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Synthetic Use of Poly[4-(diacetoxyiodo)styrene] for Organic Reactions

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Poly[4-(diacetoxyiodo)styrene] is sufficiently reactive for the iodination of aromatics, the oxidative 1,2-aryl migration of alkyl aryl ketones, the α-hydroxylation of ketones, and the oxidation of hydroquinones and sulfides similarly to (diacetoxyiodo)benzene. Here, those reactions with poly[4-(diacetoxyiodo)styrene] are very useful because of the simple operation; thus, filtration gives the crude products and recovered poly(4-iodostyrene), and then poly[4-(diacetoxyiodo)-styrene] can be regenerated by oxidation of the recovered poly(4-iodostyrene), which are reused for the same reactions.

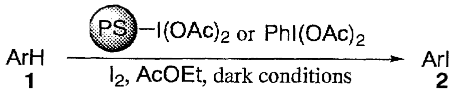
In the past two decades, trivalent iodine compounds have been widely used in organic synthesis in view of their potential utility for oxidation and radical reactions.[1] The advantages of using trivalent iodine compounds are the simple experimental operation and the low toxicity of the reagents. Among the trivalent iodine compounds, (diacetoxyiodo)-benzene has attracted significant interest because of its rich chemistry and commercial availability, while poly[4-(diacetoxyiodo)styrene] is expected to have the same reactivities as (diacetoxyiodo)benzene has. Hitherto, poly[4-(diacetoxyiodo)styrene] has been studied for a few reactions, such as the preparation of phenyl polystyryliodonium bisulfate[2] and the oxidation of amines.[3] The major advantages with the polymer-supported reagent is that the reactions can be monitored by standard methods (TLC, GC, HPLC), and the polymer reagents can be recovered by simple filtration and reused. This recycling is environmentally safe. Therefore, we carried out the iodination of aromatics, the oxidative 1,2-aryl migration of alkyl aryl ketones, the α-hydroxylation of ketones, and the oxidation of hydroquinones and sulfides, using poly[4-(diacetoxyiodo)styrene]; these reactions were compared with those using (diacetoxyiodo)benzene.[4] Furthermore, the regeneration and reuse of poly[4-(diacetoxyiodo)styrene] from the recovered poly(4-iodostyrene) were also studied. Poly[4-(diacetoxyiodo)styrene] was prepared by a literature method.[2] Commercial polystyrene, whose average molecular weight is 45000, was iodinated with $I_2/I_2O_5/H_2SO_4$ to give poly(4-iodostyrene). The degree of iodination was established by elemental analysis. Most of the phenyl groups were iodinated (88% conversion). The poly(4-iodostyrene) was then converted to poly[4-(diacetoxyiodo)styrene] by a treatment with peracetic acid.[2] The composition of poly[4-(diacetoxyiodo)styrene], which is insoluble in organic solvents, was assayed by both iodometry and elemental analysis (74% conversion).

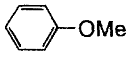
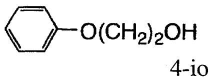
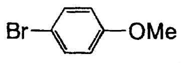
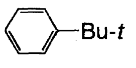
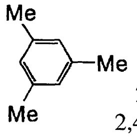
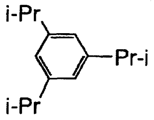
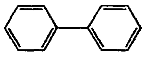
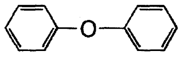
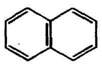
Results and Discussion

