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Biphenyl- and terphenyl-based recyclable organic trivalent iodine reagents

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Abstract—Biphenyl- and terphenyl-based recyclable trivalent iodine reagents, such as 4-bromo-4′-(diacetoxyiodo)biphenyl, 4,4′-bis(diacetoxyiodo)biphenyl, 1,4-bis[4-(diacetoxyiodo)phenyl]benzene, 4-bromo-4′-[(hydroxy)(tosyloxy)iodo]biphenyl, 4,4′-bis[(hydroxy)(tosyloxy)iodo]biphenyl, were simply prepared and their reactivities for the oxidative rearrangement of ketones to esters, TEMPO-mediated oxidation of alcohols to aldehydes or ketones, oxidative dealkylation of *N*-alkylsulfonamides to sulfonamides, and α-tosyloxylation of ketones were compared with *p*-(diacetoxyiodo)toluene and *p*-[(hydroxy)(tosyloxy)iodo]toluene to show the same reactivities and, moreover, the biphenyl- and terphenyl-based iodoarenes formed were recovered by simple filtration of the reaction mixture in every reaction. Thus, these biphenyl- and terphenyl-based trivalent iodine reagents can be used as the recyclable reagents.

1. Introduction

Recently, synthetic use of hypervalent iodines for organic synthesis has been investigated widely because of their efficient oxidizing ability and less toxicity.[1] Especially, (diacetoxyiodo)benzene (DIB), iodosylbenzene, and [(hydroxy)(tosyloxy)iodo]benzene (HTIB) are well-known reagents and the oxidative reactions can be carried out under mild conditions with easy handling, high chemoselectivity, and low toxicity.[2] Based on the broad synthetic utility of these organohypervalent iodine compounds for organic synthesis, previously, we and others reported polymer-supported hypervalent iodine reagents such as poly[4-(diacetoxy)-iodo]styrene (PSDIB), poly[4-(hydroxy)(tosyloxy)iodo]-styrene (PSHTIB), etc.[3] The major advantages of the use of these polymer-supported hypervalent iodine reagents are as follows: reactions can be monitored by standard methods such as TLC, GC, HPLC, etc., reaction products can be obtained by simple filtration to remove the polymer-supported reagent, and regeneration and reuse of the recovered polymer-supported reagents are possible. Thus, polymer-supported hypervalent iodines are environmentally friendly reagents, and have wide applicability to organic synthesis in the chemical and pharmaceutical industries. However, the introduction of high loading rate of organic trivalent iodine groups onto polystyrene is not so easy and sometimes lowers the reactivities than those observed with DIB and HTIB. Recently, Kita et al. reported an elegant approach for recyclable trivalent iodine reagents, such as 1,3,5,7-tetrakis[(diacetoxyiodo)phenyl]adamantane[4a] and tetrakis[4-(diacetoxyiodo)phenyl]methane.[4b] Thus, these are not polymers, but they are recyclable trivalent iodine reagents. This approach impressed us, since we have experienced some limitations with polymer-supported trivalent iodine reagents, for example, oxidative dealkylation of *N*-alkylsulfonamides with PSDIB does not proceed effectively. Here, as a part of our study on environmentally benign organic synthesis with hypervalent iodines, we would like to report biphenyl- and terphenyl-based recyclable trivalent iodine reagents.

2. Results and discussion

Our approach is focused on biphenyl- and terphenyl-based trivalent iodines,[5] since the diiodination of biphenyl and terphenyl is easy and the solubility of these iodo compounds is not so high. Thus, the solubility of 4-bromo-4′-iodobiphenyl, 4,4′-diiodobiphenyl, and 1,4-bis(*p*-iodophenyl)benzene in hexane is 8.4 mg/ml, 2.2 mg/ml, and slightly soluble, respectively, and even in chloroform it is 114.9 mg/ml, 32.3 mg/ml, and 0.9 mg/ml, respectively. So, it is expected that 4,4′-diiodobiphenyl and 1,4-bis(*p*-iodophenyl)benzene are the core candidates in recyclable hypervalent iodines. The iodination of 4-bromobiphenyl, biphenyl, and terphenyl proceeded smoothly with molecular iodine and iodine pentoxide in nitrobenzene in the presence of a small amount of carbon tetrachloride and sulfuric acid, as in the preparation of PSDIB from polystyrene, as shown in Scheme 1. For

