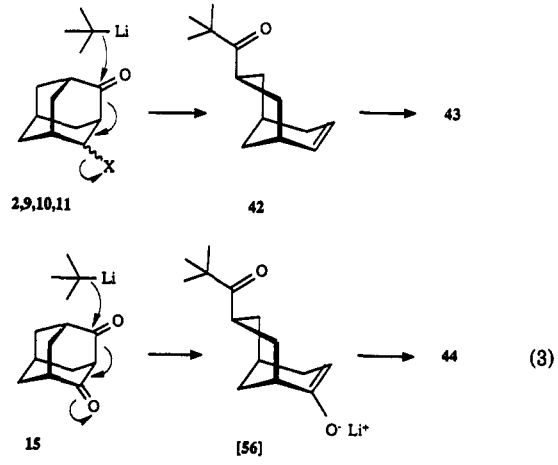


(2)

pretation was confirmed by the facts that in these reactions the di-*tert*-butyladamantanols **25** and **29** were formed as side products (halogen–*tert*-butyl exchange) and some adamantanone (**1**) was isolated.

There are two unique reduction products. In the reaction of **5** (ax-OH) the symmetrical diol **41**, a compound which does not contain any *tert*-butyl group, was found in small yield. This finding is reminiscent of some surprising reductions which we reported some years ago.[16] The second case is the conversion of **15** to **21** involving a stereoselective reduction at C-4.

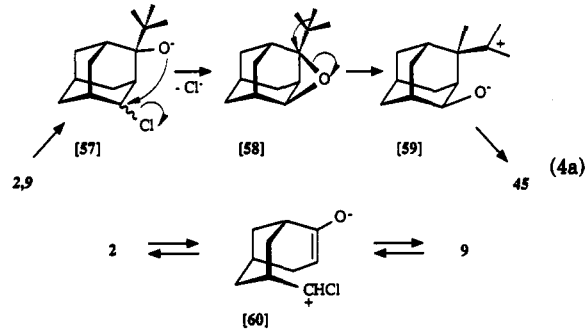
Fragmentation to form 7-endo-substituted bicyclo[3.3.1]non-2-enes often occurs during exposure of 4-equatorially substituted adamantanones to basic or acidic conditions;[1,17] 4-axially substituted adamantanones undergo this reaction with clearly lower yield. Thus, the halo ketones **2**, **9**–**11** gave the ketone **42** in a first fragmentation step; the fragmentation may be facilitated by coordination of a lithium cation to the leaving group.[18] Apparently, in the case of **3** and **4** the reduction to halogen-free products is faster. The ketone **42** was further alkylated to produce the carbinol **43**. The diketone **15** afforded the ketocarbinol **44**; eq 3 suggests plausible mechanisms.



(3)

Since no *tert*-butyl introduction at C-4 was observed in the reaction of **15**, the enolate [**56**] is assumed to be an intermediate. As can easily be proven by NOE measurements, the compounds **42**–**44** adopt the boat conformation of the saturated six-membered ring. This is in contrast to 7-endo-nitrile derivatives.[19]

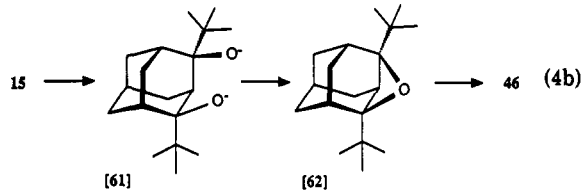
The 4-chloroadamantanones **2** and **9** afforded the ether **45** which contains a tetrahydrofuran moiety condensed to the adamantane framework. According to the mechanism proposed in eq 4a the reaction is initiated by the formation



(4a)

of the anion [**57**] which may be transformed to the oxetane [**58**] with loss of chloride. It is reasonable to assume that the ether formation is facilitated by the fact that the bulky, *tert*-butyl group presses the oxygen inward, i.e. towards C-4. A similar observation will be discussed later (eq 6). Presumably, [**58**] is rather labile and rearranged—directly or during workup—with methyl migration to the zwitterion [**59**] which combined to **45**. The C-2 stereochemistry of this product after the [**58**] → [**59**] rearrangement nicely confirms this interpretation. For this reaction sequence the chlorine atom in the equatorially substituted adamantanone **9** is in the proper stereochemical position, whereas that in the axial **2** is not. However, it is plausible that, by analogy with earlier observations,[16] compound **2** can easily isomerize to **9** under basic conditions via the fragmentation intermediate [**60**] (eq 4a).

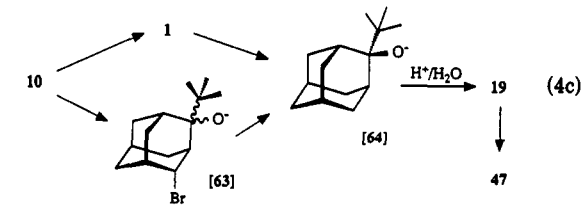
The formation of **46** from **15** can be rationalized in a similar way (eq 4b). The dialkoxide [**61**] may have formed



(4b)

the oxetane [**62**] which rearranged to the final product **46**, although **46** may also have been formed directly from [**61**] during acidic workup. The existence of the intermediate [**61**] is corroborated by the formation of the diol **40** from **15** (see above).

Starting from the bromo derivative **10**, however, 2-isopropenyl-2-methyladamantane **47** was formed (eq 4c).



(4c)

Apparently, the alkoxide [**64**], which has been produced by bromine–hydrogen exchange via **1** and/or [**63**], was protonated during workup to form **19**. This compound is prone to rearrange to **47** under acidic conditions.[10] During the mildly acidic workup (ammonium chloride), however, this reaction is rather slow so that **47** was produced here only in a small quantity. In all other reactions we could

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(19) Duddeck, H.; Kaiser, M.; Brosch, D. *Magn. Reson. Chem.* **1985**, *23*, 548.

