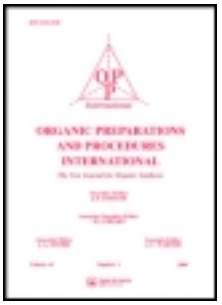

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SYNTHESIS OF 3,6-DIHALOPHENANTHRENE DERIVATIVES

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OPPI BRIEFS

SYNTHESIS OF 3,6-DIHALOPHENANTHRENE DERIVATIVES

Submitted by (10/31/05)

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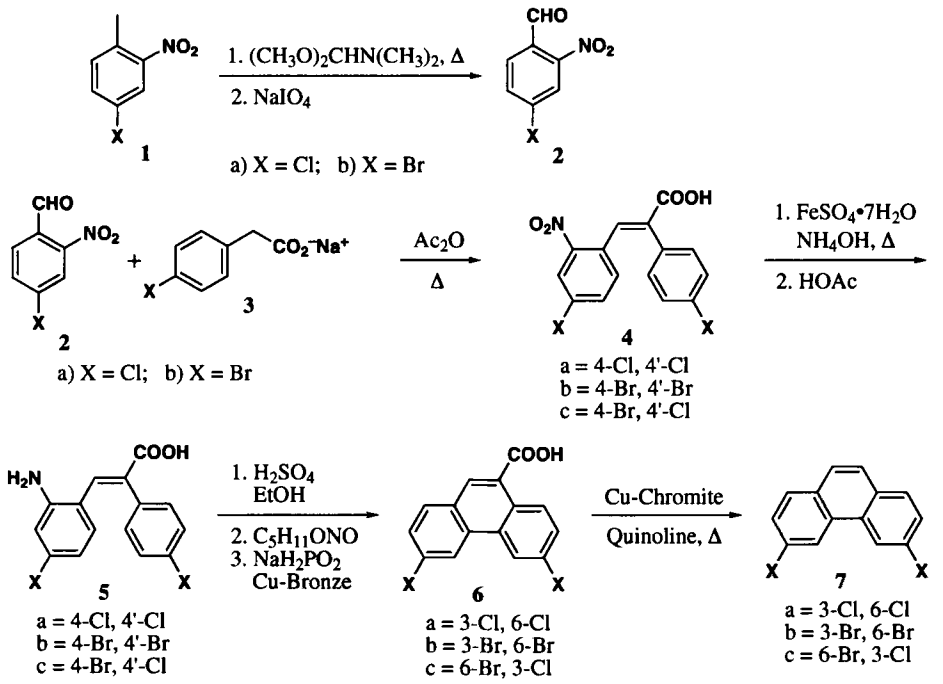
Surface functionalization of Group IV semiconductors, in particular Si(100), is one route to the formation of unique surfaces that may lead to novel applications in chemical sensing, biological recognition and molecular and optical electronics.[1-3] Our work in this area[4-7] has required the synthesis of several 3,6-dihalophenanthrene derivatives. These compounds are of interest because the distance between the halogens is approximately equal to the gap between the dimer rows formed by cleavage of a silicon wafer in the (100) direction. Cleavage results in a reconstructed surface containing ordered rows of dimerized surface atoms.[8] There is an approximate 6 Å gap between the Si-dimer rows, while each dimer is separated from the next one in the same row by approximately 4 Å. The unique chemistry of these dimers has been reviewed by several authors.[1,2,9] The 3,6-dihalophenanthrenes have a rigid backbone and appropriate halogen-halogen distance to possibly induce reactions selectively between Si-dimer rows. Thus, we required access to 3,6-dichlorophenanthrene, 3,6-dibromophenanthrene and 3-bromo-6-chlorophenanthrene to examine potential interactions with the Si(100) surface.

The synthesis of 3,6-dibromophenanthrene has been described and the compound characterized by melting point and elemental analysis.[10] However, the preparation and characterization of the related 3,6-dichlorophenanthrene and 3-bromo-6-chlorophenanthrene have not been reported. Our synthesis, based on the method of Barber and Stickings,[10] starts from the Perkin condensation of aldehydes **2** with the sodium salts of *p*-halophenylacetic acids **3** as shown in the *Scheme*. Since the yields of aldehydes **2** from the previously reported[11,12] oxidation of the corresponding *o*-nitrotoluenes **1** with Jones reagent proved to be unsatisfactory, an alternative method[13] based on the formation of arylenamines from **1**, followed by oxidative cleavage with sodium periodate was used. Both **2a** and **2b** were obtained in 80% yields using this procedure. Reduction of **4** using iron sulfate heptahydrate under basic conditions gave amino acids **5**. Deamination of **5** *via* diazotization and reduction followed by Pschorr cyclization led to 3,6-dihalophenanthrene-9-carboxylic acids **6**, which were then decarboxylated over copper chromite in quinoline to afford the desired 3,6-dihalophenanthrenes **7**.



