# Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization

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ABSTRACT: Diaryliodonium salts ( $Ar_2I^+MX_n^-$ ) possessing complex metal halide anions such as  $BF_4^-$ ,  $AsF_6^-$ ,  $PF_6^-$ , and  $SbF_6^-$  are active photoinitiators of cationic polymerization. The synthesis and characterization of a number of these compounds was carried out via a new synthetic pathway. A study of the mechanism of photolysis was conducted and observed to occur via a radical pathway. Brønsted acids produced by photolysis of the diaryliodonium salts are credited as the true initiators of cationic polymerization. A number of cationic polymerizations were carried out to demonstrate the scope of the usefulness of these new photoinitiators.

Although photoinitiated radical polymerizations have been known and investigated for a considerable period of time, the corresponding photoinitiated cationic and anionic polymerizations have received little attention. The slow development of this field has been largely due to the dearth of suitable photoinitiators capable of catalyzing ionic polymerizations. However, in the past few years considerable progress has been made, particularly in the development of photoinitiators for cationic polymerization. For example, titanium and vanadium tetrachlorides have been shown to be effective photoinitiators for the photopolymerization of isobutylene.<sup>2,3</sup> Silver<sup>4</sup> and gold<sup>5,6</sup> salts have been used in the photopolymerization of N-vinylcarbazole. Organometallic sandwich compounds such as bis(cyclopentadienyl)titanium dichloride sensitizes the cationic polymerization of 2-chloroethyl vinyl ether<sup>7</sup> while epichlorohydrin has been effectively polymerized by complexes of ferrocene and certain Lewis acids.<sup>8</sup> Anderson<sup>9</sup> has employed cyclopentadienyl manganese tricarbonyl and  $Strohmeyer^{10}$  manganese decacarbonyl as photoinitiators for the polymerization of epoxides. Last, diazonium salts have received considerable attention as photoinitiators for the polymerization of epoxides.<sup>11-14</sup>

Recently, we have discovered that diaryliodonium salts I

$$Ar-I^+-Ar'$$
  
 $MX_n^-$ 

having complex metal halide counterions  $(MX_n^{-})$  are efficient photoinitiators for the polymerization of a variety of cationically polymerizable monomers.<sup>1</sup> Diaryliodonium salts, in contrast to dialkyliodonium and alkylaryliodonium salts, are considerably more stable and can be readily isolated and purified by conventional techniques. In addition, they are indefinitely stable in the absence of light and in the presence of even such highly reactive cationically polymerizable monomers as cycloaliphatic olefin oxides.

In the present paper, we would like to report on our investigations into the synthesis and characterization of a number of active diaryliodonium salt photoinitiators as well as on the results of our investigations into the nature by which these compounds photoinitiate cationic polymerization. Further, we would like to demonstrate the general scope of their use in photoinitiated cationic polymerization by the polymerization of some selected representative monomers.

### **Experimental Section**

**Purification of Reagents and Starting Materials.** All solvents used in the photolysis and quantum yield studies were used without further purification. Reagents used in the preparation of monomers and diaryliodonium salts were reagent grade. Cyclohexene oxide, vinylcyclohexene oxide, trioxane, styrene,  $\alpha$ -methylstyrene, 2-chloroethyl vinyl ether,  $\epsilon$ -caprolactone, and oxetane were dried over cal-

cium hydride, then purified by fractional distillation. Tetrahydrofuran was freshly distilled from lithium biphenyl complex. 1,4,6-Trioxaspiro[4.4]nonane was prepared and purified according to the method of Bodenbenner.  $^{15}$ 

**Preparation of Diaryliodonium Salt Photoinitiators.** Specific examples are given of each of the three general methods employed for the synthesis of the diaryliodonium salts shown in Table I.

Method A. The Preparation of 3,3'-Dinitrodiphenyliodonium Hexafluoroarsenate. Into a 500 mL, 3-neck, round-bottom flask, equipped with a mechanical stirrer, a thermometer, and a dropping funnel, was placed a mixture of 7.7 g (0.030 mol) of iodine, 20 g (0.093 mol) of KIO<sub>3</sub>, and 80 mL of concentrated sulfuric acid. To this solution was slowly added, at 10 °C, 39.36 g (0.32 mol) of nitrobenzene. The addition was made over the course of 1 h. After the mixture had been stirred, at room temperature, for 24 h and then at 45–50 °C for 40 h, it was diluted at 5 °C with 200 mL of cold water. A precipitate was formed which was removed by filtration and washed successively with water and then ethyl ether. The product was then transferred to a 500-mL Erlenmeyer containing 200 mL of water and 17 g (0.075 mol) of KASF<sub>6</sub>. After stirring for 1 h, the 3,3'-dinitrodiphenyliodonium hexafluoroarsenate was filtered off, washed, and dried in vacuo at 60 °C to give a 29% yield of product, mp 192–195 °C.

Method B. Preparation of Diphenyliodonium Fluoroborate. Into a 500-mL, three-neck, round-bottom flask equipped with a paddle stirrer, addition funnel, thermometer, and condenser were placed 100 g (0.046 mol) of potassium iodate, 100 mL of acetic anhydride, and 90 mL (1 mol) of benzene. This mixture was cooled to -5°C and then a solution composed of 70 mL of concentrated sulfuric acid and 100 mL of acetic anhydride was added dropwise via the addition funnel. During the addition, the temperature was not permitted to rise above 5 °C. When the addition had been completed, the reaction mixture was allowed to rise to room temperature. After standing for 48 h, the reaction was again cooled to 5 °C and then 200 mL of distilled water was added at such a rate that the reaction temperature did not exceed 10 °C. At this point, 75 mL of diethyl ether was added and the reaction mixture was filtered to remove KHSO4. The aqueous layer was then extracted twice with diethyl ether and once with petroleum ether. To the aqueous solution was then added 53.5 g (1 mol) of NH<sub>4</sub>Cl. An immediate precipitate of diphenyliodonium chloride was formed which was collected by filtration, washed, and air dried.