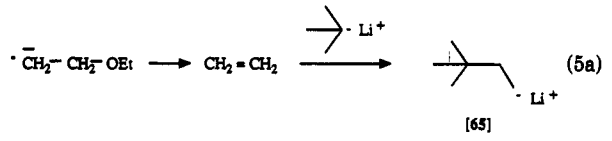
Table I. Results from the Reactions: Adamantanones + *t*-BuLi[a]. Yields after Chromatographic Purification in Parentheses

reactant (X)	addition [1]	reduction [2]	fragment [3]	*t*-Bu rearr [4]	dimethylbutyl [5]	adam. rearr [6]	oxidation [7]	reactant recovered
1	**19** (73)	–	–	–	**48** (5)	–	–	(10)
2 (axCl)	**20** (20)	–	**42** (4)	**45** (11)	–	**51** (4)	–	(38)
			43 (4)					
3 (axBr)	**25** (6)	**1** (38)	–	–	**48** (2)	–	–	–
	29 (5)	**19** (32)	–	–		–	–	–
4 (axI)	**25** (3)	**1** (50)	–	–	**50** (9)	–	–	–
		19 (15)						
5 (axOH)	**21** (67)	**41** (11)	–	–	–	–	–	–
6 (axOMe)	**22** (43)	–	–	–	–	–	–	(29)
	34 (8)							
7 (axPh)	**23** (60)	–	–	–	–	–	–	(19)
8 (axCH$_2$OH)	**24** (29)	–	–	–	–	–	**52** (14)	(33)
9 (eqCl)	–	–	**42** (19)	**45** (9)	–	–	–	(21)
			43 (38)					
10 (eqBr)	**25** (6)	**1** (33)	**43** (21)	**47** (7)	–	–	–	–
	29 (6)	**19** (5)						
11 (eqI)	**25** (3)	**1** (51)	**43** (8)	–	–	–	–	–
		19 (20)						
12 (eqOH)	**26** (32)	–	–	–	–	–	–	(29)
	35 (14)							
13 (eqOMe)	**27** (23)	–	–	–	–	–	–	(18)
	36 (42)							
14 (eqPh)[b]	{**28** + **37**}	–	–	–	–	–	**53** (5)	(23)
	1:1 (50)							
15 (=O)	**30** (17)	**21** (29)	**44** (6)	**46** (2)	**49** (1)	–	–	–
	38 (21)							
	40 (3)							
16 (=CH$_2$)	**31** (16)	–	–	–	–	–	–	(28)
	39 (31)							
17 (Me$_2$)	**32** (75)	–	–	–	–	–	–	(10)
18 ($O_2C_2H_4$)	**33** (51)	–	–	–	–	–	–	(25)

[a] The numbers in brackets refer to the reaction pathways in the respective equations 1–7. [b] Compounds in braces could not be isolated and were investigated as mixtures; ratios determined by NMR.

not find analogous substituted methylpropenyladamantanes, a fact which, however, does not rule out the formation of traces. Apparently, the occurrence of such a rearrangement is delicately dependent on the proton concentration in this pH range.

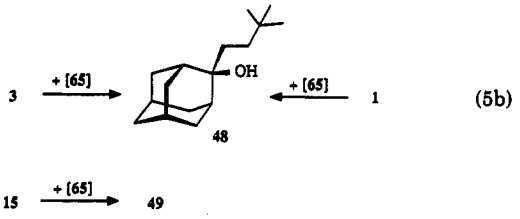
There is another class of side products (**48**–**50**) containing 3,3-dimethylbutyl substituents. Obviously, the extra ethylene group originates from the solvent diethyl ether. It has been reported before that lithium alkyls are able to attack ethers producing alkenes.[20] Moreover, the formation of higher alkanes (hexane, heptane, and octane) has been observed in the reaction of butyllithium with diethyl ether.[20c] Thus, eq 5a describes a reasonable reaction pathway producing (3,3-dimethylbutyl)lithium ([**65**]).



(5a)

[65]

The reactions **1** → **48** and **3** → **48** (eq 5b) are analogous to those affording **19** (see above, eq 1 and 2).

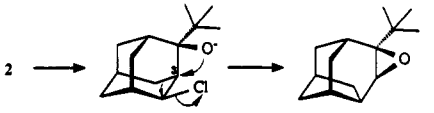


(5b)

Likewise, **49** is a side product of the reaction of **15** (eq 5b). The question why **49** only and not a tetrahydrofuran derivative analogous to **46** is formed cannot be answered. However, due to the extremely low yields of these products and the amount of material missing in the mass balance, this is not necessarily an inconsistency.

Among the products of the reaction with **4** we found a significant amount (9%) of the acetal **50**, the mode of formation of which is not obvious.

A unique example of a base-promoted adamantane → protoadamantane rearrangement is found in the reaction of **2** to **51** (eq 6). The formation of **51** is explained by the



(6)

[66] 51

attack of the negatively charged oxygen atom to C-3 in the intermediate [**66**]. Possibly, this can happen because the oxygen atom pressed inward to C-3 by the bulky *tert*-butyl group in the geminal position (cf. the formation of **45** via the assumed [**58**] in the same reaction, eq 4a). This is accompanied by a 1,2-bond shift and the production of a protoadamantane epoxide by the loss of the chloride anion which might be facilitated by coordination of a lithium ion to the chlorine atom.[18] The reaction is reminiscent of base-catalyzed pinacol rearrangements.[21] To the best of our knowledge, however, such kind of reaction has never been reported before in adamantane chemistry. Acid-promoted adamantane → protoadamantane rearrangements, however, have been published by us very recently.[22]

(20) (a) Burwell, R. L., Jr. *Chem. Rev.* **1954**, *54*, 615. (b) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, 1974; p 198 ff. (c) Ziegler, K.; Gellert, H.-G. *Liebigs Ann. Chem.* **1950**, *567*, 185.

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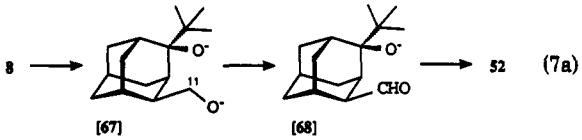
(22) Duddeck, H.; McKervey, M. A.; Rosenbaum, D. *Tetrahedron Lett.* **1990**, *31*, 4061.

Finally, two surprising reactions are mentioned which, formally, are oxidations.

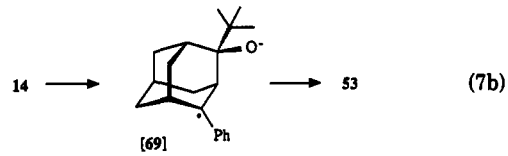
Firstly, the hydroxy ketone 8 was converted to the hemiacetal **52** in a nonnegligible yield (14%, eq 7a). It



(7a)

can be assumed that the dianion [67] may have been an intermediate in which C-11 is oxidized to form the aldehyde [68] which, after workup, undergoes a stereospecific ring formation to **52** with an 11-exo-hydroxy group. The stereospecificity can be explained by thermodynamical control of the last reaction step; molecular models clearly show that there would be a severe steric interference between the hydroxyl group and the 9-endo-hydrogen in the 11-endo-epimer of **52**. The electron acceptor, however, could not be identified, but may have been among the products which could not be isolated.

Secondly, the phenyl ketone **14** gave the diol **53** (5% yield, eq 7b). In a merely speculative explanation one may



(7b)

conceive of the formation of a benzyl radical anion [**69**] under the influence of traces of oxygen; subsequently, this intermediate is converted stereospecifically to **53**.

