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# Synthesis, properties and photolysis of new iodonium tetrakis(pentafluorophenyl)gallate photoinitiators and comparison with their indate and aluminate analogs☆

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Dedicated to Professor Dr J. W. Neckers on the occasion of his 100th birthday

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**Abstract**—A series of new iodonium tetrakis(pentafluorophenyl)gallates were synthesized in high yield via an improved preparation of the lithium gallate, their photoproducts analyzed by UV, $^{19}$F NMR and GC–MS spectra and a photolysis mechanism postulated. The stability of these photoinitiators was also compared with their borate, aluminate and indate analogs. © 2002 Published by Elsevier Science Ltd.

## 1. Introduction

Diaryl iodonium salts are important photoacid generators.[1] Tailoring the absorption characteristics of the iodonium cation, enhancing its solubility by attaching long alkyl chains, reducing toxicity and developing new and efficient synthetic routes has lead to several important advances in the field. In contrast, modification of the anion of such initiators has received little attention. In fact, varying the anion also affects the solubility, stability and toxicity of the entire salt, even the photoreactivity of the iodonium cation. The most common counterions used in iodonium salt photoacid generators are weakly nucleophilic complex inorganic anions, with the order of nucleophilicity being $SbF_6^- < AsF_6^- < PF_6^- < BF_4^-$. The most efficient cationic photoinitiators among such iodonium salts are those which contain the least nucleophilic anion $SbF_6^-$. This anion, however, has several drawbacks. Antimony is a toxic heavy metal, and the hexafluoroantimonate anion is both sensitive to humidity and has a tendency to convert to the corresponding antimony oxides, especially when these salts are stored for long periods of time. Most iodonium hexafluoroantimonates are insoluble in nonpolar media and this affects performance in silicone release resins, epoxized soybean oil and a variety of vinyl ethers. Recently it has been shown that the tetrakis(pentafluorophenyl)borate anion,[2] when paired with iodonium cations, produces better performing cationic photoinitiators than those in which the anion is $SbF_6^-$. Tetrakis(pentafluorophenyl)borate also forms more soluble compounds that are less toxic and less hydroscopic than are the $SbF_6^-$ counterparts. This discovery intrigued us so we have extended our previous work in the field of gallates.[3] Earlier we had discovered that ammonium butyltriphenylgallate, the first reported gallate photoinitiator, displayed similar photoactivity to the corresponding borate salt.

Of the group 15 elements phosphorus, arsenic and antimony, electronegativity follows in order from the element at the top of the group, phosphorus, to antimony. Likewise, of the anions $PF_6^-$. $AsF_6^-$, and $SbF_6^-$, $PF_6^-$ is the most nucleophilic, while $SbF_6^-$ is the least. Of the corresponding Brønsted acids $HPF_6$, $HAsF_6$, and $HSbF_6$, which result from the photolysis of their corresponding iodonium salts, $HPF_6$ is the weakest, and $HSbF_6$ is the strongest acid.

Electronegativity does not follow the order of elements from top to bottom in group 13. Boron (2.04), gallium (1.81) and indium (1.78) follow in order but the electronegativity of aluminum (1.61) seems out of place. We reasoned that since the electronegativity of gallium is closer to that of boron than is aluminium, it might be the better element from which to make new anions. Unlike aluminium and indium, gallium has nonmetallic character similar to boron.[4] Therefore it seemed reasonable to expect that tetrakis(pentafluorophenyl)gallate, when paired with an iodonium cation, should be an attractive photoinitiator in the manner of salts of tetrakis(pentafluorophenyl)borates.

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*Keywords*: iodonium tetrakis(pentafluorophenyl)gallates; photolysis.

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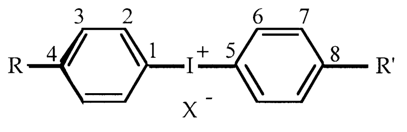


**1**: X = $Ga(C_6F_5)_4$

**2**: X = $B(C_6F_5)_4$

**3**: X = $SbF_6$

**4**: X = Cl, or OTos

| | R | R′ |
|---|---|---|
| **a** | H | H |
| **b** | $CH_3$ | $i$-$C_3H_7$ |
| **c** | $i$-$C_3H_7$ | $i$-$C_3H_7$ |
| **d** | $n$-$C_{12}H_{25}$ | $n$-$C_{12}H_{25}$ |
| **e** | H | O-$n$-$C_8H_{17}$ |
| **f** | H | $O(CH_2)_3Si(CH_3)_3$ |
| **g** | H | O-$n$-$CH_2CH(OH)C_{12}H_{25}$ |

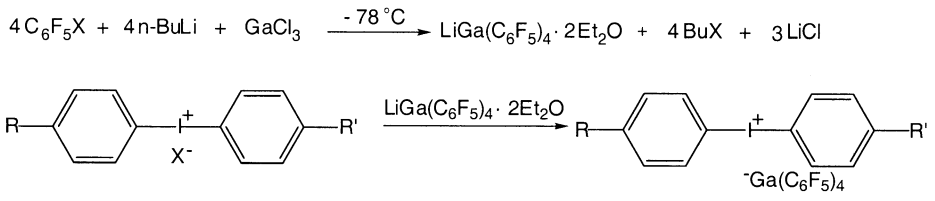
**Figure 1.** Structure of initiators used.

