3484 *J. Org. Chem.* **2000,** *65,* 3484−3488

Photolysis of ((3-(Trimethylsilyl)propoxy)phenyl)phenyliodonium Salts in the Presence of 1-Naphthol and 1-Methoxynaphthalene

Haiyan Gu, Wenqin Zhang, Kesheng Feng, and Douglas C. Neckers*[,1]

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43402

Received January 14, 2000

Direct photolysis of ((3-trimethylsilylpropoxy)phenyl)phenyliodonium salts with different counteranions (Cl^-, SbF_6^-, and $B(C_6F_5)_4^-$) in methanol leads to products by both heterolytic and homolytic processes. In the presence of 1-naphthol and 1-methoxynaphthalene, products formed by a heterolytic reaction disappear, suggesting an electron-transfer process occurs between excited 1-naphthol/1-methoxynaphthalene and the iodonium salts. In the case of 1-methoxynaphthalene, three phenylated methoxynaphthalene isomers are produced. These are produced as radical coupling products from the phenyl radical and 1-methoxynaphthalene radical cation.

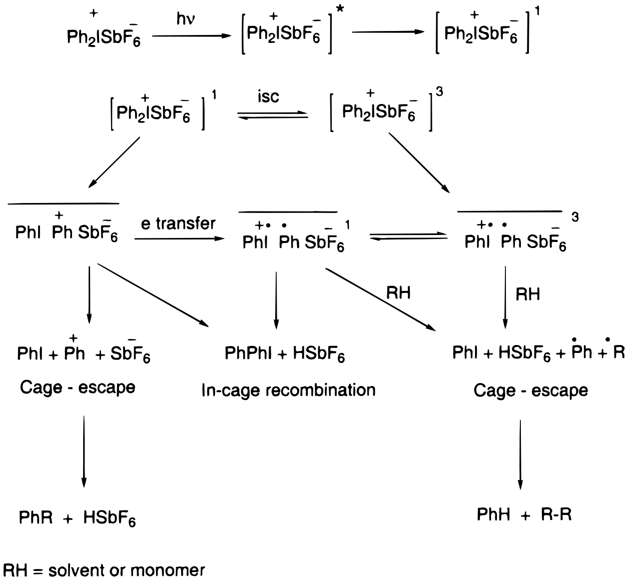
Introduction

In the past two decades, photoinitiated cationic polymerization has found a wide range of applications in fields ranging from UV−curing technologies to the microelectronics industry. Diaryliodonium salts and triarylsulfonium salts, as the most important cationic photoinitiators, have been the subject of significant activity because of their thermal stability and excellent initiating efficiency.[2]

The photochemistry of iodonium salts having nucleophilic anions was studied before they were found to be useful as cationic photoinitiators.[3] Since nucleophilic anions terminate cationic polymerization chains, iodonium salts with such anions cannot be used as initiators. Photolysis of iodonium salts with nonnucleophilic anions produces a proton, which is the species that initiates the polymerization. Early studies suggested a mechanism involving the photoinduced homolysis of a carbon−iodine bond, in direct analogy with photolysis of triarylsulfonium salts.[4−6]

Recent studies have shown that the mechanism of direct photolysis of iodonium salts is more complex than originally thought.[7,8] It involves heterolytic as well as homolytic reactions, and the effect of the solvent cage is considered to be important.[9,10] The best current mechanism for the photolysis of diphenyliodonium salts is shown in Scheme 1.[8]

Scheme 1



In addition to the direct photolysis of diaryliodonium salts, sensitized photolyses have also been studied.[11−18] Three possible mechanisms have been proposed, namely, energy transfer, electron transfer, and redox photosensitization. Triplet energy transfer was demonstrated by using acetone[8] and *m*-trifluoroacetophenone[6] as sensitizers. However, for various reasons not the least of which is the high triplet energy of most iodonium salts (64 kcal/mol), it is not practical to use such sensitizers industrially.

