Reactions of 1b in Aqueous Base. To 0.25 mL of 0.02 M **1b** in D_2O was added 0.25 mL of pH 11[14] 0.10 M carbonate buffer in D_2O. After 25 min at 25 °C, only *p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CD_2CH_2OD$ Br^- (**2b**-*d*) and/or (*p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CD_2CH_2)_2O$ $2Br^-$ were detected by ^1H NMR. The same result was obtained with the substitution of pH 10 0.10 M carbonate buffer in D_2O. With extended reaction times, conversion to **6a**/**6b** is likely, analogous to that of **1a** to **6a**.[4b,5b]

A reaction mixture was prepared from 1.0 mL of 0.02 M NaOD-D_2O and 1.0 mL of 0.002 M **1b** in D_2O. After 3 min at 25 °C, an oil had precipitated, and the reaction mixture was acidified with 20 wt % DCl-D_2O. By ^1H NMR, no organic material was detected in the supernatant solution. The oil was washed with H_2O and dried under vacuum; its ^1H NMR spectrum ($CDCl_3$) was similar to that of the crude product obtained from **1b** in 0.1 M NaOH.

As above for **1a**, 0.27 g (0.50 mmol) of **1b** in 25 mL of H_2O was treated with 25 mL of 0.2 M NaOH. The 0.20 g of crude product was chromatographed on basic alumina packed in Et_2O with MeOH-Et_2O elution. **4b** and **3b**/**3c** (7:1 mol ratio, 91 mg, 45%) eluted together with 1% MeOH-Et_2O. **4a**[1a] (13 mg, 11%) eluted with 1% MeOH-Et_2O. **5b** (trace) and **5c** (21 mg, 11%) eluted with 3% MeOH-Et_2O. **6a** (trace), **6b**, and *p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CH_2CH_2OH$ Cl^-/Br^- (2:1, 22 mg, 10%) eluted with 10-50% MeOH-Et_2O. **5a** was not detected. New compounds were identified by ^1H NMR in comparison with analogues from **1a** and by HRMS. **3b**/**3c**: calcd for $C_{32}H_{43}OP$ 474.3051, found, 474.3032. **4b**: calcd for $C_{26}H_{37}OP$ 396.2581, found 396.2551. **5b**: calcd for $C_{38}H_{48}O_2P_2$ 598.3128, found 598.3083. **5c**: calcd for $C_{50}H_{72}O_2P_2$ 766.5007, found 766.4990. **6a**: calcd for $C_{14}H_{15}O_2P$ 246.0810, found 246.0818. **6b**: calcd for $C_{26}H_{39}O_2P$ 414.2688, found 414.2686.

Stability of 2a in Aqueous Base. To 0.25 mL of 0.02 M **1a** was added 0.25 mL of 5.0 M NaOD-D_2O. After 30 min at 25 °C, the solution was acidified with 20 wt % DCl-D_2O. By ^1H NMR it contained ca. 10% $Ph_2P(O)CD_2CH_2OD$ (**6a**-*d*), with the remainder being **2a**-*d*.

Reaction of 1c in Aqueous Base. As for **1a**, 0.77 g (2.0 mmol) of **1c** in 100 mL of H_2O was treated with 100 mL of 5.0 M NaOH. The 0.80 g of crude product was chromatographed on basic alumina packed in Et_2O with MeOH-Et_2O elution. **3b** and **3c** (1:1 mol ratio, 93 mg, 14%) eluted with 1% MeOH-Et_2O. **4a**[1a] (trace) and **4b** (132 mg, 27%) eluted with 2% MeOH-Et_2O. **5b** (trace) and **5c** (144 mg, 31%) eluted with 3% MeOH-Et_2O. **6a**[5b] (trace) and **6b** (16 mg, 3%) eluted with 10% MeOH-Et_2O. *p*-$MeC_6H_4Ph_2P^+CH_2CH_2OH$ Cl^-/Br^- (52 mg, 7%) eluted with 50% MeOH-Et_2O. **5a** was not detected. New compounds were identified by ^1H NMR in comparison with analogues from **1a** and by HRMS. **3b**/**3c**: calcd for $C_{21}H_{21}OP$ 320.1330, found 320.1315. **4b**: calcd for $C_{15}H_{15}OP$ 242.0860, found 242.0844. **5b**: calcd for $C_{27}H_{26}O_2P_2$ 444.1407, found 444.1395. **5c**: calcd for $C_{28}H_{28}O_2P_2$ 458.1564, found 458.1554. **6b**: calcd for $C_{15}H_{17}O_2P$ 260.0966, found 260.0986.