Fresh Ag<sub>2</sub>O was prepared by mixing approximately equimolar aqueous solutions of AgNO3 and NaOH together and then decanting the aqueous solutions from the precipitated black  $Ag_2O$ . The  $Ag_2O$ was then washed several times with distilled water and then filtered. Next, 20 g of moist Ag<sub>2</sub>O, 31.6 g of diphenyliodonium chloride, and 10 mL of water were mixed together in a glass mortar. The reagents were thoroughly ground together until no trace of the iodonium compound could be discerned. The black slurry was then washed into a sintered glass filter and the precipitate was washed with water until 360 mL of filtrate was obtained. After transferring the filtrate to an Erlenmeyer flask, the contents were then frozen in a dry ice-acetone bath and then 25 mL of 45% HBF<sub>4</sub> were added in two portions with stirring. The reaction mixture was allowed to slowly warm to room temperature and then filtered to collect the diphenyliodonium fluroborate. The salt was dried in vacuo to give 22.1 g (60% yield) of pure product having a melting point of 136 °C (lit.<sup>16</sup> mp 136 °C).

Method C. The Preparation of 4-Methoxydiphenyliodonium Fluoroborate. Iodosobenzene diacetate was prepared by placing 40.8 g (0.2 mol) of iodobene in a 500-mL Erlenmeyer flask and then adding dropwise, with stirring, 91.2 g (0.48 mol) of 40% peracetic acid. The

		Table 1	I		
Structure and	Properties o	f Aromatic	Iodonium	Salt	Photosensitizers

			λ <sub>max</sub> (MeOH) nm			Eler	nental A	Anal	
Structure	Anion	Mp, °C	$(\epsilon_{max})$	Method		С	Н	I	Ma
	BF₄⁻	136	227 (17 800)	Α, Β	Calcd Found	39.13 40.10	$\begin{array}{c} 2.72\\ 2.65\end{array}$		$3.00 \\ 3.22$
CH,0	BF₄ <sup>-</sup>	96-100	246 (15 400)	С	Caled Found	39.20 39.39	$\begin{array}{c} 3.02\\ 3.09 \end{array}$	31.91 31.83	
	AsF <sub>6</sub> <sup>-</sup>	192-195	215 (35 000) 245 (17 000)	А	Calcd Found	$\begin{array}{c} 25.71\\ 26.00 \end{array}$	$\begin{array}{c} 1.42 \\ 1.42 \end{array}$	$\begin{array}{c} 22.68\\ 22.80\end{array}$	
	BF <sub>4</sub> <sup>-</sup>	95-100	236 (18 000)	В	Calcd Found	$\begin{array}{c}42.42\\42.51\end{array}$	$3.54 \\ 3.50$	$32.07 \\ 31.96$	
CH <sub>4</sub> CH <sub>5</sub> CH <sub>5</sub>	PF <sub>6</sub> -	169-173	237 (18 200)	В	Calcd Found	$\begin{array}{c} 37.00\\ 37.20\end{array}$	$3.08 \\ 2.83$	$29.97 \\ 28.81$	
CH , I * CH ,	$AsF_6^-$	166-167	237 (17 500)	В	Calcd Found	$\begin{array}{c} 33.74\\ 33.70\end{array}$	$\begin{array}{c} 2.81 \\ 2.92 \end{array}$		$\begin{array}{c} 15.06\\ 15.28 \end{array}$
	$BF_4^-$	80-83	238 (20 800)	В	Calcd Found	$\begin{array}{c} 50.00\\ 49.98 \end{array}$	$\begin{array}{c} 5.42 \\ 5.30 \end{array}$	$\begin{array}{c} 26.46\\ 26.55 \end{array}$	$2.29 \\ 2.30$
+<>>-1*-<>+	PF <sub>6</sub> -	173-174	238 (20 000)	В	Calcd Found	$\begin{array}{c} 44.61\\ 45.10\end{array}$	$\begin{array}{c} 4.83\\ 5.25\end{array}$		$5.76 \\ 5.07$
+ <r++< td=""><td>AsF<sub>6</sub><sup>-</sup></td><td>169-171</td><td>238 (20 700)</td><td>В</td><td>Calcd Found</td><td><math display="block">\begin{array}{c} 41.24\\ 41.28\end{array}</math></td><td><math display="block">\begin{array}{c} 4.47\\ 4.46\end{array}</math></td><td></td><td><math display="block">\begin{array}{c} 12.89\\ 12.70\end{array}</math></td></r++<>	AsF <sub>6</sub> <sup>-</sup>	169-171	238 (20 700)	В	Calcd Found	$\begin{array}{c} 41.24\\ 41.28\end{array}$	$\begin{array}{c} 4.47\\ 4.46\end{array}$		$\begin{array}{c} 12.89\\ 12.70\end{array}$
+	SbF <sub>6</sub> -	183-185	238 (21 200)	В	Caled Found	$\begin{array}{c} 38.16\\ 37.91 \end{array}$	$\begin{array}{c} 4.13\\ 4.14\end{array}$	$20.19 \\ 19.90$	19.20 19.10
	AsF <sub>6</sub> -	194-195	240 (23 000)	А	Caled Found	$\begin{array}{c} 26.72\\ 26.85 \end{array}$	$\begin{array}{c} 1.48 \\ 1.59 \end{array}$	$\begin{array}{c} 13.91 \\ 13.72 \end{array}$	
CH,CONH	AsF <sub>6</sub> <sup>-</sup>	232-234	275 (30 000)	А	Caled Found	$\begin{array}{c} 32.87\\ 33.00 \end{array}$	$2.74 \\ 2.79$	$\begin{array}{c} 21.75 \\ 21.92 \end{array}$	
Q, Q	AsF <sub>6</sub> -	268-270	264 (17 300)	С	Calcd Found	$\begin{array}{c} 30.74\\ 30.85 \end{array}$	$\begin{array}{c} 1.71 \\ 1.70 \end{array}$	$\begin{array}{c} 22.14\\ 26.80\end{array}$	$16.03 \\ 16.20$

 $^{a}$  M = B, P, As, or Sb.

reaction mixture was maintained at 30 °C by placing it in a large water bath at that temperature. After 1 h, a white precipitate had formed and the reaction mixture was cooled in ice and then filtered off and washed with water. The yield of iodosobenzene diacetate having a melting point of 154–156 °C was 89%.