In conclusion, 3,6-dichlorophenanthrene, 3,6-dibromophenanthrene and 3-bromo-6-chlorophenanthrene have been synthesized on the 100s of milligrams scale. Our modified procedure has led to an improved overall yield of **6b** from 3%[10] to 21%; our overall yield of **7b** is 15% (the overall yield for **7b** was not previously reported). In addition, we have extended the synthesis to other halogenated derivatives, **7a** and **7c**. Each compound has been fully characterized by NMR, IR and mass spectrometry. The quantities synthesized were more than sufficient to study the surface reactivity of these compounds with the Si(100) surface.

EXPERIMENTAL SECTION

Melting points were uncorrected. IR spectra were obtained as thin films. ^1H NMR and ^{13}C NMR were recorded at 300 MHz and 75 MHz, respectively, using $CDCl_3$ as the solvent, unless otherwise unless specified; coupling constants (*J*) are reported in Hz. Mass spectra were obtained on a GC-MS instrument at 70 eV.

Representative Procedure for the Oxidation of Halonitrotoluene Derivatives. 4-Chloro-2-nitrobenzaldehyde (2a).- In a 50-mL one-necked round-bottomed flask, a solution of 3.06 g (17.8 mmol) of 4-chloro-2-nitrotoluene in 7.18 g (8.00 mL, 60.2 mmol) of *N,N*-dimethylformamide dimethyl acetal containing 1.28 g (1.50 mL, 18.0 mmol) of pyrrolidine was refluxed until the reaction was complete by TLC (24 h). This solution was cooled to room temperature and added dropwise to a mechanically stirred solution of 15.4 g (71.9 mmol) of sodium periodate in 75 mL of 2:1 (v/v) water/dimethylformamide at 20°C in a three-necked round-bottomed flask. Stir-

ring was continued at 20°C until the reaction was complete by TLC (3 h). The insoluble material was removed by filtration and the filtrate was extracted with 50 mL of ethyl acetate (3x). The extract was washed with 50 mL of water (3x), dried ($MgSO_4$) and concentrated *in vacuo*. The concentrate was purified by chromatography on silica gel using 1:1 (v/v) methylene chloride/hexane to give 2.68 g (81%) of **2a** as a light yellow solid, mp 54-56°C (*lit.*[11-13] mp 58°C). IR: 1699, 1541, 1348 cm^{-1}; ^1H NMR: δ 10.4 (s, 1 H), 8.11 (d, 1 H, J = 1.6), 7.95 (dd, 1 H, J = 8.2, 1.6), 7.75 (d, 1 H, J = 8.2); ^{13}C NMR: δ 187.3, 149.2, 140.7, 134.7, 131.4, 129.8, 125.3; MS *m/z* (%): 185/187 (M^+, 0.6/0.6), 155 (100).

Anal. Calcd for $C_7H_4ClNO_3$: C, 45.31; H, 2.17; N, 7.55. Found: C, 45.12; H, 2.37; N, 7.35.

4-Bromo-2-nitrobenzaldehyde (2b) was obtained as a light yellow solid (77%), mp 97-98°C (*lit.*[10] mp 95-97°C). The spectral data matched those previously reported.[14]