It is interesting to note that in **53** a restricted phenyl group rotation is indicated by coalescence effects of its carbon and proton signals. In contrast, there is a clearly lower rotation barrier in **23** which lacks the equatorial hydroxyl group at C-4. It is conceivable that the steric constraint between the axial hydroxyl group at C-2 and the axial phenyl group at C-4 is more severe in **53** than in **28** (see below).

^{13}C NMR Spectra. In a series of papers[7] we have shown that in rigid molecules such as adamantanes the ^{13}C chemical shifts can be used to monitor intramolecular interactions of substituents. Moreover, if crowding of substituents occurs, divergence from substituent additivity in the ^{13}C chemical shifts of certain carbons reflect geometrical distorsions of the adamantane framework.[9] The present molecules containing *tert*-butyl groups are excellent candidates for an extension of these studies.

In order to trace nonadditivity effects (NAE) we used the ^{13}C chemical shifts of 2-*tert*-butyladamantan-2-ol (**19**) as a basis set and added substituent effects from 2-monosubstituted adamantanes[7,23] according to the respective position of this particular substituent in the 4-substituted 2-*tert*-butyladamantan-2-ols. Positive (negative) NAE indicate that the experimental δ value is larger (smaller) than the one calculated by this method.

In diastereomeric 2,4-dissubstituted adamantanes we had found[7b,9] that positive NAE occur at the substituted C-2 and C-4 if the two substituents are in diaxial position. However, the magnitude of these effects decrease with atomic weight if the substituents are halogens and even negative ones can be encountered for the dibromide.[7b,9] Moreover, in contrast to other stereoisomers and related 4-substituted adamantanones,[7] moderate negative divergences from additivity were found in the series of the diaxial 2,4-disubstituted adamantanes for C-3 which have been interpreted by assuming adamantane skeleton distorsions.[7b,9] These findings are confirmed by the data for 2,2,4^a-trisubstituted adamantanes where analogous and even more pronounced effects occur,[24] as well as by the data of 2,4-bis(trimethylsilyl)adamantanes[25] where even C-10 is strongly affected.

Table II. NAE Values in 4^e-Substituted 2-*tert*-Butyladamantan-2-ols with the 2-Hydroxy Group in the Axial Position (26–29)

	C-2	C-4
26 (X = OH)	+2.9	−1.8
27 (X = OCH_3)	+2.6	−0.9
28 (X = Ph)	−0.9	−2.6
29 (X = *t*-Bu)	−3.2	−5.1

In the series of 4^a-substituted 2-*tert*-butyladamantan-2-ols with the 2-hydroxy group in axial position (**20–25**) we found that NAE at C-2 and C-4 are in the range of +4 to +10 ppm, i.e. rather similar to the analogous compounds without the *tert*-butyl group. Apparently, in this type of configuration the *tert*-butyl group does not contribute significantly to further distortion of skeleton.

We could synthesize only one example of a 4^a-substituted 2-*tert*-butyladamantan-2-ols with the *tert*-butyl group in the axial position, namely **34**. If we compare its NAE at C-2 and C-4 with the respective values of its isomer **22**, we find that the NAE for C-4 is decreased in its absolute magnitude (**22**, C-2 6.7, C-4 8.0; **34**, C-2 7.1; C-4 5.9), and this might be an effect of steric interference.

C-2 and C-4 NAE values in 4^e-substituted 2-*tert*-butyladamantan-2-ols with the 2-hydroxy group in axial position (**26–29**) exhibit varying magnitudes and signs and a certain trend can be observed related to the space demand of the substituent at C-4 (Table II).

These trends in NAE values differ considerably from 2^e,4^a-disubstituted adamantanes[9] so that we have to assume a contribution from the equatorial *tert*-butyl group at C-2, which, however, is difficult to interpret.

Another striking result emerges from the NAE calculation of the tetrasubstituted diol **53** with an axial phenyl group displaying restricted rotation (vide infra). In contrast to **23** (without the 4-hydroxyl group) the NAE at C-4 is strongly negative (−5.2; **23**, +5.9) and that at C-9 strongly positive (+4.9; **23**, +2.4). Clearly, this can be interpreted in terms of steric congestion, as already revealed by the restricted rotation. The unusual C-9 value may be caused by different average orientations of the phenyl groups in **53**, **23**, and 2-phenyladamantane, i.e. different anisotropy (ring current) effects. On the other hand, the NAE in the diol **40** (with the hydroxyl groups in diaxial position) are rather similar to those in 2^a,4^a-adamantanediol (**41**)[7b,9] indicating the absence of noticeable steric effects of the *tert*-butyl group in **40**.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C). The chemical shifts were referenced to the solvent peaks (^{1}H, $CHCl_3$ δ = 7.24; ^{13}C, $CDCl_3$ δ = 77.0). For all one- and two-dimensional multipulse experiments standard Bruker software was employed.

The IR spectra were recorded in $CHCl_3$. Only significant bands are noted; ubiquitous bands, e.g. those at 2800–3000 cm^{-1} (aliphatic CH) are neglected.

Electron-impact mass spectra were recorded at (70 eV). Only peaks with intensities >10% are noted, unless they are of particular interest.

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Column chromatography was performed on Lobar columns (Merck) filled with silica gel (0.04–0.063 mm) using petroleum ether (PE) or mixtures of PE and acetone (AC). Thin-layer chromatography was performed on silica gel 60 plates (Merck) using the same eluent or eluent mixtures, respectively.

Melting points are uncorrected. As commonly found in adamantane chemistry, our compounds often were obtained as viscous oils or amorphous solids without well-defined melting points.

Syntheses. Starting Materials. Adamantanone (**1**) is commercially available. The following compounds were prepared according to known procedures: 4-substituted adamantanones **2** and **9**,[26] **3** and **10**,[23b] **4** and **11**,[26] **5** and **12**,[27] **6** and **13**,[26] as well as **7** and **14**.[28]

Adamantane-2,4-dione (**15**) was obtained in quantitative yield by Jones oxidation[29] of the alcohols **5** or **12** (or the mixture thereof).[27a]

4-Methyleneadamantanone (**16**, viscous oil) was synthesized by a Wittig-reaction (equimolar amount of methyltriphenylphosphonium bromide) with **15**: yield 40%; IR 3070, 1700 (C=O), 1650 (s); MS 162 (77, M^+), 134 (31, $M^+ - CO$), 119 (30, $M^+ - CO - CH_3$), 105 (23), 93 (100).