In this paper, we report the synthesis, characterization, stability and photolysis of a series of new iodonium tetrakis(pentafluorophenyl)gallates (**1**) (Fig. 1). In previous papers, we have reported rates of photoacid generation and photopolymerization rates in different resins.[5–7] The application of these new cationic photoinitiators and other salts have shown interesting results.

## 2. Results and discussion

### 2.1. Synthesis method of tetrakis(pentafluorophenyl)-gallate salts

Although much is known about the synthesis and properties of organogallium compounds, the first tetrakis(pentafluorophenyl)gallate salts were not reported until 1992.[8] The reaction of $Mg(C_6F_5)Br$ and $GaCl_3$ yielded a mixture of two kinds of magnesium salts $Mg[Ga(C_6F_5)_4]_2$ and $MgX_2$, that was metathesized directly with $n$-$Bu_4NF$ to obtain pure tetrabutylammonium tetrakis(pentafluorophenyl)gallate in poor yield (25%). The separation of the final product from $MgX_2$ was difficult since its solubility and that of the organic salts were very similar. In 1996, another tetrakis(pentafluorophenyl)gallate salt, $[Ph_3PNPPh_3][Ga(C_6F_5)_4]$, was synthesized using the same method.[9] The tetrakis(pentafluorophenyl)gallate anion was proven to have a tetrahedral geometry by X-ray diffraction. More recently, Kubas et al. reported an improved preparation of tetrakis(pentafluorophenyl)gallate in 1999 by which $LiGa(C_6F_5)_4$ was prepared by reaction of a slight excess of $LiC_6F_5$ with $GaCl_3$ in hexane at −78°C. In this case, a rather modest yield of 44% was obtained (Scheme 1).[10] Unfortunately this yield was still too low to prepare the designed compounds in high purity. In addition, the many byproducts would burden the isolation of product. Preparing the gallate in ether circumvented this problem. The reaction is somewhat cumbersome in that the $GaCl_3$ has to be added to the ether at −40°C due to the formation of the etherate complex, but the yields and purity of the final product are much better than those obtained by the aforementioned method. The crude lithium gallate etherate was characterized by $^{19}F$



**Scheme 1.**

**Table 1.** Melting point of diphenyliodonium salts ($Ph_2I^+X^-$)

| X | Cl | $BF_4$ | $PF_6$ | $AsF_6$ | $SbF_6$ | $B(C_6F_5)_4$ | $Ga(C_6F_5)_4$ |
|---|---|---|---|---|---|---|---|
| Mp (°C) | 233–235 | 136–138 | 138–140 | 128–130 | 125–127 | 165–166 | 153–154 |

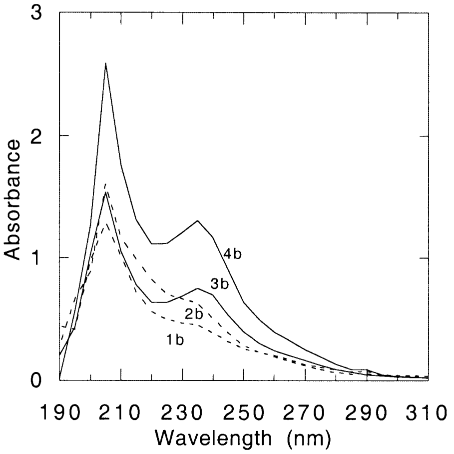


**Figure 2.** UV spectra of iodonium (**b**) salts in ethanol ($1.25\times10^{-5}$ M).

NMR, and it was found to contain minor amounts of impurities that did not affect further use. The metathsis of the lithium gallate etherate with various iodonium salts to give the desired iodonium tetrakis(pentafluorophenyl)-gallate is shown in Scheme 1.

## 2.2. Characterization of iodonium tetrakis(pentafluorophenyl)gallates

Iodonium salts paired with less nucleophilic anions typically show lower melting points.[11] For example, the order of the melting points of diphenyliodonium salts are as follows: $SbF_6^- < AsF_6^- < PF_6^- \approx BF_4^- < Cl^-$, and in the case of the tetra-aryl anions $Ga(C_6F_5)_4^- < B(C_6F_5)_4^-$ (Table 1).

