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New and Direct Approach to Hypervalent Iodine Compounds from Arenes and Iodine. Straightforward Synthesis of (Diacetoxyiodo)arenes and Diaryliodonium Salts Using Potassium μ-Peroxo-hexaoxodisulfate[#]

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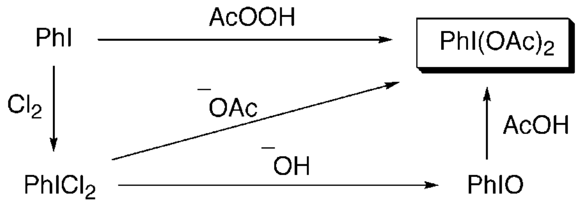
The reaction of arenes with elemental iodine, acetic acid, and potassium μ-peroxo-hexaoxodisulfate ($K_2S_2O_8$) in the presence of concentrated sulfuric acid, efficiently generated the corresponding (diacetoxyiodo)arenes in good yields. Diaryliodonium triflates were directly synthesized by reaction of arenes with elemental iodine in good yields by using $K_2S_2O_8$, AcOH, and TfOH. Diaryliodonium tosylates were also prepared from arenes and elemental iodine by using $K_2S_2O_8$, AcOH, H_2SO_4, and TsOH. The procedure involved mild conditions and a straightforward one-pot synthesis.

Molecular iodine has been widely used for iodination reactions, and its utilization has afforded many fundamental and significant processes in chemistry. However, direct use of molecular iodine for synthesizing hypervalent iodine compounds is not general, because most of them are synthesized from aromatic iodides. Recently, hypervalent iodine reagents have attracted increasing interest as green oxidants in organic synthesis due to their low toxicity, ready availability, easy handling, high efficiency and stability to air and moisture, and because they are environmentally benign alternatives to heavy metal reagents, such as lead(IV), thallium(III), and mercury(II). Hypervalent iodine compounds, such as (diacetoxyiodo)arenes, [bis(trifluoroacetoxy)iodo]arenes, [hydroxy(tosyloxy)iodo]arenes, and diaryliodonium salts, have been extensively studied, and their applications for organic synthesis have been reviewed.[1] (Diacetoxyiodo)arenes, [$ArI(OAc)_2$], and their parent compound, (diacetoxyiodo)benzene [$PhI(OAc)_2$], have been known for a long time.[2–4] Particularly, (diacetoxyiodo)benzene is a crystalline compound, is fairly stable in air, and can be stored for long periods in the dark. It is a potent, often chemoselective oxidant, and is widely used in modern organic synthesis. There are several methods for synthesizing (diacetoxyiodo)benzene. Historically, (diacetoxyiodo)benzene was prepared by Willgerodt in 1892, by simply dissolving iodosylbenzene in hot acetic acid.[5] Basically, the methods, as shown in Scheme 1, involve the reaction of iodosylbenzene with acetic acid,[5] the direct oxidation of iodobenzene in acetic acid,[4,6–10] and the reaction of (dichloroiodo)benzene with metal acetates or acetic acid.[11,12] During the course of our systematic studies on effective and easy preparations of $ArI(OAc)_2$, we have devised two methods for their synthesis from iodoarenes.[13] In most of the above methods, iodobenzene is used as a starting material to prepare (diacetoxyiodo)benzene; however, iodobenzene is readily available but expensive.

Similarly, diaryliodonium salts also represent an important class of aromatic iodine(III) derivatives. They have been used in organic synthesis mostly as arylating reagents for a large variety of organic and inorganic nucleophiles[14] and have been applied to a photochemical polymerization process as a photoacid generator[15] and to chemical amplification in imaging systems.[16] In addition, some of diaryliodonium salts also show biological activity.[17] There are many methods for preparing diaryliodonium salts,[18] but very few of them involve the syntheses of diaryliodonium triflate and tosylate salts. Most of the diaryliodonium triflates and tosylates have been prepared from (diacetoxyiodo)arenes because of their stability and easy handling. For example, diaryliodonium triflates are prepared by the reaction of aromatic substrates with (diacetoxyiodo)benzene activated with triflic acid or trifluoroacetic acid.[19,20] For the synthesis of diaryliodonium tosylates,[21,22] the preparative methods involve the reaction of [hydroxy(tosyloxy)iodo]arenes, which are prepared from (diacetoxyiodo)arenes. Therefore, once (diacetoxyiodo)arenes are available, diaryliodonium triflates and tosylates can be readily prepared.



Scheme 1.

The most ideal and fundamental procedure for (diacetoxyiodo)benzene should involve a straightforward synthesis from benzene and iodine. This procedure would give a direct and efficient method that does not involve iodobenzene. However, to the best of our knowledge, there are no methods for preparing (diacetoxyiodo)benzene directly from benzene and iodine. Very recently, Shreeve et al. have reported a direct synthesis of (diacetoxyiodo)arenes mediated by Selectfluor.[23] In the Selectfluor-mediated method, electron-rich di- and tri-substituted benzenes are used as starting materials to obtain the corresponding (diacetoxyiodo)arenes. However, it seems that this

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method cannot be applied to benzene, mono-substituted benzenes, and electron-deficient arenes due to low reactivity, judging from the Selectfluor-mediated iodination of arenes.[24]

In addition, considering the useful properties of salts and other derivatives of triflic acid,[25] the development of a simple and efficient procedure for the preparation of diaryliodonium triflates is desirable. Similarly, the most ideal procedure for diphenyliodonium triflate should involve a straightforward synthesis from benzene and iodine. In other words, it would be a direct and efficient method that does not involve the preparation of iodobenzene and (diacetoxyiodo)benzene. Preparation of diaryliodonium triflates has been studied so far by using $\mathrm{ArI(OAc)_2}$.[19,20] Very recently, we have found that diaryliodonium triflates are directly prepared by the reaction of arenes and iodine in the presence of potassium μ-peroxo-hexaoxodisulfate ($\mathrm{K_2S_2O_8}$) in TFA, followed by treatment with NaOTf.[26] However, this method requires two successive procedures to obtain triflate salts: (1) reaction of arenes and iodine and (2) exchange of the counter anion with triflate.

Herein, we wish to report a direct, easy method for the preparation of (diacetoxyiodo)benzene from benzene, together with its application to toluene and less reactive halobenzenes.[27] Furthermore, we wish to report a one-pot, easy method for the preparation of diaryliodonium triflates and tosylates from arenes and iodine.