Electron transfer, in contrast, often occurs.[11−15] Sensitized decomposition of iodonium salts in the presence of anthracene, diethoxyanthracene,[7,12] xanthene, acetophenone,[13] chlorothioxanthone,[14] and thioxanthone derivatives[15] have been reported. Steady-state photolysis,

---

[1] Contribution No. 395 from the Center for Photochemical Sciences.

[2] Crivello, J. V. Latent Developments in the Chemistry of Onium Salts. In *Radiation Curing in Polymer Science and Technology;* Fouassier, J. P., Rabek, J. F., Eds.; Elsevier: London, 1993; Vol. II, Chapter 8, pp 435−471.

[3] Knapczyk, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* **1972**, *35*, 3739.

[4] Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1.

[5] Crivello, J. V.; Lee, J. L.; Colon, D. A. *Makromol. Chem. Macromol. Symp.* **1988**, *13/14*, 145.

[6] Pappas, S. P.; Pappas, B. C.; Gatechair L. R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 69.

[7] Devoe, R. J.; Sahyun, M. R. V.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1987**, *65*, 2343.

[8] Devoe, R. J.; Sahyun, M. R. V.; Schmidt, E.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1988**, *66*, 319.

[9] Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639.

[10] Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1991**, *56*, 1838.

[11] (a) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, 16, 2441. (b) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1059.

[12] Nelson, E. W.; Carter, T. P.; Scranton A. B. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 247.

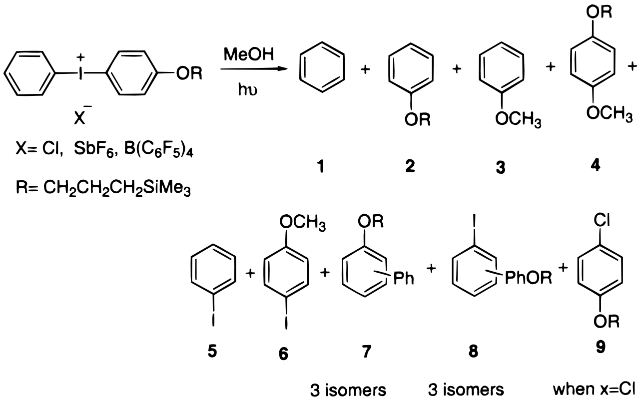
[13] Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77.

[14] Wang, X. Z.; Wang, E. J.; Fouassier, J. P. *Acta Chim. Sin.* **1992**, *58*, 492.

[15] Fouassier, J. P.; Burr, D.; Crivello, J. V. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 677.

10.1021/jo000058w CCC: $19.00

Scheme 2



laser flash photolysis,[6,7] and photo-CIDNP (chemically induced dynamic nuclear polarization) techniques[16] have been employed to study the details of the mechanism of the sensitized photolysis of iodonium salts.

Chemical sources of free radicals can also promote cationic polymerization.[16−18] Ledwith and his research group worked extensively in this area, using benzoin ether and α-hydroxyacetophenone as radical sources.[17] Sundell and co-workers studied many common radicals and found that molecules containing α-ether radicals or α-hydroxy radicals can reduce iodonium salts.[18] Bi and Neckers also demonstrated that systems consisting of a xanthene dye, an aromatic amine, and a diaryliodonium salt could function as a visible light initiating system for free radical promoted cationic polymerization.[19]

In this paper, we report studies of the photolyses of the title iodonium salts in the presence and absence of the sensitizers, 1-naphthol and 1-methoxynaphthalene. It is known that the dihydroxynaphthalene can promote cationic polymerization as initiated by iodonium salts,[20] and we were interested in the interaction between the iodonium salts and the hydroxynaphthalenes. Product analysis suggests electron transfer between the excited 1-naphthol/1-methoxynaphthalene molecule and iodonium salt. Diaryliodonium salts containing silane groups have been shown to increase iodonium salt solubility in nonpolar solvents.[21] Here we used these compounds as unsymmetrical iodonium salts to get more mechanistic information about the cleavage pathways.

Results and Discussion

Direct irradiation of the title compound with various counteranions (Cl^-, SbF_6^-, and $B(C_6F_5)_4^-$) in methanol gave 13 products in the case of Cl^- and 12 products in the case of the other compounds (Scheme 2). The products (Table 1) were detected by GC/MS, and the resulting spectra were compared with those of authentic samples excluding the iodobiaryl cases.