Acknowledgment is gratefully made to the U.S. Army Research Office and the Marathon Oil Company.

Registry No. **1a**, 5044-52-0; **1a**-*d*, 7237-37-8; **1b**, 98482-65-6; **1c**, 100449-69-2; **2a**, 7237-34-5; **2a**-*d*, 100449-72-7; **2b**-*d*, 100466-22-6; **2c**, 100449-71-6; **3a**, 23896-93-7; **3b**, 100449-76-1; **3c**, 100449-77-2; **4a**, 2096-78-8; **4b**, 100449-75-0; **5a**, 4141-50-8; **5b**, 100449-78-3; **5c**, 100466-23-7; **6a**, 887-21-8; **6a**-*d*, 100449-80-7; **6b**, 100466-24-8; **7**, 5368-62-7; **7**-*d*, 100449-73-8; *p*-$MeC_6H_4Ph_2P^+CH_2CH_2Cl,Br^-$, 100449-70-5; *p*-$MeC_6H_4Ph_2P^+CH_2CH_2Cl,Cl^-$, 100449-82-9; *p*-$MeC_6H_4PPh_2$, 1031-93-2; $BrCH_2CH_2OH$, 540-51-2; $Ph_3P^+CH_2CH_2OH,Cl^-$, 23250-03-5; $(Ph_3P^+CD_2CH_2)_2O,2Cl^-$, 100449-83-0; $Ph_3P^+CD{=}CH_2,Cl^-$, 100449-84-1; $Ph_3P^+CD_2CH_2OD,Cl^-$, 100449-85-2; $(p\text{-}n\text{-}C_{12}H_{25}C_6H_4Ph_2P^+CD_2CH_2)_2O,2Br^-$, 100449-74-9; *p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CH_2CH_2OH,Cl^-$, 100449-79-4; *p*-$MeC_6H_4Ph_2P^+CH_2CH_2OH,Cl^-$, 100449-81-8.

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Ester Cleavage by a Phenolic Quaternary Phosphonium Surfactant

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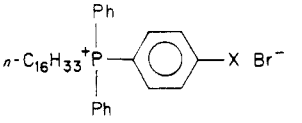
Numerous functionalized surfactants have been used to catalyze the hydrolysis of carbon and phosphorus esters.[1] Most of these have been quaternary ammonium systems. Previously, we described[2] the first functionalized quaternary phosphonium surfactants, and herein we report the synthesis and application of additional examples **1**-**3**.



1, X = OH
1a, X = O⁻
2, X = OCOMe
3, X = OMe

Reaction of *p*-$MeOC_6H_4PPh_2$ with *n*-$C_{16}H_{33}Br$ gave **3**, which was converted to **1** with hydrobromic acid. Acetylation of **1** with MeCOCl yielded **2**. By UV and ^{31}P NMR methods, micellar **1** has a pK_a of 6.6. Thus, the *p*-$C_{16}H_{33}Ph_2{}^+P$ substituent and micellization[3] combine to give an acidity enhancement of ca. 3 pK_a units relative to phenol (9.86).[4]

Phenolic **1** in comicellar form with hexadecyltrimethylammonium bromide (HTABr) was used as a catalyst for hydrolyses of *p*-nitrophenyl acetate (**4**) and sodium 4-acetoxy-3-nitrobenzenesulfonate (**5**), and the results are summarized in Tables I and II. **1**'s solubility characteristics precluded its use alone.