Results and Discussion

In our laboratory, we found a direct and efficient method for preparing $\mathrm{ArI(OAc)_2}$ in good yield from the corresponding arenes with iodine in AcOH, using commercial $\mathrm{K_2S_2O_8}$ as the oxidant. The results are given in Table 1. Addition of concentrated $\mathrm{H_2SO_4}$ was essential to generate (diacetoxyiodo)arenes. Trifluoromethanesulfonic acid was also effective, but $\mathrm{H_2SO_4}$ was more convenient for handling and workup. $\mathrm{K_2S_2O_8}$ is used as a strong oxidizing agent in many applications. It has particular advantages of being almost non-hygroscopic, stable for storage, and easy and safe to handle. Therefore, $\mathrm{K_2S_2O_8}$ was good choice for this reaction. The transformation of arenes to (diacetoxyiodo)arenes could be easily scaled up, given the advantages of $\mathrm{K_2S_2O_8}$ outlined above, together with the complete absence of effluent or by-product problems. The optimized conditions involved a slight excess of arenes. It is thought that an excess of arenes do not undergo the further reaction affording diaryliodonium salts because the amount of $\mathrm{H_2SO_4}$ is not enough to promote further reaction. Our novel diacetoxyiodination is described in Scheme 2.

Table 1. Direct Synthesis of (Diacetoxyiodo)arenes from Arenes[a)]

Entry	Arene	Time/h	Product	Yield/%[b)]
1	Benzene	20	$\mathrm{PhI(OAc)_2}$	73
2[c)]	Benzene	20	$\mathrm{PhI(OAc)_2}$	0
3[d)]	Benzene	24	$\mathrm{PhI(OAc)_2}$	70
4[e)]	Benzene	28	$\mathrm{PhI(OAc)_2}$	66
5[f)]	Benzene	30	$\mathrm{PhI(OAc)_2}$	64
6	Toluene	12	$\mathrm{4\text{-}MeC_6H_4I(OAc)_2}$	70
7	Chlorobenzene	20	$\mathrm{4\text{-}ClC_6H_4I(OAc)_2}$	71
8	Bromobenzene	20	$\mathrm{4\text{-}BrC_6H_4I(OAc)_2}$	70
9	Fluorobenzene	20	$\mathrm{4\text{-}FC_6H_4I(OAc)_2}$	69

a) The reaction of an arene (1.18 mmol) was carried out in a mixture of AcOH (5 mL), $\mathrm{I_2}$ (0.5 mmol), 1,2-dichloroethane (2 mL), and $\mathrm{H_2SO_4}$ (4 mmol) in the presence of $\mathrm{K_2S_2O_8}$ (5 mmol) at 40 °C. b) Isolated yield based on iodine atom. c) In the absence of $\mathrm{K_2S_2O_8}$. d) Benzene (1.18 mmol), AcOH (2 mL), $\mathrm{I_2}$ (0.5 mmol), 1,2-dichloroethane (2 mL), $\mathrm{H_2SO_4}$ (4 mmol), and $\mathrm{K_2S_2O_8}$ (5 mmol). e) Benzene (11.8 mmol), AcOH (20 mL), $\mathrm{I_2}$ (5 mmol), 1,2-dichloroethane (20 mL), $\mathrm{H_2SO_4}$ (40 mmol), and $\mathrm{K_2S_2O_8}$ (50 mmol). f) Benzene (59.0 mmol), AcOH (100 mL), $\mathrm{I_2}$ (25 mmol), 1,2-dichloroethane (100 mL), $\mathrm{H_2SO_4}$ (200 mmol), and $\mathrm{K_2S_2O_8}$ (250 mmol).

$$\mathrm{ArH} + \mathrm{I_2} \xrightarrow[\substack{\mathrm{AcOH,\ ClCH_2CH_2Cl} \\ 40\,^{\circ}\mathrm{C},\ 12\text{-}30\ \mathrm{h}}]{\mathrm{K_2S_2O_8,\ H_2SO_4}} \mathrm{ArI(OAc)_2}$$

Scheme 2.

$$\mathrm{ArH} + \mathrm{I_2} \xrightarrow[\substack{\mathrm{AcOH,\ ClCH_2CH_2Cl} \\ 40\,^{\circ}\mathrm{C},\ 20\ \mathrm{h}}]{\mathrm{K_2S_2O_8,\ H_2SO_4}} \mathrm{ArIO}$$

Ar = $\mathrm{2,5\text{-}Me_2C_6H_3}$ (30%)
Ar = $\mathrm{2,4,6\text{-}Me_3C_6H_2}$ (30%)
Ar = $\mathrm{4\text{-}{}^{\mathit{t}}BuC_6H_4}$ (35%)

Scheme 3.

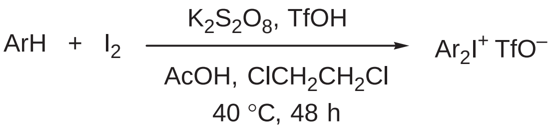
The diacetoxyiodination reaction of arenes shown in Scheme 2 was carried out at 40 °C in a mixture of AcOH, 1,2-dichloroethane, iodine, and concentrated $\mathrm{H_2SO_4}$. The presence of $\mathrm{K_2S_2O_8}$ in the reaction mixture was required, because (diacetoxyiodo)arenes did not form otherwise (Entry 2). When $\mathrm{K_2S_2O_8}$ was replaced with $\mathrm{Na_2S_2O_8}$, the final yields of $\mathrm{ArI(OAc)_2}$ were lowered by ca. 20–25%. Attempt to use $\mathrm{NaBO_3}$ for this preparation was unsuccessful. Decreasing the amount of AcOH did not affect the yield of (diacetoxyiodo)benzene (Entry 3). The reaction on as 10- or 50-fold scale larger than that in Entry 3 did not lead to the decrease in the yield (Entries 4 and 5). Toluene also gave 4-(diacetoxyiodo)toluene in good yield (Entry 6). Interestingly, arenes bearing weak deactivating groups, such as chloro, bromo, and fluoro groups, gave (diacetoxyiodo)arenes in good yields (Entries 7–9). In order to broaden the scope of this reaction, we conducted the diacetoxyiodination of xylene, mesitylene, and *tert*-butylbenzene. Actually, these substrates underwent the reaction. However, as shown in Scheme 3, we found that these reactions resulted in the formation of iodosylbenzene derivatives, respectively. Therefore, it is thought that, because these compounds are electron-rich, hydrolysis of (diacetoxyiodo)arenes occurs during the reaction or the workup procedure. This method was not applicable for arenes with strong electron-donating groups. For example, naphthalene and anisole were quickly oxidized in the reaction mixtures, but the reaction resulted in decomposition and the formation of viscous products. This method also did not work for arenes with strong electron-withdrawing groups, such as trifluoromethyl and nitro groups, due to their decreased reactivity.