A mixture of 48.9 g (0.052 mol) of iodosobenzene diacetate, 16.3 mL of anisole, 65 mL of acetic anhydride, and 725 mL of glacial acetic acid was placed in a 2000-mL 3-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and addition funnel. Then 8 mL of concentrated sulfuric acid was added dropwise maintaining the solution at <10 °C. After 45 min, there was added, with stirring, 31 g of NaBr in 150 mL of water. The white crystalline 4-methoxy-diphenyliodonium bromide was collected by filtration, washed, and dried to yield 40 g (73%) of product.

The bromide salt was converted to the corresponding fluoroborate by the same procedure described in method B using Ag<sub>2</sub>O. The yield from the bromide was 27%. After recrystallization from ethanol-ether, the product gave a melting point of 96–100 °C.

**Photolyses Studies.** Photolyses were conducted using a Hanovia 450 W medium pressure arc lamp with a measured output of 13 000  $\mu$ W/cm<sup>2</sup> from 200 to 300 nm and 13 000  $\mu$ W/cm<sup>2</sup> from 300 to 400 nm at a distance of 5 cm. Surrounding the lamp is a quartz well through which is pumped cooling water. Sample tubes were placed in a "merry-go-round" holder which is rotated continuously via a motor to provide even illumination throughout the photolysis. The entire apparatus was placed in a large thermostated water bath which controls the temperature within 1 °C.

**Photodecomposition Studies.** The photodecomposition of diaryliodonium salts was carried out by irradiating 0.1 M solutions of the salts in acetonitrile, 1:1 ethanol-water, and acetone in quartz sample tubes. Irradiations were terminated at approximately 20–25% conversion (7–8 min of irradiation) to avoid the formation of secondary photoproducts. The photolysis products were identified using a combination of two analytical techniques. The products were initially identified by a comparison of their GLC retention times with the re-

tention times obtained from authentic samples. Confirmation of structural assignment was then made using a GLC mass spectrometer.

**Kinetic Studies.** Kinetic studies were conducted in the photolysis apparatus described above. The sample tubes were constructed of quartz and sealed with a rubber septum through which aliquots were drawn for analysis. Samples consisted of  $2-5 \,\mathrm{cm}^3$  of 0.07 M solutions of the iodonium salt in acetonitrile, acetone, ethanol-water, or nitromethane. During kinetic runs, the tubes were withdrawn from the UV light, shielded with aluminum foil, and then analyzed by GLC. In all cases, the amount of iodoaromatic compound formed was taken to be equal to an equivalent quantity of diaryliodonium compound which has undergone photolysis. An internal standard, usually naphthalene, biphenyl, or decalin, was included for purposes of quantitative determination of the iodoaromatic compound. The addition of these compounds in no way affected the rates of photolysis of the diaryliodonium salts. The conditions under which the GLC analyses were performed are outlined below.

Solutions of photolysis products were chromatographed on a 6 ft UC, W90,  $\frac{1}{8}$  in. column with a helium pressure of 40 lb/in.<sup>2</sup>. Runs were programmed from 100–300 °C at a heating rate of 30 °C/min. The column was held at its upper limit for 5 min to ensure purging of the column of all residual products. Problems in analysis due to the tendency of the iodonium salts to decompose in the injection port were minimized by maintaining the injection port temperature below 180 °C. Nevertheless, the curvature in Figures 4–9 at low conversions is apparently due to the contribution of the thermolysis of the diarylic due to the curvature in the low conversion region of the curves.

In certain cases, for example, 4,4'-dimethyldiphenyliodonium salts, the photolysis of the salt was followed by NMR by monitoring the disappearance of the band at 2.24 ppm (Figure 2) assigned to the methyl protons. A comparison of the percent conversion versus time data obtained by this method shows a very close agreement between these two analytical techniques. In the study of the effect of light intensity on the rate of photolysis of diaryliodonium compounds, a commercial "Rayonet" apparatus was used. This device consists of 16 lamps disposed in a circle about a circular rotating sample holder. Regular variations in intensity can be achieved by removing a portion of the lamps.

**Quantum Yield Determinations.** The procedure for the determination of the quantum yields of diaryliodonium salts photolysis was adapted from a modification of the method described by Turro and his co-workers.<sup>17</sup>

Isolation of Spectral Regions for Quantum Yield Determinations. Isolation of the 313-nm Region. The 313-nm region of the medium-pressure mercury arc was isolated following the method described by Turro and his co-workers,<sup>17</sup> using a chemical filter solution. The filter solution consisted of a 1-cm path of 0.002 M potassium chromate in a 1% aqueous solution of potassium carbonate. This filter solution has been found to be somewhat "leaky" and to transmit some light at wavelengths greater than 400 nm. It is, therefore, necessary to apply a correction factor to the light intensity. Turro has determined this factor to be 0.56 by comparison of the light intensity measured through the filter using a benzophenone-benzhydrol actinometer with the light intensity measured using uranyl oxalate actinometry. All the quantum yields reported in this work using the potassium chromate-potassium carbonate filter have been corrected.

Isolation of the 365-nm Region. The filter system used to isolate the 365-nm region of the medium-pressure mercury arc was adapted from the one recommended by Calvert and Pitts.<sup>18</sup> This filter system consisted of a 2.0-cm solution of copper sulfate pentahydrate (400 g/L) and a Corning Glass band pass filter No. 7-37. In quantum yield measurements made at this wavelength, the usual "merry-go-round apparatus" could not be used. Instead, a  $5 \times 5 \times 5$  cm copper box was constructed with one side consisting of the glass band pass filter. A hole in the top of the box allowed insertion of a quartz sample tube. This entire apparatus was fixed in the water bath at a distance of approximately 10 cm from the light source. The above filter system has its maximum transmittance at 365 nm with less than 0.01% transmission at 313 nm and 0.1% at 404 nm. Light-intensity measurements made using this filter combination required no correction.

