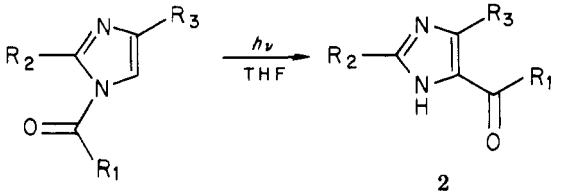
Table I. Photolysis of *N*-Acyl-2-alkylimidazoles[a]



1 2

compd	R_1	R_2	R_3	yield, %	mp, °C (solvent)[b]
2a	CH_3	CH_3	H	48	127-129 (A)
2b	CH_3	CH_3	CH_3	41	87-88 (B)
2c	CH_3	C_2H_5	H	50	120-121 (C)
2d	CH_3	C_3H_7-*n*	H	45	112-113 (C)
2e	CH_3	$CH_2C_6H_5$	H	30	154-157 (C)
2f	CH_3	$(CH_2)_2C_6H_5$	H	34	130-132 (C)
2g	CH_3	$(CH_2)_3C_6H_5$	H	48	90-91 (C)
2h	C_2H_5	CH_3	H	45	158-159 (A)
2i	CH_3	H	CH_3	39	140-142 (lit.[5] 146-149) (C)

[a] Satisfactory ^1H NMR data and analytical values (±0.4% for C, H, and N) were reported for all compounds in the table. [b] Recrystallization solvents: A, acetonitrile; B, isopropyl ether; C, ethyl acetate.

The yields in this reaction are diminished by the fact that a side reaction in this procedure is cleavage of the *N*-acetyl bond, thereby generating the original 2-substituted imidazole. This byproduct poses no severe difficulty in that it is readily removed by chromatography. Although most of the examples are straightforward, a few deserve special comment. Disubstituted imidazoles should prove to be suitable substrates as exemplified by **2b**. Example **2h** is consistent with Iwasaki's results in that other alkyl (and presumably aryl) ketones can also be utilized in this procedure. Finally, in example **2i**, only one isomer was isolated despite previous precedence which would lead one to expect formation of the 2-acetylimidazoles as well.[6]

This method may be limited to alkylimidazoles and aralkylimidazoles since, when this reaction was attempted with 1-acetylimidazole-2-carboxaldehyde, a myriad of products were detected by TLC. It is unclear as to whether this is due to the electron-withdrawing effect of the aldehyde or to complications involving homolysis of its carbonyl. Despite this drawback, this method should prove to be of value. The ease of operation, as well as the availability of a number of 2-substituted imidazoles either by classical[7] or modern methods,[1,2] make this approach attractive for the synthesis of 1*H*-5-acetyl-2-alkylimidazoles.

Experimental Section[8]

N-Acetylation of Imidazoles. The method reported by Iwasaki[4] was followed by using a 50/50 chloroform–toluene solution as the solvent in place of benzene. The following procedure is typical. A solution of 9.6 g (0.10 mol) of 2,4-dimethylimidazole in 50 mL of chloroform and 50 mL of toluene was stirred at room temperature, and 3.6 mL (0.05 mol) of acetyl chloride was added over a 1-min period. After the mixture was stirred at room temperature for 1 h, the 2,4-dimethylimidazole hydrochloride which precipitated was removed by filtration. Concentration of the filtrate left 5.9 g (100%) of 1-acetyl-2,4-dimethylimidazole as a crystalline solid: NMR ($CDCl_3$) δ 7.00 (s, 1 H), 2.68 (s, 3 H), 2.57 (s, 3 H), 2.21 (s, 3 H). This material was used directly in the photolysis reaction.

In general, the yields of the acylations were >75%. The crude product was analyzed by NMR and then used directly without further purification.

Photolysis of 1-Acetylimidazoles. A solution of 5–6 g of the *N*-acetylimidazole in 600 mL of dry THF was placed in a quartz vessel and photolyzed under nitrogen in a Rayonet reactor at 254 nm for 24 h. The mixture was then concentrated, and the residue was chromatographed over 25 times its weight of silica gel with 19:1 chloroform–methanol as the eluant. The product, which proved less polar than the imidazole byproduct, was of sufficient purity to use directly, although further purification can be achieved by recrystallization. A summary of the physical data of **2a–i** appears in Table I.