Generally, (diacetoxyiodo)arenes are activated by adding a

Table 2. Preparation of Diaryliodonium Triflates from Arenes[a)]

Entry	Arene	Product	Yield/%[b)]
1	Benzene	Ph_2I^+ TfO^-	72
2[c)]	Benzene	Ph_2I^+ TfO^-	71
3	Bromobenzene	$(4\text{-}BrC_6H_4)_2I^+$ TfO^-	55
4	Chlorobenzene	$(4\text{-}ClC_6H_4)_2I^+$ TfO^-	60
5	Fluorobenzene	$(4\text{-}FC_6H_4)_2I^+$ TfO^-	68
6	*tert*-Butylbenzene	$(4\text{-}^tBuC_6H_4)_2I^+$ TfO^-	81
7	*p*-Xylene	$(2,5\text{-}Me_2C_6H_3)_2I^+$ TfO^-	47
8	Mesitylene	$(2,4,6\text{-}Me_3C_6H_2)_2I^+$ TfO^-	56

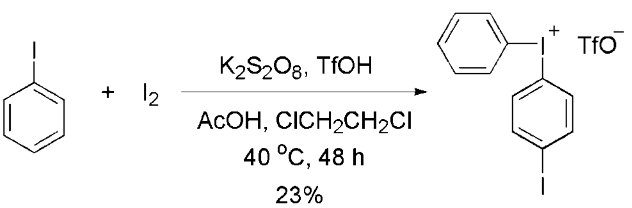
a) The reaction of an arene (10 mmol) was carried out in a mixture of AcOH (5 mL), TfOH (10 mmol), 1,2-dichloroethane (2 mL), and iodine (0.52 mmol) in the presence of $K_2S_2O_8$ (5.11 mmol) at 40 °C for 48 h. b) Isolated yield based on iodine atom. c) Benzene (100 mmol), AcOH (50 mL), TfOH (100 mmol), 1,2-dichloroethane (20 mL), iodine (5.2 mmol), and $K_2S_2O_8$ (51.1 mmol).



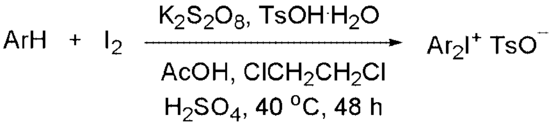
Scheme 4.

strong acid and react with arenes to give diaryliodonium salts. Since a strong acid is present in the preparation of (diacetoxyiodo)arenes, it is expected that diaryliodonium salts are formed by the reaction of the in situ generated (diacetoxyiodo)arenes on using excess aromatic substrates. Thus, one-pot preparation of diaryliodonium triflates, $Ar_2I^+OTf^-$, and tosylates, Ar_2I^+-OTs^-, from arene and iodine were examined by applying the above method. In the case of diphenyliodonium triflate, the reaction of benzene with elemental iodine was conducted in AcOH with triflic acid in the presence of commercial grade $K_2S_2O_8$ as the oxidant at 40 °C. This simple, one-pot reaction for 48 h gave diphenyliodonium triflate directly in 72% yield (Table 2, Entry 1). In order to explore the scope of this reaction, we applied it to other aromatic substrates, as shown in Scheme 4. The results are given in Table 2. Analogous to previous results,[26] use of a large excess of arenes and triflic acid was essential to obtain a better yield of diaryliodonium salts.

The preparation of diphenyliodonium triflate from benzene could easily be scaled up (Entry 2), together with the complete absence of effluent or by-product problems. Interestingly, arenes bearing weak deactivating groups such as chloro, bromo, and fluoro groups, gave diaryliodonium triflates in good yields (Entries 3–5). However, the similar reaction with iodobenzene did not give bis(4-iodophenyl)iodonium triflate, but afforded (4-iodophenyl)(phenyl)iodonium triflate in 23% yield (Scheme 5). In the reaction of iodobenzene, it is thought that the iodo group of iodobenzene is oxidized to form (diacetoxyiodo)benzene, which reacts with iodobenzene to yield the (4-iodophenyl)(phenyl)iodonium salt, as it is observed previously in the reaction of iodobenzene.[28] *tert*-Butylbenzene, *p*-xylene, and mesitylene gave bis(4-*tert*-butylphenyl)iodonium triflate, bis(2,5-dimethylphenyl)iodonium triflate, and bis(2,4,6-trimethylphenyl)iodonium triflate, respectively (Entries 6–8).



Scheme 5.



Scheme 6.

Table 3. Preparation of Diaryliodonium Tosylates from Arenes[a)]

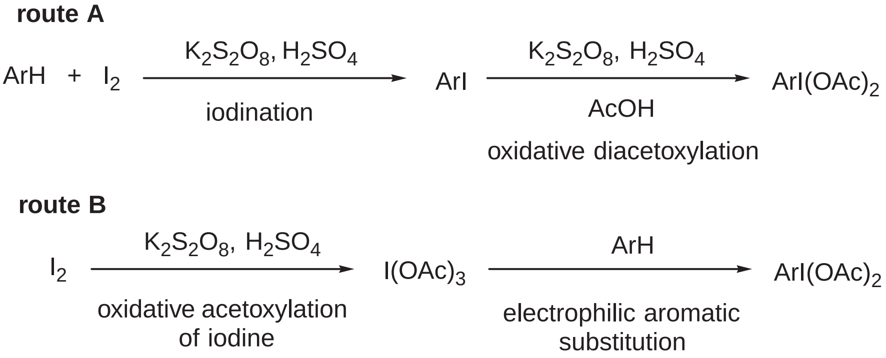
Entry	Arene	Product	Yield/%[b)]
1	Benzene	Ph_2I^+ TsO^-	67
2[c)]	Benzene	Ph_2I^+ TsO^-	65
3	Bromobenzene	$(4\text{-}BrC_6H_4)_2I^+$ TsO^-	22
4	Chlorobenzene	$(4\text{-}ClC_6H_4)_2I^+$ TsO^-	24
5	Fluorobenzene	$(4\text{-}FC_6H_4)_2I^+$ TsO^-	50
6	*tert*-Butylbenzene	$(4\text{-}^tBuC_6H_4)_2I^+$ TsO^-	85

a) The reaction of an arene (10 mmol) was carried out in a mixture of AcOH (5 mL), TsOH (2.36 mmol), H_2SO_4 (8 mmol), 1,2-dichloroethane (2 mL), and iodine (0.52 mmol) in the presence of $K_2S_2O_8$ (5.11 mmol) at 40 °C for 48 h. b) Isolated yield based on iodine atom. c) Benzene (100 mmol), AcOH (50 mL), TsOH (23.6 mmol), H_2SO_4 (80 mmol), 1,2-dichloroethane (20 mL), iodine (5.2 mmol), and $K_2S_2O_8$ (51.1 mmol).