Keywords: 4-Bromo-4′-(diacetoxyiodo)biphenyl; 4,4′-Bis(diacetoxyiodo)-biphenyl; 1,4-Bis[4-(diacetoxyiodo)phenyl]benzene; 4-Bromo-4′-[(hydroxy)-(tosyloxy)iodo]biphenyl; 4,4′-Bis[(hydroxy)(tosyloxy)iodo]biphenyl; Oxidation; Aldehyde; Ketone; Ester; α-Tosyloxyketone; Sulfonamide.
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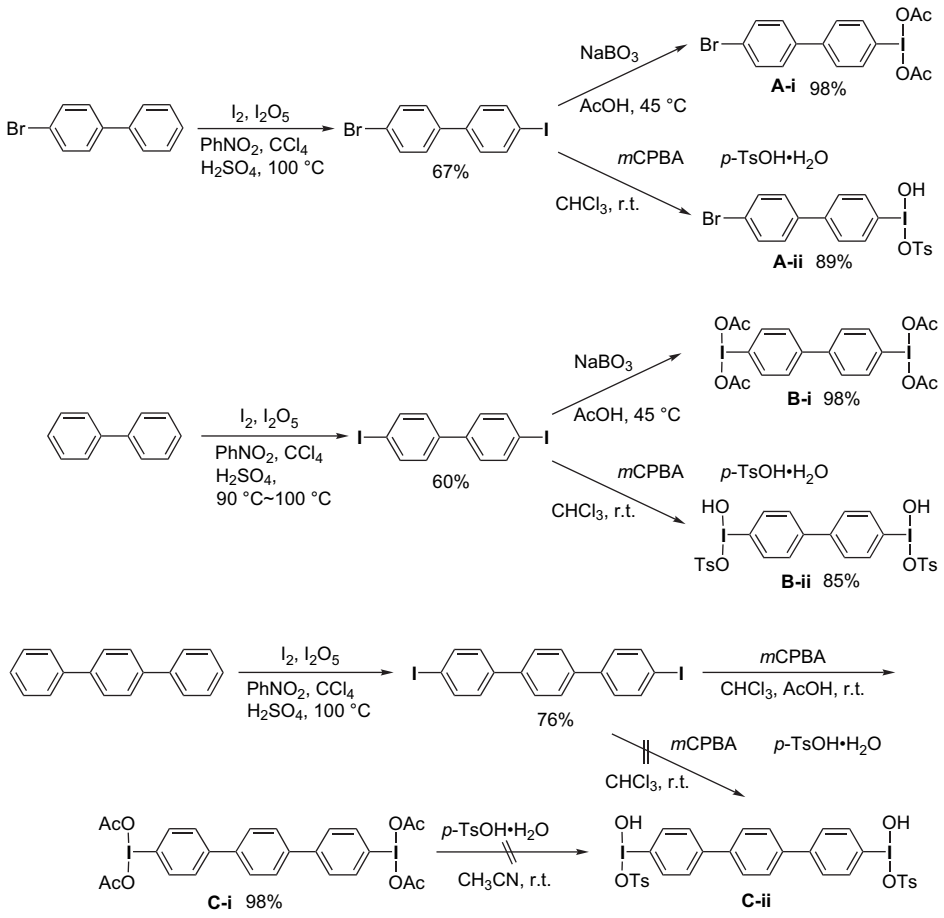


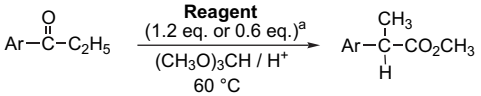
Scheme 1. Preparation of biphenyl- and terphenyl-based trivalent iodines.