In pH 9 buffer with [**1**] = [HTABr] = 0.001 M, the pseudo-first-order rate constant (k_ψ) for hydrolysis of **4** is 2.7×10^{-3} s^{-1} (entry 1). Compared to reactions with **3** substituted for **1** (entry 2), with [HTABr] = 0.002 M (entry 3), and without surfactant (entry 4), that with **1** is 2.7, 5, and 13 times faster, respectively. These facts are consistent with the involvement of **1a** in nucleophilic attack on micellar bound **4** to give **2** (eq 1), which can undergo deacylation to regenerate **1a** (eq 2). At pH 9, **1** is >99% ionized to **1a**. The reaction of eq 2 was performed independently with [**2**] = 0.0001 M and [HTABr] = 0.002 M, and k_ψ = 5.4×10^{-3} s^{-1} resulted (entry 5). Comparison of entries 1 and 5 suggests that **2** decomposes faster than it is formed under the conditions of the former, i.e., that **1** is a turnover catalyst.[5] A conclusive demonstration of **1**'s turnover capability with [**4**] > [**1**] = 0.001 M was precluded by **4**'s limited solubility. Furthermore, lower [**1**]s could not be

1a + **4**(**5**) →
2 + *p*-$NO_2C_6H_4O^-$[4-($Na^+{}^-O_3S$)-2-$NO_2C_6H_3O^-$] (1)

$$\mathbf{2} \xrightarrow[H_2O]{^-OH} \mathbf{1a} + MeCO_2^- \qquad (2)$$

(1) For a summary and examples, see: Moss, R. A.; Ihara, Y. *J. Org. Chem.* **1983**, *48*, 588 and references therein.
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Table I. Hydrolyses of 4[a] and 2 in pH 7 and 9 Buffers[b] at 25 °C

entry	pH	[HTABr], M	[1], M	[2], M	[3], M	10^3k_ψ,[c] s^{-1}
1	9	0.001	0.001			2.7
2	9	0.001			0.001	1.0
3	9	0.002				0.54
4	9					0.21
5	9	0.002		0.0001		5.4
6	9	0.01	0.01			6.3
7	9	0.01			0.01	1.5
8	9	0.02				0.93
9	9					0.21
10	9	0.02		0.0001		2.4
11	7	0.01	0.01			2.1
12	7	0.02				0.048

[a] [4] = 2×10^{-5} M in all entries but 5 and 10, wherein **2** was the substrate. [b] Entries 1–5 contained 0.4% and 6–12, 2.2% (v/v) MeCN. [c] Averages of duplicate runs; average deviations ≤6%.

Table II. Hydrolyses of 5[a] in pH 9 Buffer[b] at 25 °C

entry	[HTABr], M	[1], M	[3], M	10^3k_ψ,[c] s^{-1}
13	0.001	0.001		11
14	0.001		0.001	3.3
15	0.002			2.3
16				0.32
17	0.01	0.01		9.0
18	0.01		0.01	2.0
19	0.02			1.3
20				0.34

[a] [5] = 5×10^{-5} M. [b] Entries 13–16 and 17–20 contained 0.4% and 2.2% (v/v) MeCN, respectively. [c] Averages of duplicate runs; average deviations ≤6%.

used because the rate enhancement for 1–HTABr relative to HTABr systems dropped to negligible values.

Results comparable to those above were obtained at higher surfactant concentrations (entries 6–10), except that the cleavage of **2** (entry 10) was slower than that of **4** (entry 6). Also, two reactions were performed with **4** at pH 7, where **1** is 71% ionized. With [1] = [HTABr] = 0.01 M, $k_\psi = 2.1 \times 10^{-3}$ s^{-1} (entry 11). Compared to reactions with [HTABr] = 0.02 M (entry 12) and without surfactant (estimated $k_\psi = 2 \times 10^{-6}$ s^{-1}), that with **1** is 44 and 1050 times faster, respectively.