Actinometry. Light-intensity measurements were made using the uranyl oxalate actinometer described by Leighton and Forbes.<sup>19</sup> The quantum yields for the actinometer are 0.57 at 313 nm and 0.496 at 365 nm. A stock solution of 0.42 g of uranyl sulfate and 0.45 g of oxalic acid in 100 mL of water was prepared under dark room conditions and stored in the dark. A 2-mL aliquot of the actinometer solution was irradiated for 30 min. To this solution and a 2-mL aliquot of an unphotolyzed sample were added 2 mL of 10% H<sub>2</sub>SO<sub>4</sub>. Both samples were heated to 60–70 °C and then titrated at this temperature with 0.02 M potassium permanganate solution. The potassium permanganate solution had been standardized against sodium oxalate. The difference in the volume of permanganate required for the photolyzed and unphotolyzed solutions ( $\Delta V_A$ ) was used in the calculation of the light intensity as shown in the following equation:

$$I = \frac{2.5[\mathrm{KMnO_4}]\Delta V_\mathrm{A} \times 6.023 \times 10^{23}}{\Phi_\mathrm{A}{}^t}$$

where  $\Delta V_{\rm A}$  = the difference in volume of potassium permanganate (in liters); I = the light intensity in quanta per unit time; t = the irradiation time in seconds; and  $\Phi_{\rm A}$  = the known quantum yield of the actionmeter at a given UV region: 0.570 for the 313-nm region and 0.496 for the 365-nm region. Three samples of blanks and photolyzed solutions were titrated and the average difference in the volume of permanganate was used in the calculations. The light intensities measured using this method were found to be  $1.7 \times 10^{16}$  quanta/s at 313 nm and  $1.9 \times 10^{16}$  quanta/s at 365 nm.

**Quantum-Yield Measurements.** Standard 0.3 M solutions of iodonium salts in acetonitrile were prepared under dark room conditions. Aliquots (2 mL) were irradiated for 30 min in the photolysis apparatus. Analysis showed that conversions after this irradiation period had reached 5–10%. Conversions were purposely kept low to minimize production of secondary photoproducts.

After photolysis, the samples were shielded with aluminum foil and 1 mL of 0.02 M solution of naphthalene or biphenyl in acetonitrile was added as an internal standard. The samples were then analyzed by vapor phase chromatography. Concentrations of products in the 0.001-0.005 M range were easily detected.

To determine whether a correction factor need be applied to compensate for differences in the absorbance between the actinometer (99% absorbance) and the sample solutions, the ultraviolet absorption of the sample solutions was measured at 313 and 365 nm. These measurements were carried out in the quartz photolysis cells using a Perkin-Elmer 421 grating spectrometer. At these two wavelengths, there is less than 0.1% of the incident light which is transmitted through the sample. No correction factor was thus necessary for these determinations.

The absolute quantum yields were calculated using the following equation:

$$\Phi = \frac{[\text{product}]V \times 6.023 \times 10^{23}}{It}$$

where V = the volume of the photolysis sample; I = the light intensity at the region of study; t = the irradiation time in seconds; and [product] = concentration of the photolyzed product. For each photoinitiator salt, 3–5 quantum yield determinations were made and were averaged to give the reported value.

**Photopolymerizations.** Photopolymerizations were carried out using the same apparatus described for the photolysis studies. Monomers were dissolved in the appropriate solvent or irradiated in bulk, sealed in Pyrex ampules, and isolated by pouring the reaction mixtures into a nonsolvent for the polymer. The experimental conditions of monomer-initiator stoichiometry, temperature, and polymerization solvent are given in Tables III-VI.

#### **Results and Discussion**

**Preparation of Diaryliodonium Salt Photoinitiators.** Higher valence state iodine compounds such as diaryliodonium salts were described by Willgerodt as early as 1885.<sup>20</sup> Sandin reviewed the literature to 1942,<sup>21</sup> Beringer and Gindler to 1956,<sup>22</sup> and Banks to 1965.<sup>23</sup> Extensive work by Beringer and his co-workers has led to the development of several synthetic pathways to this class of compounds.<sup>24,25</sup>

In our work, we have used three basic synthetic pathways in the preparation of diaryliodonium salts. The choice of the specific method depended on whether the desired iodonium salt bears substituents and where they are situated. For iodonium salts having symmetrically placed substituents, two methods involving the coupling of two molecules of an aromatic substrate through electrophilic substitution were used. Aromatic substrates bearing deactivating substituents such as NO<sub>2</sub>, halogen, COOH, or CH<sub>3</sub>SO<sub>2</sub> are best coupled by the method used by Masson and co-workers<sup>26</sup> employing iodyl sulfate (method A, eq 1).

$$3 H_2 SO_4 + 4 Cl \longrightarrow + (IO)_2 SO_4$$
$$\longrightarrow 2 \left( Cl \longrightarrow \right)_2 I^+ + 2 H_3 O^+ + 4 H SO_4^- (1)$$

Diaryliodonium salts having electron-donating substituents are readily prepared by the direct coupling of their aromatic precursor compounds using an alkali iodate in a mixture of acetic acid, acetic anhydride, and sulfuric acid (method B, 2).<sup>27</sup>

$$2 + () + KIO_{4} + 2H_{2}SO_{4} + 2Ac_{2}O$$

$$\rightarrow (+ () + 2H_{2}SO_{4} + 4AcOH + [0] (2)$$

Unsymmetrical iodonium salts were prepared by the direct coupling of an aromatic compound with an iodoso compound in the presence of a strong protonic acid (method C, eq 3).<sup>21</sup>

$$\begin{array}{c} & & & \\ & & &$$

The aromatic iodoso compounds are easily prepared either

Ar-IO

OH<sup>^</sup>

Ar-ICL.