As expected from the UV spectra, the introduction of an alkoxy group to an iodonium cation shifted the maximum absorption wavelength from 236 nm in alkylated iodonium salts to approximately 250 nm. The hypochromic effect of the tetrakis(pentafluorophenyl)gallate anion was also observed. In order to stabilize the ion pair compound, the negative charge delocalized over the large size of the anion, and the positive charge of the iodine was delocalized over the aromatic ring of the iodonium cation as well. Accordingly, the $\pi\rightarrow\pi^*$ electronic transition energy of the electron-deficient aromatic ring was increased. Therefore, at the same wavelength (236 nm), the intensity of absorption was reduced in the order of **1b**<**2b**<**3b**<**4b** (Fig. 2).

The $^{13}$C NMR spectra of C1 and C5 of **1b**, **2b**, **3b** and **4b** (as labeled in Fig. 1) are shifted upfield, and those of C4 and C8 shifted downfield by a change in anion from $Cl^-$ to $Ga(C_6F_5)_4^-$. Consistent results are also obtained from the $^1$H NMR spectra of H3 and H7 (Table 2). This suggests that the positive charge of iodine on the cation gets more delocalized into the aryl ring as the anion goes from $Cl^-$ to $Ga(C_6F_5)_4^-$.

In the $^{19}$F NMR spectra, fluorine absorptions of the $C_6F_5$ group of **1b** shift downfield when compared to **2b**, since the electronegativity of gallium is lower than that of boron. Likewise the gallate anion is less nucleophilic than

**Table 2.** Selected NMR data for iodonium (**b**) salts (ppm)

| | $^{13}$C NMR | | | | $^1$H NMR | | $^{19}$F NMR | | |
|---|---|---|---|---|---|---|---|---|---|
| | C1 | C5 | C4 | C8 | H3 | H7 | *m*-F | *o*-F | *p*-F |
| **1b** | 107.04 | 107.19 | 146.28 | 156.74 | 7.389 | 7.348 | −123.2 | −158.4 | −163.7 |
| **2b** | 107.03 | 107.18 | 146.35 | 156.82 | 7.382 | 7.348 | −132.8 | −163.0 | −166.8 |
| **3b** | 108.52 | 108.58 | 144.59 | 155.07 | 7.333 | 7.286 | | | |
| **4b** | 115.89 | 116.10 | 141.47 | 152.07 | 7.186 | 7.149 | | | |

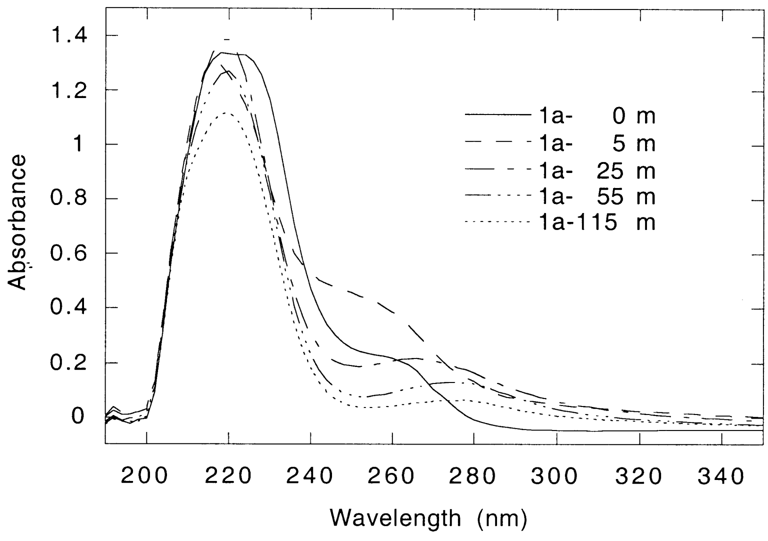


**Figure 3.** Photolysis of **1a** in ethanol ($1.25\times10^{-5}$ M) at 254 nm recorded by UV spectra.

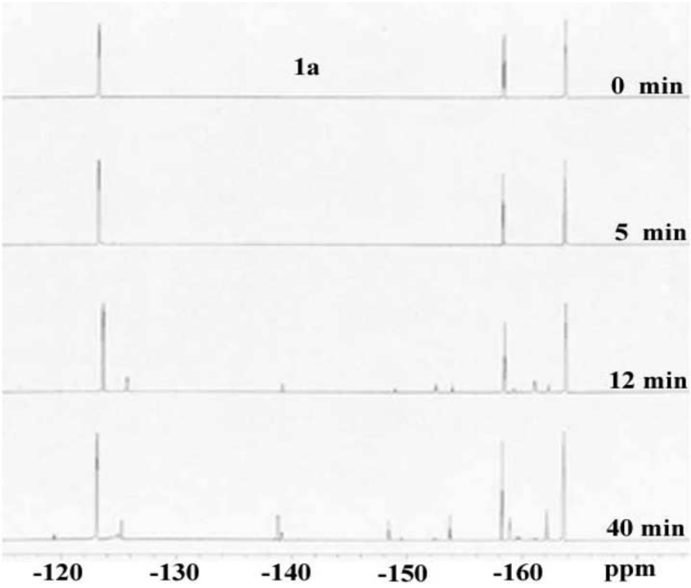


**Figure 4.** Photolysis of **1a** in $CDCl_3$ at 254 nm followed by $^{19}F$ NMR.

is the borate. Therefore, anion nucleophilicity can be correlated with the $^{1}H$ and $^{13}C$ NMR data of the iodonium cation or by $^{19}F$ NMR data of anion.