Representative Procedure for the Perkin Condensation: (2*E*)-(4-Chloro-2-nitrophenyl)-2-(4-chlorophenyl)prop-2-enoic Acid (4a).- Sodium 4-chlorophenylacetate (**3a**) was prepared by dissolving 1.55 g (9.09 mmol) of 4-chlorophenylacetic acid in 50 mL of deionized water containing 0.38 g (9.75 mmol, 5% excess) of sodium hydroxide. The solution was rotary evaporated and dried under vacuum overnight resulting in 1.75 g of **3a**. A solution of 1.62 g (8.74 mmol) of **2a** in 60 mL of acetic anhydride was added to 1.75 g (9.09 mmol) of solid **3a** in a one-necked round-bottomed flask fitted with a condenser and a thermometer. The solution, which quickly turned light yellow, was heated at 80°C for 25.5 h while being monitored by TLC. During the first 5 h, the solution was periodically stirred. After completion, 220 mL of water was added slowly while maintaining the temperature between 110-120°C. The reaction mixture was cooled and extracted with 100 mL of ether (3x). The combined ethereal extracts were washed with 100 mL of water (3x), extracted with 100 mL of 2.0 M sodium hydroxide (3x), and the basic extract was washed with 50 mL of ether (3x). The basic extract was acidified to a pH of 4 with 3.0 M hydrochloric acid, and the product was extracted into 100 mL of ether (3x). The ethereal layer was washed with 100 mL of water (3x), dried ($MgSO_4$) and concentrated to give an orange solid. This solid was dried under vacuum overnight to give 2.67 g (91%) of crude **4a**, which was used without further purification. An analytical sample was obtained by recrystallization from 4:1 (v/v) acetic acid/water to give bright orange crystals, mp 178-180°C.

IR: 3500-2580, 1697, 1529, 1349 cm^{-1}; ^1H NMR: δ 13.1 (s, 1 H), 8.19 (d, 1 H, J = 2.2), 7.99 (s, 1 H), 7.62 (dd, 1 H, J = 8.5, 2.2), 7.34 (dd, 2 H, J = 8.7, 2.2), 7.12 (dd, 2 H, J = 8.7, 2.2), 6.97 (d, 1 H, J = 8.5); ^{13}C NMR: δ 167.2, 148.4, 136.5, 134.4, 133.5, 133.4, 133.3, 133.2, 132.6, 132.1, 130.2, 128.1, 124.5.

Anal. Calcd for $C_{15}H_9Cl_2NO_4$: C, 53.28; H, 2.68; N, 4.14. Found: C, 53.57; H, 2.65; N, 3.99.

(2*E*)-(4-Bromo-2-nitrophenyl)-2-(4-bromophenyl)prop-2-enoic Acid (4b) was obtained as orange rods (75%), mp 205-207°C (*lit.*[10] mp 204-206°C). IR: 3550-2550, 1695, 1528, 1348 cm^{-1}; ^1H NMR: δ 13.1 (s, 1 H), 8.30 (d, 1 H, J = 1.9), 7.96 (s, 1 H), 7.75 (dd, 1 H, J = 8.2, 1.9), 7.45 (d, 2 H, J = 8.5), 7.05 (d, 1 H, J = 8.5), 6.89 (d, 2 H, J = 8.5); ^{13}C NMR: δ 167.9, 149.2, 137.3, 137.1, 135.1, 134.4, 134.0, 133.1, 131.7, 131.2, 128.0, 122.2, 122.0.

(2*E*)-(4-Bromo-2-nitrophenyl)-2-(4-chlorophenyl)prop-2-enoic Acid (4c) was obtained as orange rods (91%), mp 186-188°C. IR: 3650-2300, 1696, 1530, 1345 cm^{-1}; ^1H NMR: δ 13.1 (s, 1 H), 8.29 (d, 1 H, *J* = 1.9), 7.97 (s, 1 H), 7.74 (dd, 1 H, *J* = 8.5, 1.6), 7.32 (d, 2 H, *J* = 8.5), 7.14 (d, 2 H, *J* = 8.5), 6.90 (d, 1 H, *J* = 8.5); ^{13}C NMR: δ 170.4, 148.5, 138.8, 136.4, 133.4, 133.0, 131.9, 131.7, 130.1, 128.0, 127.9, 123.0, 122.9.

Anal. Calcd for $C_{15}H_9BrClNO_4$: C, 47.09; H, 2.37; N, 3.66. Found: C, 47.07; H, 2.37; N 3.62.