Acknowledgment. We are grateful to Dr. M. S. Kellogg and Mr. T. Blizniak for their helpful suggestions.

Registry No. **1a**, 3720-89-6; **1b**, 52757-00-3; **1c**, 84694-85-9; **1d**, 84694-86-0; **1e**, 84694-87-1; **1f**, 84694-88-2; **1g**, 84694-89-3; **1h**, 84694-90-6; **1i**, 61553-60-4; **2a**, 78210-66-9; **2b**, 56536-44-8; **2c**, 84694-91-7; **2d**, 84694-92-8; **2e**, 84694-93-9; **2f**, 84694-94-0; **2g**, 84694-95-1; **2h**, 84694-96-2; **2i**, 23328-91-8; 2-methylimidazole, 693-98-1; 2,4-dimethylimidazole, 930-62-1; 2-ethylimidazole, 1072-62-4; 2-*n*-propylimidazole, 50995-95-4; 2-benzylimidazole, 14700-62-0; 2-phenethylimidazole, 84694-97-3; 2-(3-phenylpropyl)imidazole, 13682-31-0; 4-methylimidazole, 822-36-6.

(6) It is possible that <5% of this material is formed, but if so, it was not detected.

(7) For example, 2-benzyl-, 2-phenethyl-, and 2-(3-phenylpropyl)-imidazole were all prepared by using the method of: Lawson, J. K. *J. Am. Chem. Soc.* **1953**, *75*, 3398.

(8) ^1H NMR spectra were obtained on a Varian T-60 spectrometer. Melting points are uncorrected and were obtained in open capillaries on a Thomas-Hoover melting point apparatus. Solvents and reagents were commercially available unless otherwise noted and were used directly. Tetrahydrofuran (THF) was dried over 4A molecular sieves before use.

π Route to 3-Substituted Noriceanes

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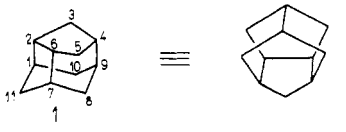
Received June 18, 1982

Noriceane[1] (1) is an interesting rigid and symmetrical



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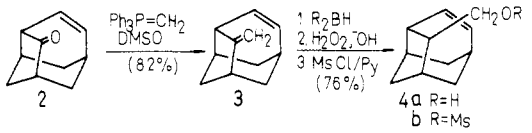
molecule, consisting of two cyclopentane and three cyclo-

0022-3263/83/1948-0898$01.50/0

Scheme I



hexane rings, two in the non-twist-boat and one in the chair conformation. It is more strained by 11 kcal/mol[2,3] than iceane,[4] from which it can be formally derived by replacement of a methano bridge with a direct bridgehead–bridgehead bond.

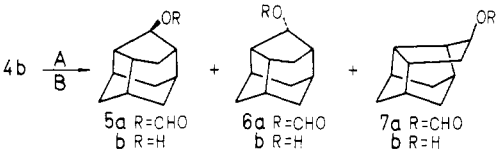
The only synthetic approach to the noriceane system has been through highly strained 3,5-didehydronoriceane, available by a photochemically induced intramolecular [2 + 2] cycloaddition of tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene.[5] Catalytic hydrogenolysis of 3,5-didehydronoriceane afforded the parent hydrocarbon, noriceane (**1**),[5] while oxymercuration followed by sodium borohydride reduction yielded 3-*endo*-noriceanol.[6] Acetolysis of the tosylate derived from this alcohol gave a mixture of 3-*exo*-acetoxynoriceane, 10-*exo*-acetoxy-2,4-ethanonoradamantane, and 2,4-ethenonoradamantane.[7] Oxidation of 3,5-didehydronoriceane with thallium(III) or lead(IV) acetate produced mixtures of the 3,5-diacetoxynoriceanes and 10,11-diacetoxy-2,4-ethanonoradamantane,[6] while bromination as well as iodination yielded mixtures of the corresponding 3,5-dihalogenonoriceanes and 10,11-dihalogeno-2,4-ethanonoradamantanes.[8]

In this work we have studied a new, more direct approach to the noriceane system involving the intramolecular nucleophilic addition of the protoadamantene double bond onto the ionizing 2-*endo*-[(sulfonyloxy)methyl] center.[9] This π-bond-assisted ionization process was expected to lead to the 3-noriceanyl cation and its derivatives.[10,11]