In pH 9 buffer with [1] = [HTABr] = 0.001 M, $k_\psi = 11 \times 10^{-3}$ s^{-1} for hydrolysis of **5** (entry 13). This value is 3, 5, and 34 times greater than k_ψs for reactions with the substitution of **3** for **1** (entry 14), with [HTABr] = 0.002 M (entry 15), and without surfactant (entry 16), respectively. Attack of **1a** on micellar bound **5** (eq 1) is implicated, analogous to that on **4**. Since k_ψ for deacylation of **2** (entry 5) is less than k_ψ for hydrolysis of **5**, **1** does not function as a turnover catalyst in this case. Comparable results were obtained at higher surfactant concentrations (entries 17–20).

Moss and Dix[3] studied cleavage of **4** by *n*-$C_{16}H_{33}Me_2N^+CH_2C_6H_4XH$-*p*,$Br^-$ (**6**, X = O; **7**, X = S) comicellized with HTABr. In pH 8 buffer at 25 °C, where **6** is 48% and **7** >99% ionized, $k_\psi = 0.0123$ s^{-1} with [6] = [HTABr] = 0.01 M, and 0.034 s^{-1} with [7] = 0.0075 M and [HTABr] = 0.01 M. Although **6** and **7** are kinetically superior, **1** does possess the advantage of modest turnover capability at pH 9.

Experimental Section

General Procedures. ^1H NMR spectra were recorded at 270 MHz with Me_4Si as internal standard in $CDCl_3$ and ^{31}P NMR spectra at 109.1 MHz with 85% phosphoric acid as external standard (by substitution). Fast atom bombardment (FAB) mass spectra were obtained on a VG-ZAB 1F spectrometer with glycerol as sample matrix.

Materials and Solvents. **4** (Aldrich) was recrystallized from EtOH, mp 78–79.5 °C (lit.[6a] mp 79.5–80 °C), and **5**, mp >300 °C (lit.[6b] mp >300 °C), was prepared by a literature procedure. HTABr (Aldrich) was purified by recrystallization from 4:1 (v/v) Me_2CO–MeOH to give material with a cmc of 9.0×10^{-4} M (H_2O) (lit.[7] 9.2×10^{-4} M). For kinetic studies, H_2O (HPLC-grade) was purified as before,[2] and MeCN (HPLC-grade) was used as received. All synthetic procedures were under N_2.

Diphenyl(*p*-methoxyphenyl)hexadecylphosphonium Bromide (3). *p*-$MeOC_6H_4PPh_2$, mp 66–68 °C (lit.[8] mp 68–69 and 78–79 °C), was prepared by a literature procedure.[8] A mixture of 2.92 g (9.99 mmol) of *p*-$MeOC_6H_4PPh_2$ and 3.36 g (11.0 mmol) of *n*-$C_{16}H_{33}Br$ (Aldrich) in 10 mL of $MeNO_2$ was degassed (N_2), held at 80 °C for 3.5 h, concentrated to 5 mL, and added to 200 mL of Et_2O. At −10 °C, 4.1 g (69%) of crude product precipitated as an oil, which was chromatographed on a 3.5 × 30 cm column of silica gel packed in $CHCl_3$ with 300 mL each of $CHCl_3$ and 1:1 $CHCl_3$–Et_2O and 1 L of 1:19 MeOH–$CHCl_3$. With the last solution 3.50 g (59%) of **3** eluted as an oil: ^1H NMR δ 7.19–7.84 (m, 14 H, Ar H), 3.92 (s, 3 H, CH_3O), 3.63 (br m, 2 H, CH_2P), 1.63 (m, 4 H, $CH_2CH_2CH_2P$), 1.24 (m, 24 H, $(CH_2)_{12}$), 0.87 (t, 3 H, CH_3); FAB HRMS calcd for $C_{35}H_{50}BrOP$ (cation) 517.3599, found 517.3597.