The ethylene acetal of **16** was prepared by acetalization with glycol in benzene and a trace of *p*-toluenesulfonic acid in nearly quantitative yield. In a one-pot reaction the crude acetal was hydroborated,[30] and subsequently the acetal was hydrolyzed in HCl/methanol to give **8** in 47% yield: IR 3540–3220 (br, OH), 1700 (C=O); MS 180 (58, M^+), 162 (53, $M^+ - H_2O$), 150 (44, $M^+ - CH_2O$), 149 (50, $M^+ - CH_3O$), 134 (18, $M^+ - H_2O - C_2H_4$), 121 (99, $M^+ - CH_3O - CO$), 93 (64), 79 (100).

4,4-Dimethyladamantanone (**17**) was synthesized according to a known procedure.[31]

Finally, adamantane-2,4-dione ethylene acetal (**18**, viscous oil) could be prepared by acetalization of the alcohols **5** or **12** (or the mixture thereof) with glycol in benzene and a trace of *p*-toluenesulfonic acid and subsequent Jones oxidation; the total yield was 90%.

Reactions of the 4-Substituted Adamantanones 1–18 with *tert*-Butyllithium (General Procedure). Under dry argon a solution of the respective 4-substituted adamantanone in dry diethyl ether (Et_2O) was prepared. While cooling with ice a 1.7 M solution of *tert*-butyllithium (*t*-BuLi) in pentane was added dropwise, and the combined mixture stirred overnight at room temperature. Then, it was cooled with ice again and hydrolyzed by adding saturated aqueous NH_4Cl dropwise. The aqueous layer was extracted with ether and the combined organic layers were dried over Mg_2SO_4, filtered, and evaporated. If possible, the obtained crude material was separated into the pure compounds by column chromatography (CC).

Reaction of Adamantanone (1) with *tert*-Butyllithium. **1** (0.539 g, 3.59 mmol) in 50 mL, of Et_2O, 5 mL, of *t*-BuLi; CC, PE/AC (40:1).

Fraction 1: 2-*tert*-butyladamantan-2-ol (**19**, 447.8 mg, 2.15 mmol); colorless viscous oil; yield 60%; IR 3615 (w, OH), 1365 (m, $C(CH_3)_3$); MS 193 (0.6, $M^+ - CH_3$), 151 (100, $M^+ - C_4H_9$), 123 (12), 107 (10), 81 (23), 67 (15), 57 (17, $C_4H_9^+$), 41 (21); HRMS found m/z 175.1490, calcd for $C_{13}H_{19}$ 175.1487.

Fraction 2: mixture of **19** and 2-(3,3-dimethylbutyl)-adamantan-2-ol[32] (**48**, 141 mg) (2.3:1, according to NMR), corresponding to **19**; 98 mg; 0.47 mmol; yield 13%. **48**: 43 mg; 0.18 mmol; yield 5%. IR and MS data of **48**, vide infra (reaction of **3**).

Fraction 3: **1** (55 mg, 10%).

Reaction of 4^e-Chloroadamantan-2-one[32] (2) with *tert*-Butyllithium. **2** (402 mg, 2.18 mmol) in 60 mL of Et_2O, 4 mL of *t*-BuLi; CC, PE/AC (200:1).

Fraction 1: 4-*endo*-*tert*-butyl-3,4-*exo*-epoxyprotoadamantane[32] (**51**, 19.8 mg, 0.10 mmol); colorless viscous oil; yield 4%; IR 1370 (m, $C(CH_3)_3$); MS 206 (14, M^+), 191 (23, $M^+ - CH_3$), 149 (30, $M^+ - C_4H_9$), 121 (38, $M^+ - C_4H_9 - CO$), 107 (29), 93 (36), 79 (73), 67 (30), 57 (88), 41 (100).

Fraction 2: 2^e-*tert*-butyl-4^a-chloroadamantan-2^a-ol[32] (**20**, 104 mg, 0.43 mmol); colorless glassy solid; yield 20%; IR 3565 (OH), 1365 (m, $C(CH_3)_3$), 1070 (m, CCl); MS 206 (1, $M^+ - HCl$), 187/185 (14/44, $M^+ - C_4H_9$), 149 (30, $M^+ - C_4H_9 - HCl$), 121 (100, $M^+ - C_4H_9 - HCl - CO$), 93 (17), 79 (29), 67 (12), 57 (27), 41 (25%); HRMS found m/z 185.0734, calcd for $C_{10}H_{14}O^{35}Cl$ 185.0733.

Fraction 3: 7-*endo*-(di-*tert*-butylhydroxymethyl)bicyclo-[3.3.1]non-2-ene[32] (**43**, 20.5 mg, 0.08 mmol); yield 4%; colorless solid; mp 45–7 °C; IR 3620 (m, OH), 3020 (m, C=CH), 1395, 1370 (s, $C(CH_3)_3$), 690; MS 207 (13, $M^+ - C_4H_9$), 189 (3, $M^+ - C_4H_9 - H_2O$), 175 (2), 143 (18, $(C_4H_9)_2COH^+$), 121 (8), 87 (42, $C_5H_{10}OH^+$), 57 (100, $C_4H_9^+$); HRMS found m/z 207.1750, calcd for $C_{14}H_{23}O$ 207.1749.

Fraction 4: 7-*endo*-pivaloylbicyclo[3.3.1]non-2-ene (**42**, 15.9 mg, 0.08 mmol); yield 4%; colorless glassy solid; IR 3010 (m, C=CH), 1690 (s, C=O), 1365 (m, $C(CH_3)_3$); MS 206 (2.6, M^+), 149 (36, $M^+ - C_4H_9$), 121 (100, $M^+ - C_4H_9 - CO$), 93 (40), 79 (60), 67 (24), 57 (37), 41 (35).

Fraction 5: 2,11,11-trimethyl-15-oxa-2,4-ethanoadamantane[32] (**45**, 50.3 mg, 0.24 mmol); yield 11%; colorless viscous oil; IR 1365 (m, $C(CH_3)_3$), 1225 (m, C–O); MS 207 (4, $M^+ + 1$), 206 (1, M^+), 191 (30, $M^+ - CH_3$), 133 (33, $M^+ - (CH_3)_2O - CH_3$), 106 (42), 93 (30), 91 (30), 79 (30), 43 (41), 41 (30); HRMS found m/z = 206.1663, calcd for $C_{14}H_{22}O$ 206.1671.

Fraction 6: **2** (152 mg, 38%).

Reaction of 4^e-Chloroadamantan-2-one[32] (9) with *tert*-Butyllithium. **9** (1.038 g, 5.62 mmol) in 100 mL of Et_2O, 10 mL of *t*-BuLi; CC, PE/AC (200:1).