Figure 1. Infrared spectrum of 4,4'-dimethyldiphenyliodonium hexafluoroarsenate (KBr disk).



Figure 2.  $^{13}\mathrm{C}$  spectrum of 4,4′-dimethyldiphenyliodonium hexafluoroarsenate in DMSO- $d_{6}$ .

by the oxidation of the corresponding iodoaromatic compounds with peracetic acid or by the chlorination of the iodoaromatic compound and subsequent hydrolysis of the iodoaromatic dichlorides (eq 4).

Iodonium salts prepared by the three methods described above have as their counterions the bisulfate anion. Since the bisulfate salts are often rather hygroscopic and somewhat unstable, one generally isolates the stable halide salts by metathesis (e.g., eq 5).

$$Ar_2I^+HSO_4^- + NH_4Cl \rightarrow Ar_2I^+Cl^- + NH_4HSO_4 \quad (5)$$

For use in photoinitiators in cationic polymerization, iodonium salts having complex metal halide anions  $(MX_n^{-})$  were desired. It was therefore necessary to consider methods of changing the halide salts to one of these complex anion salts. Two methods have been reported in the literature for the preparation of iodonium fluoroborates and are described in eq 6.

The first method a involves the conversion of the iodonium halide to the corresponding hydroxide with basic silver oxide, followed by acidification with fluoroboric acid.<sup>28,19</sup> In our hands, this method gives fair yields of fluoroborates. A second method b, involving the direct metathesis of diaryliodonium halides with silver fluoroborate, gives good yields of the desired fluoroborates. Apart from a few diaryliodonium fluoroborate salts which have been reported in the literature, diaryliodonium salts possessing other complex metal halide anions do not appear to have been prepared.

We have found that diaryliodonium salts having the  $PF_6^-$ ,

 $AsF_6^-$ , or  $SbF_6^-$  anions can be prepared directly from their corresponding bisulfates by metathesis with such acids as  $HPF_6$ ,  $HAsF_6$ , and  $HSbF_6$  or their alkali metal salts (eq 7).

$$\operatorname{Ar}_{2}I^{+}\operatorname{HSO}_{4}^{-} + \operatorname{YMX}_{n} \rightleftharpoons \operatorname{Ar}_{2}I^{+}\operatorname{MX}_{n}^{-} + \operatorname{YHSO}_{4} \quad (7)$$

where Y = H, Na, K, etc., and  $MX_n^- = PF_6^-$ ,  $AsF_6^-$ , and  $SbF_6^-$ . The above reaction constitutes a convenient and direct synthesis of these compounds.

A summary of a number of diaryliodonium salts prepared during the course of this work together with their melting points, UV spectral characteristics, and elemental analysis are reported in Table I. The salts shown in Table I are all white crystalline compounds indefinitely stable in the absence of light. Repeated recrystallizations gave analytically pure salts in most cases; however, certain salts having low melting points resisted purification by this technique. After some investigation, it was found that by simply passing a methylene chloride solution of the salt through a column of neutral alumina and then triturating the solution with ether, analytically pure samples of these salts could be obtained.

Figures 1 and 2 show the infrared and <sup>13</sup>C NMR spectra for 4,4'-dimethyldiphenyliodonium salts and are typical for this class of compounds. In both the infrared and NMR spectra of compounds appearing in Table I, it was noted that for a series of salts having the same cationic structure, the character of the  $MX_n^-$  anion has little effect on the spectra. This suggests that these diaryliodonium salts are ionic in nature.<sup>23</sup>

The same observation can be made with respect to the ultraviolet spectra of diaryliodonium salts. While the nature of the anion plays little role in determining position of the UV absorption bands, a change in the substituents does cause shifts in the position and the intensity of these bands. In Figure 3 is shown a composite UV spectrum of a number of diaryliodonium salts having the same anion (AsF<sub>6</sub><sup>-</sup>) but differing in the structure of their cation. These spectra were all recorded at the same molar concentration so that a direct comparison of their extinction coefficients can be made. The spectra all possess strong absorption bands in the regions 190–200 and 230–250 nm with only very small absorption at wavelengths greater than 300 nm.

**Photodecomposition of Diaryliodonium Salts.** It has been recognized for some time that diaryliodonium salts are photosensitive.<sup>23</sup> Determination of the products of the photochemical decomposition of diphenyliodonium iodide in chloroform showed the presence of mainly iodobenzene with benzene, biphenyl, and iodine also present in lesser amounts.<sup>30,31</sup> Photolysis of diphenyliodonium hydroxide in aqueous sodium hydroxide gives as the main products 4-iodobiphenyl and biphenyl. Minor products also formed were terphenyls and iodoterphenyls.<sup>32</sup> Radical mechanisms for these two photodecomposition studies have been proposed. Recently, Knapczyk, Lubinkowski, and McEwen<sup>33</sup> studied the photodecomposition of diphenyliodonium fluoroborate,



Figure 3. Ultraviolet spectra of substitued diaryliodonium salts.

Scheme I

$$\operatorname{Ar}_{2}\mathrm{I}^{+}\mathrm{X}^{-} \xrightarrow{h_{\nu}} [\operatorname{Ar}_{2}\mathrm{I}^{+}\mathrm{X}^{-}]^{*}$$
(a)

$$[Ar_2I^+X^-]^* \rightarrow Ar_-I^+ + Ar_+ + X^-$$
 (b)

$$Ar-I^{+} \cdot + S-H \to Ar-I^{+}-H + S \cdot$$
 (c)

$$Ar-I^+-H \rightarrow Ar-I + H^+$$
 (d

Major

$$[\operatorname{Ar}_{2}I^{+}X^{-}]^{*} + S - H \rightarrow [\operatorname{Ar}-SH]^{+} + \operatorname{Ar}I + X^{-}$$
(e)

$$[Ar-SH]^+ \rightarrow Ar-S + H^+$$
(f)

nitrate, and chloride in 2-propanol at 253.7 nm. The products for the photolysis include benzene, acetone, iodobenzene, biphenyl phenylisopropyl ether, and Brønsted acids derived from the anion. A photochemically initiated chain reaction was proposed as the mechanism in the photolysis involving the solvent derived hydroxyisopropyl radical as the chain carrier.