Iodination of Aromatic Compounds. The iodination of aromatics with [bis(trifluoroacetoxy)iodo]benzene[5] and (diacetoxyiodo)benzene[6] has been reported. Based on these results, the iodination of aromatics with poly[4-(diacetoxyiodo)styrene] was carried out in ethyl acetate at room temperature or 60 °C, and the same reaction was carried out with (diacetoxyiodo)benzene under the same conditions, in order to compare the reactivities. The results are given in Table 1. The reactivity of substrates depends on the electronic density of the aromatic rings. Thus, anisole and 2-phenoxyethanol were monoiodinated at room temperature. Alkylbenzenes were also iodinated in good yields. Though it was difficult to control the number of iodination of mesitylene, 1,3,5-triisopropylbenzene gave only 1-iodo-2,4,6-triisopropylbenzene in good yield. Alkylbenzenes with bulkier alkyls, as 1,3,5-tri-*t*-butylbenzene, were not iodinated. In contrast, propiophenone was not iodinated with either poly-[4-(diacetoxyiodo)styrene] or with (diacetoxyiodo)benzene. Benzothiophene was also iodinated at the β-position in 60% yield with poly[4-(diacetoxyiodo)styrene] (Conditions A). Thus, poly[4-(diacetoxyiodo)styrene] is useful for the iodination of aromatics, except for electron-poor aromatics.

Oxidative 1,2-Aryl Migration of Alkyl Aryl Ketones. Tamura et al. have reported that (diacetoxyiodo)benzene promotes the 1,2-aryl migration of propiophenones to methyl 2-phenylpropanoates and acetophenones to methyl phenylacetates in methanol or trimethyl orthoformate.[7] Singh has also reported the 1,2-aryl migration of acetophenone to methyl α-methoxyphenylacetate with (diacetoxyiodo)-benzene in trimethyl orthoformate.[8] These reactions were carried out with poly[4-(diacetoxyiodo)styrene] instead of (diacetoxyiodo)benzene. The reactivity of poly[4-(diacetoxyiodo)styrene] was compared with that of (diacetoxyiodo)benzene under the same conditions; the results are given in Table 2. Thus, 1,2-aryl migration of propiophenone, 1-(4-fluorophenyl)propan-1-one, 1-(4-methylphenyl)propan-1-one, and 1-(4-methoxyphenyl)propan-1-one with poly-[4-(diacetoxyiodo)styrene] successfully occurred to give the corresponding rearranged products in good yields, similarly

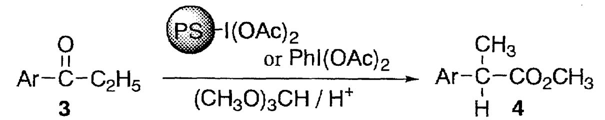
Table 1. Iodination of Aromatic Compounds[a)]



ArH		(molar ratio) (PS)–I(OAc)$_2$		2/Yields (%) PhI(OAc)$_2$
 OMe		(0.5/0.6/0.6)	(0.5/2.4/2.4)	(0.5/0.6/0.6)
		(A)	**(B)**	**(A)**
	4-iodo	56	—	85
	2,4-diiodo	—	99	—
 O(CH$_2$)$_2$OH		(0.5/1.2/1.2)		(0.5/1.2/1.2)
		(C)		**(C)**
	4-iodo	85		92
	2,4-diiodo	3		Trace
 Br, OMe		(0.5/1.2/1.2)	(0.5/1.8/1.8)	(0.5/1.2/1.2)
		(D)	**(D)**	**(D)**
	2-iodo	65	94	99
 Bu-*t*		(0.5/0.6/0.6)	(0.5/2.4/2.4)	(0.5/0.6/0.6)
		(B)	**(B)**	**(B)**
	4-iodo	41	85	70
 Me, Me, Me		(0.5/1.2/1.2)	(0.5/2.4/2.4)	(0.5/1.2/1.2)
		(B)	**(B)**	**(B)**
	2-iodo	72	—	4
	2,4-diiodo	28	79	96
	2,4,6-triiodo	—	7	—
 i-Pr, Pr-i, i-Pr		(0.5/1.5/1.5)	(0.5/2.3/2.3)	(0.5/1.5/1.5)
		(B)	**(B)**	**(B)**
	2-iodo	81	93	99
		(0.5/1.2/1.2)	(0.5/3.6/3.6)	(0.5/1.2/1.0)
		(B)	**(B)**	**(B)**
	4-iodo	43	16	12
	4,4′-diiodo	2	84	87
 O		(0.5/1.2/1.2)	(0.5/2.4/2.4)	(0.5/1.2/1.0)
		(B)	**(B)**	**(B)**
	4-iodo	70	—	28
	4,4′-diiodo	15	99	70
		(0.5/1.2/1.2)		(0.5/1.2/1.2)
		(B)		**(B)**
	1-iodo	63		69