In Scheme 1 it is shown that, after light absorption, the diaryliodonium salts undergo both heterolysis and homolysis. Homolysis leads to an aryl radical and an aryliodonium radical cation, which in the solvent cage recombine to form the iodobiaryls **8a**−**c**. The structures and the possible route to formation of these three isomers are shown in Scheme 3. After diffusing outside of the solvent cage, the aryl radical abstracts a H atom from solvent forming benzene (**1**) and **2**. Therefore, we assign these two products as products formed by a homolytic pathway. In the case of heterolysis, a neutral iodoarene and an aryl cation are formed. The latter is expected to be trapped by methanol to form anisole (**3**) and 1-methoxy-4-(3-(trimethylsilyl)propoxy)benzene (**4**), or by Cl^- to form **9** in the case of chloride salt. We assign these products as those formed by the heterolytic pathway (Scheme 4). How the three isomeric biaryls **7** form is still unclear. In principle, two possibilities exist. One is electrophilic substitution of the aryl cation on the arene. The other is radical substitution of the aryl radical on the arene. Since neither biphenyl nor 4,4′-(3-(trimethyl)silylpropoxy)biphenyl was detected, out-cage radical coupling is excluded. Also in methanol, the possibility of electrophilic substitution is rare. So radical substitution is considered the route to formation of these products. The *para* isomer dominates among these three isomers, and the ratio of *ortho* plus *meta* to *para* is about 1:10. The structure of the anion has little effect on the distribution of photoproducts (Table 1). This is consistent with what was found in the case of diphenyliodonium salts.[8]

Irradiation of the target iodonium salts in the presence of 1-naphthol gave just four products. The products formed by heterolytic reactions and via in-cage recombination disappeared. We attribute this observation to an electron transfer between the excited naphthol molecules and the diaryliodonium salts (Scheme 5).

Electron transfer produces a naphthol radical cation and diaryliodine radical. The latter decomposes at a diffusion controlled rate to an iodoarene and the aryl radical so no heterolytic products or in-cage recombination products are formed. Although a decrease in the concentration of 1-naphthol is obvious, no naphthol-derived photoproducts that could be attributed to coupling of 1-naphthol radical cation and phenyl radical could be detected. Our explanation is that 1-naphthol radical cation easily loses a proton forming the naphthoxy radical. Since naphthoxy radicals often form higher molecular weight materials, these would not be detected under our conditions by GC/MS.

To provide further evidence for this hypothesis, the photolysis of these compounds in the presence of 1-methoxynaphthalene was carried out (Table 1). Under these conditions, products formed by a heterolytic reaction as well as the iodobiaryls **8** disappear. However, some *para* biaryl **7** remains among the photoproducts although the *ortho* and *meta* isomers are not formed. In this case, we propose the *para* isomer arises from phenyl radical substitution on the iodoarene which releases an iodine atom. In addition to these products, three other new peaks were observed by GC/MS. These products are isomers that correspond to an analysis of $C_{17}H_{14}O$. From the fragmentaion patterns (219, 191 and 165) we assign these products to be the isomers 2, 4, 5-phenyl-1-methoxynaphthalene. A possible mechanism for formation of these isomers is shown in Scheme 6. The 1-methoxynaphthalene radical cation couples with a phenyl radical releasing a proton. Since the methyl group is not a good leaving group in radical displacement processes,

---

[16] Goez, M.; Ecert, G.; Muller, U. *J. Phys. Chem.* A **1999**, *103*, 5714.

[17] (a) Ledwith, A. *Makromol. Chem. Suppl.* **1978**, *3*, 348. (b) Abdul-Rasoul, F. A. M.; Ledwith, A.; Yagci, Y. *Polymer* **1978**, *19*, 1219. (c) Abdul-Rasoul, F. A. M.; Ledwith, A. *Polym. Bull.* **1978**, *1*, 1.

[18] Sundell, P. E.; Jonsson, S.; Hult, A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1525.