### 2.3. Photolysis of diphenyliodonium tetrakis(pentafluorophenyl)gallate and tetrakis(pentafluorophenyl)-borate

The simplest diphenyliodonium salts **1a** and **2a** were chosen to conveniently compare the photolysis of iodonium gallate with the corresponding borate. The UV spectra in the ethanol were followed during irradiation. As can be seen from Fig. 3, several absorption bands emerged between 240 and 300 nm, causing the growth of the curve during the first 5 min. Later in the photolysis these bands disappeared gradually, and the maximum absorption shifted from 258 to 276 nm. The UV spectra obtained from **2a** exhibited the same shape. This suggested that the same photoproducts were obtained from the same mechanism during their photolyses.

Since the photoproducts of the iodonium cation contain no fluorine, the byproducts formed by the cation of **1a** and **2a** should not be detectable by $^{19}F$ NMR. Any change in the fluorine NMR would then be due to changes in the nature of the anion. Upon the photolysis of **1a** in a Rayonet photoreactor, we found that after 12 min, byproducts containing fluorine gradually resulted. The $^{19}F$ NMR peaks that resulted coincided with peaks deriving from known compound $HC_6F_5$ ($\delta$, $-138$, $-153$, $-161$) and suspected byproduct $Ga(C_6F_5)_3$ ($\delta$, $-125$, $-152$, $-162$) (Fig. 4).

In the case of **2a**, similar products, identified by two known compounds: $HC_6F_5$ and $B(C_6F_5)_3$ ($\delta$, $-136$, $-156$, $-163$),

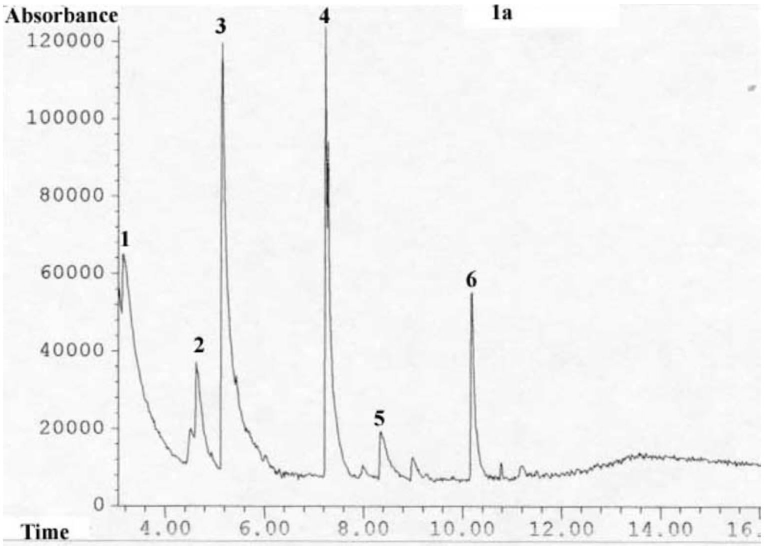


**Figure 5.** Photoproducts of **1a** in $CDCl_3$ at 254 nm recorded by GC–MS.

began to appear in 40 min. This suggests the Brønsted acid $HGa(C_6F_5)_4$, derived from the photolysis of the gallate salt, was less stable thermally than $HB(C_6F_5)_4$. In order to confirm that the acid would more likely be decomposed thermally rather than photochemically, we carried out the following experiment. In NMR tubes, anhydrous HCl solution in ether was added to the solutions of $KGa(C_6F_5)_4$ and $KB(C_6F_5)_4$ in $CDCl_3$ under argon. The $HGa(C_6F_5)_4$ and $HB(C_6F_5)_4$ solutions thus prepared were then monitored by $^{19}F$ NMR at room temperature without light irradiation. It was found that $HGa(C_6F_5)_4$ decomposed to give $HC_6F_5$ and $Ga(C_6F_5)_3$ faster than the $HB(C_6F_5)_4$.

The same solutions of **1a** and **2a** in $CDCl_3$ were irradiated for four more hours at 254 nm. The samples were analyzed by GC–MS. It can be seen from Fig. 5 that MS identified six photoproducts of **1a**. They include the first generation photoproducts described previously:[12] iodobenzene **3** (as labeled on GC spectrum) (5.2 min), biphenyl **5** (8.2 min) and iodobiphenyl **6** (10.2 min); the thermal decomposition product pentafluorobenzene **1** (3.2 min); the second generation photoproducts iodopentafluorobenzene **2** (4.8 min) and pentafluorophenylbenzene **4** (7.3 min). Products **1**, **2** and **4** have not been reported before. The photolysis of **2a** gave the similar peaks in the GC spectrum, the six photoproducts are identical in MS spectra.