Representative Procedure for Nitro Reduction: (2*E*)-(2-Amino-4-chlorophenyl)-2-(4-chlorophenyl)prop-2-enoic Acid (5a).- In a 300-mL three-necked round-bottomed flask fitted with a mechanical stirrer in a water bath at 80°C, 11.3 g (40.6 mmol) iron sulfate heptahydrate was dissolved in 45 mL of water. The solution was made basic by adding 100 mL of 6.0 M ammonium hydroxide. After thermal equilibration, a warm solution of 1.72 g (5.09 mmol) of **4a** in 15 mL of 2.0 M ammonium hydroxide was added slowly, and the mixture was stirred at 80°C until the reaction was complete by TLC (*ca.* 1.5 h). A small amount of activated charcoal was added and the hot solution was filtered through a pad of Celite®. The Celite® was washed with 75 mL of boiling 2.0 M ammonium hydroxide (at least 4x) until there was no precipitation upon the addition of 3.0 M acetic acid to the filtrate. The filtrate and washes were combined and adjusted to a pH of approximately 6 using 3.0 M acetic acid. This resulted in a yellow product that turned white upon standing. The product was extracted with 100 mL of ether (3x), washed with 100 mL of water (3x), dried ($MgSO_4$) and concentrated to give a yellow-brown solid. This solid was dried under vacuum overnight to give 1.33 g (85%) of **5a**, which was used without further purification. Recrystallization of a small amount of the solid from 65:35 (v/v) ethanol/water gave **5a** as a light brown solid, mp 195-197°C.

IR: 3293-1820, 1667 cm^{-1}; ^1H NMR (d_6-DMSO): δ 12.7 (s, 1 H), 7.66 (s, 1 H), 7.36 (dd, 2 H, *J* = 8.5, 1.6), 7.15 (dd, 2 H, *J* = 8.5, 1.6), 6.70 (d, 1 H, *J* = 2.2), 6.37 (d, 1 H, *J* = 8.5), 6.26 (dd, 1 H, *J* = 8.5, 2.2), 5.72 (br s, 2 H); ^{13}C NMR (d_6-DMSO): δ 168.2, 152.6, 149.4, 135.9, 135.2, 133.3, 131.9, 131.6, 131.2, 128.2, 117.4, 115.2, 114.4.

Anal. Calcd for $C_{15}H_{11}Cl_2NO_2$: C, 58.46; H, 3.60; N, 4.46. Found: C, 58.46; H, 3.67; N, 4.29.

(2*E*)-(2-Amino-4-bromophenyl)-2-(4-bromophenyl)prop-2-enoic Acid (5b) was obtained as a light brown solid (63%), mp 186-188°C (*lit.*[10] mp 188-191°C). IR: 3782-3085, 1659 cm^{-1}; ^1H NMR (d_6-DMSO): δ 12.7 (s, 1 H), 7.64 (s, 1 H), 7.47 (d, 2 H, *J* = 7.9), 7.07 (d, 2 H, *J* = 7.9), 6.85 (s, 1 H), 6.31 (dd, 2 H, *J* = 7.9, 2.3), 5.70 (br s, 2 H); ^{13}C NMR (d_6-DMSO): δ 169.2, 150.6, 137.0, 136.6, 133.2, 132.7, 132.3, 132.1, 123.8, 121.6, 119.0, 118.8, 118.4.

(2*E*)-(2-Amino-4-bromophenyl)-2-(4-chlorophenyl)prop-2-enoic Acid (5c) was obtained as a light brown solid (80%), mp 214-217°C. IR: 3775-3113, 1694 cm^{-1}; ^1H NMR (d_6-DMSO): δ 12.7 (s, 1 H), 7.64 (s, 1 H), 7.35 (dd, 2 H, *J* = 8.4, 1.9), 7.14 (dd, 2 H, *J* = 8.4, 1.9), 6.86 (d, 1 H, *J* = 2.2), 6.38 (dd, 1 H, *J* = 8.4, 1.9), 6.31 (d, 1 H, *J* = 8.4) 5.70 (br s, 2 H); ^{13}C NMR (d_6-DMSO): δ 169.3, 150.6, 137.0, 136.2, 133.1, 132.9, 132.7, 132.4, 129.2, 123.8, 119.1, 118.8, 118.5.

Anal. Calcd for $C_{15}H_{11}BrClNO_2$: C, 51.09; H, 3.15; N, 3.97. Found: C, 51.24; H, 2.88; N, 3.86.