Results and Discussion

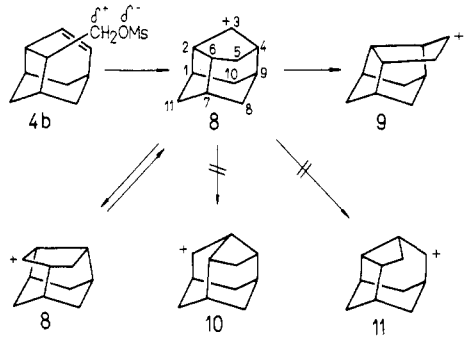
The starting material, 2-*endo*-[(mesyloxy)methyl]-protoadamantene (**4b**), was prepared in 62% overall yield from 2-protoadamantenone (**2**, Scheme I). We obtained this ketone in 20% yield by thermal cyclization of 7-(allyloxy)cycloheptatriene[12] using a modified procedure for isolation; the products (2- and 10-protoadamantenone) were not separated directly but were reduced first to alcohols, which were separated easily by a single column chromatography run and then reoxidized to the ketones.

Scheme II[a]



[a] A: HCOOH, 55 °C, 5 h. B: 65% aqueous diglyme/Na_2CO_3, reflux, 12 h.

Scheme III



This procedure was superior in our hands to direct separations of 2- and 10-protoadamantenones by either column chromatography or preparative GC. More than 80% of **2** was isolated from the product mixture by using this procedure, while only half of this amount could be isolated by the direct separations in a reasonable time. Ketone **2** was readily converted (82%) to 2-methyleneprotoadamantene (**3**) by Corey's modification[13] of the Wittig reaction. Selective hydroboration of diene **3** with disiamylborane followed by oxidation of the resulting organoborane with alkaline hydrogen peroxide afforded 80% of 2-*endo*-(hydroxymethyl)protoadamantene (**4a**). Alcohol **4a** was esterified (95%) to mesylate **4b** by the standard procedure.[4b]

Mesylate **4b** was solvolyzed in two media: 98% formic acid at 55 °C and in 65% aqueous diglyme in the presence of sodium carbonate at reflux (Scheme II). Formolysis yielded 78% of three formates, **5a–7a**, in the ratio 1:1:5 (by quantitative ^{13}C NMR). The formates were reduced with $LiAlH_4$ to the corresponding alcohols, **5b–7b** (1:1:5), which were readily separated by column chromatography on silica gel. Hydrolysis of mesylate **4b** in 65% aqueous diglyme afforded 70% of a 1:1.3:1.4 mixture of the same three alcohols (**5b–7b**), which were obtained from the formates, and 13% of an olefin. Alcohols **5b–7b** were identified as 3-*exo*- and 3-*endo*-noriceanol and 10-*exo*-2,4-ethanonoradamantanol, respectively, by comparing their ^{13}C NMR, ^{1}H NMR, IR, and mass spectra with the spectral data reported[6,7] for these compounds. The olefin was shown to be 2,4-ethenonoradamantane.[7,14] For unambiguous confirmation of the structures of the alcohols they were oxidized to ketones. Alcohols **5b** and **6b** produced the same ketone, 3-noriceanone, which was subsequently reduced to noriceane (**1**) by the Wolff–Kishner reaction.[6] Alcohol **7b** yielded 2,4-ethano-10-noradamantanone.[7]

The mechanism probably involves intramolecular nucleophilic addition of the protoadamantene double bond onto the ionizing 2-*endo*-[(mesyloxy)methyl] center leading to the 3-noriceanyl cation (**8**, Scheme III), which rearranges subsequently by a 1,2-C,C shift to the thermodynamically

