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New Alkyliodonium Derivatives Stabilized by Ammonium or Phosphonium Groups

Viktor V. Zhdankin,* Jeff A. Callies, Kari J. Hanson, Jessica Bruno

Department of Chemistry, University of Minnesota-Duluth, Duluth, Minnesota 55812

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Abstract: Alkyliodine(III) dichlorides **2a,b** and bis(trifluoroacetate) **4**, which are stabilized due to the presence of the electron-withdrawing trialkylammonium or triphenylphosphonium groups, can be prepared from readily available iodomethyl phosphonium and ammonium salts **1a,b**. Decomposition of dichlorides **2** in the solution affords chloromethyl phosphonium and ammonium salts **3**; the structure of the chloromethyl phosphonium salt **3b** (as a tetrachloroiodinate) was established by a single-crystal X-ray analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Derivatives of polyvalent iodine with an alkyl substituent at iodine generally are highly unstable and can exist only as short-lived reactive intermediates in the oxidation of alkyliodides and some other reactions.[1] For example, the low temperature reaction of iodomethane with chlorine results in the formation of a yellow precipitate of (dichloroiodo)methane which rapidly decomposes above -28 ^{o}C.[1b] The introduction of an electron-withdrawing substituent into the alkyl moiety leads to a stabilization of the molecule; for example, (dichloroiodo)methylsulfones, $ArSO_2CH_2ICl_2$,[2a] 1-(dichloroiodo)-1*H*,1*H*-perfluoroalkanes, $R_fCH_2ICl_2$,[3] and tosylates, $R_fCH_2I(OH)OTs$,[4] are known, relatively stable and useful compounds. Several examples of iodonium salts, $R_2I^+X^-$, with one or two aliphatic alkyl groups were generated and investigated by NMR spectroscopy at low temperatures and some of them even were isolated in the form of highly unstable crystalline products.[5] The only known examples of stable alkyliodonium salts are polyfluoroalkyl(aryl)iodonium salts, $R_fI(Ph)X$[6,7] and (arylsulfonylmethyl)phenyliodonium triflates, $ArSO_2CH_2I(Ph)OTf$.[2b] Polyfluoroalkyl(aryl)iodonium salts have found some practical application as electrophilic polyfluoroalkylating reagents.[7]

In this paper, we report the preparation of the novel alkyliodine(III) dichlorides **2** (eq. 1) which are stabilized due to the presence of the electron-withdrawing trialkylammonium or triphenylphosphonium groups. The starting iodides **1a** and **1b** were prepared by the reaction of diiodomethane with triethylamine or triphenylphosphine, respectively, followed by anion exchange with an aqueous solution of $NaBF_4$.[8a] Chlorination of salts **1a,b** in a dichloromethane solution at about -10 ^{o}C afforded dichlorides **2** in the form of yellow precipitates. Compounds **2** were isolated as relatively stable, non-hygroscopic, light-yellow microcrystalline solids.[8b]

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* *E-mail: vzhdanki@d.umn.edu* *FAX: (218) 726 7394*

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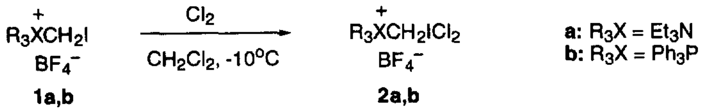
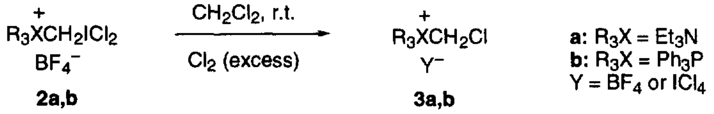


$$\underset{\mathbf{1a,b}}{\overset{+}{R_3XCH_2I}\ BF_4^-} \xrightarrow[CH_2Cl_2,\ -10^{\circ}C]{Cl_2} \underset{\mathbf{2a,b}}{\overset{+}{R_3XCH_2ICl_2}\ BF_4^-} \qquad \text{(eq. 1)}$$