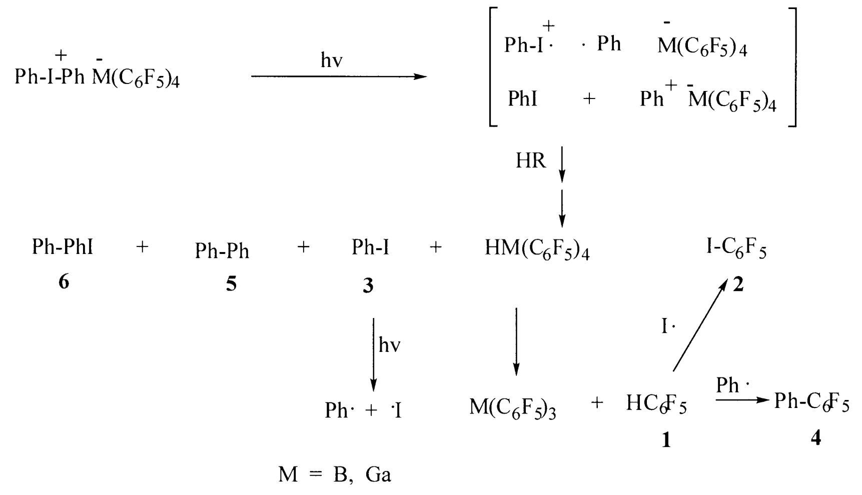
The studies above reveal that like diphenyliodonium tetrakis(pentafluorophenyl)borate, diphenyliodonium gallate undergoes both homolytic and heterolytic cleavages of the carbon–iodine bond to generate reactive radical, cation and cation–radical intermediates including phenyl radical, phenyl cation and iodophenyl radical–cation upon irradiation, which then undergo the further reactions with a proton source HR, most likely solvent or an impurity, to form a Brønsted superacid $HGa(C_6F_5)_4$ and the first generation photoproducts **3**, **5** and **6**. Thereafter, the acid decomposes thermally to yield compound **1**, which reacts with both iodine and phenyl radical to give the second generation photoproducts **2** and **4**. The mechanism is depicted in detail in Scheme 2.

### 2.4. Iodonium tetrakis(pentafluorophenyl)aluminate and tetrakis(pentafluorophenyl)indate

A quantitative scale for Lewis acidity of $MF_3$, where M is an element of group 13, has recently been reported.[13] The order of the Lewis acid strength was $AlF_3>InF_3GaF_3BF_3$. It is reasonable to conclude that when the iodonium salts are photolyzed, the strength of the yielded Brønsted acids should follow the order: $HAl(C_6F_5)_4>'''$ $HIn(C_6F_5)_4>HGa(C_6F_5)_4>HB(C_6F_5)_4$. With this in mind, we successfully prepared the iodonium tetrakis(pentafluorophenyl)aluminate and the corresponding indate by using the same method as gallate. TLC confirmed products were pure under argon. However, good clean NMR spectra could not be obtained due to the instability of both salts. However, the correct peaks were prominent and clearly visible in both spectra. (4-Octyloxyphenyl)phenyliodonium tetrakis(pentafluorophenyl)indate exhibited excellent solubility and photoactivity in epoxy silicone resins when the operations were conducted under an inert argon atmosphere. However, both the iodonium aluminate and indate decomposed when stored under an ambient environment as shown by $^1H$ and $^{19}F$ NMR. Since it is both air and moisture sensitive, the iodonium aluminate was almost completely decomposed after 1 h. The iodonium indate lasted 4 days before it decomposed completely. In contrast, the iodonium gallate did not decompose to a degree that could be detected, even when stored for over one year. Accordingly the stability of these iodonium salts increased as a function of the anion: $Al(C_6F_5)_4^-<In(C_6F_5)_4^-<Ga(C_6F_5)_4^-<B(C_6F_5)_4^-$.

## 3. Conclusions

A synthetic method has been developed to prepare a series of new iodonium tetrakis(pentafluorophenyl)gallates in high yield. The physical properties of different iodonium salts were compared. It was found that the decrease of the nucleophilicity from $Cl^-$, $SbF_6^-$ to $B(C_6F_5)_4^-$ and $Ga(C_6F_5)_4^-$ could be correlated with melting points, UV and NMR spectra. A photolysis mechanism, involving two new photoproducts iodopentafluorobenzene and pentafluorophenylbenzene, was postulated. These second-generation



Scheme 2.

photoproducts resulted from the decomposition of the Brønsted superacid $HGa(C_6F_5)_4$, which was stronger but less stable than $HB(C_6F_5)_4$. In addition, the iodonium tetrakis(pentafluorophenyl)aluminate and the corresponding indate also were synthesized. Both of these compounds displayed very poor stability. However, the iodonium tetrakis(pentafluorophenyl)gallates could be stored for over a year at ambient temperature without decomposition.

