for all the spin trapping experiments. The radical ions were generated in situ by using a special electrochemical cell.[8a]

Registry No. DTBN, 118921-33-8; $DTBN^{\bullet-}$, 118921-34-9; $DTBN^+$, 119008-54-7; TTBN, 24973-59-9; PMNB, 84802-28-8; $PMNB^+$, 118921-35-0; $TTBN^-$, 61278-22-6; $TTBN^+$, 34530-62-6; $PhNO^{\bullet-}$, 34480-22-3; CH_3, 2229-07-4; CH_2CH_3, 2025-56-1; $CH_2CH{=}CH_2$, 1981-80-2; $CH(CH_3)_2$, 2025-55-0; $C(CH_3)_3$, 1605-73-8; $C(O)C(CH_3)_3$, 50694-27-4; $C(O)CH(CH_3)_2$, 35586-36-8; SCH_2CH_3, 14836-22-7; $P(O)(OEt)_2$, 31682-65-2; 4-oxo-2,6-di-*tert*-butyl-1,4-dihydrobenzene-1-iminoxyl, 118921-37-2; 4-oxo-2,3,5,6-tetramethoxy-1,4-dihydrobenzene-1-iminoxyl, 118921-38-3; 2,6-di-*tert*-butylaniline, 2909-83-3; 4-(benzoyloxy)-2,6-di-*tert*-butylnitrosobenzene, 25798-70-3; 2,6-di-*tert*-butylphenylhydronitroxide, 118921-36-1.

Single-Step Reductive Isomerization of Unsaturated Polycyclics to $C_{4n+6}H_{4n+12}$ Diamondoid Cage Hydrocarbons with Sodium Borohydride/Triflic Acid[1]

George A. Olah,* An-hsiang Wu, Omar Farooq, and
G. K. Surya Prakash

*The Donald P. and Katherine B. Loker Hydrocarbon
Research Institute and Department of Chemistry,
University of Southern California,
Los Angeles, California 90089-1661*

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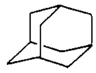
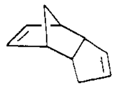
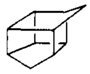
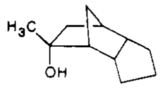
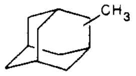
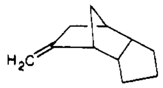
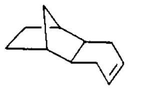
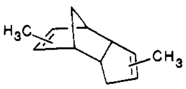
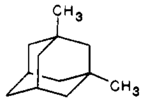
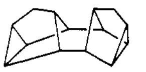
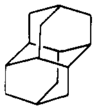
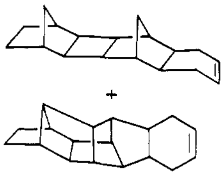
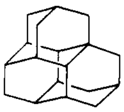
Introduction

Following the first isolation of adamantane and diamantane by Landa et al. from crude oil[2a] and Prelog's subsequent multistep synthesis,[2b] substantial interest arose in adamantanoid polycyclic cage hydrocarbons of $C_{4n+6}H_{4n+12}$ composition.[3] Adamantane, diamantane, and later triamantane were prepared in 19,[4-6] 65,[7-14] and 60%[15-18] yield, respectively, by Lewis acid ($AlCl_3$, $AlBr_3$, $AlBr_3$–sludge) catalyzed isomerization of their various strained polycyclic saturated precursors.

Table I

R′H (reactant)	RH (product)	yield,[a] %
		95
		96
		97
		92
		95
		90
		90
		99
		92

[a] Isolated yield. [b] 1-Methyladamantane was the major product.

Subsequent developments[19-22] led to an improved (60%) yield of adamantane by gas-phase isomerization of isomeric trimethylenenorbornane ($C_{10}H_{16}$) precursors over chlorinated platina.[23] We have recently reported that the polycyclic cage hydrocarbons, adamantane and diamantane, can be conveniently prepared in quantitative yield by isomerization of their corresponding hydrogenated (saturated) precursors with $B(OTf)_3$, $B(OTf)_3$–CF_3SO_3H, and SbF_5–CF_3SO_3H superacids, either neat or in Freon-113 solution.[24-26] Near quantitative isomerization of isomeric

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$C_{18}H_{24}$ saturated precursors to triamantane in superacid media was promoted by 1-haloadamantane serving as a source of 1-adamantyl cation for hydride abstraction.[26]

The needed saturated strained polycyclic precursors of $C_{4n+6}H_{4n+12}$ composition in the reported preparations[24-26] were obtained by catalytic hydrogenation of their readily available unsaturated progenitors using Adams and related hydrogenation catalysts. Preceding procedure by necessity thus represents an additional hydrogenation step of some complexity and expense.

We have previously reported the use of $NaBH_4$–CF_3SO_3H as an effective reagent system for ionic hydrogenation of tertiary aryl, cycloalkylmethyl alcohols[27] in ether solution. We now report the use of this reagent system in Freon-113 solution for the mild reductive isomerization of the strained unsaturated polycyclic compounds to their corresponding diamondoid cage hydrocarbons of $C_{4n+6}H_{4n+12}$ composition in a single step operation with nearly quantitative yields.