[19] Bi, Y.; Neckers, D. C. *Macromolecules* **1994**, *27*, 3683.

[20] Feng, K. S.; Neckers, D. C. U.S. Patent applied for.

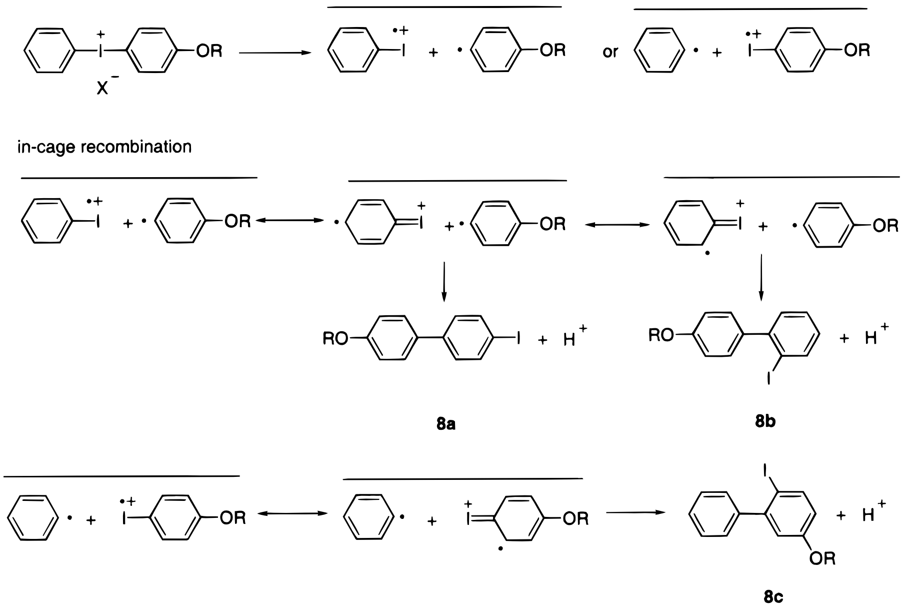
[21] Ger. Offen. DE 4, 4142, 3237, 1993.

Table 1. Concentrations[a] and Distributions (%)[b] of Photoproducts

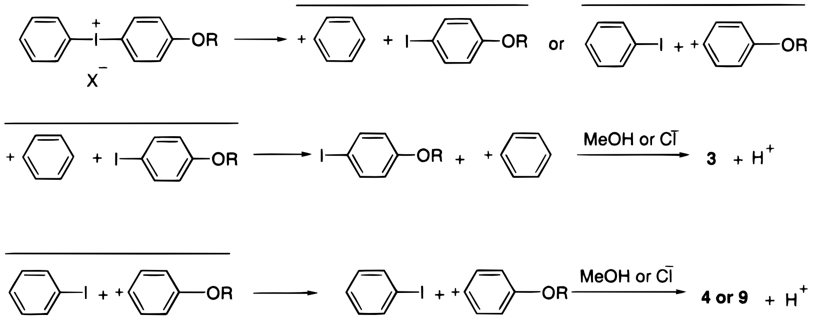
X^-	ED[f]	**1**	**2**	**3**	**4**	**9**	**5**	**6**	**7**	**8**[c]
Cl	none	14[a] (13)[b]	8.7 (8)	2.8 (3)	3.5 (3)	5.7 (5)	19 (18)	24 (23)	13 (12)	15 (14)
Cl	NA[d]	15 (22)	15 (22)				14 (21)	24 (35)		
Cl	MN[e]	15.8 (27)	8.9 (15)				12.6 (22)	20.0 (34)	1 (2)	
SbF_6	none	5.2 (12)	4.8 (11)	1.2 (2)	2.2 (5)		8.2 (18)	11 (25)	5.2 (12)	6.4 (14)
SbF_6	NA	15 (28)	99 (18)				10 (19)	19 (35)		
SbF_6	MN	11.3 (30)	5.5 (15)				6.8 (18)	13.2 (35)	0.6 (2)	
$B(C_6F_5)_4$	none	6.6 (14)	6 (13)		2.2 (5)		9.4 (20)	13 (29)	5.8 (13)	3.0 (6)
$B(C_6F_5)_4$	NA	20 (22)	12 (13)				11 (12)	50 (54)		
$B(C_6F_5)_4$	MN	18.7 (28)	10.7 (16)				15.4 (23)	21.2 (32)	0.9 (1)	

