Single-Step One-Carbon Ring Homologation of Cyclic and Polycyclic Hydrocarbons via Their Methyl Alcohols or Carboxylic Acids with Sodium Borohydride/Triflic Acid[1]

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Introduction

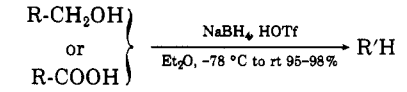
When an incipient primary carbenium ion center is generated adjacent to an alicyclic ring, the latter undergoes ring expansion,[2-6] initially giving a ring expanded alicyclic tertiary carbenium ion, which upon aqueous workup yields the corresponding tertiary alcohols. This methodology is used for the preparation of ring-expanded tertiary alicyclic alcohols generally under solvolytic (hydrolytic) conditions of the corresponding esters (frequently tosylates, although other esters such as nosylates, brosylates, acetates, etc. are also used).[2] To obtain the parent ring-expanded hydrocarbons necessitates subsequent reduction of the alcohols. Certain ring-expanded polycyclic hydrocarbons, such as homoadamantane, were prepared by catalytic hydrogenation of homoadamantene synthesized in a multistep procedure via ring homologation of adamantanone.[2b,c]

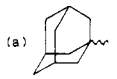
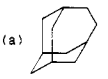
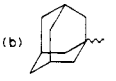
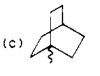
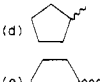
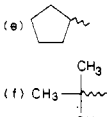
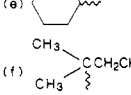
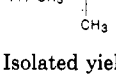
We have previously reported[7] the use of $NaBH_4$–CF_3SO_3H and HCOOH–CF_3SO_3H as effective reducing agents for the preparation of aryl-substituted polycyclic hydrocarbons from their corresponding alcohols. Recently, we have also reported[1] the effective use of $NaBH_4$–CF_3SO_3H system in Freon-113 for reductive isomerization of strained unsaturated polycyclic compounds to the corresponding diamondoid cage hydrocarbons of $C_{4n+6}H_{4n+12}$ composition. We now want to report the convenient one-pot preparation of ring-expanded polycyclic hydrocarbons from their corresponding methyl alcohols or carboxylic acids with $NaBH_4$–CF_3SO_3H.

Results and Discussion

When to a heterogeneous mixture of $NaBH_4$ and 1-adamantanemethyl alcohol in diethyl ether at −78 °C triflic acid is added dropwise and the reaction mixture is slowly warmed up to room temperature, homoadamantane was obtained in near quantitative yield after aqueous bicarbonate workup. The procedure when applied to other alicyclic methyl alcohols as shown in Table I gave ring-homologated hydrocarbons in near quantitative yield. Attempted reactions with $NaBH_4$–CF_3COOH and HCOO-H–CF_3SO_3H, on the other hand, gave only the corresponding trifluoroacetate and formate esters, respectively, of the alcohols, and no hydrocarbon product was obtained.

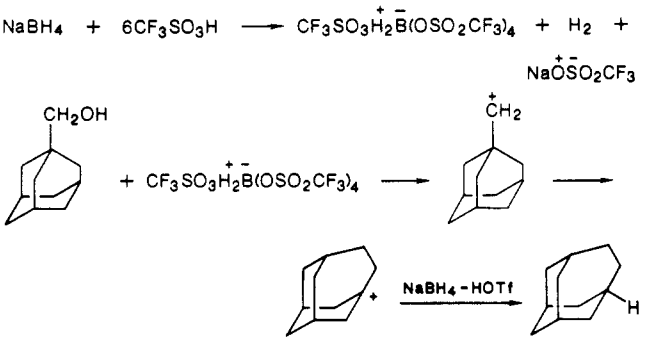
Table I



R	R′	yield,[a] % from RCH_2OH	yield,[a] % from RCOOH
 (a)	 (a)	97	96
 (b)	 (b)	98	98
 (c)	 (c)	98	98
 (d)	 (d)	96	96
 (e)	 (e)	96	95
 (f)	(f)	95	95

[a] Isolated yield.

Scheme I



Since carboxylic acids can be easily reduced to the corresponding methyl alcohols with complex hydrides or with BH_3–THF complex, we found that ring-expanded hydrocarbons can also be obtained directly from the appropriate polycyclic carboxylic acid precursors using the $NaBH_4$–HOTf system. The results (Table I) show that the ring-homologated polycyclic hydrocarbons can be conveniently obtained in near quantitative yield from both the appropriate methyl alcohol or carboxylic acids.

All the ring-homologated hydrocarbons in the present investigation were prepared in etheral solvent. When reactions of the methyl alcohol or carboxylic acid precursors (Table I) were carried out in a lower polarity solvent such as Freon-113, further reductive isomerization can take place. Homoadamantane for example gives methyladamantanes (with 1-methyladamantane predominating). In the reaction with excess CF_3SO_3H, $NaBH_4$ gives conjugate-Brønsted protic superacid $CF_3SO_3H_2^+B(OSO_2CF_3)_4^-$[8] via intermediately formed $B(OSO_2CF_3)_3$.[9] The in situ generated protic superacid similarly to $B(OSO_2CF_3)_3$ itself ionizes the cycloalkylmethyl alcohols such as 1-adamantanemethyl alcohol (Scheme I) to form via

(1) Synthetic Methods and Reactions. 136. Part 135, see: Olah, G. A.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Org. Chem.*, preceding paper in this issue.

