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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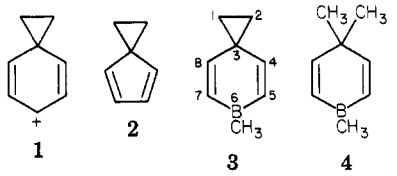
The phenonium ion (1) and related spiro-conjugated systems have been actively investigated for over 30 years.[2,3] Evidence (especially ^1H and ^{13}C NMR chemical shifts) show that the phenonium ion has extensive charge delocalization involving the cyclopropyl ring.[4] On the other hand, the question 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-

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(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.
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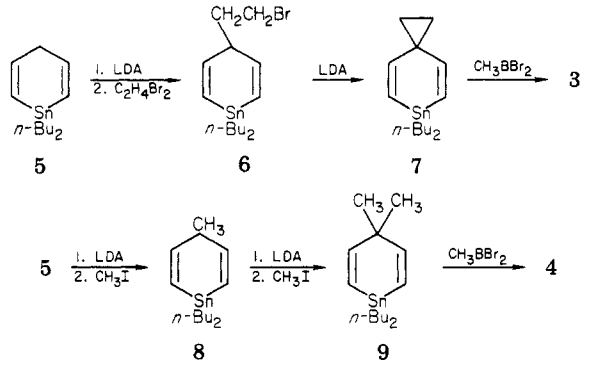
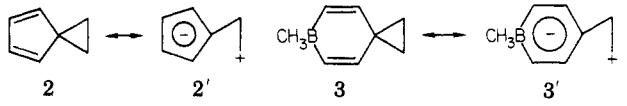


giospecific since only the indicated *gem*-dimethyl isomer **9** is obtained. Exchange of **7** and **9** with methylboron dibromide affords the desired bora dienes **3** and **4**, respectively.

Results and Discussion

The ^1H and ^{13}C NMR chemical shift values of **3**, **4**, **7**, and **9** are shown in Figure 1. Of particular note is the large downfield shift of the cyclopropyl protons of **3** compared with those of **7**. This low-field signal is comparable to that shown by **2** (δ 1.62),[5a,9] although considerably upfield from the signal of **1** (δ 4.80).[4] For compound **2** this shift has been associated with an electron donation from the cyclopropane ring, which in valence-bond terms involves structures such as **2'**.[5] Analogous borabenzene anion structures **3'** might be written for **3**.



Comparison of the ^1H chemical shifts of **3** with those of **4** shows that the $H_{5,7}$ signal of **3** is 0.35 ppm downfield while the $H_{4,8}$ signal is 0.35 ppm upfield of the corresponding signals of **4**. The spectra of stannanes **7** and **9** show that the signals for $H_{5,7}$ have essentially identical chemical shift values, while the signal of $H_{4,8}$ of **7** is 0.70 ppm upfield from that of **9**. Similar upfield shifts are observed in other cyclopropylcarbinyl systems.[10] The relatively smaller upfield shift of $H_{4,8}$ and the downfield shift of $H_{5,7}$ are consistent with a small diamagnetic ring current implied by structure **3'**.

It should be possible to gauge the importance of the electron donation indicated by structure **3'** from ^{13}C[11] and ^{11}B[12] chemical shift values, since these values are particularly sensitive to charge density effects. Electron donation suggests that the cyclopropane carbon signals should experience downfield shifts relative to suitable model compounds while the ring atoms should be shifted upfield. However, the cyclopropane signals of **3** are not unusual. The C_1 signal of **3** at δ 18.7 is not much different from the C_1 signal of **7** at δ 19.2 or that of C_2 of 1,1-dimethylcyclopropane at δ 17.0.[13] For comparison, the C_1 signal of **1** at δ 59.7 is far downfield.[4]

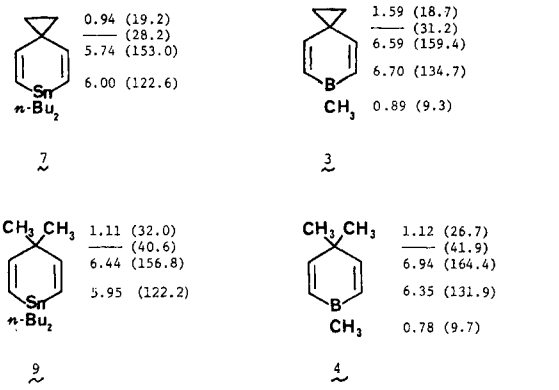


Figure 1. ^1H NMR and ^{13}C NMR (in parentheses) chemical shift values for compounds **3**, **4**, **7**, and **9**. The signals for the butyl groups of **7** and **9** have been omitted. For consistency the numbering system of **3** and **7** has been used for **4** and **9**.