Representative Procedure for Phenanthrene Ring Closure. 3,6-Dichlorophenanthrene-9-carboxylic Acid (6a).- In a 250-mL one-necked round-bottomed flask, 1.12 g (3.63 mmol) of **5a** was suspended in 20 mL of ethanol and 0.4 mL of conc. sulfuric acid was added with stirring to give the anilinium salt as a thick paste. After cooling to room temperature, 0.53 g (0.60 mL, 5.8 mmol) of isoamyl nitrite was added, and this resulted in a clear solution. Over 1 h, the diazonium salt precipitated out of solution as a fine powder.

A solution of 4.25 g (25.0 mmol) of calcium hypophosphite in 35 mL of hot water was added to a solution of 3.20 g (25.8 mmol) of sodium carbonate monohydrate in 25 mL of hot water. After filtering to remove the calcium carbonate, the solution was poured into a 250-mL one-necked round-bottomed flask in a 50°C water bath, and 20 mg of copper-bronze powder and a magnetic stir bar were added. The diazonium salt suspension was poured into this solution with stirring. The reaction was complete by TLC after 15 min. The resulting orange solid was collected, dissolved in ether and filtered to remove traces of copper-bronze. The aqueous filtrate was also extracted with 50 mL of ether (3x). The two ethereal solutions were combined, washed with 100 mL of water (3x), dried ($MgSO_4$), and concentrated. The crude product was dried under vacuum overnight to give 1.08 g of a sticky orange residue. The residue was sublimed twice at 240°C under vacuum to give 0.81 g (2.78 mmol, 76%) of **6a** as a light yellow solid, mp 261-263°C. This material was used without further purification. Recrystallization from chlorobenzene gave an analytical sample of **6a** as a white solid, mp 281-283°C.

IR: 3520-2300, 1698 cm^{-1}; ^1H NMR (d_6-DMSO): δ 13.5 (s, 1 H), 9.06 (m, 2 H), 8.93 (d, 1 H, *J* = 8.5), 8.60 (s, 1 H), 8.23 (d, 1 H, *J* = 8.5), 7.78 (apparent t, 2 H, *J* = 8.5); ^{13}C NMR (d_6-DMSO): δ 168.2, 161.4, 134.6, 132.6, 131.9, 131.7, 131.5, 130.9, 128.7, 128.4, 128.3, 127.4, 126.6, 123.3, 123.0.

Anal. Calcd for $C_{15}H_8Cl_2O_2$: C, 61.88; H, 2.77. Found: C, 61.71; H, 2.67.

3,6-Dibromophenanthrene-9-carboxylic Acid (6b) was obtained as a light yellow solid (57%), mp 292-294°C (*lit.*[10] mp 290-292°C). IR: 3283-2248, 1694 cm^{-1}; ^1H NMR (d_6-DMSO): δ 13.5 (s, 1 H), 9.90 (m, 2 H), 8.84 (d, 1 H, *J* = 8.8), 8.59 (s, 1 H), 8.13, (d, 1 H, *J* = 8.8), 7.81 (dd, 2 H, *J* = 8.5, 2.1), 7.78 (dd, 1 H, *J* = 8.5, 2.1); ^{13}C NMR (d_6-DMSO): δ 168.1, 131.9, 131.8, 131.7, 131.6, 131.0, 130.9, 128.9, 128.4, 127.6, 126.7, 126.2, 126.0, 123.5, 121.4.

3-Bromo-6-chlorophenanthrene-9-carboxylic Acid (6c) was obtained as a light yellow solid (67%), mp 270-272°C. IR: 3365-2314, 1694 cm^{-1}; ^1H NMR (d_6-DMSO): δ 13.6 (s, 1 H), 9.26 (s, 1 H), 9.14 (d, 1 H, *J* = 2.3), 9.03 (d, 1 H, *J* = 9.0), 8.68 (s, 1 H), 8.23 (d, 1 H, *J* = 9.0), 8.01 (dd, 1 H, *J* = 9.0, 2.3), 7.90 (dd, 1 H, *J* = 9.0, 2.3); ^{13}C NMR (d_6-DMSO): δ 166.7, 131.2, 130.5, 130.1, 129.6, 129.3, 128.8, 127.5, 126.9, 126.8, 126.0, 125.2, 124.6, 122.1, 121.8.

Anal. Calcd for $C_{15}H_8BrClO_2$: C, 53.68; H, 2.40. Found: C, 53.52; H, 2.14.