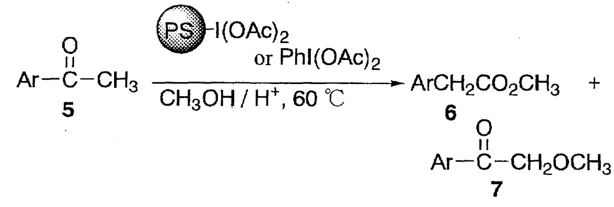
a) Molar ratio indicates ArH/Trivalent Iodine Compound/Iodine (mmol). Conditions **A**: Stirred for 16 h at r.t. **B**: Stirred for 16 h at 60 °C. **C**: Stirred for 4 h at r.t. **D**: Stirred for 5 h at 60 °C.

Table 2. Oxidative 1,2-Aryl Migration of Alkyl Aryl Ketones



Ar	Reaction time	4, Yields (%) PhI(OAc)$_2$	 (PS)–I(OAc)$_2$
p-FC$_6$H$_4$-	5 h, r.t.	81	80
C$_6$H$_5$-	2 h, 60 °C	85	81
p-CH$_3$C$_6$H$_4$-	2 h, 60 °C	91	89
p-CH$_3$OC$_6$H$_4$-	1 ~ 3 h, 60 °C	93	87

Molar ratio of trivalent iodine compound/ketone was 1.2/1.0



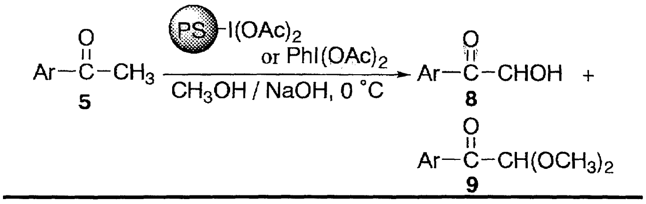
Ar	Reaction time	6/7, Yields (%) PhI(OAc)$_2$	 (PS)–I(OAc)$_2$
C$_6$H$_5$-	1	56/21	41/14
p-CH$_3$C$_6$H$_4$-	1	67/11	41/10

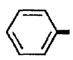
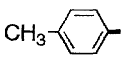
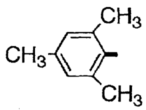
Molar ratio of trivalent iodine compound/ketone was 1.2/1.0

to (diacetoxyiodo)benzene. Moreover, acetophenone and 1-(4-methylphenyl)ethan-1-one were also successfully converted to methyl phenylacetate and methyl 4-methylphenylacetate in methanol together with 2-methoxy-1-phenylethan-1-one and 2-methoxy-1-(4-methylphenyl)ethan-1-one, respectively. Therefore, poly[4-(diacetoxyiodo)styrene] is very useful for the oxidative 1,2-aryl migration of alkyl aryl ketones.

α-Hydoxylation of Ketones. α-Hydroxylation of ketones and esters with iodosylbenzene,[9] (diacetoxyiodo)benzene,[9] and [bis(trifluoroacetoxy)iodo]benzene,[10] respectively, is known. Thus, α-hydroxylation of acetophenone derivatives with poly[4-(diacetoxyiodo)styrene] in the presence of sodium hydroxide in methanol was carried out to give the corresponding α-hydroxy ketones in moderate yields (Table 3). However, there is a slight difference: A small amount of 2,2-dimethoxy-1-phenylethan-1-one derivatives was formed as by-products in reactions with poly[4-(diacet-