(1) Norwurtzitane or tetracyclo[5.3.1.0^{2,6}.0^{4,9}]undecane.
(2) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(3) Godleski, S. A.; Schleyer, P. v. R.; Osawa, E. *J. Chem. Soc., Chem. Commun.* **1976**, 38. Godleski, S. A.; Schleyer, P. v. R.; Osawa, E.; Inamoto, Y.; Fujikura, Y. *J. Org. Chem.* **1976**, *41*, 2596.
(4) (a) Cupas, C. A.; Hodakowski, L. *J. Am. Chem. Soc.* **1974**, *96*, 4668. (b) Tobler, H.; Klaus, R. O.; Ganter, C. *Helv. Chim. Acta* **1975**, *58*, 1455. (c) Hamon, D. P. G.; Taylor, G. F. *Tetrahedron Lett.* **1975**, 155.
(5) Katsushima, T.; Yamaguchi, R.; Kawanisi, M. *J. Chem. Soc., Chem. Commun.* **1975**, 692.
(6) Katsushima, T.; Yamaguchi, R.; Iemura, S.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3318.
(7) Katsushima, T.; Yamaguchi, R.; Kawanisi, M.; Osawa, E. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3313.
(8) Katsushima, T.; Yamaguchi, R.; Iemura, S.; Kawanisi, M. *J. Chem. Soc., Chem. Commun.* **1980**, 133. Katsushima, T.; Yamaguchi, R.; Iemura, S.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3324.
(9) Ganter and co-workers have used an analogous approach for the synthesis of iceane (wurtzitane).[4b]
(10) This reaction could theoretically lead also to the considerably more strained 2,4-methano-5-protoadamantyl cation 11.
(11) Such cyclization processes were classified originally by Winstein as the π-route cyclizations (Winstein, S.; Carter, P. *J. Am. Chem. Soc.* **1961**, *83*, 4485).
(12) Cupas, C. A.; Schumann, W.; Heyd, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 3237.
(13) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 866.
(14) Katshushima, T.; Yamaguchi, R.; Kawanisi, M.; Osawa, E. *J. Chem. Soc., Chem. Commun.* **1976**, 39.

more stable 2,4-ethano-10-noradamantyl cation (**9**).[15] Cation **8** could theoretically isomerize by 1,2-C,C shifts to four species: **8** (degenerate isomerization), **9**, 2,4-methano-10-adamantyl cation (**10**), and 2,4-methano-5-protoadamantyl cation (**11**). These isomerizations would involve migrations of the C(1)–C(2), C(4)–C(9), C(2)–C(6), and C(4)–C(5) bonds, respectively. However, cations **10** and **11** should be considerably less stable than **9**,[3,15a] and, in addition, the vacant C(3)$^+$ orbital in **8** is unfavorably arranged for the bond migrations which would lead to these two cations. Therefore, the isomerization of **8** to **9** is highly preferred.[16]

Cations **8** and **9** react with water and formic acid, yielding the corresponding alcohols and formates. Since water is a stronger nucleophile than formic acid, formation of the 3-substituted noriceanes is favored in 65% aqueous diglyme, while the 10-substituted 2,4-ethanonoradamantane derivative is formed preferably in formic acid. Therefore, the noriceane/2,4-ethanonoradamantane product ratio can be controlled by choosing the appropriate solvent.[17]

The 3-noriceanyl cation, formed in the acetolysis of 3-*endo*-noriceanyl tosylate, yielded exclusively the 3-exo-substituted noriceane product owing to a severe steric hindrance at the endo side.[7] Formation of both 3-*exo*- and 3-*endo*-noriceane products in the formolysis and hydrolysis of mesylate **4b** can be explained by different conformations[18] of the 3-noriceanyl cation originated from mesylate **4b** and 3-*endo*-noriceanyl tosylate. In addition, the sulfonate counterion location in the intermediary ion pair should be different in each case. Both these arguments are in good agreement with the higher ratio of the exo to endo products obtained in the less nucleophilic and more polar solvent, formic acid. Exclusive formation of the 10-exo-substituted 2,4-ethanonoradamantane derivatives in the formolysis and hydrolysis of mesylate **4b**, as well as in the acetolysis[7] of 3-noriceanyl tosylate, may be interpreted in terms of a steric hindrance at the endo side of the 2,4-ethano-10-noradamantyl cation (**9**).

In summary, hydrolysis of 2-*endo*-[(mesyloxy)-methyl]protoadamantene (**4b**) in 65% aqueous diglyme yielded 70% of a 1:1.3:1.4 mixture of 3-*exo*- and 3-*endo*-noriceanol (**5b**, **6b**) and 10-*exo*-2,4-ethanonoradamantanol (**7b**), which were readily separated. Formolysis of **4b** afforded 78% of the three corresponding formates in the ratio 1:1:5. Consequently, the π-route cyclization of **4b** appears to be a method of choice for preparation of 3-exo- and 3-endo-substituted noriceanes, as well as 10-exo-substituted 2,4-ethanonoradamantanes.