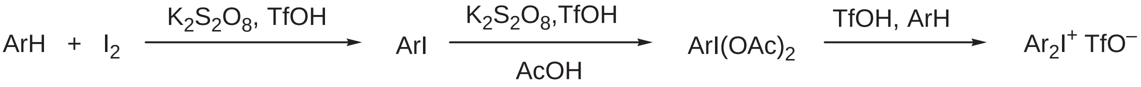
This method was not applicable to arenes with strong electron-donating groups. For example, in the case of anisole, the reaction mixture was quickly oxidized as indicated by the formation of a black solution, but no diaryliodonium salts were obtained. In addition, arenes with strong electron-withdrawing groups, such as trifluoromethyl and nitro groups, could not be used due to their decreased reactivity.

Similarly, it was applied to the synthesis of diaryliodonium tosylates, $Ar_2I^+TsO^-$. Diphenyliodonium tosylate, Ph_2I^+-OTs^-, was prepared from benzene and iodine in the presence of AcOH, H_2SO_4, 1,2-dichloroethane, and *p*-toluenesulfonic acid monohydrate with $K_2S_2O_8$ at 40 °C. In order to explore the scope of this reaction, we applied it to other aromatic substrates in Scheme 6. The results are given in Table 3. Arenes bearing weak deactivating groups, such as chloro, bromo, and fluoro groups, gave diaryliodonium tosylates (Entries 3–5). *tert*-Butylbenzene gave bis(4-*tert*-butylphenyl)iodonium tosylate in good yield (Entry 6). This method was not applicable for electron-rich arenes, such as anisole, mesitylene, and *p*-xylene, and for arenes with strong electron-withdrawing groups, such as trifluoromethyl and nitro groups, due to their decreased reactivity.

Mechanistically, there are two possible routes for generating (diacetoxyiodo)arenes, as shown in Scheme 7: route A is the iodination of arenes, followed by oxidative diacetoxylation



Scheme 7.



Scheme 8.

of iodoarenes leading to (diacetoxyiodo)arenes, and route B is the generation of triacetoxyiodine(III), followed by electrophilic aromatic substitution to give (diacetoxyiodo)arenes. The latter route may be probable, because $I(OAc)_3$ is a reactive electrophile and can react with aromatic substrates. According to Shreeve's result,[23] $I(OAc)_3$ is only effective for tri-substituted electron-rich aromatics such as mesitylene and 1-*tert*-butyl-3,5-dimethylbenzene. In our case, however, our method is effective for benzene and electron-deficient, less reactive halobenzenes. Actually, (diacetoxyiodo)benzene was not obtained by the same reaction for 11 h without benzene followed by treatment with benzene. Therefore, a plausible route is the former one. In order to detect the intermediate iodoarene in route A, we examined the reaction with a smaller amount of $K_2S_2O_8$. When benzene was allowed to react with iodine in the presence of 2 molar amounts of $K_2S_2O_8$ under the same conditions, iodobenzene was formed in 66% yield, together with $PhI(OAc)_2$ in 21% yield. We have already shown that the reaction of iodobenzene with $K_2S_2O_8/H_2SO_4$ in AcOH effectively proceeds to give (diacetoxyiodo)benzene.[13a] Therefore, it is thought that, once iodoarenes form, they are immediately oxidized to give $ArI(OAc)_2$ under the reaction conditions.

In the formation of diaryliodonium triflates, it is possible that there are three major steps: iodination of arenes, diacetoxylation of iodoarenes, and arylation of (diacetoxyiodo)arenes (Scheme 8). The key step is the formation of (diacetoxyiodo)arenes. As it is discussed above, the formation of (diacetoxyiodo)arenes is an efficient process from arenes and iodine promoted by $K_2S_2O_8$. Then, once (diacetoxyiodo)arenes are formed, they are immediately activated by trifluoromethanesulfonic acid to react with excess aromatic compounds, yielding diaryliodonium triflates.[19] In the case of diaryliodonium tosylates, the reaction proceeds similarly to that for the formation of diaryliodonium triflates. However, (diacetoxyiodo)arenes are activated by H_2SO_4 and react with excess arenes to yield diaryliodonium sulfates, because diaryliodonium salts do not form without H_2SO_4. Finally, the anion exchanges with tosylate.

Conclusion

In conclusion, we have demonstrated novel, simple, and one-pot procedures for the preparations of (diacetoxyiodo)arenes, diaryliodonium triflates, and diaryliodonium tosylates. These processes involve a fundamental process composed of arenes and elemental iodine. (Diacetoxyiodo)arenes were obtained in good yields by the reaction promoted by $K_2S_2O_8$ and concentrated H_2SO_4 in AcOH. Diaryliodonium triflates were prepared in good yields by using excess arenes in the presence of $K_2S_2O_8$ and TfOH. This new method also afforded diaryliodonium tosylates by the reaction of excess arenes with elemental iodine in the presence of $K_2S_2O_8$, H_2SO_4, TsOH in AcOH. Since the present one-pot procedures can be scaled up easily, it is expected that this procedures will be used widely for many purposes.

The present methods described above cover relatively electron-rich to weakly deactivated aromatic substrates, and it involves fundamental starting materials (simple arenes, elemental iodine, and commercial $K_2S_2O_8$). The simple and convenient one-pot procedures for (diacetoxyiodo)arenes, diaryliodonium triflates and diaryliodonium tosylates have a significant advantage over the previous reported ones.

Experimental

General. Melting points were determined with a Yanaco micro-melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer and the chemical shifts are expressed in parts per million downfield from tetramethylsilane. Elemental analysis was conducted by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University.