Fraction 1: **43** (563.2 mg, 2.13 mmol); yield 38%.

Fraction 2: **42** (215.4 mg, 1.04 mmol); yield 19%.

Fraction 3: **45** (103 mg, 0.50 mmol); yield 9%.

Fraction 4: **9** (213 mg, 21%).

Reaction of 4^a-Bromoadamantan-2-one[32] (3) with *tert*-Butyllithium. **3** (1.013 g, 4.42 mmol) in 80 mL of Et_2O, 10 mL of *t*-BuLi; CC, PE/AC (300:1).

Fraction 1: 2^e,4^a-di-*tert*-butyladamantan-2^a-ol[32] (**25**, 70.6 mg, 0.27 mmol); yield 6%; colorless viscous oil; IR 3650 (w, OH), 1375 (m, $C(CH_3)_3$); MS 231 (3, $M^+ - CH_3 - H_2O$), 207 (100, $M^+ - C_4H_9$), 189 (15, $M^+ - C_4H_9 - H_2O$), 151 (19, $C_{10}H_{15}O^+$), 133 (12), 121 (13), 95 (20), 79 (20), 57 (75), 41 (33); HRMS found m/z 207.1748, calcd for $C_{14}H_{23}O$ 207.1749.

Fraction 2: 2^e,4^e-di-*tert*-butyladamantan-2^a-ol[32] (**29**, 63 mg, 0.24 mmol); yield 5%; colorless solid; mp 50–1 °C; IR 3610 (m, OH), 1365 (m, $C(CH_3)_3$); MS 231 (3, $M^+ - CH_3 - H_2O$), 207 (100, $M^+ - C_4H_9$), 189 (11, $M^+ - C_4H_9 - H_2O$), 151 (18), 134 (40), 119 (13), 91 (25), 79 (36), 57 (98, $C_4H_9^+$); HRMS found m/z 231.2108, calcd for $C_{17}H_{27}$ 231.2113.

Fraction 3: **19** (298 mg, 1.43 mmol); yield 32%.

Fraction 4: **48** (32.5 mg, 0.10 mmol); yield 2%; colorless viscous oil; IR 3600 (w, OH), 1365 (m, $C(CH_3)_3$); MS 235 (1, $M^+ - 1$), 151 (100, $M^+ - C_6H_{13}$), 91 (13), 79 (10); HRMS found m/z 235.2062, calcd for $C_{16}H_{27}O$ 235.2062.

Fraction 5: **1** (25 mg, 38%).

Reaction of 4^e-Bromoadamantan-2-one[32] (10) with *tert*-Butyllithium. **10** (600 mg, 2.62 mmol) in 80 mL of Et_2O, 6 mL of *t*-BuLi; CC, PE/AC (300:1).

Fraction 1: **25** (43.8 mg, 0.17 mmol); yield 6%.

Fraction 2: 2-methyl-2-isopropenyladamantane (**47**, 35.4 mg, 0.19 mmol); yield 7%; colorless viscous oil; IR 3095 (w, $=CH_2$); MS 190 (26, M^+), 175 (100, $M^+ - CH_3$), 135 (10, $C_{10}H_{15}^+$), 133 (10), 119 (16), 105 (14), 93 (26), 79 (34), 67 (18), 41 (28); HRMS found m/z 190.1722, calcd for $C_{14}H_{22}$ 190.1721.

Fraction 3: **43** (148 mg, 0.56 mmol); yield 21%.

Fraction 4: **29** (39.5 mg, 0.1 mmol); yield 6%.

Fraction 5: **19** (28.6 mg, 0.14 mmol); yield 5%.

Fraction 6: **1** (128 mg, 33%).

Reaction of 4^a-Iodoadamantan-2-one[32] (4) with *tert*-Butyllithium. **4** (720 mg, 2.61 mmol) in 90 mL of Et_2O, 7 mL of *t*-BuLi; CC, PE/AC (100:1).

Fraction 1: 2,2-bis(3′,3′-dimethylbutoxy)adamantane (**50**, 77.3 mg, 0.23 mmol); yield 9%; colorless viscous oil; IR 1365 (m,

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$C(CH_3)_3$), 1020 (s-m, C–O); MS 235 (70, $M^+ - C_6H_{13}O$), 151 (100, $C_{10}H_{14}OH^+$), 85 (15), 79 (29), 57 (25), 43 (22), 41 (22); HRMS found m/z 235.2057, calcd for $C_{16}H_{27}O$ 235.2062.

Fraction 2: 25 (21.4 mg, 0.08 mmol); yield 3%.

Fraction 3: 19 (82.7 mg, 0.40 mmol); yield 15%.

Fraction 4: 1 (196 mg, 50%).

Reaction of 4^e-Iodoadamantan-2-one[32] (11) with *tert*-Butyllithium. 11 (48 mg, 1.76 mmol) in 60 mL of Et_2O, 5 mL of *t*-BuLi; CC, PE/AC (100:1).

Fraction 1: 43 (38.6 mg, 0.1 mmol); yield 8%.

Fraction 2: 19 (72.6 mg, 0.3 mmol); yield 20%.

Fraction 3: 25 (13.8 mg, 0.05 mmol); yield 3%.

Fraction 4: 1 (135.5 mg, 51%).

Reaction of 4^a-Hydroxyadamantan-2-one[32] (5) with *tert*-Butyllithium. 5 (1.054 g, 6.34 mmol) in 100 mL of Et_2O, 10 mL of *t*-BuLi; CC, PE/AC (10:1).

Fraction 1: 2^e-*tert*-butyladamantane-2^a,4^a-diol[32] (21, 956 mg, 4.26 mmol); yield 67%; colorless solid; dec >100 °C; IR 3605 (m, OH), 3410 (s, br, OH), 1075 (s, C–O); MS 206 (2, $M^+ - H_2O$), 167 (10, $M^+ - C_4H_9$), 149 (66, $M^+ - C_4H_9 - H_2O$), 121 (100), 93 (37), 79 (55), 57 (43), 41 (58); HRMS found m/z 206.1663, calcd for $C_{14}H_{22}O$ 206.1671.

Fraction 2: 2^a,4^a-dihydroxyadamantane[9,32] (41, 135.5 mg, 11%).

Reaction of 4^e-Hydroxyadamantan-2-one[32] (12) with *tert*-Butyllithium. 12 (970 mg, 5.84 mmol) in 100 mL of Et_2O, 10 mL of *t*-BuLi; CC, PE/AC (10:1).