## 4. Experimental

### 4.1. General

All inert manipulations were performed under an argon atmosphere using standard techniques. Reagents and solvents were purchased from Aldrich and used without further purification techniques unless otherwise noted. (4-Octyloxyphenyl)phenyliodonium tosylate (**4e**) was obtained from General Electric Silicones. (2-Hydroxytetradecyloxyphenyl)phenyliodonium hexafluoroantimonate (**3g**) (CD1012) was purchased from Sartomer. (4-Isopropylphenyl)-4-methylphenyliodonium tetrakis(pentafluorophenyl)-borate (**2b**) (Rhodorsil 2074) was obtained from Rhodia. Diphenyliodonium tetrafluoroborate, diphenyliodonium hexafluorophosphorate, diphenyliodonium hexafluoroarsenate, diphenyliodonium hexafluoroantimonate, (4-isopropylphenyl)-4-methylphenyl-iodonium hexafluoroantimonate (**4b**), bis(4-isopropylphenyl)iodonium chloride (**4c**), bis(docecylphenyl)iodonium chloride (**4d**) and [4-(3-trimethylsilylpropyloxy)phenyl]phenyliodonium tosylate (**4f**), were prepared as described previously.[14] Diphenyliodonium tetrakis(pentafluorophenyl)borate (**2a**) was prepared according to the reported procedure.[2]

$^1H$ and $^{13}C$ NMR spectra were taken with a Varian Gemini 200 NMR spectrometer. $^{19}F$ NMR spectra were taken with a Unity Plus 400 NMR spectrometer, using $CFCl_3$ as an external reference. GC/MS were taken on a Hewlett–Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m×0.25 mm ID×0.25 mm film thickness DB-5 ms column (J&B Scientific), interfaced to an HP 2623A data processor. UV–visible spectra were obtained using an HP 8452 diode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab Inc. in Norcross, GA. Silica gel chromatography was performed using silica gel (40 μm, 32–63 μm) purchased from Scientific Adsorbents Incorporated. Thin layer chromatography was performed on Sigma-Aldrich plates (layer thickness: 250 μm, particle size 5–17 μm, pore size 60 Å) purchased from Aldrich. Melting points are uncorrected.

*Caution*: Preliminary toxicology studies of (4-octyloxyphenyl)phenyl-iodonium tetrakis(pentafluorophenyl)gallate (**1e**) indicate potent dermal toxicity.[15]

**4.1.1. Lithium tetrakis(pentafluorophenyl)gallate etherate $LiGa(C_6F_5)_4 \cdot 2(Et_2O)$.** To a 125 mL four-neck round-bottom flask, equipped with a magnetic stirrer, a thermometer and a solid-addition funnel, 50 mL of anhydrous ether was added and cooled to about −40°C under an argon atmosphere. The $GaCl_3$ (5.2 g, 29.55 mmol) was added via the solid-addition funnel in portions.

Into a dry 500 mL four-neck round bottom flask, equipped with a thermometer, two addition funnels and magnetic stirrer, was placed anhydrous ether (200 mL) and bromopentafluorobenzene (30 g, 121.46 mmol) and cooled to below −75°C. A 2.5 M solution of *n*-butyl lithium (47.4 mL, 118.50 mmol) in hexane was added dropwise over 4.0 h. The mixture was stirred for another hour, at −78°C.

A solution of gallium chloride was added dropwise to the above mixture over 1.0 h. The mixture was kept for 3–5 h at −78°C and allowed to gradually warm to room temperature. A white precipitate of LiCl appeared. The solution was stirred for another 5 h and then filtered to remove the LiCl. The filtrate was concentrated to give a gray white solid. This crude product was washed with anhydrous hexane (4×30 mL) and then vacuum dried overnight at room temperature to give a white solid 22.97 g of lithium tetrakis(pentafluorophenyl)gallate etherate [$LiGa(C_6F_5)_4 \cdot 2 Et_2O$], crude yield: 87%. The hydroscopic product was stored under an argon atmosphere. $^1H$ NMR ($CDCl_3$) $\delta$ 3.46 (q, 2H, $J$=7.0 Hz, $CH_2$), 1.18 (t, 3H, $J$=7.0 Hz, $CH_3$); $^{19}F$ NMR ($CDCl_3$) $\delta$ −124.2 (sm, 2F), −158.2 (sm, 1F), −164.0 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 260 (1533). The crude product was used directly without further purification.