Optimized Procedure for Preparing (Diacetoxyiodo)arenes from Arenes. General Procedure (Table 1, Scheme 2): A solution of an appropriate arene (1.18 mmol) in a mixture of AcOH (5 mL), 1,2-dichloroethane (2 mL), concentrated H_2SO_4 (4 mmol), and I_2 (0.5 mmol) was heated with stirring to 40 °C for 15 min. Next, $K_2S_2O_8$ (5 mmol) was added portionwise over 10 min, and the stirring was continued until TLC analysis indicated completion of reaction. Reaction needed 12–30 h. After the reaction was completed, water (10 mL) was added. The precipitate was collected by filtration under reduced pressure, washed with CH_2Cl_2 (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with dichloromethane (3 × 10 mL) and finally washed with H_2O (10 mL). The extracts were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by washing with hexane (20 mL) or recrystallized from AcOH. Large-scale (Table 1, Entry 5) synthesis was conducted for (diacetoxyiodo)benzene in a similar manner. A solution of benzene (4.62 g, 59 mmol), AcOH (100 mL), 1,2-dichloroethane (100 mL), concentrated H_2SO_4 (200 mmol), and I_2 (6.34 g, 25 mmol) was heated with stirring to 40 °C. Next, $K_2S_2O_8$ (250 mmol) was added portionwise over 20 min, and the stirring was continued 30 h. Workup of the reaction mixture gave the product (10.79 g, 64%).

(Diacetoxyiodo)benzene: 0.245 g (73%); mp 160–161 °C (lit.[29] mp 161.1–162.2 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, $J = 7.5$ Hz, 2H, ArH), 7.59 (t, $J = 7.5$ Hz, 1H, ArH), 7.51 (t, $J = 7.5$ Hz, 2H, ArH), 2.0 (s, 6H, $MeCO_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.27, 134.81, 131.61, 130.83, 121.50, 20.21.

1-(Diacetoxyiodo)-4-methylbenzene: 0.248 g (70%); mp 107–108 °C (lit.[29] mp 106–110 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, $J = 7.8$ Hz, 2H, ArH), 7.09 (d, $J = 7.8$ Hz, 2H, ArH), 2.49 (s, 3H, Me), 2.27 (s, 6H, $MeCO_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.36, 142.06, 134.95, 132.25, 111.72, 21.29, 20.36.

4-Chloro-1-(diacetoxyiodo)benzene: 0.261 g (71%); mp 112–113 °C (lit.[29] mp 109.8–113.2 °C); ^{1}H NMR (300 MHz, CD_3OD) δ 8.06 (d, $J = 8.7$ Hz, 2H, ArH), 7.57 (d, $J = 8.7$ Hz, 2H, ArH), 1.94 (s, 6H, $MeCO_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.38, 138.34, 136.25, 131.12, 118.74, 20.22.

4-Bromo-1-(diacetoxyiodo)benzene: 0.291 g (70%); mp 121–122 °C (lit.[7] mp 120–122 °C); ^{1}H NMR (300 MHz, CD_3OD) δ 8.0 (d, $J = 8.4$ Hz, 2H, ArH), 7.71 (d, $J = 8.4$ Hz, 2H, ArH), 1.94 (s, 6H, $MeCO_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.37, 136.33, 134.03, 126.66, 119.49, 20.22.

1-(Diacetoxyiodo)-4-fluorobenzene: 0.241 g (69%); mp 175–176 °C (lit.[29] mp 177.0–179.8 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11–8.06 (m, 2H, ArH), 7.17 (m, 2H, ArH), 2.01 (s, 6H, $MeCO_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.39, 164.18 (d, $J_{CF} = 252.82$ Hz, CF), 137.46 (d, $J_{CF} = 9.22$ Hz, *C*CF), 118.41 (d, $J_{CF} = 22.87$ Hz, *C*CCF), 115.42, 20.17.

1-Iodosyl-2,4-dimethylbenzene:[30] 0.077 g (30.4%); mp 118–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H, Me), 2.54 (s, 3H, Me), 7.25 (d, $J = 6.6$ Hz, 2H, ArH), 7.81 (d, $J = 6.6$ Hz, 2H, ArH), 7.9 (s, 1H, ArH).

1-Iodosyl-2,4,6-trimethylbenzene:[31] 0.078 g (29.5%); mp 148–150 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.18 (s, 2H, ArH), 2.5 (s, 6H, Me), 2.34 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.26, 143.63, 131.75, 118.99, 26.09, 20.85.

4-*tert*-Butyl-1-iodosylbenzene: 0.101 g (35.2%); mp 182–184 °C (lit.[32] mp 189 °C); ^{1}H NMR (300 MHz, CD_3OD) δ 8.07 (d, $J = 8.7$ Hz, 2H, ArH) 7.55 (d, $J = 8.7$ Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.57, 136.19, 130.40, 112.48, 36.05, 31.33.

Optimized Procedure for Preparing Diaryliodonium Triflates from Arenes. General Procedure (Table 2, Scheme 4): A solution of the appropriate arene (10 mmol), molecular iodine (0.52 mmol), AcOH (5 mL), TfOH (10 mmol) and 1,2-dichloroethane (2 mL) was heated with stirring to 40 °C. After the iodine dissolvved, $K_2S_2O_8$ (5.11 mmol) was added. The reaction mixture was stirred at that temperature for 48 h. After completion of the reaction, water (12 mL) was added. The resulting precipitates were collected by filtration under reduced pressure, washed with CH_2Cl_2 (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with CH_2Cl_2 (4 × 10 mL). The extracts were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed by evaporation. The crude product was washed with Et_2O (3 × 3 mL), and recrystallized from CH_2Cl_2/hexane. Large scale (Table 2, Entry 2) synthesis was conducted for diphenyliodonium triflate in a similar manner. A solution of benzene (7.8 g, 100 mmol), AcOH (50 mL), 1,2-dichloroethane (20 mL), TfOH (100 mmol), and I_2 (1.32 g, 5.2 mmol) was heated with stirring to 40 °C. After the iodine dissolved, $K_2S_2O_8$ (51.1 mmol) was added and the stirring was continued 48 h. Workup of the reaction mixture gave pure product (3.16 g, 71%).

Diphenyliodonium Triflate: 0.324 g (72%); mp 177–178 °C (lit.[33] mp 178–180 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, $J = 8.1$ Hz, 4H, ArH), 7.66 (t, $J = 8.1$ Hz, 2H, ArH), 7.51 (t, $J = 8.1$ Hz, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.39, 133.56, 133.10, 121.78 (q, $J_{CF} = 316.5$ Hz, SO_2CF_3), 115.80.

Bis(4-bromophenyl)iodonium Triflate: 0.334 g (55%); mp 190–191 °C (lit.[34] mp 198 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.4$ Hz, 4H, ArH), 7.67 (d, $J = 8.4$ Hz, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.12, 136.24, 128.69, 121.73 (q, $J_{CF} = 316.42$ Hz, SO_2CF_3), 114.25.