Representative Procedure for Decarboxylation. 3,6-Dichlorophenanthrene (7a).- A 50-mL one-necked round-bottomed flask fitted with a condenser was charged with a solution of 0.26 g (0.89 mmol) of **6a** in 5 mL of freshly distilled quinoline and 0.05 g of powdered copper

chromite.[10,15] This solution was refluxed under nitrogen until the reaction was complete by TLC (8 h). After cooling to 80°C, the reaction mixture was poured into 45 mL of conc. hydrochloric acid, boiled for 15 min, filtered and washed with water. The resulting black powder was dried and sublimed at 160°C under vacuum resulting in 0.11 g (0.45 mmol, 49%) of **7a** as a white solid, mp 159-163°C. Recrystallization from *n*-hexane resulted in white needles, mp 171-173°C. IR: 1501, 1413, 913, 651 cm^{-1}; ^1H NMR: δ 8.54 (d, 2 H, J = 1.9), 7.82 (d, 2 H, J = 8.5), 7.69 (s, 2 H), 7.57 (dd, 2 H, J = 8.5, 1.9); ^{13}C NMR: δ 132.9, 130.7, 129.9, 127.7, 126.6, 126.5, 122.3; MS *m/z* (%): 246/248/250 (M^+, 100/67/11).

Anal. Calcd for $C_{14}H_8Cl_2$: C, 67.95; H, 3.26. Found: C, 67.71; H, 3.26.

3,6-Dibromophenanthrene (7b) was obtained as a white solid (73%), mp 184-188°C (*lit.*[10] mp 188-191°C). IR: 1501, 1405, 834 cm^{-1}; ^1H NMR: δ 8.68 (d, 2 H, J = 1.6), 7.74 (d, 2 H, J = 8.5), 7.68 (dd, 4 H, J = 8.5, 1.6); ^{13}C NMR: δ 130.7, 130.6, 130.4, 130.1, 126.7, 125.5, 121.1; MS *m/z* (%): 334/336/338 (M^+, 44/85/41), 176 (100).

3-Bromo-6-chlorophenanthrene (7c) was obtained as a white solid (67%), mp 171-173°C. IR: 1497, 1411, 911, 742 cm^{-1}; ^1H NMR: δ 8.5 (d, 1 H, J = 1.6), 8.33 (d, 1 H, J = 1.9), 7.62 (d, 1 H, J = 8.5), 7.58-7.46 (complex, 4 H), 7.38 (dd, 1 H, J = 8.5, 1.9); ^{13}C NMR: δ 131.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 125.9, 124.8, 124.7, 123.7, 120.5, 119.3, 98.2; MS *m/z* (%): 290/292/294 (M^+, 78/100/25).

Anal. Calcd for $C_{14}H_8BrCl$: C, 57.67; H, 2.77. Found: C, 57.64; H, 2.52.

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THE SELECTIVE SOLID-PHASE OXIDATION OF ALCOHOLS AND OTHER ORGANIC SUBSTRATES BY 3,5-DIMETHYLPYRAZOLIUM FLUOROCHROMATE

Submitted by (11/07/06)

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Selective oxidation has been a fundamental procedure in organic chemistry and finds application not only in basic research and in the pharmaceutical industries but is also regarded as a core technology for the conversion of petroleum based materials or bio-mass based feed stocks to useful chemicals.[1] Although a wide variety of oxidants, catalysts and reaction systems have been developed for the purpose, Cr(VI)-based oxidants are extensively used owing to their excellent performance under mild conditions with high efficiency and operational simplicity. Endeavors have been made to overcome the problems of over-oxidation and diminished selectivity. This has led to the development of a number of oxidants such as Collins reagent,[2] CrO_3-3,5-dimethylpyrazole complex,[3] pyridinium chlorochromate(VI) (**PCC**),[4] pyridinium dichromate (**PDC**),[5] 2,2'-bipyridinium chlorochromate (**BiPCC**),[6] pyridinium fluorochromate(VI) (**PFC**),[7] quinolinium fluorochromate(VI) (**QFC**),[8,9] imidazolium fluorochromate(VI) (**IFC**),[10] 3,5-dimethylpyrazolium fluorochromate(VI) (**DmpzHFC**),[11] tetramethylammonium fluorochromate(VI) (**TMAFC**)[12] and benzimidazolium fluorochromate(VI) (**BIFC**).[13] However, some of the distinctive features of **DmpzHFC** compared to its companion reagents are quite evident from