Results and Discussion

When to a mixture of dicyclopentadiene (tricyclo[5.2.1.0^{2,6}]deca-3,8-diene) and $NaBH_4$ in Freon-113[27] CF_3SO_3H is added dropwise with vigorous stirring under dry nitrogen and the reaction is allowed to continue for 4–6 h from -30 °C to room temperature, adamantane was obtained in quantitative yield after appropriate workup. Similarly when Binor-S[11] (hepatocyclo[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane, 4 + 4 dimer of norbornadiene) was reacted with $NaBH_4$–CF_3SO_3H under the same reaction condition, diamantane was obtained as the sole product. When the procedure was applied to an isomeric mixture of $C_{18}H_{20}$ (heptacyclooctadecene) synthesized[18] through C_4 elaboration of Binor-S[11] triamantane was obtained in nearly quantitative yield (92%). So far no unsaturated C_{10}, C_{14}, and C_{18} hydrocarbon precursors have been used for the preparation of adamantane, diamantane, and triamantane directly. Thus, the $NaBH_4$–HOTf system is the most effective for the reductive isomerization of unsaturated precursors for diamandoid cage hydrocarbons. The results are summarized in Table I.

$$R'H \xrightarrow[\text{Freon-113, -30 °C to rt}]{NaBH_4, CF_3SO_3H,} RH$$

Superacidic triflic acid reacting with $NaBH_4$ effectively hydrogenates unsaturated hydrocarbon precursors (ionic hydrogenation).[1] The in situ hydrogenated strained polycyclic precursors undergo rearrangement to the desired cage compounds by in situ generated $B(OSO_2CF_3)_3$ based superacid[25] formed from reaction of CF_3SO_3H with $NaBH_4$. The detailed investigation of in situ formation of superacid from the reaction of CF_3SO_3H with $NaBH_4$ will be reported elsewhere.[28]

The presently developed procedure offers advantages for the preparation of adamantanoid cage compounds in that the procedure eliminates the use of preprepared hydrogenated precursors by using expensive Adams and related catalysts and that the hydrogenation and isomerization are carried out as a single operation. Furthermore, even carbonyl precursors, alcohol as well as pentacyclic precursor (such as bishomocubane) also undergoes effective reductive isomerization (see Table I) to their respective diamondoid hydrocarbons.

Experimental Section

Sodium borohydride, tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, tricyclo[5.2.1.0^{2,6}]decan-8-one, methylcyclopentadiene dimer were available from Aldrich in the highest purity and were used as received. 4-Tricyclo[6.2.1.0^{2,7}]undecene[29a] and pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (1,3-bishomocubane) were prepared according to literature procedure.[29b,c] 8-Methyl-8-tricyclo[5.2.1.0^{2,6}]decanol was prepared from the corresponding ketone and methyllithium.[30] 8-Methylenetricyclo[5.2.1.0^{2,6}]decane was prepared according to our recent procedure.[31] Heptacyclo[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane (Binor-S) and the Diels–Alder adduct, the unsaturated precursor for triamantane, were available in our laboratory from previous work.[32]

Trifluoromethanesulfonic (triflic) acid (3 M) was distilled prior to use. Freon-113 (Aldrich) and diethyl ether were dried over P_2O_5 and sodium metal, respectively, under reflux.

Gas chromatographic analysis was carried out on a Varian Model 3700 gas chromatograph equipped with a quartz silica capillary column coated with DB-1. GC–MS spectra were recorded on a Finnigan Mat Model 700 GC–MS spectrometer equipped with an ion-trap detector and interfaced with a Varian Associates Model 3500 gas chromatograph. NMR spectra were recorded on a Varian (VXR-200) superconducting NMR spectrometer.

General Method of Preparation of Diamondoid Hydrocarbons. To a well-stirred heterogeneous mixture of the unsaturated hydrocarbon precursors (usually 7.6 mmol) and $NaBH_4$ (22.8 mmol) in dry Freon-113 (~40 mL) cooled to -30 °C is added 12 mL (137 mmol) of triflic acid dropwise over a period of $^1/_2$ h under dry argon or nitrogen. During the addition of acid (exothermic reaction) the system is further cooled to -78 °C, and after the addition of acid the system is slowly warmed to room temperature over a period of 3–5 h, and the reaction is continued for a total of 18 h. Usual workup with ice–bicarbonate, extraction with CH_2Cl_2, drying the extracted solution over anhydrous Na_2SO_4, and removal of solvent gave crude cage hydrocarbon product, which subsequently was purified by column chromatography (alumina, hexane). The isolated products were characterized by GC, GC–MS, and ^{13}C NMR spectroscopy.[33,34]

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. Binor-S, 13002-57-8; sodium borohydride, 16940-66-2; triflic acid, 1493-13-6; tricyclo[5.2.1.0^{2,6}]decan-8-one, 13380-94-4; tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, 77-73-6; pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 6707-86-4; 8-methyl-8-tricyclo[5.2.1.0^{2,6}]decanol, 118798-26-8; 8-methylenetricyclo[5.2.1.0^{2,6}]decanol, 64937-28-6; tricyclo[6.2.1.0^{2,7}]undec-4-ene, 91465-71-3; dimethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene, 26472-00-4; 1,4:5,10-dimethanobenzo[*b*]biphenylene, 51520-81-1; 3,10:4,9-ethanediylidenepentaleno[1,2-*b*]naphthalene, 62870-28-4; adamantane, 281-23-2; methyladamantane, 30583-25-6; 1,3-dimethyladamantane, 702-79-4; diamantane, 2292-79-7; triamantane, 13349-10-5.

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