Bis(4-chlorophenyl)iodonium Triflate:[26] 0.294 g (60%); mp 175–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, $J = 8.7$ Hz, 4H, ArH), 7.53 (d, $J = 8.7$ Hz, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.41, 138.08, 133.22, 121.74 (q, $J_{CF} = 316.5$ Hz, SO_2CF_3), 113.55.

Bis(4-fluorophenyl)iodonium Triflate:[26] 0.332 g (68%); mp 167–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25–8.21 (m, 4H, ArH), 7.31 (t, $J = 8.7$ Hz, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.35 (d, $J_{CF} = 252.22$ Hz, *C*F), 139.31 (d, $J_{CF} = 9.3$ Hz, *C*CCF), 121.78 (q, $J_{CF} = 316.5$ Hz, SO_2CF_3), 120.50 (d, $J_{CF} = 23.47$ Hz, *C*CF), 110.11.

Bis(4-*tert*-butylphenyl)iodonium Triflate:[26] 0.453 g (81%); mp 164–165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, $J = 8.4$ Hz, 4H, ArH), 7.54 (d, $J = 8.4$ Hz, 4H, ArH), 1.28 (s, 18H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.61, 136.15, 130.39, 121.78 (q, $J_{CF} = 317.1$ Hz, SO_2CF_3), 35.99, 31.32.

(4-Iodophenyl)(phenyl)iodonium Triflate: 1.27 g (23%) mp 138–140 °C (lit.[35] mp 144–148 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, $J = 8.4$ Hz, 2H, ArH), 7.91 (q, $J = 8.4$ Hz, 4H, ArH), 7.68 (t, $J = 8.4$ Hz, 1H, ArH), 7.55 (t, $J = 8.4$ Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.29, 137.75, 136.47, 133.77, 133.24, 121.79 (q, $J_{CF} = 315.9$ Hz, SO_2CF_3), 116.07, 115.16, 100.61.

Bis(2,4-dimethylphenyl)iodonium Triflate: 0.238 g (47%); mp 192–193 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 2H, ArH), 7.41 (s, 4H, ArH), 2.59 (s, 6H, Me), 2.35 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.40, 139.22, 138.28, 135.07, 132.63, 121.79 (q, $J_{CF} = 315.8$ Hz, SO_2CF_3), 119.4, 24.98, 20.45. Found: C, 41.91; H, 3.72%. Calcd for $C_{17}H_{18}O_3IF_3S$: C, 41.98; H, 3.70%.

Bis(2,4,6-trimethylphenyl)iodonium Triflate: 0.298 g (56%); mp 190–192 °C (lit.[34] mp 192–193 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (s, 4H, ArH), 2.53 (s, 12H, Me), 2.34 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.20, 143.55, 133.74, 121.76 (q, $J_{CF} = 316.42$ Hz, SO_2CF_3), 118.94, 26.09, 20.84.

Optimized Procedure for Preparing Diaryliodonium Tosylates from Arenes. General Procedure (Table 3, Scheme 6): A solution of the appropriate arene (10 mmol), molecular iodine (0.52 mmol), AcOH (5 mL), H_2SO_4 (8 mmol), TsOH (2.36 mmol), and 1,2-dichloroethane (2 mL) was heated with stirring to 40 °C. After the iodine dissolved, $K_2S_2O_8$ (5.11 mmol) was added. The reaction mixture was stirred at that temperature for 48 h. After completion of the reaction, water (12 mL) was added. The resulting precipitate was collected by filtration under reduced pressure, washed with CH_2Cl_2 (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with CH_2Cl_2 (4 × 10 mL). The extracts were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed by evaporation. The crude product was washed with Et_2O (3 × 3 mL) and recrystallized from CH_2Cl_2/hexane. Large scale synthesis (Table 3, Entry 2) was conducted for diphenyliodonium tosylate in a similar manner. A solution of benzene (7.8 g, 100 mmol), AcOH (50 mL), 1,2-dichloroethane (20 mL), H_2SO_4 (80 mmol), TsOH (23.6 mmol), and I_2 (1.32 g, 5.2 mmol) was heated with stirring to 40 °C. After the iodine dissolved, $K_2S_2O_8$ (51.1 mmol) was added, and the stirring was continued 48 h. Workup of the reaction mixture gave pure product (3.07 g, 65%).

Diphenyliodonium Tosylate: 0.313 g (67%); mp 178–179 °C (lit.[22] mp 179–180 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, $J = 8.1$ Hz, 4H, ArH), 7.68 (d, $J = 8.1$ Hz, 2H, ArH), 7.62 (t, $J = 8.1$ Hz, 2H, ArH), 7.47 (t, $J = 8.1$ Hz, 4H, ArH), 7.17 (d, $J = 8.1$ Hz, 2H, ArH), 2.31 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.67, 141.52, 136.39, 133.44, 133.04, 129.78, 126.9, 115.98, 21.31.

Bis(4-bromophenyl)iodonium Tosylate: 0.137 g (22%); mp 200–201 °C (lit.[36] mp 203 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, $J = 8.4$ Hz, 4H, ArH), 7.66 (d, $J = 8.4$ Hz, 6H, ArH), 7.20 (d, $J = 8.4$ Hz, 2H, ArH), 2.36 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.64, 138.15, 136.25, 133.92, 129.82, 128.66, 126.93, 114.50, 21.34.

Bis(4-chlorophenyl)iodonium Tosylate:[37] 0.131 g (24%); mp 205–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, $J = 7.8$ Hz, 4H, ArH), 7.65 (d, $J = 7.8$ Hz, 2H, ArH), 7.49 (d, $J = 7.8$ Hz, 4H, ArH), 7.20 (d, $J = 7.8$ Hz, 2H, ArH), 2.35 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.66, 140.37, 138.11, 137.33, 133.24, 129.82, 126.92, 113.78, 21.32.

Bis(4-fluorophenyl)iodonium Tosylate: 0.255 g (50%); mp 189–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 4H, ArH), 7.67 (d, $J = 7.2$ Hz, 2H, ArH), 7.25–7.2 (m, 6H, ArH), 2.34 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.20 (d, $J_{CF} = 252.22$ Hz, *C*F), 143.60, 141.64, 139.33 (d, $J_{CF} = 9.22$ Hz, *C*CCF), 129.83, 126.91, 120.39 (d, $J_{CF} = 22.87$ Hz, *C*CF), 110.33, 21.3. Found: C, 46.64; H, 3.04%. Calcd for $C_{19}H_{15}O_3IF_2S$: C, 46.73; H, 3.07%.