[a] Concentrations were obtained from GC data using dodecane as internal standard. [b] Distributions were calculated from the sum of the concentrations listed. In the case of MN, new products were not included. [c] Concentration of 8 was estimated using the same coefficients as for 7. [d] NA is 1-naphthol. The ratio of iodonium salt to NA is 1:5. [e] MN is 1-methoxynaphthalene. The ratio of iodonium salt to MN is 1:5. [f] Electron donor.

Scheme 3



Scheme 4



most of the 1-methoxynaphthalene radical cation is returned to 1-methoxynaphthalene by reverse electron transfer. Consequently, the concentration of 1-methoxynaphthalene does not change significantly (<5%).

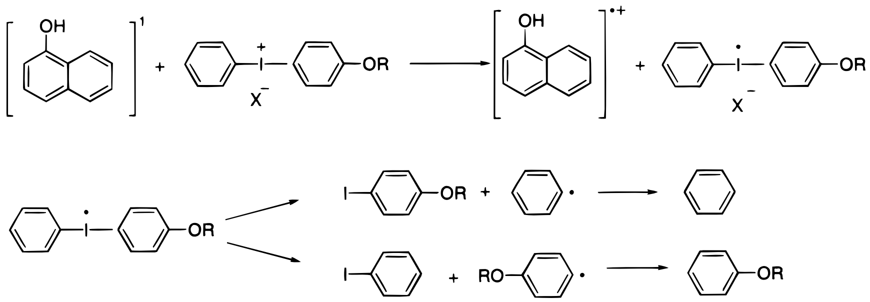
Experimental Section

General Information. GC measurements were carried out on a Hewlett-Packard 5890 instrument (FID detector), with a 30 m J&W DB-1 capillary column. GC/MS spectra were determined at an ionizing voltage of 70 eV. Elemental analyses were obtained from Atlantic Microlab Inc. HRMS were obtained from Mass Spectrometry Laboratory of the University of Illinois at Urbana-Champaign. (3-Chloropropyl)trimethylsilane was purchased from Gelest Inc. All other reagents were purchased from Aldrich Chemical Co. and used as received, unless otherwise noted.

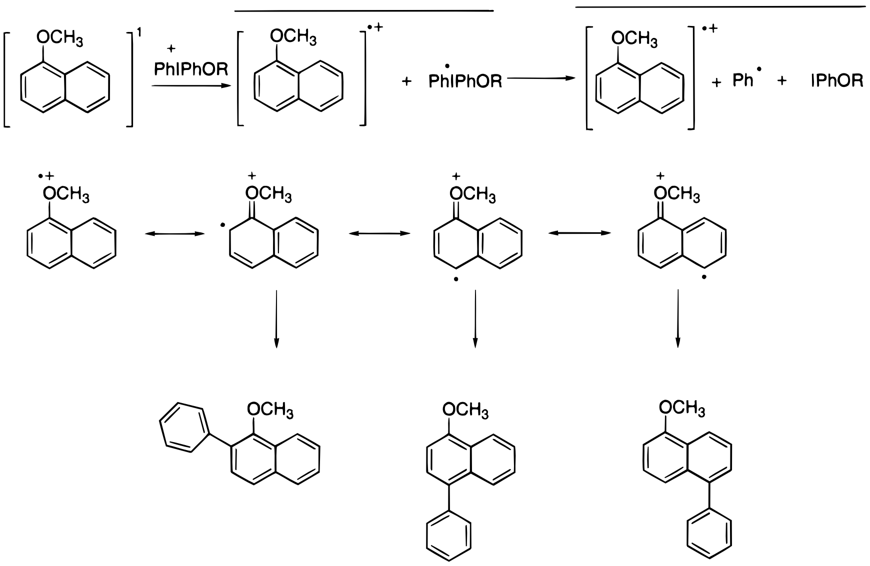
General Procedures for Irradiation and Product Detection A 4 mL vial containing a dilute (~0.01 M) solution of the iodonium salts with or without electron donors (~0.05 M) was degassed with dry argon for ca. 10 min. It was then irradiated for 5 min at ambient temperature in Rayonet PRP-100 photoreactor equipped with 15 300 nm GEF8T5/BLB lamps. After photolysis, 5 mL of pentane containing dodecane as internal standard was added to extract the photoproducts while 5 mL of water was added. GC/MS was performed to identify the products, and GC was used to quantify the concentrations and distributions of the photoproducts.