### 4.2. General procedure for the preparation of iodonium tetrakis(pentafluorophenyl)gallates

In a 50 mL round-bottom flask, lithium tetrakis(pentafluorophenyl)gallate etherate (6 mmol) was dissolved in 25 mL $CH_2Cl_2$. A solution of the corresponding iodonium chloride or tosylate (5 mmol) in 25 mL $CH_2Cl_2$ was added dropwise with stirring at room temperature. The reaction mixture becomes cloudy as the corresponding lithium salt precipitates out of solution. After the solution was stirred for 2 h in the absence of light, the salt was filtered, and the solvent removed to give a sticky residue.

The crude product was chromatographed through a short plug of silica gel (3–5 cm in length) by elution with the mixture of $CH_2Cl_2$ and hexane (1:1) to give the desired iodonium tetrakis(pentafluorophenyl)gallate as a solid or a light yellow sticky oil. The product was vacuum dried overnight in the dark.

**4.2.1. Diphenyliodonium tetrakis(pentafluorophenyl)-gallate (1a).** Compound **1a** was obtained from diphenyliodonium chloride in 68% yield as a white powder: mp 153–154°C. $^1H$ NMR ($CDCl_3$) $\delta$ 7.22–7.90 (m, 10H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 151.12 (m, $Ga(C_6F_5)_4$), 146.56 (m, $Ga(C_6F_5)_4$), 142.14 (m, $Ga(C_6F_5)_4$), 138.77 (m, $Ga(C_6F_5)_4$), 134.81, 134.56, 133.90, 110.74; $^{19}F$ NMR ($CDCl_3$) $\delta$ −124.1 (sm, 2F), −158.5 (sm, 1F), −164.2 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 258 (6226). Anal. calcd for $C_{36}H_{10}F_{20}GaI$: C, 42.43; H, 0.99. Found: C, 42.51; H, 1.00.

**4.2.2. (4-Isopropylphenyl)-4-methylphenyliodonium tetrakis(pentafluoro-phenyl)gallate (1b).** Compound **1b** was obtained from (4-isopropylphenyl)-4-methylphenyliodonium chloride **4b** in 85% yield as a white powder: mp 92–94°C. $^1$H NMR ($CDCl_3$) $\delta$ 1.12 (d, 6H, $J$=7.0 Hz), 2.37 (s, 3H), 2.86 (m, 1H), 7.26 (t, 4H, $J$=8.8 Hz), 7.62 (d, 4H, $J$=8.4 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 151.14 (m, $Ga(C_6F_5)_4$), 146.57 (m, $Ga(C_6F_5)_4$), 142.15 (m, $Ga(C_6F_5)_4$), 138.89 (m, $Ga(C_6F_5)_4$), 156.74, 146.28, 134.72, 134.41, 132.03, 107.19, 107.04, 34.18, 24.72, 23.30, 21.39; $^{19}$F NMR ($CDCl_3$) $\delta$ −123.2 (sm, 2F), −158.4 (sm, 1F), −163.7 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 236 (22,037). Anal. calcd for $C_{40}H_{18}F_{20}GaI$: C, 44.69; H, 1.69. Found: C, 44.62; H, 1.82.

**4.2.3. Bis(4-isopropylphenyl)iodonium tetrakis(pentafluorophenyl)gallate (1c).** Compound **1c** was obtained from bis(4-isopropylphenyl)iodonium chloride **4c** in 84% yield as a white powder: mp 116–118°C. $^1$H NMR ($CDCl_3$) $\delta$ 1.25 (d, 6H, $J$=7.0 Hz), 2.99 (m, 2H), 7.39 (d, 4H, $J$=8.8 Hz), 7.77 (d, 4H, $J$=8.8 Hz); $^{19}$F NMR ($CDCl_3$) $\delta$ −123.1 (sm, 2F), −158.4 (sm, 1F), −163.7 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 236 (26,611). Anal. calcd for $C_{42}H_{22}F_{20}GaI$: C, 45.73; H, 2.01. Found: C, 45.41; H, 2.12.

**4.2.4. Bis(docecylphenyl)iodonium tetrakis(pentafluorophenyl)gallate (1d).** Compound **1d** was obtained from bis(docecylphenyl)iodonium chloride **4d** in 59% yield as a slightly yellow sticky oil. $^1$H NMR $\delta$ ($CDCl_3$) 0.87 (s, 6H), 1.24 (m, 36H), 1.58 (m, 4H), 2.64 (t, 4H, $J$=7.0 Hz), 7.34 (d, 4H, $J$=8.8 Hz), 7.76 (d, 4H, $J$=8.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 151.17 (m, $Ga(C_6F_5)_4$), 146.54 (m, $Ga(C_6F_5)_4$), 142.18 (m, $Ga(C_6F_5)_4$), 138.89 (m, $Ga(C_6F_5)_4$), 151.17, 134.69, 133.78, 107.08, 35.67, 31.89, 30.89, 29.61, 29.47, 29.32, 29.18, 22.66, 10.07; $^{19}$F NMR ($CDCl_3$) $\delta$ −123.1 (sm, 2F), −158.5 (sm, 1F), −163.7 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 236 (22,970). Anal. calcd for $C_{60}H_{58}F_{20}GaI$: 53.16; H, 4.31. Found: C, 53.47; H, 4.34.