It was of considerable interest to determine whether the mechanism of photolysis of diaryliodonium salts is the same in solvents other than 2-propanol. In addition, studies were initiated to determine the relative order of photosensitivity as well as the effects of structure on their photosensitivity and the influences of solvent, temperature, atmosphere, and intensity of incident light on their rates of photolysis.

When the photolysis of 4,4'-di-*tert*-butyldiphenyliodonium fluoroborate was conducted as a 0.07 M solution in acetonitrile using a 450 W Hanovia medium-pressure mercury arc lamp, the products which were obtained and identified by means of GLC mass spectroscopy are shown in eq 8. The major product of photolysis is 4-*tert*-butyliodobenzene. Smaller amounts of *tert*-butylbenzene, two isomeric di-*tert*butylbiphenyls, and 4-*tert*-butylphenol are also present accompanied by trace quantities of 4-*tert*-butylacetanilide, and 4-*tert*-butylphenyl-*tert*-butyliodobenzene.

Additional photolysis and GLC mass spectral analyses were carried out on 4,4'-di-*tert*-butyldiphenyliodonium salts having the  $PF_6^-$ ,  $AsF_6^-$ , and  $SbF_6^-$  counterions in acetonitrile, eth-anol-water, and acetone. In all cases, the major products observed were identical with those obtained in the photolysis study of the  $BF_4^-$  salt. Slightly different minor and trace products were obtained in ethanol-water and acetone resulting from reaction of those solvents with the products of photolysis.

To account for all the observed products, the presence of two mechanisms must be invoked. Except for 4-*tert*-butylphenol and 4-*tert*-butylacetanilide, the remaining products can be explained by a radical mechanism. To rationalize the presence of the later products, an alternate mechanism must be put forth.

In the light of the above results, we would like to propose the following general mechanism for the photolysis of diaryliodonium salts (Scheme I) which is similar to that proposed by Knapczyk and his co-workers.<sup>33</sup>

The major pathway involves the facile decomposition of the excited iodonium compound to an aryliodo radical-cation, an aryl radical, and an anion. This process should be highly efficient due to the very low bond energy of the C-I bond (26-27 kcal/mol).<sup>32</sup> The fate of the aryl radicals generated in step (b) is to give rise to the *tert*-butylbiphenyl products by dimerization and 4-*tert*-butylbenzene via hydrogen abstraction from the solvent S-H. Confirmation that *tert*-butylbenzene is produced by hydrogen abstraction from the solvent was obtained by performing the photolysis in acetonitrile- $d_3$ . In this case, monodeuterated *tert*-butylbenzene was obtained and identified by GLC mass spectroscopy. 4-*tert*-Butylphenyl-*tert*-butylphenyl-radical on 4-*tert*-butyliodobenzene.

Interaction of the aryliodo radical-cation with the solvent (step c) generates a protonated iodoaromatic compound which rapidly deprotonates (step d) and a radical derived from the solvent.

The minor pathway which seems to be taking place simultaneously with the above radical process is shown in steps e and f of Scheme I. Reaction of the solvent with the excited iodonium compound generates a cationic species  $[Ar-SH]^+$ . Further loss of a proton gives products in which an aryl group is attached to the solvent (4-tert-butylphenol and 4-tertbutylacetanilide).<sup>34</sup>

Further support for the mechanism of Scheme I was obtained by the simultaneous photolysis of two diaryliodonium salts, 4,4'-di-*tert*-butyldiphenyliodonium hexafluoroarsenate and 4,4'-dichlorodiphenyliodonium hexafluoroarsenate, in acetonitrile. This reaction gives rise to a mixture of products among which 4,4'-dichlorobiphenyl, 4,4'-di-*tert*-butylbiphenyl, and the crossover product 4-*tert*-butyl-4'-chlorobi-





Figure 4. Photodecomposition study of a 0.07 M solution of 4,4'dimethyldiphenyliodonium hexafluoroarsenate in acetonitrile.



**Figure 5.** Photolysis of 0.07 M solution of 4,4'-dimethyliodonium hexafluoroarsenate in acetonitrile using quartz and Pyrex filtered light.

phenyl have been identified. The results of this experiment suggest that the photolysis of diaryliodonium salts does not take place within a "cage" and that the aryl radicals produced have sufficient lifetimes to diffuse from reaction site and to give crossover products.

During the photolysis, the  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ , and  $SbF_6^$ anions associated with the diaryliodonium salts remain unchanged and appear in the products as the corresponding Brønsted acids. These acids are, therefore, the ultimate initiators when diaryliodonium salts are employed in the cationic photopolymerization of various monomers.

Figure 4 shows a plot of the data obtained in a study of the photolysis of 4,4'-dimethyldiphenyliodonium hexafluoroar-



**Figure 6.** Effect of air on the photodecomposition of 4,4'-dimethyldiphenyliodonium hexafluoroarsenate in acetone.



**Figure 7.** Photodecomposition of 4,4'-dimethyldiphenyliodonium hexafluoroarsenate in acetone at different light intensities.

senate in acetonitrile. The data were obtained by following the formation of 4-iodotoluene by GLC. Nearly identical data were obtained by following the disappearance of the methyl protons at  $\delta$  2.24 ppm in the starting material by <sup>1</sup>H NMR. As the curve indicates, photolysis is quite rapid with approximately 50% reaction occurring within 30 min.

When the photolysis of 4,4'-dimethyldiphenyliodonium hexafluoroarsenate was carried out using Pyrex filtered light which contains only radiation at wavelengths greater than 300 nm, a considerable decrease in the rate of photolysis was noted as shown in Figure 5. At these wavelengths the rate of photolysis of the diaryliodonium salt is still surprisingly rapid, particularly in view of the fact that absorption is occurring in the tail of the large band at 237 nm. This conclusion, in turn, suggests an appreciable quantum yield of photolysis at wavelengths above 300 nm.