3-(Trimethylsilyl)propyl Phenyl Ether (I). The title compound was synthesized from (3-chloropropyl)trimethylsilane and sodium phenolate trihydrate using typical Williamson ether reaction conditions. After 4 h, water was added to the reaction mixture and three portions of hexane were used to extract the product. NaOH solution (0.1 N) and saturated NaCl

Scheme 5



Scheme 6



solution were used to wash the organic layers several times. A pale yellow liquid was obtained in 94% yield after evaporation of the hexane. The compound was characterized by ^{1}H NMR and HR-MS. ^{1}H NMR (CDCl$_3$, 200 Hz): δ 7.24−7.32 (m, 2H), 6.87−6.93 (m, 3H), 3.91 (t, 2H, J = 7.0 Hz), 0.57−0.66 (m, 2H), −0.02 to 0.06 (m, 9H). HR-MS: calcd for m/z 208.1284, found m/z 208.1288.

(3-(Trimethylsilyl)propoxyphenyl)phenyliodonium Chloride (II). The chloride salt was synthesized from **I** and iodobenzene diacetate by following a literature procedure.[3] The crude product was purified by recrystallization from acetonitrile to obtain white crystals, mp 169−170 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.85−7.98 (m, 4H), 7.21−7.41 (m, 3H), 6.74 (d, 2H, J = 8.8 Hz), 3.84 (t, 3H, J = 6.6 Hz), 1.64−1.79 (m, 2H), 0.49−0.57 (m, 2H), −0.07 to 0.06 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 161.1 (C), 136.7 (CH), 134.2 (CH), 130.9 (CH), 130.4 (CH), 120.6 (C), 117.3 (CH), 108.8 (C), 70.8 (CH$_2$), 23.5 (CH$_2$), 12.4 (CH$_2$), −1.8 (CH$_3$). Anal. Calcd: C, 48.40; H, 5.42. Found: C, 48.19; H, 5.40.

(3-(Trimethylsilyl)propoxyphenyl)phenyliodonium Hexafluoroantimoniate. The title compound was synthesized from the chloride salt **II** and NaSbF$_6$ by following a modified procedure as described by Crivello.[4] Instead of filteration of the precipitate after the addition of water, methylene chloride was used to extract the product. After rotatory evaporation, a waxy solid was obtained, mp 93−95 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.95−7.99 (m, 4H), 7.41−7.64 (m, 3H), 6.93 (d, J = 9.2 Hz), 3.91 (t, 2H, J = 6.6 Hz), 1.67−1.83 (m, 2H), 0.52−0.61 (m, 2H), −0.06 to 0.06 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 163.3 (C), 137.9 (CH), 134.7 (CH), 133.0 (CH), 132.7 (CH), 119.1 (CH), 112.7 (C), 98.8 (C), 71.4 (CH$_2$), 23.3 (CH$_2$), 12.4 (CH$_2$), −1.8 (CH$_3$). Anal. Calcd: C, 33.41; H, 3.74. Found: C, 33.60; H, 3.73.

Potassium Tetrakis(pentafluorophenyl)borate. This compound was obtained following a procedure described by Fouassier.[22] The^{19}F NMR spectrum was consistent with that found in the literature.