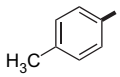
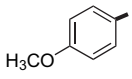
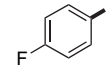
the preparation of 4-bromo-4′-(diacetoxyiodo)biphenyl (**A-i**), 4,4′-bis(diacetoxyiodo)biphenyl (**B-i**),[6] and 1,4-bis[4-(diacetoxyiodo)phenyl]benzene (**C-i**), there are two methods. The first method is the oxidation of iodo compounds with sodium peroxoborate in acetic acid as a standard method,[7] and the second one is the oxidation with *m*CPBA in a mixture of chloroform and acetic acid as shown in Scheme 1.[4] 4-Bromo-4′-[(hydroxy)(tosyloxy)iodo]biphenyl (**A-ii**) and 4,4′-bis[(hydroxy)(tosyloxy)iodo]biphenyl (**B-ii**) were directly prepared with *m*CPBA and *p*-toluenesulfonic acid monohydrate in chloroform, based on our previous report.[8] 1,4-Bis[4-(hydroxy)(tosyloxy)iodophenyl]benzene (**C-ii**) could not be prepared cleanly by the direct preparation of 1,4-bis(*p*-iodophenyl)benzene with *m*CPBA and *p*-toluenesulfonic acid monohydrate or by the exchange reaction of 1,4-bis[4-(diacetoxyiodo)phenyl]benzene (**C-i**) with *p*-toluenesulfonic acid monohydrate, as a traditional method.

2.1. Oxidative 1,2-aryl migration of alkyl aryl ketones

1,2-Aryl migration of propiophenones with the present trivalent iodine reagents **A-i**, **B-i**, and **C-i** in trimethyl orthoformate was carried out effectively, based on the previous report,[9] and the reactivities were compared with that of standard *p*-(diacetoxyiodo)toluene (**D-i**) as shown in Table 1. Since biphenyl- and terphenyl-based reagents **B-i** and **C-i** have two trivalent iodine groups, the mole amount used is reduced to a half-millimole amount of trivalent iodine reagents **A-i** and **D-i**. Thus, the results indicate that the present trivalent iodine

Table 1. Oxidative 1,2-aryl migration of alkyl aryl ketones to esters with reagents **A-i**–**D-i**



Reagent	Ar–	Time (h)	Yields (%)	
			Product	Recovery[b]
A-i		2	91	81
B-i			85	84
C-i			88	94
D-i			88	(—)
A-i		2	88	90
B-i			85	84
C-i			88	96
D-i			92	(—)
A-i		3	89	80
B-i			91	80
C-i			88	90
D-i			92	(—)
A-i		5[c]	86	81
B-i			84	84
C-i			87	94
D-i			82	(—)

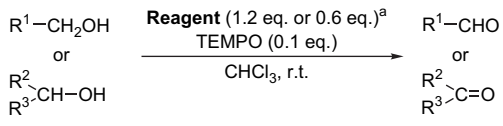
[a] For **B-i** and **C-i**: 0.6 equiv, and for **A-i** and **D-i**: 1.2 equiv.
[b] Yield of 4,4′-diiodobiphenyl, 4-bromo-4′-iodobiphenyl, or 1,4-bis(*p*-iodophenyl)benzene.
[c] Reaction was carried out at room temperature.

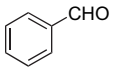
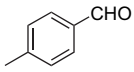
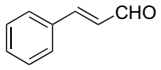
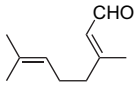
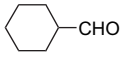
reagents **A-i**, **B-i**, and **C-i** showed the same reactivity to give the rearranged esters in high yields, as with the standard reagent **D-i**. Here, 4-bromo-4′-iodobiphenyl, 4,4′-diiodobiphenyl, and 1,4-bis(*p*-iodophenyl)benzene formed as byproducts could be recovered in high yields by simple filtration of the reaction mixture, though *p*-iodotoluene could not be recovered at all. Generally, the collecting ability is slightly decreased in the order of 1,4-bis(*p*-iodophenyl)benzene, 4,4′-diiodobiphenyl, and 4-bromo-4′-iodobiphenyl. Thus, after the reaction with 1,4-bis[4-(diacetoxyiodo)phenyl]benzene (**C-i**), 1,4-bis(*p*-iodophenyl)benzene was recovered quantitatively by simple filtration.