Bis(4-*tert*-butylphenyl)iodonium Tosylate:[38] 0.495 g (85%); mp 250–251 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, $J = 7.8$ Hz, 4H, ArH), 7.69 (d, $J = 7.8$ Hz, 2H, ArH), 7.51 (d, $J = 7.8$ Hz, 4H, ArH), 7.18 (d, $J = 7.8$ Hz, 2H, ArH), 1.28 (s, 18H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.52, 141.70, 141.47, 136.18, 130.36, 129.78, 126.97, 112.48, 36.03, 31.35, 21.36.

References

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1 Reviews on organohypervalent iodine compounds and their applications in organic synthesis: a) A. Varvoglis, *Chem. Soc. Rev.* **1981**, *10*, 377. b) M. Ochiai, *Rev. Heteroat. Chem.* **1989**, *2*, 92. c) R. M. Moriarty, R. K. Vaid, G. F. Koser, *Synlett* **1990**, 365. d) R. M. Moriarty, R. K. Vaid, *Synhesis* **1990**, 431. e) A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH, Weinheim, **1992**. f) P. J. Stang, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. g) O. Prakash, N. Sainai, P. K. Sharma, *Synlett* **1994**, 221. h) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123. i) T. Umemoto, *Chem. Rev.* **1996**, *96*, 1757. j) Y. Kita, T. Takada, H. Thoma, *Pure Appl. Chem.* **1996**, *68*, 627. k) V. V. Zhdankin, *Rev. Heteroat. Chem.* **1997**, *17*, 133. l) A. Varvoglis, *Hypervalent Iodine in Organic Synthesis*, Academic, San Diego, CA, **1997**. m) T. Kitamura, Y. Fujiwara, *Org. Prep. Proced. Int.* **1997**, *29*, 409. n) A. Varvoglis, *Tetrahedron* **1997**, *53*, 1179. o) T. Muraki, H. Togo, M. Yokoyama, *Rev. Heteroat. Chem.* **1997**, *17*, 213. p) A. Kirschning, *Eur. J. Org. Chem.* **1998**, *11*, 2267. q) V. V. Zhdankin, P. J. Stang, *Tetrahedron* **1998**, *54*, 10927. r) A. Varvoglis, S. Spyroudis, *Synlett* **1998**, 221. s) Y. Kita, M. Egi, T. Takada, H. Thoma, *Synthesis* **1999**, 885. t) T. Wirth, V. H. Hirt, *Synthesis* **1999**, 1271. u) *Chemistry of Hypervalent Compounds*, ed. by K. Akiba, VCH, New York, NY, **1999**, p. 359. v) V. V. Grushin, *Chem. Soc. Rev.* **2000**, *29*, 315. w) S. S. Chaudhari, *Synlett* **2000**, 278. x) H. Togo, M. Katohgi, *Synlett* **2001**, 565. y) T. Wirth, *Angew. Chem., Int. Ed.* **2001**, *40*, 2812. z) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523. aa) H. Togo, K. Sakuratani, *Synlett* **2002**, 1966. bb) *Hypervalent Iodine Chemistry*, ed. by T. Wirth, Springer, Berlin, Heidelberg, **2003**. cc) P. J. Stang, *J. Org. Chem.* **2003**, *68*, 2997. dd) H. Thoma, Y. Kita, *Adv. Synth. Catal.* **2004**, *346*, 111.

2 C. Willgerodt, *Die Organischen Verbindungen Mit Mehrwertigem Jod*, Enke Verlag, Stuttgart, **1914**.

3 Reviews on (diacetoxyiodo)arenes: a) E. B. Merkushev, *Russ. Chem. Rev.* **1987**, *56*, 826. b) A. Kirschning, *J. Prakt. Chem./Chem.-Ztg.* **1998**, *340*, 184. c) G. Pohnert, *J. Prakt. Chem.* **2000**, *342*, 731. d) H. Thoma, *Yakugaku Zasshi* **2000**, *120*, 620; *Chem. Abstr.* **2000**, *133*, 222460. e) M. Arisawa, H. Thoma, Y. Kita, *Yakugaku Zasshi* **2000**, *120*, 1061; *Chem. Abstr.* **2001**, *134*, 29586.

4 a) J. G. Sharefkin, H. Salzman, *Org. Synth.*, **1973**, Coll. Vol. *V*, 660. b) J. Cao, N. Yang, X. Yu, *Jingxi Huagong Zhongjianti* **2003**, *33*, 36; *Chem. Abstr.* **2004**, *141*, 104208. c) R. Kaguyama, Jpn. Kokai Tokkyo Koho JP 2003238496, **2003**; *Chem. Abstr.* **2003**, *139*, 197258.

5 C. Willgerodt, *Ber. Dtsch. Chem. Ges.* **1892**, *25*, 3494.

6 A. McKillop, D. Kemp, *Tetrahedron* **1989**, *45*, 3299.

7 P. Kazmierczak, L. Skulski, *Synthesis* **1998**, 1721.

8 P. Kazmierczak, L. Skulski, L. Kraszkiewicz, *Molecules* **2001**, *6*, 881.

9 a) A. Zielinska, L. Skulski, *Molecules* **2002**, *7*, 806. b) A. Zielinska, L. Skulski, *Molecules* **2005**, *10*, 190.

10 C. Rocaboy, A. Gladysz, *Chem. Eur. J.* **2003**, *9*, 88.

11 N. W. Alcock, T. D. Waddington, *J. Am. Chem. Soc.* **1963**, *85*, 4103.

12 B. Karele, O. Neilans, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1970**, 587; *Chem. Abstr.* **1971**, *74*, 42033.

13 a) M. D. Hossain, T. Kitamura, *Synthesis* **2005**, 1932. b) M. D. Hossain, T. Kitamura, *J. Org. Chem.* **2005**, *70*, 6984.