(2) (a) Gutsche, C. D.; Redmore, D. *Carbocyclic Ring Expansion Reactions*; Academic Press: New York, 1968. (b) Schleyer, P. v. R.; Funke, E.; Liggero, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 3965. (c) Nordlander, J. E.; Wu, F.; Jindal, S. P.; Hamilton, J. B. *J. Am. Chem. Soc.* **1969**, *91*, 3962. (d) Nordlander, J. E.; Jindal, S. P.; Schleyer, P. v. R.; Fort, R. C., Jr.; Harper, J. J.; Nicholas, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 4475.

(3) McElrath, E. N.; Fritz, R. M.; Brown, C.; LeGall, C. Y.; Duke, R. B. *J. Org. Chem.* **1960**, *25*, 2195.

(4) (a) Winstein, S.; Morse, B. K.; Grunwald, E.; Schreiber, K. C.; Corse, J. *J. Am. Chem. Soc.* **1952**, *74*, 1113. (b) Roberts, D. D. *J. Org. Chem.* **1964**, *29*, 294. (c) Cox, E. F.; Caserio, M. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 2719.

(5) (a) Bly, R. S., Jr.; Dryden, H. S., Jr. *Chem. Ind. (London)* **1959**, 1287. (b) Wilcox, C. F., Jr.; Chibber, S. S. *J. Org. Chem.* **1962**, *27*, 2332. Leny, G. Ph.D. Thesis, Univerisity of Paris, France, 1964.

(6) (a) Dauben, W. G.; Rogan, J. B. *J. Am. Chem. Soc.* **1957**, *79*, 5002. (b) Wiberg, K. B., Lowry, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188. (c) Bixler, R. L.; Niemann, C. *J. Org. Chem.* **1958**, *23*, 742.

(7) Olah, G. A.; Wu, A.; Farooq, O. *J. Org. Chem.*, in press.

(8) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1984**, *49*, 4591.

(9) Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Olah, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2560.

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neighboring C–C bond insertion the desired ring-expanded carbenium ion, which is then reduced to give the hydrocarbon product.

Experimental Section

1-Adamantanemethyl alcohol, 1-adamantanecarboxylic acid, 3-noradamantanecarboxylic acid, cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, and neopentylcarboxylic acid and alcohol were available from Aldrich. 3-Noradamantanemethyl alcohol was prepared from the corresponding carboxylic acid by reduction with $LiAlH_4$. 1-Norbornanemethyl alcohol was prepared by reduction of the corresponding carboxylic acid prepared according to literature procedure.[10]

Sodium borohydride (Aldrich) and trifluoromethanesulfonic (triflic) acid (3 M) were commercially available. The latter was distilled prior to use. Diethyl ether was dried over sodium under reflux prior to use.

Gas chromatographic analysis was carried out on a Varian (Model 3700) Gas Chromatograph with use of a quartz silica capillary column coated with DB-1. Mass spectroscopic analysis was performed on a Finnigan Mat Model 700 GC–MS spectrometer. NMR spectra were recorded on a Varian-200 MHz (VXR-200) superconducting NMR spectrometer.

General Method of Reductive Isomerization of Cycloalkylmethyl Alcohols and Carboxylic Acids to Homologated Hydrocarbons. To a well-stirred heterogeneous mixture of 1.0 g (6.02 mmol) of 1-adamantane methyl alcohol in diethyl ether and 0.46 g (12.04 mmol) of $NaBH_4$ taken in a three-necked flask cooled to −78 °C under dry nitrogen flow was added 6.4 mL (72.24 mmol) of triflic acid dropwise over a period of $^1/_2$ h. After the addition of acid the reaction mixture was slowly warmed up to room temperature at which stirring was continued for an additional 2 h. Quenching the reaction mixture in ice–bicarbonate followed by extraction in methylene chloride, drying the reaction solution over anhydrous $MgSO_4$, and removal of solvent afforded crude homoadamantane, which subsequently was purified by column chromatography (silica gel/hexane). Reduction of all other cycloalkylmethyl alcohols and carboxylic acids was similarly carried out except that in the case of carboxylic acids higher ratio of carboxylic acid:$NaBH_4$:HOTf ≈ 1:3:18 was used.