Table 3. α-Hydoxylation of Ketones

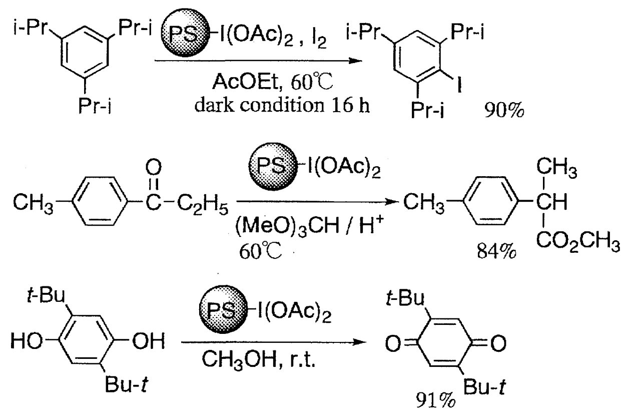


Ar			 CH$_3$		 CH$_3$, CH$_3$, CH$_3$	
	8	**9**	**8**	**9**	**8**	**9**
(PS)–I(OAc)$_2$	52	8	34	10	70	12
PhI(OAc)$_2$	83	—	63	—	44	—

oxyiodo)styrene].

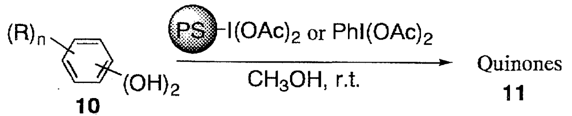
Oxidations of Hydroquinones and Sulfides. The oxidations of hydroquinones[11] and sulfides[12] with (diacetoxyiodo)benzene are known. Thus, here, the oxidation of hydroquinones and sulfides with poly[4-(diacetoxyiodo)styrene] was carried out and the same reactivities as (diacetoxyiodo)benzene were again observed (Table 4). However, there was a big difference in the oxidation of diaryl sulfides (Table 5). Under the same conditions, the major product with poly[4-(diacetoxyiodo)styrene] was sulfone, while that with (diacetoxyiodo)benzene was sulfoxide. The reason for the difference in the oxidation of diaryl sulfides between poly[4-(diacetoxyiodo)styrene] and (diacetoxyiodo)benzene is probably that the diaryl sulfoxide formed does not come out from the polymer inside because of the π–π weak interaction between the polystyrene skeleton and diaryl sulfoxides. Therefore, further oxidation to sulfone occurred.

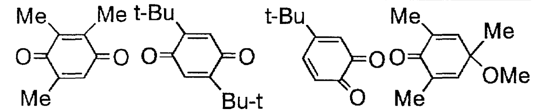
Regeneration and Reuse of Poly[4-(diacetoxyiodo)styrene] from Recovered Poly(4-iodostyrene). Finally, the regeneration and reuse of poly[4-(diacetoxyiodo)styrene] were studied. Thus, after these reactions, poly(4-iodostyrene), to which poly[4-(diacetoxyiodo)styrene] was converted, was recovered by simple filtration in over 80% yield (Scheme 1). The recovered poly(4-iodostyrene) was then dissolved in chloroform at 60 °C and precipitated by the addition of methanol. Its elemental analysis showed that the recovered poly(4-iodostyrene) maintains the same number of iodine atoms as the initially prepared poly(4-iodostyrene). Here, the compositions of elements C, H, I are almost the same in both basic poly(4-iodostyrene) (88% conversion) and recovered poly(4-iodostyrene) (87% conversion). The recovered poly(4-iodostyrene) was again oxidized to poly[4-(diacetoxyiodo)styrene] with peracetic acid, and its composition was assayed again both by iodometry and by elemental analysis, and the composition of elements C, H, I in regenerated poly[4-(diacetoxyiodo)styrene] was 64% conversion (basic poly[4-(diacetoxyiodo)styrene]: 74% conversion). Then, reactions with regenerated poly[4-(diacetoxyiodo)styrene] were carried out as shown below, and the same yields of the iodination products from 1,3,5-triisopropylbenzene, 1,2-aryl migrated product from 1-(4-methylphenyl)propan-1-one, and 2,5-di-*t*-butylbenzoquinone were obtained, though the yields were slightly diminished. Here, the regeneration of poly[4-(diacetoxyiodo)styrene] was successful. In conclusion, poly[4-(diacetoxyiodo)styrene] has sufficient reactivity in these ionic reactions, such as the iodination of aromatic compounds, the oxidative 1,2-aryl migration of alkyl aryl ketones, the α-hydroxylation of ketones, and the oxidation of hydroquinones and sulfides. These reactions proceed in heterogeneous solutions. After reactions with poly[4-(diacetoxyiodo)styrene], the generated poly(4-iodostyrene) could be recovered by simple filtration in good yields, and the poly[4-(diacetoxyiodo)styrene] could be regenerated and reused.