**4.2.5. (4-Octyloxyphenyl)phenyliodonium tetrakis(pentafluorophenyl)-gallate (1e).** Compound **1e** was obtained from (4-octyloxyphenyl)phenyliodonium tosylate **4e** in 86% yield as a slightly yellow sticky oil. $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, 3H, $J$=7.2 Hz), 1.34 (m, 10H), 1.80 (m, 2H), 3.94 (t, 2H, $J$=7.2 Hz), 6.90–7.90 (m, 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 151.15 (m, $Ga(C_6F_5)_4$), 146.48 (m, $Ga(C_6F_5)_4$), 142.16 (m, $Ga(C_6F_5)_4$), 138.64 (m, $Ga(C_6F_5)_4$), 164.18, 137.45, 133.97, 133.77, 133.54, 119.83, 112.06, 97.16, 69.23, 31.70, 29.16, 29.10, 28.70, 25.75, 22.59, 14.02; $^{19}$F NMR ($CDCl_3$) $\delta$ −123.2 (sm, 2F), −158.4 (sm, 1F), −163.7 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 250 (17,310). Anal. calcd for $C_{44}H_{26}F_{20}GaOI$: C, 46.06; H, 2.28. Found: C, 46.15; H, 2.32.

**4.2.6. [4-(3-Trimethylsilylpropyloxy)phenyl]phenyliodonium tetrakis(penta-fluorophenyl)gallate (1f).** Compound **1f** was obtained [4-(3-trimethylsilylpropyloxy)phenyl]phenyliodonium tosylate **4f** in 73% yield as a slightly yellow sticky oil. $^1$H NMR ($CDCl_3$) $\delta$ 0.56 (t, 2H, $J$=7.2 Hz), 1.78 (m, 2H), 3.94 (t, 2H, $J$=7.2 Hz), 6.96–7.91 (m, 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 151.15 (m, $Ga(C_6F_5)_4$), 146.46 (m, $Ga(C_6F_5)_4$), 142.14 (m, $Ga(C_6F_5)_4$), 138.69 (m, $Ga(C_6F_5)_4$), 164.24, 137.51, 133.87, 133.76, 133.59, 119.89, 110.92, 96.93, 71.80, 23.41, 12.31, −1.94; $^{19}$F NMR ($CDCl_3$) $\delta$ −123.2 (sm, 2F), −158.4 (sm, 1F), −163.7 (sm, 2F); UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 250 (15,880). Anal. calcd for $C_{42}H_{24}F_{20}GaSiOI$: C, 43.89; H, 2.10. Found: C, 44.17; H, 2.24.

**4.2.7. (2-Hydroxytetradecyloxyphenyl)phenyliodonium tetrakis(pentafluoro-phenyl)gallate (1g).** Compound **1g** was obtained from (2-hydroxytetra-decyloxyphenyl)phenyliodonium hexafluoroantimonate **3g** in 80% yield as a slightly yellow sticky oil. $^1$H NMR ($CDCl_3$) $\delta$ 0.85 (t, 3H, $J$=7.2 Hz), 1.23 (m, 20H), 1.54 (m, 2H), 2.03 (d, 1H, $J$=4.0 Hz), 3.97 (m, 3H), 6.98–7.80 (m, 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 151.17 (m, $GaC_6F_5$), 146.49 (m, $GaC_6F_5$), 142.12 (m, $GaC_6F_5$), 138.71 (m, $GaC_6F_5$), 162.35, 137.45, 134.12, 133.94, 133.65, 119.93, 108.59, 98.02, 71.32, 69.39, 37.33, 34.38, 33.00, 31.91, 29.62, 26.67, 25.39, 22.77, 22.68, 14.11; $^{19}$F NMR ($CDCl_3$) $\delta$ −123.1 (sm, 2F), −158.3 (sm, 1F), −163.7 (sm, 2F; UV (EtOH) $\lambda_{max}$ ($\varepsilon$) 248 (15,157). Anal. calcd for $C_{50}H_{38}F_{20}GaO_2I$: C, 48.14; H, 3.07. Found: C, 48.23; H, 3.19.

### 4.3. Photolysis of diphenyliodonium tetrakis(pentafluorophenyl)gallate and diphenyliodonium tetrakis-(pentafluorophenyl)borate

Solutions ($2.2\times10^{-4}$ M) of diphenyliodonium gallate **1a** and of the corresponding borate **2a** in ethanol were irradiated in a Rayonet photoreactor ($\lambda$=254 nm), and their UV spectra were recorded as a function of time. Solutions of **1a** and **2a** in $CDCl_3$ in NMR tubes were irradiated in a Rayonet photoreactor ($\lambda$=254 nm) to monitor their photolysis by $^{19}$F NMR. The final photolysis products were analyzed by GC–MS.

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