Experimental Section

Purity of all compounds was controlled by GC. ^{13}C NMR and ^{1}H NMR spectra were taken on a JEOL FX100 and/or a JEOL FX90Q spectrometer, IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer, and mass spectra were obtained on a Kratos MS25 mass spectrometer. The quantitative analyses with ^{13}C NMR were performed by a combination of long pulse intervals (120 s) to assure complete relaxation of all ^{13}C nuclei in the products and a gated decoupling, which eliminated the Overhauser enhancements.[19] GC analyses were carried out on a Varian Aerograph 940 or 1800 gas chromatograph on stainless-steel analytical (150 cm, 2 mm i.d.) or capillary columns (10 m, 0.5 mm i.d.). Melting points were determined in sealed capillary tubes completely immersed in oil by using a Thiele apparatus and are uncorrected.

2-Protoadamantenone (2) was obtained in 20% overall yield by pyrolysis of 7-(allyloxy)cycloheptatriene[12] (21 g, 140 mmol) at 200 °C for 24 h and with the following procedure for isolation. The crude pyrolysis product was steam distilled to give a 1:1:0.2 mixture (11 g) of 2- and 10-protoadamantenone and a byproduct.[20] The mixture of the ketones was reduced with $LiAlH_4$ (1.5 g, 38 mmol) in dry ether (150 mL) at reflux for 6 h. The excess of $LiAlH_4$ was destroyed with wet ether (100 mL) followed by water. The ether solution was dried ($MgSO_4$) and the solvent evaporated, yielding a 1:1:0.2 mixture (10.5 g) of 2- and 10-protoadamantenol and the byproduct.[20] The mixture of the alcohols was readily separated by column chromatography on neutral alumina (activity II/III) with pentane–ether (9/1 to 1/1) as the eluent. The order of elution was as follows: the byproduct, 2-protoadamantenol, and 10-protoadamantenol. Pure 2-protoadamantenol (4.3 g, 29 mmol) was oxidized with pyridinium chlorochromate (9.4 g, 44 mmol) in methylene chloride (100 mL). The reaction mixture was stirred at room temperature for 5 h, and ether (300 mL) was added. The resulting solution was decanted off the solid material, washed with 10% sodium hydroxide solution (3 × 200 mL), 5% hydrochloric acid solution (2 × 200 mL), and water (2 × 200 mL), and dried ($MgSO_4$). Evaporation of the solvent yielded 2-protoadamantenone (**2**): 4.0 g (95%; ≥97% pure by GC, DEGS, 130 °C); ^{13}C NMR ($CDCl_3$) δ 212.8 (s, 1 C), 142.0 (d, 1 C), 127.0 (d, 1 C), 49.9 (d, 1 C), 48.7 (d, 1 C), 37.1 (t, 1 C), 37.0 (t, 1 C), 34.9 (t, 1 C), 31.5 (d, 1 C), 31.3 (d, 1 C). The ^{1}H NMR, IR, and mass spectral data are in complete agreement with those reported previously.[12]

2-Methyleneprotoadamantene (3). A dry nitrogen atmosphere was maintained during the entire preparation. Sodium hydride (1.92 g, 40 mmol, as a 50% dispersion in mineral oil) was washed in the reaction flask with several portions of pentane to remove the mineral oil. Dimethyl sulfoxide (20 mL, freshly distilled from CaH_2) was added, and the resulting mixture was stirred for 1 h at 75–80 °C. The mixture was then cooled to room temperature, and a warm solution of methyltriphenylphosphonium iodide (16.16 g, 40 mmol, dried overnight over P_2O_5 in vacuo) in dry dimethyl sulfoxide (30 mL) was added dropwise over a period of 30 min. To the resulting bright orange-green mixture was added a solution of **2** (2.96 g, 20 mmol) in dry dimethyl sulfoxide (35 mL). The reaction mixture was stirred at 58–60 °C for 4 h, cooled to room temperature, and poured into water (200 mL). The resulting mixture was extracted with pentane (3 × 100 mL), and the combined extracts were dried ($MgSO_4$). The solvent was evaporated, and the crude product was purified by column chromatography on neutral alumina (activity I) with pentane as the eluent to give **3**: 2.4 g (82%; ≥98% pure by GC, DEGS, 90 °C); ^{13}C NMR ($CDCl_3$) δ 159.3, 137.2, 133.4, 99.6, 46.8, 43.2, 42.2, 37.7, 33.9, 33.7, 32.0; ^{1}H NMR ($CDCl_3$) δ 6.4–5.9 (m, 2 H), 4.6–4.3 (m, 2 H), 3.3–1.3 (complex m, 10 H, maxima at δ 1.7 and 1.75); IR (KBr) 3060 (w), 3030 (m), 2920 (s), 2860 (s), 1660 (m), 1630 (w), 1460 (w), 865 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{11}H_{14}$: C, 90.34; H, 9.66. Found: C, 90.05; H, 9.58.