Fraction 1: 2^a-*tert*-butyladamantane-2^e,4^e-diol[32] (35, 180 mg, 0.80 mmol); yield 14%; colorless solid; mp 91–2 °C; IR 3650 (m, OH), 3500 (m, br, OH), 1370 (m, $C(CH_3)_3$), 1220 (s, C–O); MS 224 (0.1, M^+), 167 (60, $M^+ - C_4H_9$), 149 (16, $M^+ - C_4H_9 - H_2O$), 121 (100), 93 (18), 79 (28), 57 (22), 43 (21), 41 (21).

Fraction 2: 2^e-*tert*-butyladamantane-2^a,4^e-diol[32] (26, 423.6 mg, 1.89 mmol); yield 32%; colorless solid; mp 87–8 °C; IR 3610 (m, OH), 3450 (m, br, OH), 1220 (s, CO); MS 206 (1, $M^+ - H_2O$), 167 (64, $M^+ - C_4H_9$), 149 (16, $M^+ - C_4H_9 - H_2O$), 121 (100), 93 (18), 79 (28), 67 (13), 57 (17), 41 (20); HRMS found m/z 206.1671, calcd for $C_{14}H_{22}O$ 206.1671.

Fraction 3: 12 (283 mg, 29%).

Reaction of 4^a-Methoxyadamantan-2-one[32] (6) with *tert*-Butyllithium. 6 (500 mg, 2.77 mmol) in 100 mL of Et_2O, 6 mL of *t*-BuLi; CC: PE/AC (500:1).

Fraction 1: 2^e-*tert*-butyl-4^a-methoxyadamantan-2^a-ol[32] (22, 285.4 mg, 1.20 mmol); yield 43%; colorless solid; mp 56–7 °C; IR 3415 (s, OH), 2835 (m, OCH_3), 1088 (s, C–O); MS 206 (1, $M^+ - CH_3OH$), 181 (10, $M^+ - C_4H_9$), 149 (74, $M^+ - C_4H_9 - CH_3OH$), 121 (100, $M^+ - C_4H_9 - CH_3OH - CO$), 93 (24), 79 (32), 67 (12), 57 (18), 41 (23); HRMS found m/z 206.1671, calcd for $C_{14}H_{22}O$ 206.1671.

Fraction 2: 2^a-*tert*-butyl-4^a-methoxyadamantan-2^e-ol[32] (34, 50.2 mg, 0.21 mmol); yield 8%; colorless solid; mp 71–2 °C; IR 3615 (w, OH), 2835 (w, OCH_3), 1105 (s, C–O); MS 206 (1, $M^+ - CH_3OH$), 181 (20, $M^+ - C_4H_9$), 149 (84, $M^+ - C_4H_9 - CH_3OH$), 121 (100), 93 (22), 79 (35), 67 (15), 57 (22), 41 (32).

Fraction 3: 6 (147 mg, 29%).

Reaction of 4^e-Methoxyadamantan-2-one[32] (13) with *tert*-Butyllithium. 13 (200 mg, 1.11 mmol) in 50 mL of Et_2O, 3 mL of *t*-BuLi; CC, PE/AC (500:1).

Fraction 1: 2^a-*tert*-butyl-4^e-methoxyadamantan-2^e-ol[32] (36, 112.1 mg, 0.47 mmol); yield 42%; colorless solid; mp 54–5 °C; IR 3615 (w, OH), 2825 (w, OCH_3), 1100 (s, C–O); MS 181 (40, $M^+ - C_4H_9$), 149 (65, $M^+ - C_4H_9 - CH_3OH$), 121 (100, $M^+ - C_4H_9 - CH_3OH - CO$), 93 (16), 67 (11), 57 (18), 41 (21).

Fraction 2: 2^e-*tert*-butyl-4^e-methoxyadamantan-2^a-ol[32] (27, 60 mg, 0.2 mmol); yield 23%; colorless viscous oil; IR 3610 (w, OH), 2825 (w, OCH_3), 1100 (s, C–O); MS 220 (1, $M^+ - H_2O$), 181 (24, $M^+ - C_4H_9$), 149 (56, $M^+ - C_4H_9 - CH_3OH$), 121 (100, $M^+ - C_4H_9 - CH_3OH - CO$), 93 (28), 79 (40), 67 (18), 41 (59); HRMS found m/z 181.1229, calcd for $C_{11}H_{17}O_2$ 181.1229.

Fraction 3: 13 (36 mg, 18%).

Reaction of 4^a-Phenyladamantan-2-one[32] (7) with *tert*-Butyllithium. 7 (1 g, 4.42 mmol) in 100 mL of Et_2O, 10 mL of *t*-BuLi; CC, PE/AC (100:1).

Fraction 1: 2^e-*tert*-Butyl-4^a-phenyladamantan-2^a-ol[32] (23, 760 mg, 2.67 mmol); yield 60%; colorless viscous oil; IR 3590 (m, OH), 3400 (m, br, OH), 1365 (m, $C(CH_3)_3$); MS 251 (3, $M^+ - H_2O - CH_3$), 227 (100, $M^+ - C_4H_9$), 167 (8), 149 (50, $M^+ - C_4H_9 - C_6H_6$), 121 (75, $M^+ - C_4H_9 - C_6H_6 - CO$), 91 (46), 79 (16), 77 (8, $C_6H_5^+$), 57 (18), 41 (19).

Fraction 2: 7 (190 mg, 19%).

Reaction of 4^e-Phenyladamantan-2-one[32] (14) with *tert*-Butyllithium. 14 (830 mg, 3.67 mmol) in 100 mL of Et_2O; 9 mL of *t*-BuLi; CC, PE/AC (100:1).

Fraction 1: mixture of 2^e-*tert*-butyl-4^e-phenyladamantan-2^a-ol[32] (28) and 2^a-*tert*-butyl-4^e-phenyladamantan-2^e-ol[32] (37) (1:1.1, from NMR) (530 mg, 1.86 mmol); yield 50%; colorless viscous oil; IR 3620 (m, OH), 1365 (m, $C(CH_3)_3$); MS 284 (1, M^+), 267 (12, $M^+ - OH$), 266 (58, $M^+ - H_2O$), 227 (100, $M^+ - C_4H_9$), 209 (16, $M^+ - C_4H_9 - H_2O$), 155 (19), 149 (18, $M^+ - C_4H_9 - C_6H_6$), 121 (40), 91 (54), 79 (14), 77 (10), 57 (30), 41 (27); HRMS found m/z 266.2032, calcd for $C_{20}H_{26}$ 266.2035.