Scheme 1. Reactions with regenerated poly[4-(diacetoxyiodo)styrene].

Table 4. Oxidation of Benzenediols

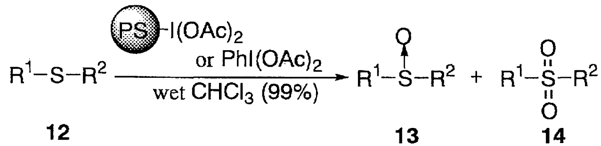


	11, Yields (%)			
				
PS–I(OAc)$_2$	91	92	82	36
PhI(OAc)$_2$	94	96	72	38

Experimental

^{1}H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-

Table 5. Oxidation of Sulfides



	13/**14**, Yields (%)							
	R^1 = R^2 = Bu-*n*		R^1 = C$_6$H$_5$,	R^2 = C$_2$H$_5$	R^1 = R^2 = C$_6$H$_5$		R^1 = R^2 = C$_6$H$_4$CH$_3$-*p*	
	13	**14**	**13**	**14**	**13**	**14**	**13**	**14**
PS–I(OAc)$_2$	84	—	37	41	—	75	2	84
PhI(OAc)$_2$	84	—	84	13	85	3	85	8

GSX400 and JEOL-JNM-GSX500 spectrometers. The chemical shifts are expressed in ppm downfield from TMS in δ units. The mass spectra were recorded on a JEOL-JMS-AMII15 spectrometer. IR spectra were measured with JASCO FT/IR-200 spectrometer. Microanalyses of H, C, and I were performed with a Perkin Elmer-2400 elemental analyzer at Chemical Analysis Center of Tsukuba University. The melting points were determined on a Yamato Melting Points Apparatus (Model MP-211). Wakogel C-200 and Silica Gel 50 (Merck) were used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Iodination of Polystyrene: A mixture of 16 g of polystyrene (Aldrich 33165-1), 16 g of iodine, 6 g of diiodine pentaoxide, 40 ml of carbon tetrachloride, and 30 ml of 50% sulfuric acid in 200 ml of nitrobenzene was kept at 90 °C for 40 h. After the reaction, the reaction mixture was diluted with 100 ml of chloroform; precipitation then occurred upon the addition of methanol (1500 ml). The precipitates were collected by filtration. Elemental analysis showed C, 44.20; H, 3.24; I, 52.07%. This result indicates that 88% of the phenyl ring in polystyrene was iodinated.

Preparation of Poly[4-(diacetoxyiodo)styrene]: Hydrogen peroxide (30%, 40 ml) was added dropwise to an acetic anhydride solution (145 ml) at 0 °C. The solution was slowly warmed to room temperature and stirred overnight. To this solution, poly(4-iodostyrene) (8 g) was added. Then, the solution was kept at 40 °C overnight. At the end of the reaction, ether was added and the product was collected by filtration. Elemental analysis showed: C, 39.46; H, 3.57; I, 38.43%. These results indicate that 78% of the iodophenyl ring in poly(4-iodostyrene) was converted to a 4-(diacetoxyiodo)phenyl ring.

General Procedure for Iodination: A mixture of aromatics (0.5 mmol), poly[4-(diacetoxyiodo)styrene] or (diacetoxyiodo)benzene (0.9 mmol), and iodine (0.9 mmol) in dry ethyl acetate (5 ml) was stirred for 5 h at 60 °C under dark conditions and an argon atmosphere. The resulting solution was quenched with aq Na_2SO_3. Ether was then added into the solution to precipitate polymer species. The solution was filtered to remove any polymer species, and the filtrate was poured into aq Na_2SO_3 and extracted with ether. The extract was dried over Na_2SO_4 and evaporated under reduced pressure; the residual oil was purified by preparative TLC on silica gel using hexane.