2-*endo*-(Hydroxymethyl)protoadamantene (4a). To a solution of $NaBH_4$ (765 mg, 20.25 mmol) and 2-methyl-2-butene (3.78 g, 54 mmol) in diglyme (20 mL, freshly distilled from $LiAlH_4$ in vacuo), stirred at 0 °C in a dry nitrogen atmosphere, was added boron trifloride etherate (3.36 mL, ca. 27 mmol, freshly distilled from CaH_2) dropwise in a period of 5 min. The resulting mixture was stirred at room temperature for 30 min and then cooled to −5 °C. A solution of **3** (1.32 g, 9 mmol) in dry diglyme (6 mL) was added in one portion, the reaction mixture was stirred for 15 min at 0 °C, and then 3 M sodium hydroxide solution (18 mL) was added rapidly followed by slow dropwise addition of 30%

(15) (a) Since all cations in question are secondary, their relative thermodynamic stabilities should roughly parallel the relative stabilities of the corresponding hydrocarbons. (b) Empirical force field calculations predicted 2,4-ethanonoradamantane to be 3 (Allinger force field) or 6 kcal/mol (Engler force field) more stable than noriceane.[3]

(16) Degenerate rearrangement of **8** probably also takes place.

(17) Substituted 2,4-ethanonoradamantane derivatives are not readily available. 2,4-Ethano-10-noradamantanone was prepared (in a mixture with 2,9-ethano-10-noradamantanone) by the copper-catalyzed decomposition of 2-*endo*-noradamantyl methyl diazoketone followed by intramolecular C–H insertion of the resulting oxocarbene.[3] The only other compound used as a precursor for 2,4-ethanonoradamantanes has been 3,5-didehydronoriceane.[6–8,14]

(18) Cf.: Farcasiu, D.; Kascheres, C.; Schwartz, L. H. *J. Am. Chem. Soc.* **1972**, *94*, 180.

(19) Shoolery, J. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 79.

(20) 3-Oxatricyclo[5.3.1.0^{4,10}]undeca-5,8-diene.[12]

hydrogen peroxide (18 mL). After an additional 15-min period of being stirred at 0 °C, the reaction mixture was extracted with ether (3 × 50 mL). The combined extracts were washed with water (3 × 100 mL) and dried ($MgSO_4$). The solvent was evaporated, and the crude product was purified by column chromatography on neutral alumina (activity II/III) with 1:1 pentane–ether mixture as the eluent, followed by sublimation to yield **4a**: 1.18 g (80%; ≥98% pure by GC, DEGS, 160 °C); mp 129–131 °C; ^{13}C NMR ($CDCl_3$) δ 139.4 (d, 1 C), 129.1 (d, 1 C), 62.6 (t, 1 C), 49.3 (d, 1 C), 43.2 (t, 1 C), 39.4 (d, 1 C), 39.2 (t, 1 C), 37.8 (d, 1 C), 34.1 (d, 1 C), 32.5 (d, 1 C), 26.5 (t, 1 C); ^1H NMR ($CDCl_3$) δ 6.4 (dd, $J_1 \simeq J_2 \simeq 8.5$ Hz, 1 H), 5.8 (dd, $J_1 = 8.5$ Hz, $J_2 = 6.5$ Hz, 1 H), 3.7 (dd, $J_1 = 7$ Hz, $J_2 = 3.5$ Hz, 2 H), 3.0–1.1 (complex m, 12 H, maximum at δ 1.5); IR (KBr) 3320 (s), 3025 (m), 2920 (s), 2860 (s), 1630 (w), 1465 (m), 1005 (s), 690 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 164 (M^+, 33), 135 (63), 115 (40), 91 (90), 79 (100). Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.83. Found: C, 80.40; H, 9.99.