Fraction 2: 2^e-*tert*-butyl-4^a-phenyladamantane-2^a,4^e-diol[32] (53, 50.7 mg, 0.17 mmol); yield 5%; colorless solid; dec >85 °C; IR 3595 (s, OH), 3450 (w, br, OH), 1365 (m, $C(CH_3)_3$); MS 283 (3, $M^+ - OH$), 282 (13, $M^+ - H_2O$), 267 (11, $M^+ - H_2O - CH_3$), 225 (65, $M^+ - H_2O - C_4H_9$), 210 (28), 197 (28, $M^+ - H_2O - C_4H_9 - CO$), 155 (26), 117 (22), 105 (100), 91 (64), 78 (39, $C_6H_6^+$), 77 (42, $C_6H_5^+$), 57 (56), 41 (45); HRMS found m/z 282.1979, calcd for $C_{20}H_{26}O$ 282.1984.

Fraction 3: 14 (192 mg, 23%).

Reaction of 4^a-(Hydroxymethyl)adamantan-2-one[32] (8) with *tert*-Butyllithium. 8 (300 mg, 1.66 mmol) in 6 mL of Et_2O, 3 mL of *t*-BuLi; CC, PE/AC (10:1).

Fraction 1: 2-*tert*-butyl-15-*exo*-hydroxy-16-oxa-2,4-ethanoadamantane[32] (52, 54.4 mg, 0.23 mmol); yield 14%; colorless solid; mp 93–5 °C; IR 3600 (w, OH), 3405 (w, br, OH), 1365 (m, $C(CH_3)_3$), 1080 (m, C–OH); MS 236 (3, M^+), 190 (14, $M^+ - HCO_2H$), 179 (35, $M^+ - C_4H_9$), 150 (57, $M^+ - C_4H_9 - CHO$), 133 (63, $M^+ - HCO_2H - C_4H_9$), 121 (25), 105 (19), 91 (100), 79 (49), 67 (28), 57 (72), 41 (67); HRMS found m/z 236.1777, calcd for $C_{15}H_{24}O_2$ 236.1776.

Fraction 2: 2^e-*tert*-butyl-4^a-(hydroxymethyl)adamantan-2^a-ol[32] (24, 115.4 mg, 0.48 mmol); yield 29%; colorless glassy solid; IR 3615 (w, OH), 3420 (w, br, OH), 1365 (m, $C(CH_3)_3$), 1045 (m, C–OH); MS 221 (4, $M^+ - OH$), 220 (20, $M^+ - H_2O$), 181 (21, $M^+ - C_4H_9$), 163 (91, $M^+ - C_4H_9 - H_2O$), 145 (15, $M^+ - C_4H_9 - 2H_2O$), 135 (100, $C_{10}H_{15}^+$), 121 (26), 93 (51), 91 (53), 79 (70), 67 (52), 57 (80), 41 (86); HRMS found m/z 220.1828, calcd for $C_{15}H_{24}O$ 220.1827.

Fraction 3: 8 (100.2 mg, 33%).

Reaction of Adamantane-2,4-dione (15) with *tert*-Butyllithium. 15 (1.09 g, 6.67 mmol) in 100 mL of Et_2O, 10 mL of *t*-BuLi; CC, PE/AC (15:1).

Fraction 1: 4-*tert*-butyl-2,11,11-trimethyl-15-oxa-2,4-ethanoadamantane[32] (46, 27.4 mg, 0.10 mmol); yield 2%; colorless viscous oil; IR 1365 (m, $C(CH_3)_3$), 1170 (m, C–O); MS 247 (41, $M^+ - CH_3$), 204 (11, $M^+ - (CH_3)_2CO$), 148 (12), 105 (18), 91 (28), 79 (34), 67 (22), 57 ($C_4H_9^+$, 100).

Fraction 2: 7-*endo*-(di-*tert*-butylhydroxymethyl)bicyclo-[3.3.1]nonan-2-one[32] (44, 109 mg, 0.39 mmol); yield 6%; colorless viscous oil; IR 3615 (w, OH), 3460 (w, br, OH), 1700 (s, C=O), 1370 (m, $C(CH_3)_3$); MS 233 (4, $M^+ - OH - 2CH_3$), 205 (23, $M^+ - C_4H_9 - H_2O$), 187 (19, $M^+ - C_4H_9 - 2H_2O$), 149 (13, $M^+ - 2C_4H_9 - OH$), 143 (33), 138 (20, $M^+ - 2C_4H_9 - CO$), 121 (33), 107 (19), 93 (22), 87 (71), 67 (22), 57 (100), 41 (31); HRMS found m/z 223.1698, calcd for $C_{14}H_{23}O_2$ 223.1698.

Fraction 3: 2^e-*tert*-butyl-4^e-(3,3-dimethylbutyl)adamantane-2^a,4^a-diol[32] (49, 23.9 mg, 0.08 mmol); yield 1%; colorless solid; dec >110 °C; IR 3595 (w, OH), 3380 (m, br, OH), 1365 (m, $C(CH_3)_3$), 1090 (m, C–O); MS 290 (3, $M^+ - H_2O$), 233 (73, $M^+ - H_2O - C_4H_9$), 215 (52, $M^+ - 2H_2O - C_4H_9$), 177 (16), 163 (12), 149 (27), 121 (34), 113 (32), 85 (20), 57 (100), 43 (36).

Fraction 4: 2^e,4^e-di-*tert*-butyladamantane-2^a,4^a-diol[32] (40, 50 mg, 0.18 mmol); yield 3%; colorless solid; dec >80 °C; IR 3600 (w, OH), 3330 (m, br, OH), 1365 (m, $C(CH_3)_3$), 1080 (m, C–O); MS 262 (7, $M^+ - H_2O$), 247 (32, $M^+ - H_2O - CH_3$), 205 (52, $M^+ - H_2O - C_4H_9$), 187 (40, $M^+ - 2H_2O - C_4H_9$), 149 (15), 131 (13), 121 (25), 107 (20), 93 (21), 79 (20), 57 (100), 41 (45); HRMS found m/z 262.2298, calcd for $C_{18}H_{30}O$ 262.2297.

Fraction 5: 2^a-*tert*-butyl-4-oxoadamantan-2^e-ol[32] (38, 316.4 mg, 1.42 mmol); yield 21%; colorless solid; mp 105–8 °C; IR 3605 (m, OH), 3390 (m, br, OH), 1700 (s, C=O), 1365 ($C(CH_3)_3$), 1060 (m, C–O); MS 222 (3, M^+), 165 (100, $M^+ - C_4H_9$), 137 (33, M^+ –

C_4H_9 – CO), 119 (37, $M^+ - C_4H_9 - CO - H_2O$), 109 (10), 91 (20), 79 (19), 67 (19), 57 (46), 55 (30), 41 (35).