Diphenyl(4-hydroxyphenyl)hexadecylphosphonium Bromide (1). A solution of 3.00 g (5.02 mmol) of **3** in 60 mL of 48% hydrobromic acid was refluxed for 4 h. At 25 °C the resultant oil was extracted into 100 mL of $CHCl_3$. The aqueous layer was further extracted with two 50-mL portions of $CHCl_3$, and the combined extracts were washed with two 50-mL portions of H_2O and dried (Na_2SO_4) to give 2.19 g (75%) of crude product, which was chromatographed on a 3.5 × 28 cm column of silica gel packed in $CHCl_3$ with 150 mL of $CHCl_3$ and 300 mL of 1:19 MeOH–$CHCl_3$. The surfactant eluted with the latter to give 1.90 g (65%) of **1** as a wax: mp 110–115 °C; ^1H NMR δ 10.37 (s, 1 H, OH), 7.28–7.78 (m, 14 H, Ar H), 3.21 (m, 2 H, CH_2P), 1.59 (m, 4 H, $CH_2CH_2CH_2P$), 1.24 (m, 24 H, $(CH_2)_{12}$), 0.87 (t, 3 H, CH_3); FAB HRMS calcd for $C_{34}H_{48}OP$ (cation) 503.3443, found 503.3425. For equimolar **1** and HTABr in pH 9 buffer (see below) at 25 °C, a critical micelle concentration of 5.0×10^{-5} M was determined as described previously.[9]

Diphenyl(*p*-acetoxyphenyl)hexadecylphosphonium Bromide (2). To a solution of 0.88 g (1.5 mmol) of **1** and 0.34 g (4.3 mmol) of pyridine in 5 mL of $CHCl_3$ at 0 °C was added 0.22 g (2.8 mmol) of MeCOCl. The resultant mixture was held for 30 min each at 0 °C and 60 °C. After the addition of 15 mL of $CHCl_3$, it was washed with two 10-mL portions of 10% hydrobromic acid and two 10-mL portions of saturated aqueous NaBr and dried (Na_2SO_4) to give 0.76 g (81%) of crude product. This material was chromatographed on a 12.5 × 36 cm column of silica gel packed in $CHCl_3$ with 150 mL of $CHCl_3$ and 300 mL of 1:33 MeOH–$CHCl_3$, and 0.63 g (67%) of **2** eluted as an oil with the latter: ^1H NMR δ 7.48–7.98 (m, 14 H, Ar H), 3.81 (m, 2 H, PCH_2), 2.36 (s, 3 H, CH_3CO), 1.62 (m, 4 H, $CH_2CH_2CH_2P$), 1.19–1.24 (m, 24 H, $(CH_2)_{12}$), 0.89 (t, 3 H, CH_3); FAB HRMS calcd for $C_{36}H_{50}O_2P$ (cation) 545.3548, found 545.3573.

Kinetic Studies. Runs were performed at 25.0 ± 0.1 °C on a Cary Model 2300 UV-VIS-NIR spectrophotometer in pH 7 and 9 buffers (0.06 M phosphate, μ = 0.13, and 0.0125 M borate, μ = 0.025, respectively). Reactions of **4** and **5** were generally monitored to ≥95% completion by the appearance of *p*-$NO_2C_6H_4O^-$ at 400 nm (λ_{max}) and 4-($Na^+{}^-O_3S$)-2-$NO_2C_6H_3O^-$ at 415 nm (λ_{max} 410 nm), respectively. Rate constants resulted from computer-generated least-squares plots of log ($A_\infty - A_t$) vs. time; A_∞ was determined by calculation[10] for entries 12 and 16 and by experiment for others. All runs gave good first-order kinetics (r > 0.999). A MeCN solution of **1** or **3** was added to HTABr(if appropriate)–buffer within a 1-cm cuvette containing a star-shaped