2.2. TEMPO-mediated oxidation of alcohols to aldehydes or ketones

TEMPO-mediated oxidation of primary alcohols and secondary alcohols[10] with the present trivalent iodine reagents **A-i**, **B-i**, and **C-i** in chloroform proceeded smoothly at room temperature to provide the corresponding aldehydes and ketone in good yields, and the reactivities were compared again with standard *p*-(diacetoxyiodo)toluene (**D-i**) as shown in Table 2. In trivalent iodine reagents **B-i** and **C-i**, a half-millimole amount of the reagents was used, based on that of trivalent iodine reagents **A-i** and **D-i**, and 10 mol % of TEMPO was used for effective oxidation. Again, the results indicate that trivalent iodine reagents **A-i**, **B-i**, and **C-i** showed the same reactivity as with the standard reagent **D-i**. Here, 4-bromo-4′-iodobiphenyl, 4,4′-diiodobiphenyl, and 1,4-bis(*p*-iodophenyl)benzene formed as byproducts could be recovered in high yields by simple filtration of the reaction mixture, though *p*-iodotoluene could not be recovered at all. TEMPO-mediated oxidation of cinnamyl alcohol with regenerated **C-i** provided cinnamaldehyde in high yields, together with high recovery of 1,4-bis(*p*-iodophenyl)benzene.

Table 2. TEMPO-mediated oxidation of alcohols to aldehydes or ketone with reagents **A-i**–**D-i**



Reagent	Product	Time (h)	Yields (%)	
			Product	Recovery[b]
A-i		2	98	93
B-i			93	89
C-i			99	96
D-i			97	(—)
A-i		2	93	75
B-i			90	89
C-i			90	96
D-i			94	(—)
A-i		2	71	86
B-i			73	83
C-i			95	94
			97[c]	93[c]
			97[d]	95[d]
D-i			99	(—)
A-i		2	81	84
B-i			79	90
C-i			79	92
D-i			89	(—)
A-i		24	95	93
B-i			95	89
C-i			97	95
D-i			100	(—)
A-i	$CH_3(CH_2)_{10}$–CHO	16	65	96
B-i			65	88
C-i			66	92
D-i			91	(—)
A-i		24	100	80
B-i			97	86
C-i			100	94
D-i			99	(—)

[a] For **B-i** and **C-i**: 0.6 equiv, and for **A-i** and **D-i**: 1.2 equiv.
[b] Yield of 4,4′-diiodobiphenyl, 4-bromo-4′-iodobiphenyl, or 1,4-bis(*p*-iodophenyl)benzene.
[c] Yield with the first regenerated **C-i**.
[d] Yield with the second regenerated **C-i**.

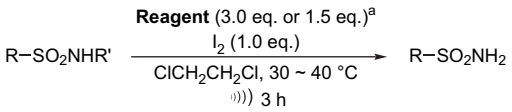
2.3. Sonochemical dealkylation of *N*-alkylsulfonamides

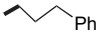
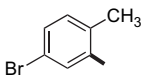
Previously, we reported sonochemical oxidative dealkylation of *N*-alkylsulfonamides with DIB in the presence of iodine to form the corresponding free sulfonamides and aldehydes.[11] Based on the report, *N*-alkylsulfonamides were treated with the present trivalent iodine reagents **A-i**, **B-i**, and **C-i** in the presence of iodine in 1,2-dichloroethane under ultrasonic irradiation conditions to generate the corresponding free sulfonamides in good yields as shown in Table 3. Again, the results indicate that trivalent iodine reagents **A-i**, **B-i**, and **C-i** have the same reactivity as that of standard reagent **D-i**. 4-Bromo-4′-iodobiphenyl, 4,4′-diiodobiphenyl, and 1,4-bis(*p*-iodophenyl)benzene formed as byproducts could be recovered in high yields by simple filtration of the reaction mixture, though *p*-iodotoluene could not be recovered at all.