Conversion of Propiophenone to Methyl 2- Phenylpropanoate: Sulfuric acid (2 mmol) was added dropwise to a solution of poly[4-(diacetoxyiodo)styrene] or (diacetoxyiodo)benzene (1.2 mmol), and propiophenone (1.0 mmol) in 3 ml of trimethyl orthoformate at 0 °C. The reaction mixture was stirred for 2 h at 60 °C under an argon atmosphere and quenched with water (10 ml). Ether was then added to the solution, and the polymer species was removed by filtration. The filtrate was poured into water, extracted with ether, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on silica gel.

General Procedure for Oxidation of Hydroquinone: Hydroquinone (1 mmol) was added to poly[4-(diacetoxyiodo)styrene] or (diacetoxyiodo)benzene (1.3 mmol), in methanol (5 ml). The mixture was stirred for 2 h at room temperature under an argon atmosphere. Then, the reaction mixture was filtered. The filtrate was evaporated and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 5/1) to give a pure quinone derivative.

General Procedure for Oxidation of Sulfide: Sulfide (1 mmol) was added to poly[4-(diacetoxyiodo)styrene] or (diacetoxyiodo)benzene (2.0 mmol), in chloroform (5 ml) containing 1% of water. The mixture was stirred for 72 h at 40 °C under an argon atmosphere. The reaction mixture was then filtered. The filtrate was evaporated and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 5/1) to give pure sulfoxide and sulfone.

Purification of Recovered Poly(4-iodostyrene). From the recovered poly(4-iodostyrene), 3 g was dissolved in $CHCl_3$ (50 ml) at 60 °C and then precipitation occurred upon the addition of methanol. The precipitates (2.5 g) were collected by filtration and dried. Elemental analysis of the recovered poly(4-iodostyrene) showed C, 44.32; H, 3.42; I, 51.63%. This result indicates that the number of the iodine groups in poly(4-iodostyrene) was 87% (the basic one: 88%). Elemental analysis of regenerated poly[4-(diacetoxyiodo)-styrene] showed C, 38.41; H, 3.72; I, 39.06%. This result indicates again that 64% of the 4-iodophenyl ring in poly(4-iodostyrene) was converted to 4-(diacetoxyiodo)phenyl ring.

1-Iodo-2,4,6-triisopropylbenzene: Oil, bp = 115 °C/2.5 mmHg (lit, 173—175 °C/28 mmHg[13], 1 mmHg = 133.322 Pa); IR (neat) 2950, 1565, 1460, and 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 1.24$ (12H, d, $J = 6.8$ Hz), 1.25 (6H, d, $J = 7.0$ Hz), 2.87 (1H, sept, $J = 7.0$ Hz), 3.39 (2H, sept, $J = 7.0$ Hz), 6.95 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 23.43$ (p), 23.98 (p), 33.88 (t), 39.26 (t), 105.71 (q), 122.07, (t), 148.83 (q), 150.77 (q); MS (EI) Found: m/z 330 (M^+). Calcd for $C_{15}H_{22}I$: M, 330.

Diiodomesitylene: Mp 79.0—80.3 °C (lit, 82 °C[14]); IR (KBr) 2975, 1440, 1375, and 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 2.42$ (6H, s), 2.92 (3H, s), 7.00 (1H, s); MS (EI) Found: m/z 372 (M^+). Calcd for $C_9H_{10}I_2$: M, 372.

Iodomesitylene: Mp 30—31 °C (lit, 30.5—31 °C[13]); IR (KBr) 2975, 1440, 1373, and 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 2.24$ (3H, s, CH_3), 2.42 (6H, s, CH_3), 6.89 (2H, s, Ar); MS (EI) Found: m/z 246 (M^+). Calcd for $C_9H_{11}I$: M, 246.