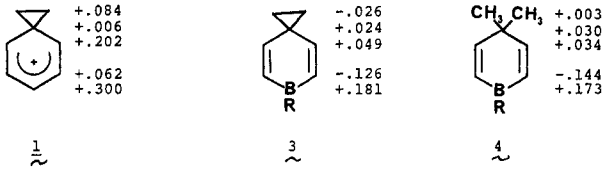


Figure 2. Total charges of **1**, **3**, and **4** (R = H) from STO-3G calculations. The total charges are the sum of σ and π charges on carbon together with the hydrogen contributions.

Comparison of the ^{11}B and ^{13}C NMR of the boradienyl rings of **3** and **4** shows only small differences. Thus the $C_{4,8}$ signal of **3** is 5.0 ppm upfield from that of **4**, while the signal of $C_{5,7}$ is 2.8 ppm downfield. Since similar although smaller differences are observed in the ^{13}C chemical shifts of **7** and **9**, only a portion of the differences between **3** and **4** can be ascribed to charge density effects. The ^{11}B chemical shift values of **3** and **4** are δ 56.5 and 58.3, respectively. Although the ^{11}B chemical shift of **3** is 1.8 ppm upfield of that of **4**, its value is well outside the range shown by borabenzene anions (δ 20–30).[14]

In summary, the small upfield NMR shifts shown by $C_{4,8}$ and B_6 of **3** are consistent with a small increase in electron density at these positions. However, the small magnitude of the difference between **3** and **4** is inconsistent with any large differences in electron distribution. In order to check this conclusion we have performed STO-3G calculations (without geometry optimization) on **1**, **3**, and **4**. Total charge densities are shown in Figure 2. There are no meaningful differences between **3** and **4**, although **1** does show charge delocalization onto the cyclopropane ring.

In conclusion, we find no evidence for extensive cyclopropyl conjugation in compound **3**. However, the ^1H NMR spectrum of **3** shows unusual chemical shift values similar to those observed for **2** and related systems.[5a,9] Recent structural and dipole moment data support a significant cyclopropyl conjugation for **2**.[5c] Perhaps similar data on **3** might also indicate cyclopropyl conjugation.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen or argon. Solvents were dried by using standard procedure and distilled immediately before use. The mass spectra were determined at a 70-eV ionizing voltage by using a Finnigan 4023 spectrometer. Combusion analyses were performed by the Spang Microanalytical Laboratory, Eagle Harbor, MI.

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NMR Spectra. All NMR spectra were obtained by using a Bruker WH-360 spectrometer. The spectra were measured from dilute $CDCl_3$ solutions with Me_4Si as an internal standard for ^1H and ^{13}C NMR spectra while external boron trifluoride etherate was used to calibrate the ^{11}B NMR spectra.

Where possible the ^1H NMR spectral assignments were made from the relative intensities of the signals. The assignment of the olefinic signals of **3** and **4** could be made since the protons trans to boron show signals broadened by coupling to ^{11}B, while the geminal protons do not.[15] The relative assignment of the olefinic protons of **7** and **9** was made from the ^{119}Sn satellite signals. The protons trans to tin are more strongly coupled than the geminal protons.[16] These olefinic signals show first-order AB patterns.