a: $R_3X = Et_3N$
b: $R_3X = Ph_3P$

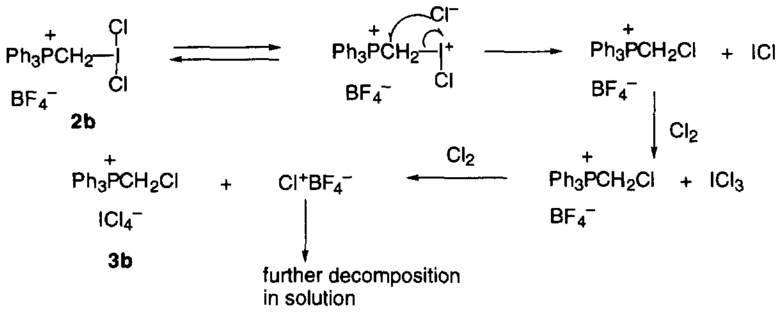
Products **2** were identified by spectral data and elemental analysis.[8b] In particular, the ^1H NMR of **2a** displayed the characteristic signal of methylene protons of the $-CH_2ICl_2$ group at $\delta = 6.17$ ppm, shifted about 1 ppm downfield compared to the starting iodide **1a**. Solutions of compounds **2a** and **2b** in organic solvents in the presence of chlorine have a relatively low stability at room temperature. Their decomposition can be monitored by NMR and the final products, chloromethyl phosphonium and ammonium salts **3a,b**, can be isolated as stable, crystalline compounds (eq. 2).



$$\underset{\mathbf{2a,b}}{\overset{+}{R_3XCH_2ICl_2}\ BF_4^-} \xrightarrow[Cl_2\ (excess)]{CH_2Cl_2,\ r.t.} \underset{\mathbf{3a,b}}{\overset{+}{R_3XCH_2Cl}\ Y^-} \qquad \text{(eq. 2)}$$

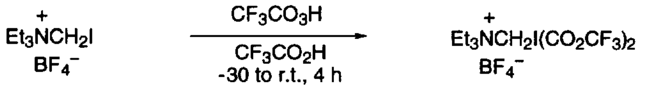
a: $R_3X = Et_3N$
b: $R_3X = Ph_3P$
$Y = BF_4$ or ICl_4

The structure of the chloromethyl phosphonium salt **3b** (as a tetrachloroiodinate) was unambiguously established by a single-crystal X-ray analysis (see Figure 1). The formation of **3b** can be rationalized by the mechanism outlined in Scheme 1. This mechanism includes fragmentation of dichloride **2b** by internal nucleophilic substitution with the formation of chloromethyl phosphonium ion and iodine chloride followed by the chlorination of ICl to tetrachloroiodate and the anion exchange in the final product.



Scheme 1

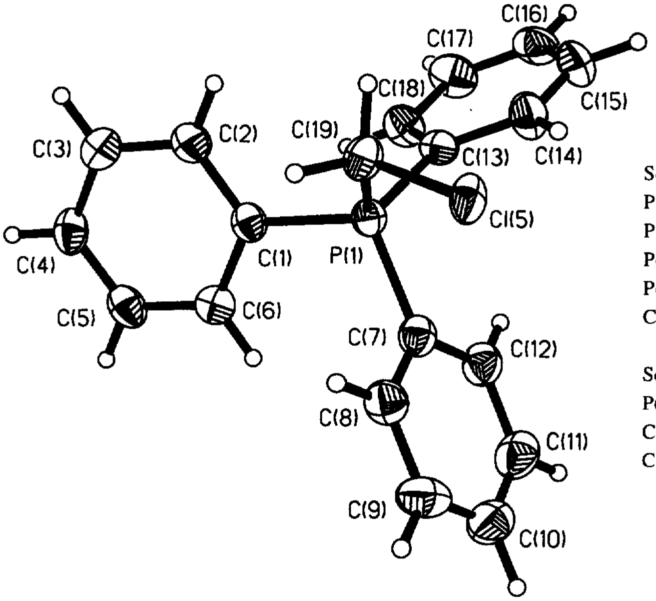
Oxidation of the phosphonium salt **1b** by peroxytrifluoroacetic acid at -30 °C resulted in complete decomposition. Under similar conditions, reaction of the ammonium salt **1a** afforded white precipitate of bis(trifluoroacetate) **4** (eq. 3), which had a low stability at room temperature and could not be completely characterized.



$$\overset{+}{\mathrm{Et_3NCH_2I}}\ \mathrm{BF_4^-}\ \xrightarrow[\mathrm{CF_3CO_2H},\ -30\text{ to r.t., 4 h}]{\mathrm{CF_3CO_3H}}\ \overset{+}{\mathrm{Et_3NCH_2I(CO_2CF_3)_2}}\ \mathrm{BF_4^-}$$

1a **4** (eq. 3)

In conclusion, we have prepared novel alkyliodine(III) dichlorides **2** which are stabilized due to the presence of the electron-withdrawing trialkylammonium or triphenylphosphonium groups. Decomposition of these compounds in solution affords chloromethyl phosphonium and ammonium salts **3**. Our further investigation of compounds **2** and **4** as potential precursors to the novel and synthetically attractive iodonium salts and ylides is in progress.