2-*endo*-[(Mesyloxy)methyl]protoadamantene (4b). To a solution of **4a** (492 mg, 3 mmol) in dry pyridine (10 mL) stirred at −10 °C was added slowly mesyl chloride (435 mg, 3.8 mmol). The reaction mixture was stirred between −10 and 0 °C for 1 h and then poured onto ice (20 g). The resulting mixture was extracted with ether (3 × 20 mL). The combined extracts were washed with 5% hydrochloric acid solution (2 × 20 mL), saturated sodium bicarbonate solution (2 × 30 mL), and water (50 mL) and then dried ($MgSO_4$). Evaporation of the solvent yielded mesylate **4b** (690 mg, 95%), which was used without purification in the next step: ^{13}C NMR ($CDCl_3$) δ 140.5, 128.6, 71.0, 45.4, 42.9, 39.4, 38.9, 37.7, 37.0, 34.1, 32.3, 26.2; ^1H NMR ($CDCl_3$) δ 6.5 (dd, $J_1 \simeq J_2 \simeq 8$ Hz, 1 H), 5.8 (dd, $J_1 = 8$ Hz, $J_2 = 6.5$ Hz, 1 H), 4.3 (d, $J = 6.6$ Hz, 2 H), 3.0 (s, 3 H), 3.0–1.3 (complex m, 11 H, maximum at δ 1.5); IR (KBr) 3040 (m), 3030 (m), 2930 (s), 2870 (m), 2850 (m), 1660 (w), 1630 (w), 1470 (m), 1345 (s), 1330 (s), 1175 (s), 970 (s), 945 (s), 840 (s), 750 (m), 705 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.45; H, 7.49; S, 13.24. Found: C, 59.74; H, 7.61; S, 12.95.

Formolysis of 4b. A solution of mesylate **4b** (690 mg, 2.85 mmol) in 98% formic acid (30 mL) was stirred at 55 °C for 5 h, cooled to room temperature, and poured onto ice (50 g). The resulting mixture was extracted with ether (3 × 50 mL). The combined extracts were washed with saturated sodium bicarbonate solution (2 × 50 mL) and dried ($MgSO_4$). Removal of the solvent in vacuo yielded a mixture of formates (410–440 mg, 75–80%). The ^{13}C NMR spectrum indicated the presence of three components in the ratio 1:1:5. The crude mixture of formates was reduced with $LiAlH_4$ (110 mg, 3 mmol) in dry ether (50 mL) at reflux for 3 h. The excess of $LiAlH_4$ was destroyed with wet ether (20 mL) followed by water. The ether solution was decanted off and dried ($MgSO_4$). Evaporation of the solvent yielded a mixture of products (370 mg, 96%), which consisted of three alcohols in the ratio 1:1:5 (by quantitative ^{13}C NMR). The alcohols were separated by column chromatography on silica gel with ethyl acetate–cyclohexane (5/95 to 30/70) as the eluent, sublimed in vacuo, and identified by comparison of their ^{13}C NMR, ^1H NMR, IR, and mass spectra with the spectral data reported[6,7] for 3-*exo*- and 3-*endo*-noriceanol and 10-*exo*-2,4-ethanonoradamantanol. Yields: 3-*exo*-noriceanol (**5b**), 45 mg (≥95% pure by quantitative ^{13}C NMR, mp 244–246 °C), 3-*endo*-noriceanol (**6b**), 50 mg (≥95% pure by quantitative ^{13}C NMR; mp 268–271 °C), 10-*exo*-ethanonoradamantanol (**7b**), 230 mg (≥97% pure by GC, DEGS, 160 °C; mp 124–126 °C).