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stirrer. Then 4-MeCN or 5-H_2O was added, and the resultant solution was stirred intermittently. Runs with 2 as substrate were performed analogously and were monitored by the appearance of 1a at 288 nm (λ_{max}); A_∞ was determined by experiment. A MeCN solution was used for its addition to HTABr–buffer. In no run was there evidence for hydrolytic cleavage of the phosphonium salt as found[11] in other systems at higher pH.

pK_a of 1. The pK_a of 1 was measured by UV[3] and ^{31}P NMR methods. In the former, three buffers containing 0.002 M HTABr were prepared at pH 2.0 (0.013 M HCl, μ = 0.13 (KCl)), 7.0 (0.06 M phosphate, μ = 0.13), and 12.0 (0.025 M phosphate, μ = 0.13). To each 1–MeCN was added to give 1.0×10^{-4} M 1 and 0.4% (v/v) MeCN. Absorbances (A) were measured for each solution at 25 °C at 5-nm intervals over the range of 240–300 nm. The ratio $(A_{7.0} - A_{2.0})/(A_{12.0} - A_{7.0})$ was taken as $[A^-]/[HA]$ and was calculated at each wavelength. An average value of 3.81 was obtained (with exclusion of anomalous data from 260–280 nm) to give pK_a = 7.0 – log 3.81 = 6.4. In the NMR method, three buffers containing 0.01 M HTABr were prepared at pH 2.0 and 7.0 (same as above) and at 10.8 (0.0125 M borate, μ = 0.13 (KCl)). To each 1–MeCN was added to give 0.01 M 1 and 2.2% (v/v) MeCN. ^{31}P NMR chemical shifts of 19.45, 18.50, and 17.92, respectively, were obtained. The ratio $[A^-]/[HA]$ was determined from $\delta_{7.0} = X_{A^-}\delta_{10.8} + X_{HA}\delta_{2.0}$ and $X_{A^-} + X_{HA} = 1$, wherein X = mole fraction. A value of 1.63 was obtained to give pK_a = 7.0 – log 1.63 = 6.8. The average pK_a (6.6) from the UV and NMR methods was used in the text.

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Registry No. 1, 100466-58-8; 2, 100466-59-9; 3, 100466-60-2; 4, 830-03-5; 5, 4134-83-2; HTABr, 57-09-0; p-$MEOC_6H_4PPh_2$, 896-89-9; n-$C_{16}H_{33}Br$, 112-82-3.

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Unexpected Formation of 1,4,7,9-Tetrafluorodiamantane in the Reaction of 1,4,9-Tribromodiamantane with $NO_2^+BF_4^-$/Pyridinium Polyhydrogen Fluoride (PPHF)

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Recently we reported[1] the preparation and NMR spectroscopic (^{13}C and ^{19}F) study of a series of bridgehead mono- and polyfluorinated adamantanes and diamantanes. The bridgehead fluorides were conveniently prepared in excellent yields from the corresponding bromo compounds using $NO_2^+BF_4^-$ pyridinium polyhydrogen fluoride (PPHF).[2] In that study we reported the preparation of two bridgehead difluorodiamantanes (namely, 1,6-difluorodiamantane and 4,9-difluorodiamantanes). The similar conversion of adamantanoid halides to fluorides was also possible by the action of elemental fluorine.[3] In continuation of our studies we were interested in preparing the tri- and tetrafluorodiamantanes from the corresponding bromo compounds. We now report our results in the reaction of 1,4,9-tribromodiamantane,[4] (1) with excess $NO_2^+BF_4^-$/PPHF reagent which gave, unexpectedly, 1,4,7,9-tetrafluorodiamantane (2).