Selected bond lengths (Å):
P(l)-C(7) 1.787(5)
P(l)-C(1) 1.788(4)
P(l)-C(13) 1.789(4)
P(l)-C(19) 1.833(5)
C(19)-Cl(5) 1.844(5)

Selected bond angles (°):
P(1)-C(19)-Cl(5) 114.3(2)
C(l)-P(1)-C(13) 111.0(2)
C(7)-P(1)-C(l) 110.3(2)

Figure 1. X-Ray Crystal Structure of Compound **3b** (ICl_4 anion not shown).

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8. ***Selected Experimental Procedures:***

(a) Preparation of (Iodomethyl)triethylammonium Tetrafluoroborate (1a): A solution of triethylamine (7.0 mL, 50.4 mmol) and diiodomethane (5.0 mL, 62.1 mmol) in methylene chloride (15 ml) was stirred and refluxed for 24 hours. The solution was cooled to room temperature. The resulting crystals of $(ICH_2NEt_3)^+I^-$were washed on filter with methylene chloride (3x10 mL) and dried under vacuum. The product was then dissolved in a saturated aqueous solution of sodium tetrafluoroborate for an anion exchange. The resulting aqueous solution was extracted with methylene chloride (5x10mL) and the methylene chloride layer dried over sodium sulfate. The solution was evaporated, the residual solid was dried under vacuum to afford the off-white crystalline product **1a** in almost quantitative yield; mp 175 °C; IR (KBr): 2965, 2904, 1300, 1264, 1068 (B-F) cm^{-1}; ^1H NMR (CD_3CN): δ 4.84 (s, 2H, CH_2), 3.34 (quartet, 6H, CH_2), 1.26 (triplet, 9H, CH_3).

(b) [(Dichloroiodo)methyl]triethylammonium Tetrafluoroborate (2a): Chlorine gas was introduced to the stirred solution of (iodomethyl)triethylammonium tetrafluoroborate **1a** (0.918 g, 2.5 mmol) in methylene chloride (50 mL) at -10 °C. The solution turned yellow and pale yellow crystals of **2a** precipitated out. The resulting crystals were washed on filter with methylene chloride (3x10 mL) and dried by suction on a cold filter to give 0.921 g (84%) of [(dichloroiodo)methyl]triethylammonium tetrafluoroborate **2a**; mp 163 °C (dec); IR (KBr): 2960, 2905, 1300, 1265, 1068 (B-F) cm^{-1}; ^1H NMR (CD_3CN): δ 6.17 (s, 2H, CH_2), 3.65 (quartet, 6H, CH_2), 1.39 (triplet, 9H, CH_3).

[(Dichloroiodo)methyl]triphenylphosphonium Tetrafluoroborate (2b): Chlorine gas was introduced to the stirred solution of (iodomethyl)triphenylphosphonium tetrafluoroborate **1b** (2.09 g, 4.3 mmol) in methylene chloride/trifluoroacetic acid (50 mL/3.5mL) at -10 °C. The solution turned yellow with no precipitate. Ethyl ether was added to the cold solution and pale yellow crystals of **2b** precipitated out. The resulting crystals were washed on filter with ether (2x5 mL) and dried by suction on a cold filter to give 0.963 g (40.3%) of [(dichloroiodo)methyl]triphenylphosphonium tetrafluoroborate **2b**; mp 182 °C (dec.); IR (KBr): 3007 (Ar), 2941 (CH_2), 1068 (B-F) cm^{-1}; ^1H NMR ($CDCl_3$/trifluoroacetic acid 20:1): δ 7.81 - 7.71 (m, 15H, Ph), 6.00 (d, 2H, CH_2). Anal. Calcd for $C_{19}H_{17}BCl_2F_4IP$: C, 40.68; H, 3.03. Found: C, 40.92; H, 3.13.