Photolysis of 4,4'-dimethylphenyliodonium hexafluoroarsenate at various temperatures from 15 to 35 °C yielded



Figure 8. Effect of anion structure on the photodecomposition of  $(CH_3Ph)_2I^+X^-$  salts in acetone.

identical photodecomposition curves. Temperature thus has no effect on the rates of photolysis of these compounds.

We were especially anxious to determine whether oxygen would inhibit the photolysis of diaryliodonium salts since we have already shown that the photolysis proceeds largely by a radical process. Also, it has been claimed by other investigators<sup>33</sup> that the inhibition of the formation of benzene in the presence of oxygen and other radical scavengers in the photolysis of diphenyliodonium salts is indicative of a photoinitiated chain reaction. Oxygen is also known to be an efficient quencher of excited states in certain photochemical reactions. For purposes of comparison, two photolyses of 4,4'-dimethyldiphenyliodonium hexafluoroarsenate were performed. The first experiment was conducted in air and the second was repeatedly vacuum freeze-thaw degased and then sealed. The curves in Figure 6 show identical behavior within experimental error with respect to the formation of 4-iodotoluene. Analogous results were obtained in a photolysis study conducted in the presence of a twofold molar excess of the radical trap 2,6-di-tert-butyl-4-methylphenol. The absence of a decrease in photolysis rates in the presence of the phenol suggests that if radical chain processes are involved in the photoinduced decomposition of diaryliodonium salts, the kinetic chain length must be very short.



Figure 9. Effect of cation structure on the photodecomposition of various diaryliodonium salts in acetone.

Table II

12 - 4 - - 2

	1 Diarynodonium 3	Saits
	Φ	
Diaryliodonium salt	313.0 nm	365.0 nm
$\left(CH - O\right)_{2} I^{+} As F_{6}^{-}$	0.21	
$\left( - + \right)_{2} I^{+} AsF_{6}^{-}$	0.20	0.19
$\left( - + \right)_{2} I^{*} PF_{e}^{-}$	0.22	
$\left( - + \right)_{2} I^{+} SbF_{e}^{-}$	0.22	

Figure 7 shows a plot of the data obtained in a study of the percent photolytic conversion of 4,4'-dimethyldiphenyliodonium hexafluoroarsenate at three different intensities of incident light. As the light intensity is reduced by one-half and

		Table III		
Photoinitiated	Cationic	Polymerization	of Olefin	Monomers <sup>a</sup>

Monomer (mol)	Photoinitiator (mol)	Solvent (mL)	Irrad time, min	[n], dL/g	Yield, %
(0.277)	$CH_{1}O \longrightarrow I^{+} \longrightarrow BF_{4}^{-} (0.000\ 65)$	CH <sub>2</sub> Cl <sub>2</sub> (13)	6	0.06	89
(0,1)	CH.0 $ O$ $I^+ - O$ $BF_4^- (0.00027)$	$CH_2Cl_2(1)$	6	0.65	97
Cl (0,015)	$\left( \begin{array}{c} - + & \bigcirc \end{array} \right)_{2} I^{+} PF_{\epsilon} (0.000.03)$	CH <sub>2</sub> Cl <sub>2</sub> (8.5)	5	0.15	74

<sup>a</sup> All polymerizations were carried out at 25 °C.

Photoinitiated Cationic Polymerization of Epoxide Monomers <sup>a</sup>							
Monomer (mol)	Photoinitiator (mol)	Irrad time, min	$\frac{[n]}{M_n}$ , dL/g or $\frac{M_n}{M_n}$ by GPC	Yield, %			
Cl (0.038)	$\left( \begin{array}{c} & & \\ & & \\ & & \\ \end{array} \right)_{2} 1^{+} \mathrm{PF_{6}^{-}} (0.00021)$	15	6900	59			
0 (0,05)	$\left(CH_{-} \bigcirc \right)_{2} I^{+} A \varepsilon F_{6}^{-} (0.001)$	15	0.24	67			
0 (0,023)	$\left( \right)_{2} I^{+}SbF_{6}^{-} (0.00006)$	1.5	0.23 10,700	93			

Table IV

<sup>a</sup> All polymerizations were carried out at 25 °C in bulk.

Photoinitiated Cationic Polymerization of Cyclic Ether and Acetal Monomers <sup>a</sup>							
Monomer (mol)	Photoinitiator (mol)	Solvent (mL)	Irrad time, min	[n], dL/g or $M_n$ by GPC	Yield, %		
0 0 (0.056)	$\left(\left\langle \bigcirc \right\rangle_{2}^{-} I^{+} PF_{6}^{-} (0.003)\right)$	$CH_2Cl_2$ (5)	20		27		
(0.31)	$\left( - + \right)_{2} I^{+} PF_{6}^{-} (0.003)$		60	43 800	52		
(0.31)	$\left( \begin{array}{c} - \\ - \\ \end{array} \right)_2 I^* As F_6^-  (0.0015)$		60	49 000	32		
(0.31)	$\left(\begin{array}{c} - \\ - \\ - \\ - \\ - \\ - \\ 2 \end{array}\right)^{-} \mathbf{I}^{+} \mathbf{Sb} \mathbf{F}_{6}^{-}  (0.0015)$		60	67 000	34		
O (0,019)	$\left(\begin{array}{c} \\ \end{array}\right)_{2} \mathbf{I}^{\dagger} \mathbf{PF_{6}^{-}} (0.000 \ 0.2)$		6	0.19	57		

<sup>a</sup> All polymerizations were carried out at 25 °C.