2,4-Diiodoanisole: Mp 42.5—43.5 °C; IR (KBr) 2930, 1565, 1470, 1280, and 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 3.85$ (3H, s), 6.51 (1H, d, $J = 8.7$ Hz), 7.50 (1H, dd, $J = 8.7$, 1.9 Hz), 7.96 (1H, d, $J = 2.2$ Hz); MS (EI) Found: m/z 360 (M^+). Calcd for $C_7H_6OI_2$: M, 360.

4-Bromo-2-iodoanisole: Oil (lit, mp 64 °C[15]); IR (neat) 2930, 1570, 1470, 1280, and 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 3.86$ (3H, s), 6.62 (1H, d, $J = 8.9$ Hz), 7.34 (1H, dd, $J = 8.9$, 2.4 Hz), 7.80 (1H, d, $J = 2.4$ Hz). Found; C, 26.64; H, 1.94%. Calcd for C_7H_6OBrI; C, 26.87; H, 1.93%. MS (EI) Found: m/z 312 (M^+). Calcd for $C_7H_6O^{79}BrI$: M, 312.

4-Iodo-*t*-butylbenzene: Oil, bp 90 °C/12.5 mmHg (lit, 258 °C/760 mmHg[16]); IR (neat) 2960, 1490, 1395, and 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 1.29$ (9H, s), 7.06 (2H, d, $J = 8.7$ Hz), 7.53 (2H, d, $J = 8.7$ Hz); MS (EI) Found: m/z 260 (M^+). Calcd for $C_{10}H_{13}I$: M, 260.

4,4′-Diiodobiphenyl: Mp 206.0—206.5 °C (lit, 204 °C[17]); IR (KBr) 3060, 1900, 1580, 1470, 1065, 995, and 800 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 7.28$ (4H, d, $J = 8.7$ Hz), 7.76 (4H, d, $J = 8.7$ Hz).

Bis(4-iodophenyl) Ether: Mp 141.0—141.5 °C (lit, 140—141 °C[17]); IR (KBr) 3080, 1890, 2840, 1575, 1480, 1250, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 6.76$ (4H, d, $J = 8.9$ Hz), 7.63 (4H, d, $J = 8.9$ Hz).

2-(4-Iodophenoxy)ethanol: Mp 73.5—74.5 °C; IR (KBr) 3300, 2900, 1580, 1480, 1240, 1080, and 1800 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 2.10$ (1H, bd, $J = 8.1$ Hz), 3.96 (2H, t, $J = 4.0$ Hz), 4.03 (2H, q, $J = 4.3$ Hz), 6.69 (2H, d, $J = 9.2$ Hz), 7.55 (2H, d, $J = 8.8$ Hz); HRMS (FAB) Found: m/z 263.9656 (M^+). Calcd for $C_8H_9O_2I$: M^+, 263.9647.

Methyl 2-Phenylpropanoate: Bp 65 °C/2.5 mmHg (lit, 104—105 °C/18 mmHg[7]); IR (neat) 2980, 1740, 1600, 1495, 1455, 1210, and 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.50 (3H, d, J = 7.2 Hz, 3.66 (3H, s), 3.73 (1H, q, J = 7.2 Hz), 7.24—7.35 (5H, m).

Methyl 2-(4-Methoxyphenyl)propanoate: IR (neat) 2980, 2960, 2840, 1740, and 1340 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.47 (3H, d, J = 7.2 Hz), 3.65 (3H, s), 3.68 (1H, q, J = 7.2 Hz), 3.79 (3H, s), 6.86 (2H, dt, J = 8.7 and 2.0 Hz), 7.22 (2H, dt, J = 8.7 and 2.0 Hz).

Methyl 2-(4-Fluorophenyl)propanoate: IR (neat) 2980, 2960, 1740, and 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.48 (3H, d, J = 7.2 Hz), 3.66 (3H, s), 3.71 (1H, q, J = 7.2 Hz), 7.00 (2H, tt, J = 8.7 and 2.1 Hz), 7.26 (2H, ddt, J = 8.7, 5.3, and 2.1 Hz).