14 a) S.-K. Kang, T. Yamaguchi, P.-S. Ho, W.-Y. Kim, H.-C. Ryu, *J. Chem. Soc., Perkin Trans. 1* **1998**, 841. b) D.-J. Chen, Z.-C. Chen, *Synlett* **2000**, 1175. c) L. Wang, Z.-C. Chen, *Synth. Commun.* **2000**, *30*, 3607. d) L. Wang, Z.-C. Chen, *J. Chem. Res.* **2000**, 372. e) U. Radhakrishnan, P. J. Stang, *Org. Lett.* **2001**, *3*, 859. f) T. Zhou, Z.-C. Chen, *J. Chem. Res.* **2001**, 235. g) T. Zhou, Z.-C. Chen, *Synth. Commun.* **2002**, *32*, 887. h) T. Zhou, Z.-C. Chen, *Synth. Commun.* **2002**, *32*, 903. i) Y. Makioka, Y. Fujiwara, T. Kitamura, *J. Organomet. Chem.* **2000**, *611*, 509.

j) D. V. Davydov, I. P. Beletskaya, G. Leninsky, *Tetrahedron Lett.* **2002**, *43*, 6217. k) T. Zhou, Z.-C. Chen, *Heteroat. Chem.* **2002**, *13*, 617. l) L. Wang, Z.-C. Chen, Q.-G. Zheng, *Chin. J. Chem.* **2002**, *20*, 1457. m) F.-Y. Wang, Z.-C. Chen, Q.-G. Zheng, *J. Chem. Res., Synop.* **2003**, 810. n) B.-X. Zhang, T. Nuka, Y. Fujiwara, T. Yamaji, Z. Hou, T. Kitamura, *Heterocycles* **2004**, *64*, 199. o) J. V. Crivello, U. Bulut, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *88*, 290. p) R.-S. Hou, H.-M. Wang, Y.-C. Lin, L.-C. Chen, *J. Chin. Chem. Soc.* **2005**, *52*, 1029.

15 a) J. V. Crivello, *Adv. Polym. Sci.* **1984**, *62*, 1. b) S. P. Pappas, *Prog. Org. Coat.* **1985**, *13*, 35. c) Y. Yagci, W. Schnabel, *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 161. d) C. G. Wilson, M. J. Bowden, *CHEMTECH* **1989**, *19*, 182.

16 H. Ito, M. Ueda, *J. Photopolym. Sci. Technol.* **1989**, *2*, 1.

17 G. F. Koser, in *The Chemistry of Functional Groups, Supplement D*, ed. by S. Patai, Z. Rappoport, Wiley, New York, **1983**, Chap. 25.

18 a) F. M. Beringer, M. Dresler, E. M. Gindler, C. C. Lumpkin, *J. Am. Chem. Soc.* **1953**, *75*, 2705. b) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, E. Sommer, *J. Am. Chem. Soc.* **1959**, *81*, 342. c) F. M. Beringer, I. Lillien, *J. Am. Chem. Soc.* **1960**, *82*, 725. d) F. M. Beringer, J. W. Dehn, M. Winicov, *J. Am. Chem. Soc.* **1960**, *82*, 2948. e) M. Schmeisser, K. Dahmen, P. Sartori, *Chem. Ber.* **1970**, *103*, 307. f) F. M. Beringer, L. L. Chang, *J. Org. Chem.* **1972**, *37*, 1516. g) P. J. Stang, R. Tykwinski, V. V. Zhdankin, *J. Heterocycl. Chem.* **1992**, *29*, 815. h) N. S. Zefirov, T. M. Kasumov, A. S. Koz'min, V. D. Sorokin, P. J. Stang, V. V. Zhadankin, *Synthesis* **1993**, 1209. i) W. Tyrra, H. Butter, D. Naumann, *J. Fluorine Chem.* **1993**, *60*, 79. j) T. M. Kasumov, V. K. Brel, A. S. Kozmin, N. S. Zefirov, *Synthesis* **1995**, 775.

19 T. Kitamura, J. Matsuyuki, H. Taniguchi, *Synthesis* **1994**, 147.

20 A. Shah, V. W. Pike, D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1* **1997**, 2463.

21 G. F. Koser, R. H. Wettach, C. S. Smith, *J. Org. Chem.* **1980**, *45*, 1543.

22 V. W. Pike, F. Butt, A. Shah, D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1* **1999**, 245.

23 C. Ye, B. Twamley, J. M. Shreeve, *Org. Lett.* **2005**, *7*, 3961.

24 a) M. Zupan, J. Iskra, S. Stavber, *Tetrahedron Lett.* **1997**, *38*, 6305. b) S. Stavber, P. Kralj, M. Zupan, *Synlett* **2002**, 598. c) S. Stavber, P. Kralj, M. Zupan, *Synthesis* **2002**, 1513. d) S. Stavber, M. Jereb, M. Zupan, *Chem. Commun.* **2002**, 488. e) J. Pavlinac, M. Zupan, S. Stavber, *J. Org. Chem.* **2006**, *71*, 1027.

25 For reviews see: a) R. D. Howells, J. D. Mc Cown, *Chem. Rev.* **1977**, *77*, 69. b) P. J. Stang, M. Hanack, L. R. Subramanian, *Synthesis* **1982**, 85. c) P. J. Stang, M. R. White, *Aldrichimica Acta* **1983**, *16*, 15. d) W.-Y. Huang, Q.-Y. Chen, in *The Chemistry of Sulfonic Acids, Esters and Their Derivatives*, ed. by S. Patai, Z. Rappoport, Wiley-Interscience, Chichester, **1991**, Chap. 21.

26 M. D. Hossain, Y. Ikegami, T. Kitamura, *J. Org. Chem.* **2006**, *71*, 9903.

27 For a preliminary report, see: M. D. Hossain, T. Kitamura, *Tetrahedron Lett.* **2006**, *47*, 7889.

28 M. D. Hossain, T. Kitamura, *Tetrahedron* **2006**, *62*, 6955.

29 J. E. Leffler, L. J. Story, *J. Am. Chem. Soc.* **1967**, *89*, 2333.

30 J. G. Sharefkin, H. Salzman, *Anal. Chem.* **1963**, *35*, 1428.

31 G. Zeev, M. Atif, *J. Mol. Catal. A: Chem.* **1999**, *142*, 367.

32 Y. Fuseya, K. Adachi, Y. Suzuki, I. Shimamura, K. Nakamura, *Ger. Offen.* **1977**, 56; *Chem. Abstr.* **1977**, *87*, 125359.

33 J. L. Dektar, N. P. Hacker, *J. Org. Chem.* **1990**, *55*, 639.

34 P. J. Stang, V. V. Zhdankin, R. Tykwinski, N. S. Zefirov, *Tetrahedron Lett.* **1991**, *32*, 7497.

35 T. Kitamura, J. Matsuyuki, K. Nagata, R. Furuki, H. Taniguchi, *Synthesis* **1992**, 945.

36 E. Johannes, H. Carsten, L. Thomas, G. Rene, H. C. Heinz, *J. Labelled Comp. Radiopharm.* **2004**, *47*, 429.

37 D. B. Haydock, J. J. Smithers, *Ger. Offen.* **1976**, 36; *Chem. Abstr.* **1976**, *85*, 45203.

38 H. H. Schurz, K. L. Busch, *Org. Mass Spectrom.* **1992**, *27*, 604.