(3-(Trimethylsilyl)propoxyphenyl)phenyliodonium Tetrakis(pentafluorophenyl)borate. The title compound was obtained from metathesis of the chloride salt **II** and KB(C$_6$F$_5$)$_4$ in CH$_2$Cl$_2$. The crude product was purified by filtering through a thin layer of neutral alumina to produce a solid, mp 48−51 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.67−7.83 (m, 5H), 7.47−7.56 (m, 2H), 6.98 (d, J = 9.6 Hz), 3.96 (t, 2H, J = 6.6 Hz), 1.65−1.83 (m, 2H), 0.53−0.62 (m, 2H), −0.05 to 0.06 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 164.1 (C), 150.5 (d, C, J = 23.9 Hz), 140.5 (d, C, J = 23.5 Hz), 138.6 (C), 137.5 (CH), 133.9 (CH), 133.8 (CH), 133.5 (CH), 119.8 (CH), 112.1 (C), 97.3 (C), 71.7 (CH$_2$), 23.4 (CH$_2$), 12.3 (CH$_2$), −2.0 (CH$_3$). ^{19}F NMR (CDCl$_3$): δ −132.8 (sm, 2F), −162.8(m, 1F), −166.7 (sm, 2F). Anal. Calcd: C, 46.26; H, 2.22. Found: C, 46.24; H, 2.24.

3-(Trimethylsilyl)propyl 4-Chlorophenyl Ether. The title compound was synthesized from 4-chlorophenol and (3-chloropropyl)trimethylsilane using typical Williamson ether reaction conditions. The product was isolated and purified as above (93%), and then characterized by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.15−7.21 (m, 2H), 6.74−6.74 (m, 2H), 3.84 (t, 2H, J = 7.0 Hz), 1.67−1.82 (m, 2H), 0.52−0.61 (m, 2H), −0.05 to 0.02 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 157.7 (CH), 129.2 (C), 125.2 (CH), 115.7 (C), 70.9 (CH$_2$), 23.8 (CH$_2$), 12.5 (CH$_2$), −1.8 (CH$_3$). HR-MS: calcd for m/e 242.0895, found m/e 242.0893.

3-(Trimethylsilyl)propyl 4-Iodophenyl) Ether. The title compound was synthesized from 4-iodophenol and (3-chloropropyl)trimethylsilane using typical Williamson ether reaction conditions and purified as mentioned above. The yield was 91%. The product was characterized by ^{1}H NMR, ^{13}C NMR,

---

[22] Castellanos, F.; Fouassier, J. P.; Priou, C.; Cavezzan, J. *J. Appl. Polym. Sci.* **1996**, *60*, 705.

and HR-MS. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.49−7.54 (m, 2H), 6.61−6.67 (m, 2H), 3.85 (t, 2H, J = 6.6 Hz), 1.67−1.83 (m, 2H), 0.52−0.61 (m, 2H), −0.02−0.06 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 158.9 (CH), 138.1 (C), 116.8 (C), 82.4 (CH), 70.7 (CH$_2$), 23.7 (CH$_2$), 12.5 (CH$_2$), −1.8 (CH$_3$). HR-MS: calcd for *m*/*z* 334.0250, found *m*/*z* 334.0243.

3-(Trimethylsilyl)propyl 4-Phenylphenyl Ether. The title compound was synthesized from 4-phenylphenol and (3-chloropropyl)trimethylsilane using typical Williamson ether reaction conditions. A white waxy solid, mp 44−45 °C, was obtained (92%). The product was characterized by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.22−7.54 (m, 7H), 6.89−6.97 (m, 2H), 3.92 (t, 2H, J = 6.6 Hz), 1.70−1.86 (m, 2H), 0.54−0.63 (m, 2H), −0.05 to 0.06 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 158.6 (C), 140.8 (C), 133.5 (C), 128.7 (CH), 128.1 (CH), 126.7 (CH), 126.6 (CH), 70.7 (CH$_2$), 23.9 (CH$_2$), 12.6 (CH$_2$), −1.7 (CH$_3$). HR-MS: Calcd for *m*/*z* 284.159 64, found *m*/*z* 284.159 65.

Acknowledgment. The authors gratefully acknowledge financial support from the United Soybean Board (Project No. 9412). We also thank Dr. John Malpert for helpful discussions. One of us (H.G.) is a Fellow of the McMaster Endowment.

JO000058W