Methyl 2-(4-Methylphenyl)propanoate: IR (neat) 2955, 1740, 1515, 1460, 1205, and 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.48 (3H, d, J = 7.2 Hz), 2.33 (3H, s), 3.65 (3H, s), 3.69 (1H, q, J = 7.2 Hz), 7.13 (2H, d, J = 8.1 Hz), 7.19 (2H, d, J = 8.1 Hz).

Methyl (4-Methylphenyl)acetate: Bp 85 °C/2.5 mmHg (lit, 108—112 °C/9 mmHg[18]); IR (neat) 2950, 1740, 1515, 1435, 1260, 1160, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.33 (3H, s), 3.59 (2H, s), 3.68 (3H, s), 7.13 (2H, d, J = 8.2 Hz), 7.17 (2H, d, J = 8.2 Hz).

Methyl Phenylacetate: Bp 80 °C/2.5 mmHg (lit, 90—92 °C/5 mmHg[7]); IR (Neat) 3030, 2955, 1740, 1605, 1495, 1260, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.63 (2H, s), 3.69 (3H, s), 7.26—7.35 (5H, m).

2-Methoxy-1-(4-methylphenyl)ethan-1-one: IR (neat) 2925, 1695, 1610, 1450, 1200, 1130, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.42 (3H, s), 3.51 (3H, s), 4.69 (2H, s), 7.27 (2H, d, J = 8.2 Hz) 7.83 (2H, d, J = 8.2 Hz).

2,3,5-Trimethyl-1,4-benzoquinone: Mp 27—28 °C (lit, 29 °C[19]); IR (KBr) 3060, 2880, 1650, and 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.01 (3H, q, J = 1.1 Hz), 2.03 (3H, q, J = 1.1 Hz), 2.04 (3H, d, J = 1.7 Hz), 6.56 (1H, q, J = 1.7 Hz).

4-*t*-Butyl-1,2-benzoquinone: Mp 65 °C (lit, 65 °C[19]); IR (KBr) 2990, 2880, 1660, and 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.24 (9H, s), 6.29 (1H, dd, J = 2.4 and 0.7 Hz), 6.40 (1H, dd, J = 10.4 and 0.7 Hz), 7.19 (1H, dd, J = 10.4 and 2.4 Hz).

2,6-Di-*t*-butyl-1,4-benzoquinone: Mp 144—146 °C (lit, 150—151 °C[19]); IR (KBr) 2870, 1650, and 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.27 (18H, s), 6.48 (2H, s).

4-Methoxy-2,4,6-trimethyl-2,5-cyclohexadien-1-one: Mp 43 °C (lit, 43—44 °C[19]); IR (KBr) 2990, 2890, 1670, and 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.37 (3H, s), 1.92 (6H, s), 3.15 (3H, s), 6.50 (2H, bs).

2-Hydroxy-1-mesitylethan-1-one: IR (neat) 3060, 2980, 1680, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.26 (3H, s), 2.29 (6H, s), 3.65 (1H, s), 3.67 (2H, s), 6.87 (2H, s).

2-Hydroxy-1-phenylethan-1-one: Mp 87 °C (lit, 86—88 °C[20]).

2-Hydroxy-1-(4-methylphenyl)ethan-1-one: Mp 88—89 °C (lit, 89—89.5 °C[21]).

Di(*p*-tolyl) Sulfoxide: Mp 91 °C (lit, 92 °C[22]).

Di(*p*-tolyl) Sulfone: Mp 156 °C (lit, 158 °C[22]).

Diphenyl Sulfoxide: Mp 70 °C (lit, 70 °C[22]).

Diphenyl Sulfone: Mp 126 °C (lit, 127 °C[22]).

Dibutyl Sulfoxide: Bp 120 °C/1.2 mmHg (lit, 120 °C/1.2 mmHg[23]).

Ethyl Phenyl Sulfoxide: Bp 102 °C/2 mmHg (lit, 102 °C/2 mmHg[24]).

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