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

Registry No. 1-Adamantanemethyl alcohol, 770-71-8; 1-adamantanecarboxylic acid, 828-51-3; homoadamantane, 281-46-9; 3-noradamantanemethyl alcohol, 17471-43-1; 3-noradamantanecarboxylic acid, 16200-53-6; adamantane, 281-23-2; 1-norbornanemethyl alcohol, 2064-02-0; 1-norbornanecarboxylic acid, 18720-30-4; bicyclo[2.2.2]octane, 280-33-1; cyclobutanemethyl alcohol, 4415-82-1; cyclobutanecarboxylic acid, 3721-95-7; cyclopentane, 287-92-3; cyclopentanemethyl alcohol, 3637-61-4; cyclopentanecarboxylic acid, 3400-45-1; cyclohexane, 110-82-7; neopentylmethyl alcohol, 75-84-3; neopentylcarboxylic acid, 75-98-9; 2-methylbutane, 281-23-2; 1-methyladamantane, 768-91-2.

(10) Bixler, R. L.; Niemann, C. *J. Org. Chem.* **1958**, *23*, 7421.

Rate Enhancement of Nucleophilic Substitution Reactions in Phosphate Esters. Influence of Conformational Transmission on the Rate of Solvolysis of Alkyl Diphenylphosphinates

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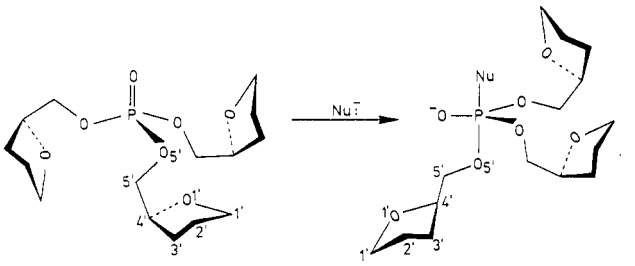
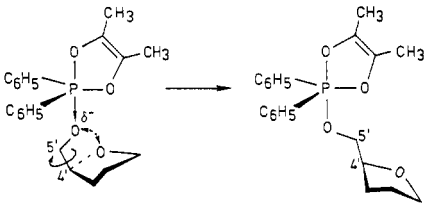
Introduction

The concept of conformational transmission in pentacoordinated (P(V)) trigonal-bipyramidal (TBP) phosphorus compounds has received considerable attention during the past few years.[1] In these studies it has been shown that phosphorus compounds possessing the common POCCO fragment are subject to a conformational rearrangement around the central C–C linkage of this fragment if the coordination state of the phosphorus atom is increased from four (P(IV)) to five (P(V)-TBP).

Scheme I



Scheme II



The incorporation of an additional ligand in a P(IV) geometry causes a considerable change in the intrinsic chemical bonding properties of the central phosphorus atom,[2] resulting in an enhanced electron density on the axially located oxygens linked directly to phosphorus. In its turn, this effect is transmitted into a conformational change around the central C–C linkage of the axially located OCCO moiety. The actual conformation of the OCCO atomic sequence is changed from the well-known gauche orientation in the P(IV) state to a pronounced anti orientation of the two vicinally orientated oxygen atoms in the P(V)-TBP state. The result of this conformational change is visualized in Scheme I.

In recent ^{13}C NMR variable-temperature studies on a series of stable oxyphosphoranes, the impact of the conformational transmission effect on the rate of intramolecular ligand reorganization in pentacoordinated oxyphosphoranes has been described.[3] In these studies it was demonstrated that pseudorotation in P(V)-TBP compounds exhibiting the conformational transmission effect is 2–4 times faster as compared to that in their counterparts in which this effect is absent. It was shown that, with the acceptance of the intermediacy of a square-pyramidal (SP) transition state in controlling the pseudorotation rate, conformational transmission in the basal ligands of the SP is responsible for the lowering of the free energy barrier of the pseudorotation process.

(1) (a) Koole, L. H.; Lanters, E. J.; Buck, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5451. (b) Koole, L. H.; van Kooyk, R. J. L.; Buck, H. M. *J. Am. Chem. Soc.* **1985**, *107*, 4032. (c) Meulendijks, G. H. W. M.; van Es, W.; de Haan, J. W.; Buck, H. M. *Eur. J. Biochem.* **1986**, *157*, 421. (d) De Vries, N. K.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 150. (e) Van Genderen, M. H. P.; Koole, L. H.; Olde Scheper, B. C. C. M.; van de Ven, L. J. M.; Buck, H. M. *Phosphorus Sulfur* **1987**, *32*, 173. (f) De Vries, N. K.; Buck, H. M. *Phosphorus Sulfur* **1987**, *31*, 267. (g) Van Genderen, M. H. P.; Buck, H. M. *Magn. Reson. Chem.* **1987**, *25*, 872.

(2) Holmes, R. R. *Pentacoordinated Phosphorus*; American Chemical Society: Washington, 1980; Vols. 1 and 2 (ACS Monograph No. 175 and 176).

(3) (a) De Keijzer, A. E. H.; Koole, L. H.; Buck, H. M. *J. Am. Chem. Soc.* **1988**, *110*, 5995, (b) De Keijzer, A. E. H.; Buck, H. M. *J. Org. Chem.* **1988**, *53*, 4827.

0022-3263/89/1954-1453$01.50/0