Fraction 6: 2^e-*tert*-butyl-4-oxoadamantan-2^a-ol[32] **30** (245.4 mg, 1.10 mmol); yield 17%; colorless solid; mp 108–110 °C; IR 3605 (m, OH), 3410 (s, br, OH), 1710 (s, C=O), 1365 (m, $C(CH_3)_3$), 1075 (s, C–O); MS 222 (1, M^+), 165 (100, $M^+ - C_4H_9$), 137 (31, $M^+ - C_4H_9 - CO$), 119 (26, $M^+ - C_4H_9 - CO - H_2O$), 95 (13), 79 (12), 67 (16), 57 (31), 55 (22), 40 (29); HRMS found m/z = 222.1620, calcd for $C_{14}H_{22}O_2$ 222.1620.

Fraction 7: **21** (435.7 mg, 1.94 mmol); yield 29%.

Reaction of 4-Methyleneadamantan-2-one (16) with *tert*-Butyllithium. **16** (340 mg, 2.10 mmol); in 100 mL of Et_2O, 4 mL of *t*-BuLi; CC, PE.

Fraction 1: 2^e-*tert*-butyl-4-methyleneadamantan-2^a-ol[32] (**31**, 74.9 mg, 0.34 mmol); yield 16%; colorless viscous oil; IR 3600 (w, OH), 3080 (w, C=CH_2), 1365 (m, $C(CH_3)_3$); MS 220 (2, M^+), 163 (100, $M^+ - C_4H_9$), 135 (85), 107 (21), 93 (36), 79 (26), 67 (12), 57 (34), 41 (30).

Fraction 2: 2^a-*tert*-butyl-4-methyleneadamantan-2^e-ol[32] (**39**, 145 mg, 0.66 mmol); yield 31%; colorless viscous oil; IR 3600 (w, OH), 1365 (m, $C(CH_3)_3$); MS 220 (6, M^+), 163 (100, $M^+ - C_4H_9$), 135 (99), 121 (12), 107 (28), 93 (48), 79 (36), 57 (43), 41 (42).

Fraction 3: **16** (9 mg, 28%).

Reaction of 4,4-Dimethyladamantan-2-one (17) with *tert*-Butyllithium. **17** (600 mg, 3.37 mmol); in 120 mL of Et_2O; 6 mL of *t*-BuLi; CC, PE.

Fraction 1: 2^e-*tert*-butyl-4,4-dimethyladamantan-2^a-ol[32] (**32**, 597.3 mg, 2.53 mmol); yield 75%; colorless viscous oil; IR 3625 (m, OH), 1365 (m, $C(CH_3)_3$), 1090 (m, C–OH); MS 218 (3, $M^+ - H_2O$), 179 (100, $M^+ - C_4H_9$), 161 (18, $M^+ - C_4H_9 - H_2O$), 151 (12), 119 (16), 95 (38), 81 (18), 57 (24), 41 (30); HRMS found m/z 218.2034, calcd for $C_{16}H_{26}$ 218.2034.

Fraction 2: **17** (61 mg, 10%).

Reaction of Adamantane-2,4-dione 4-(Ethylene acetal) (18) with *tert*-Butyllithium. **18** (641.3 mg, 3.08 mmol); in 100 mL of Et_2O; 7 mL of *t*-BuLi; CC, PE/AC (15:1).

Fraction 1: 2^e-*tert*-Butyl-4-oxoadamantan-2^a-ol 4-(ethylene acetal)[32] (**33**, 420 mg, 1.58 mmol); yield: 51%; colorless viscous oil; IR 3600 (m, OH), 3460 (w, br, OH), 1395 (w, $C(CH_3)_3$), 1365 (m, $C(CH_3)_3$); MS 266 (1, M^+), 209 (57, $M^+ - C_4H_9$), 165 (100, $M^+ - C_4H_9 - C_2H_4O$), 137 (30), 119 (35), 91 (14), 79 (12), 60 (38, $C_2H_4O_2^+$), 57 (40), 43 (46).

Fraction 2: **18** (162 mg, 25%).

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Supplementary Material Available: Tables of ^1H and ^{13}C NMR chemical shifts and positional assignments for compounds **1–40** and **42–53** (^1H NMR) and compounds **7, 8, 14–40,** and **42–53** (^{13}C NMR) and ^1H and ^{13}C NMR spectra for compounds **20–40** and **42–53** (75 pages). Ordering information is given on any current masthead page.

Reactions of Substituted 2-*tert*-Butyladamantan-2-ols

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The reaction of substituted 2-*tert*-butyladamantan-2-ols with triethylsilane and/or hydriodic acid is described. In addition to the expected hydrocarbons, interesting rearrangement products were observed in many cases. Reaction mechanisms are presented to rationalize the experimental results.

Introduction

In the preceding paper[1] we described the synthesis of a number of substituted 2-*tert*-butyladamantan-2-ols.[2] In order to synthesize a series of adamantane compounds carrying *tert*-butyl groups in secondary positions without a geminal substituent we wanted to reduce these carbinols to the corresponding hydrocarbons. To our surprise, however, we found many interesting products of other types of reaction.

Results

We employed two different reaction procedures to obtain substituted 2-*tert*-butyladamantanes. The first involved the exposure of the carbinols to triethylsilane in trifluoroacetic acid and methylene chloride (reaction type I),[2] a procedure suitable for removal of the hydroxy group to obtain the corresponding alkanes. The results were quite surprising and differed in part from our expectations. The molecular structures of the products and reaction details are listed in Chart I and in Table I (reaction type I), respectively. For comparison, some of the carbinols were treated with hydriodic acid (reaction type II, Table I) which is also a reducing reagent.

In general, the overall yields of the reactions were between 60 and 80%, only in a few cases were they lower. These values refer to isolated compounds after chromatographic separation and/or purification. The isolation procedure involving reduced-pressure distillation of the solvent on a rotary evaporator frequently caused losses of material due to the volatility of many of the adamantanes not containing polar groups.

It should be noted that Saba and Fry[2] used tri-*n*-hexylsilane for their alcohol reduction reactions. We found, however, that there is no significant difference in employing triethylsilane, apart from the fact that the reaction product triethylsilane—presumably hexaethyldisiloxane—could be removed more easily due to its lower boiling point.

The structural elucidation of the reaction products was again a crucial factor in this work and is the basis of all discussions of reaction mechanisms. For the methods employed see the preceding paper.[1]

The NMR data obtained are collected in the Tables II (^{13}C) and II (^1H) in the supplementary material.

(1) Duddeck, H.; Rosenbaum, D. *J. Org. Chem.*, preceding paper in this issue.

(2) (a) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628. (b) Saba, J. L.; Fry, J. L. *Ibid.* **1983**, *105*, 533.

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