Table VI Photoinitiated Polymerization of Some Miscellaneous Monomers <sup>a</sup>					
Monomer (mol)	Photoinitiator (mol)	Írrad time	[n], dL/g	Yield, %	
(0.05)	$\left(\begin{array}{c} - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ 2 \end{array}\right)^{-} I^{+} PF_{s}^{-}  (0.000\ 13)$	13 min	0.66	82	
(0.05)	$\left(\begin{array}{c} \\ \\ \end{array}\right)_{2} I^{*} As F_{e}^{-} (0.000 \ 13)$	10 min		14	
(0.0154)	$\left(\begin{array}{c} \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	1 h	0.40	80	
(0.0154)	$\left( - \frac{1}{2} \right)_{2} l^{+} AsF_{e}^{-} (0.000 l5)$	1 h	0.13	55	

<sup>4</sup> All polymerizations were carried out at 25 °C in bulk. <sup>b</sup> Irradiation was followed by heating 1 h at 60 °C.

then by one-quarter, the percent conversion falls by almost exactly the same amount. There is thus a linear dependence of the rate of photolysis on the light intensity.

The effects of different anions on the photolysis rates of two diaryliodonium salts having the same cations are shown in Figure 8. In this figure it is apparent that within experimental error the two curves for 4,4'-dimethyldiphenyliodonium fluoroborate and the corresponding hexafluoroarsenate are identical. Similarly, the curves obtained for the analogous  $PF_6^-$  and  $SbF_6^-$  salts show the same photolysis rates as for

Table V

the  $BF_4^-$  and  $AsF_6^-$  salts. It appears that the anion plays no role in determining the photosensitivity of the iodonium salt. Further, this observation suggests that the amounts of different Brønsted acids generated from such a series of iodonium compounds per unit time are also identical. Employing this concept, one can use such a series of diaryliodonium salts to compare the ability among various HMX<sub>n</sub> acids to initiate cationic polymerization in various monomer systems.

Figure 9 shows the data collected in a study of the effects of variations in cation structure on their relative photolysis rates. There are minor variations in the rates of photolysis of these compounds; however, the curves are all of approximately the same shape and reach the same degree of conversion (75-80%) within 30 min.

**Quantum-Yield Measurements.** Since measurement of the photodecomposition rates of diaryliodonium salts indicated that they undergo rapid photolysis even at long wavelengths, it was of considerable interest to determine the quantum yields of some representative compounds. For this reason and because of the limitations of our equipment, we chose to measure the quantum yields at two wavelengths, namely, 313 and 365 nm.

In Table II are given the results of the quantum-yield determinations on four diaryliodonium salts. A few generalized statements may be made with regard to these data. Measurement of the intensity data using the method employed in these experiments is subject to an estimated error of approximately 50%.<sup>17</sup> Hence, the quantum yield values reported here should also be understood to contain a certain amount of inherent error. Nevertheless, the determinations contained in Table II were made by averaging 3–5 separate quantumyield and light-intensity measurements. In all cases, the data were found to exhibit only slight variations in their values and to be highly reproducible.

The quantum yields for all the salts shown in this table are all of the order 0.20 and are indicative of the highly efficient nature of the photolysis of these salts. These values are surprising in view of the fact that absorption is occurring only in the region of the small extinction coefficient ( $\epsilon \sim 10$ ) tail of the major absorption band  $\lambda_{\rm max} 237-238$  nm.

Out earlier conclusion from the measurement of the photolysis rates that the structure of the cation and not the anion of the diaryliodonium salt plays the dominant role in determining the photosensitivity of the compound is confirmed in the quantum-yield results. For the series of 4,4'-di-*tert*-butyldiphenyliodonium salts having the AsF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and SbF<sub>6</sub><sup>-</sup> anions, the quantum yields are all within experimental error.

**Photopolymerization Studies.** Diaryliodonium salts possessing complex metal halide anions photoinitiate the cationic polymerization of a wide variety of monomers among which are included olefins, cyclic ethers, cyclic sulfides, cyclic acetals, and lactones. It is the intent of this paper only to describe the general scope of these polymerizations. Thus, neither the conditions of the polymerizations nor the yields and molecular weights of the resulting polymers which have been described here have been optimized. In subsequent papers, we will report more detailed studies which have been conducted on specific monomer-photoinitiator systems.

The scope of cationic polymerizations which can be photoinitiated using diaryliodonium salts is very large. Tables III-V include members of most of the major classes of cationically polymerizable monomers. The rate and extent of polymerization are dependent both on the reactivity of the specific monomer and on which acid (HBF<sub>4</sub>, HPF<sub>6</sub>, HAsF<sub>6</sub>, or HSbF<sub>6</sub>) is generated on photolysis of the diaryliodonium salt. Polymerization rates range from those which require long irradiations followed by heating to proceed at satisfactory rates to those which are complete after a few minutes irradiation at room temperature.

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- (34) One of the referees suggested that the trace products 4-tert-butylphenol and 4-tert-butylacetanilide may arise by the interaction of the tertbutylphenyl radical with the solvent or impurities instead of via the photoassisted solvolysis pathway put forth by us in Scheme I. Specifically, the referee suggests that reaction of the 4-tert-butylphenyl radical with water or oxygen produces 4-tert-butylphenol and reaction with acetamide produces tert-butylacetanilide. We think that this proposal is unlikely. Aryl radicals generated by other methods in aqueous solution do not lead to the formation of phenols (M. Gomberg and W. E. Bachman, J. Am. Chem. Soc., 46, 2339 (1924); N. Kornblum, Org. React., 2, 262 (1944)). The major reactions of aryl radicals are dimerization and hydrogen abstraction. Although the reaction of the tert-butylphenyl radical with oxygen cannot be ruled out as a source of the phenol, it is doubtful since it has been reported that this type of reaction is very slow. (L. H. Toporcer, R. E. Dessy, and S. I. E. Green, J. Am. Chem. Soc., 87, 1236 (1965).) We were not able to detect the presence of acetamide in the solvent by GLC mass spectroscopy so this must be ruled out as the source of 4-tert -butylacetanilide. The compound, 2-phenylacetonitrile, which the referee proposes would occur by coupling of the tert-butyl radical and the ·CH2-CN radical, is not present within the limits of detection of our instrument.