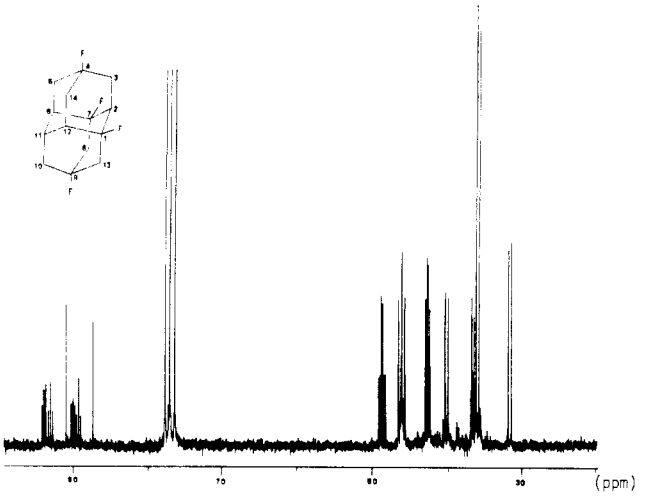
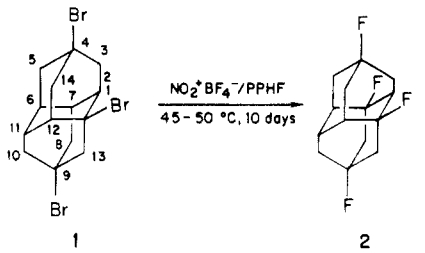


Figure 1. ^{13}C NMR spectrum of 1,4,7,9-tetrafluorodiamantane (2) in $CDCl_3$ at room temperature.



1 2

Results and Discussion

1,4,9-Tribromodiamantane (1) was prepared according to literature procedure[4] by ionic bromination of diamantane. The elemental analysis and ^{13}C NMR spectral characteristics [δ^{13}C: 70.2 (s), 60.2 (s), 59.6 (s), 59.3 (t), 48.6 (t), 47.8 (d), 47.3 (t), 44.7 (t), 41.9 (d), 38.2 (d)] correspond well with the structure, and the melting point (190–192 °C) is very close to that reported in the literature[4b] (193–195 °C).

Reaction of 1 with excess $NO_2^+BF_4^-$ in 70% pyridinium polyhydrogen fluoride (PPHF) at 45–50 °C in an autoclave for 10 days gave in 72% yield a tetrafluorocompound with molecular formula $C_{14}H_{16}F_4$ as determined by elemental analysis (see Experimental Section for details). ^{19}F NMR[5] of the product showed three signals at $\delta(^{19}F)$ –142.9 (1 F), –146.8 (1 F), and –150.4 (2 F). These are in the region of bridgehead ^{19}F chemical shift.[1] Also, the absence of any observable ^{19}F–^1H coupling indicates that all the fluorine atoms are at the bridgehead position. The ^{1}H noise-decoupled ^{13}C NMR spectrum in $CDCl_3$ is shown in Figure 1. It shows ten ^{13}C multiplets (^{13}C–^{13}F coupling), indicating a C_s symmetry in the diamantane skeleton. The ^{13}C chemical shifts along with their proton multiplicites (obtained using APT experiment[6]) are listed in the Table I.

The spectral characteristics (both ^{13}C and ^{19}F) indicate that the product is 1,4,7,9-tetrafluorodiamantane (2). Every individual ^{13}C–^{19}F multiplet in the ^{13}C NMR spec-

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(2) (a) Olah, G. A.; Shih, J. G.; Singh, B. P.; Gupta, B. G. B. *Synthesis* **1983**, 713. (b) The present method of ionic fluorination is well suited for tertiary and adamantanoid halides but seems to be limited to those tertiary alkyl halides which cannot undergo olefin-forming elimination.
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(4) (a) Gund, T. M.; Schleyer, P. v. R. *Tetrahedron Let.*. **1971**, 1583. (b) Gund, T. M.; Schleyer, P. v. R.; Unruh, G. D.; Gleicher, G. J. *J. Org. Chem.* **1974**, *39*, 2995.
(5) ^{19}F chemical shifts are with respect to $CFCl_3$. Negative sign indicates shielding.
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