Hydrolysis of 4b in 65% Aqueous Diglyme. A solution of mesylate **4b** (690 mg, 2.85 mmol) and sodium carbonate (604 mg, 5.7 mmol) in 65% aqueous diglyme (40 mL) was stirred at reflux overnight, cooled to room temperature, and poured into water (100 mL). The resulting mixture was extracted with ether (3 × 50 mL); the extracts were combined, washed with water (3 × 70 mL), and dried ($MgSO_4$). Evaporation of the solvent yielded a mixture of products (392 mg, 84%), which consisted of 2,4-ethenonoradamantane[7,14] and three alcohols, **5b–7b**, in the ratio 1:1.3:1.4 (by quantitative ^{13}C NMR). The product mixture was separated by column chromatography as described above to give 2,4-ethenonoradamantane (56 mg), 3-*exo*-noriceanol (**5b**, 83 mg), 3-*endo*-noriceanol (**6b**, 105 mg), and 10-*exo*-2,4-ethanonoradamantanol (**7b**, 110 mg). ^{13}C NMR, ^1H NMR, IR, and mass spectra of these alcohols were identical with those of the products obtained in the formolysis of mesylate **4b** followed by the $LiAlH_4$ reduction.

Acknowledgment. This work was supported by a grant from the Research Council of the Republic of Croatia (SIZ II). We thank Drs. Z. Meić and N. Blažević for recording the ^{13}C NMR and mass spectra, respectively.

Registry No. **2**, 28673-75-8; **3**, 33566-64-2; **4a**, 84499-57-0; **4b**, 84499-58-1; **5a**, 84499-59-2; **5b**, 77419-08-0; **6a**, 84580-98-3; **6b**, 77480-47-8; **7a**, 84499-60-5; **7b**, 77419-11-5; 7-(allyloxy)cycloheptatriene, 28673-74-7; 10-protoadamantenone, 28673-76-9; 2-protoadamantenol, 84580-02-9; 10-protoadamantenol, 84580-97-2.

6-Methyl-6-boraspiro[2.5]octa-4,7-diene, a Boron Analogue of the Phenonium Ion[1]

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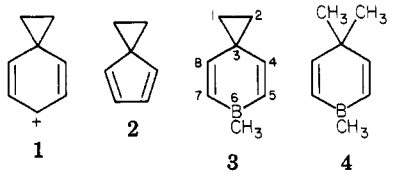
Received August 25, 1982

The phenonium ion (1) and related spiro-conjugated systems have been actively investigated for over 30 years.[2,3] Evidence (especially ^1H and ^{13}C NMR chemical shifts) show that the phenonium ion has extensive charge delocalization involving the cyclopropyl ring.[4] On the other hand, the question whether neutral molecules such as spiro[2.4]hepta-4,6-diene (**2**) involve similar spiro conjugation has been more controversial.[5,6] In this context we felt that an examination of **3**, the neutral boron analogue of the phenonium ion might be of interest. We now report on the synthesis of **3** and on a comparison of its ^1H, ^{13}C, and ^{11}B NMR spectra with the model compound **4**.



Both **3** and **4** were easily prepared from 1,1-dibutylstannacyclohexa-2,5-diene (**5**) via the alkylation-boron exchange scheme outlined above. Treating **5** with lithium diisopropylamide (LDA) in tetrahydrofuran produces the corresponding lithium stannacyclohexadienide which can be alkylated exclusively at the 4-position to afford **6**[7] or **8**,[8] respectively. Treating **6** with LDA affords **7**. Interestingly, further alkylation of **8** with methyl iodide is re-

(1) Based in part on the Ph.D. thesis of S.T.A.-O., The University of Michigan, 1982.
(2) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863; **1952**, *74*, 2129.
(3) For a review see: Lancelot, C. J.; Cram. D. J.; Schleyer, P. v. R. In Olah, G. A.; Schleyer, P. v. R. "Carbonium Ions"; Wiley: New York, 1972; Vol. 3, pp 1347–1483.
(4) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6877.
(5) (a) Clark, R. A.; Fiato, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 4736. (b) Gleiter, R.; Heilbronner, E., de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 1029. (c) Staley, S. W.; Howard, A. E.; Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Lind, G. *J. Am. Chem. Soc.* **1980**, *102*, 3639; **1981**, *103*, 2961.
(6) (a) Chiang, J. F.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 2885. (b) Schoeller, W. W.; Dahm, J. *Tetrahedron* **1973**, *29*, 3237. (c) Van De Ven, L. J. M.; De Haan, J. W. *J. Magn. Reson.* **1975**, *19*, 31.
(7) (a) Jutzi, P.; Baumgärtner, J. *J. Organomet. Chem.* **1978**, *148*, 247. (b) Ashe, A. J., III,; Abu-Orabi, S. T. *J. Org. Chem.*, in press.
(8) Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.

0022-3263/83/1948-0901$01.50/0