In the ^{13}C NMR spectra of **3** and **4** the relative assignment of the olefinic signals could be made since the signal for the α-carbons were broadened by ^{11}B quadrapole relaxation while those of the β-carbons were not.[17] The relative assignment of the olefinic signals of **7** and **9** was based on the larger value of $^1J(^{119}Sn^{13}C)$ than $^2J(^{119}Sn^{13}C)$.[16]

MO Calculations. The STO-3G calculations[18] were performed on an Amdahl 470-V8 computer by using a computer program by Binkley et al.[19] The geometries employed were as follows. Bond lengths (in angstroms) for **1** and **3**: C_1C_2, 1.494; C_2C_3, 1.546; C_3C_4, 1.54; C_4C_5, 1.36; C_5C_6 (C_5B_6), 1.54; all CH, 1.08; BH, 1.16. Bond angles for **1** and **3**: $C_1C_2C_3$, 61.1°; $C_1C_3C_2$, 57.7°; all internal angles in the six-membered rings, 120°. Bond lengths (in angstroms) for **4**: C_1C_3, 1.54; C_3C_4, 1.54; C_4C_5, 1.36; C_5B_6, 1.54; C_1H, 1.09; other CH, 1.08; BH, 1.16. Bond angles for **4**: $C_1C_3C_2$, 109.5°; all internal angles in the six-membered ring, 120°.

4,4-Dimethyl-1,1-dibutylstannacyclohexa-2,5-diene. A solution of lithium diisopropylamide was prepared by treating 3.1 g (31 mmol) of diisopropylamine in 30 mL of tetrahydrofuran with 9.6 mL of 2.13 N *n*-butyllithium in hexane. This was added to 6.4 g (20 mmol) of 4-methyl-1,1-dibutyl-1-stannacyclohexa-2,5-diene[8] in 25 mL of tetrahydrofuran at −78 °C. The color changed to a dark green-brown on addition. After 15 min addition of an excess (7 g) of methyl iodide discharged the color. The reaction mixture was added to 100 mL of water. After separation of the layers, the aqueous layer was extracted with 70 mL of ether. The combined organic fractions were washed with water and then dried over anhydrous sodium sulfate. Distillation afforded 2.6 g (39%) of product: bp 105 °C (0.5 torr); mass spectrum, *m/e* (relative intensity) 328 (0.43, M^+ for $C_{15}H_{28}{}^{120}Sn$), 271 (100, M − C_4H_9); ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 6 H), 0.94 (t, J = 7.8 Hz, 4 H), 1.11 (s, 6 H), 1.32 (m, 4 H), 1.50 (m, 4 H), 5.95 (d, J = 14.6 Hz, 2 H, $^2J(^{119}SnH)$ = 84 Hz), 6.44 (d, J = 14.5 Hz, 2 H, $^3J(^{119}SnH)$ = 123 Hz). ^{13}C NMR ($CDCl_3$) δ 10.53, 13.62, 26.89, 29.11 (C_4H_9), 31.98 (CH_3), 40.6 (C), 122.2 ($^1J(^{119}Sn^{13}C)$ = 391.85 Hz, CH), 156.8 (CH). Anal. Calcd for $C_{15}H_{28}Sn$: C, 55.06; H, 8.64. Found: C, 54.99; H, 8.72.

6,6-Dibutyl-6-stannaspiro[2.5]octa-4,7-diene. In the same manner, 1,1-dibutyl-4-(β-bromoethyl)stannacyclohexa-2,5-diene[7] (4.2 g, 10.3 mmol) was treated with 10.5 mmol of lithium diisopropylamide. The reaction mixture was allowed to stir at 25 °C for 2 h and then worked up as before. Distillation of the mixture gave the product: 2.10 g (62%); bp 90–95 °C (0.001 torr); Anal. Calcd for $C_{15}H_{26}Sn$: mass spectrum, *m/e* 269 (M^+ − C_4H_9); ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 6 H), 0.94 (s, 4 H), 0.96 (t, J = 7.9 Hz, 4 H), 1.33 (m, 4 H), 1.52 (m, 4 H), 5.74 (d, J = 14.3 Hz, $^2J(^{119}SnH)$ = 113 Hz), 6.00 (d, J = 14.2 Hz, $^3J(^{113}SnH)$ = 84 Hz); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.6, 26.9, 29.1 (C_4H_9), 19.7 (c-C_2H_4), 122.62 (CH, $^1J(^{119}Sn^{13}C)$ = 391.85 Hz), 153.0 (CH). Anal. Calcd for $C_{15}H_{26}Sn$: C, 55.42; H, 8.06. Found: C, 55.47; H, 8.13.

1,4,4-Trimethylboracyclohexa-2,5-diene. 1,1-Dibutyl-4,4-dimethyl-1-stannacyclohexa-2,5-diene (2.6 g, 8 mmol) was cooled to −78 °C under an argon atmosphere. Methylboron dibromide (1.5 g, 8 mmol) was added dropwise with stirring. A large precipitate formed. The reaction mixture was allowed to warm to 25 °C. The product was purified by pot-to-pot distillation at 25 °C (1.5 torr): mass spectrum, *m/e* (relative intensity) 120 (12, M^+ for $C_8H_{13}{}^{11}B$), 105 (100, M − CH_3); ^1H NMR ($CDCl_3$) δ 0.78 (s, 3 H), 1.12 (s, 6 H), 6.35 (d, J = 11.8 Hz, 2 H), 6.95 (d, J = 11.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 9.7 (br s, BCH_3), 26.7 (CH_3), 41.9 (C), 131.9 (br s, BCH), 164.5 (CH); ^{11}B NMR δ 58.3. Anal. Calcd for $C_8H_{13}B$: C, 80.07; H, 10.92. Found: C, 79.86; H, 11.02.

6-Methyl-6-boraspiro[2.5]octa-4,7-diene. To a solution of 1.5 g (4.2 mmol) of 6,6-dibutyl-6-stannaspiro[2.5]octa-4,7-diene in 10 mL of pentane at −78 °C was added 0.79 g (4.2 mmol) of methylboron dibromide in 10 mL of pentane. During the addition, the color darkened and a precipitate formed. The mixture was allowed to warm to 25 °C for 1 h. After removal of the solvent at reduced pressure, the product (0.4 g, 80%) was collected by pot-to-pot distillation at 25 °C (0.3 torr): mass spectrum, *m/e* (relative intensity) 118 (79, M^+ for $C_8H_{11}{}^{11}B$), 103 (100, M − CH_3). ^1H NMR ($CDCl_3$) δ 0.89 (s, 3 H), 1.59 (s, 4 H), 6.59 (d, J = 11.7 Hz, 2 H), 6.70 (d, J = 11.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.3 (br s, BCH_3), 18.7 (c-C_2H_4), 31.3 (C), 134.7 (br s, BCH), 159.4 (CH). ^{11}B NMR ($CDCl_3$) δ 56.5. Anal. Calcd for $C_8H_{11}B$: C, 81.44; H, 9.40. Found: C, 81.05; H, 9.27.

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Registry No. **1**, 29631-20-7; **3**, 84787-60-0; **4**, 84787-61-1; **6**, 66546-66-5; **7**, 84787-62-2; **8**, 57242-05-4; **9**, 84787-63-3.

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The Anion from 2,3-Dimethylnaphthalene/Tetramethylethylenediamine/*n*-Butyllithium: An Unusual Ambident Aromatic Nucleophile

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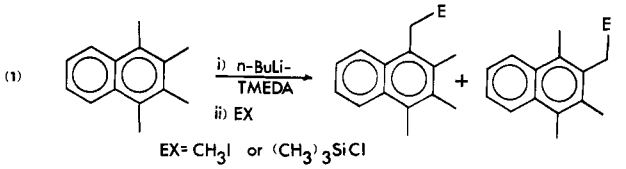
We were interested in improving the bromination of 2,3-dimethylnaphthalene (**1**) to 2-bromomethyl-3-methylnaphthalene (**2**), which we have used previously in connection with the synthesis of benzannelated dimethyldihydropyrenes.[1] Hart's procedure,[2] which uses excess *n*-BuLi/tetramethylethylenediamine (TMEDA) for monoanion formation in a series of polymethylnaphthalenes, followed by an electrophilic quench as shown, for example, in eq 1, seemed to offer a most attractive synthesis of **2**.



We thus employed these conditions with **1** but found somewhat unexpected results. Quenching the deep red anion **3** with D_2O or with CH_3I gave the expected benzylic

(1) R. H. Mitchell, R. J. Carruthers, and L. Mazuch, *J. Am. Chem. Soc.*, **100**, 1007 (1978).

(2) E. Dunkelblum and H. Hart, *J. Org. Chem.*, **44**, 3482 (1979).

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