2.4. α-Tosyloxylation of ketones

α-Tosyloxyketones are a very important strategic precursor for the direct construction of various heterocyclic

Table 3. Sonochemical dealkylation of *N*-alkyl-sulfonamides with reagents **A-i**–**D-i**

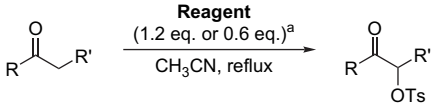


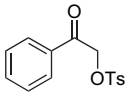
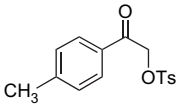
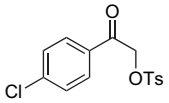
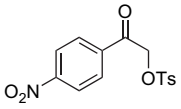
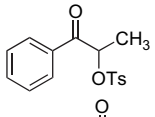
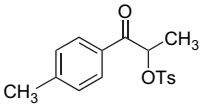
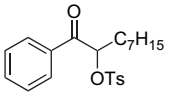
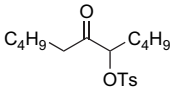
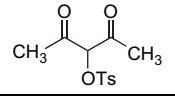
Reagent	R−	R'−	Yields (%)	
			Product	Recovery[b]
A-i		−CH_2CH_3	77	92
B-i			80	94
C-i			76	98
D-i			71	(—)
A-i			87	92
B-i			100	94
C-i			89	99
D-i			97	(—)
A-i[c]		−CH_2CH_3	66	90
B-i[c]			66	98
C-i[c]			58	98
D-i[c]			64	(—)

[a] For **B-i** and **C-i**: 1.5 equiv, and for **A-i** and **D-i**: 3.0 equiv.
[b] Yield of 4,4′-diiodobiphenyl, 4-bromo-4′-iodobiphenyl, or 1,4-bis(*p*-iodophenyl)benzene.
[c] Reaction was carried out for 6 h.

compounds such as thiazoles, oxazoles, selenazoles, imidazoles, pyrazoles, benzofurans, and lactones; and HTIB and PSHTIB are the sole reagents for the direct preparation of α-tosyloxyketones from ketones[2c,12] or alcohols.[13] Since biphenyl-based reagent **B-ii** has two trivalent iodine groups, a half-millimole amount of the reagent was used based on that of trivalent iodine reagents **A-ii** and **D-ii**. Here, various ketones were treated with the present trivalent iodine reagents **A-ii** and **B-ii** under refluxing conditions in acetonitrile to provide the corresponding α-tosyloxyketones in good yields as shown in Table 4. Again, the results indicate that the trivalent iodine reagents **A-ii** and **B-ii** have the same reactivity as that of the standard reagent **D-ii**. 4-Bromo-4′-iodobiphenyl and 4,4′-diiodobiphenyl formed as byproducts could be recovered in high yields by simple filtration of the reaction mixture, though *p*-iodotoluene could not be recovered at all.

Table 4. α-Tosyloxylation of ketones with reagents **A-ii**, **B-ii**, and **D-ii**



Reagent	Product	Time (h)	Yields (%)	
			Product	Recovery[b]
A-ii			85	88
B-ii		4	85	88
D-ii			87	(—)
A-ii			81	93
B-ii		8	84	81
D-ii			91	(—)
A-ii			92	84
B-ii		8	87	81
D-ii			95	(—)
A-ii			79	78
B-ii		8	88	81
D-ii			87	(—)
A-ii			81	93
B-ii		4	84	81
D-ii			91	(—)
A-ii			82	83
B-ii		4	86	74
D-ii			85	(—)
A-ii			81	81
B-ii		8	79	84
D-ii			80	(—)
A-ii[c]			77	87
B-ii[c]		8	72	82
D-ii[c]			65	(—)
A-ii			90	91
B-ii		4	83	84
D-ii			70	(—)

[a] For **B-ii**: 0.6 equiv and for **A-ii** and **D-ii**: 1.2 equiv.
[b] Yield of 4,4′-diiodobiphenyl and 4-bromo-4′-iodobiphenyl.
[c] Reaction was carried out at 60 °C.

3. Conclusion

4-Bromo-4′-(diacetoxyiodo)biphenyl (**A-i**), 4,4′-bis(diacetoxyiodo)biphenyl (**B-i**), and 1,4-bis[4-(diacetoxyiodo)-phenyl]benzene (**C-i**) could be used for the oxidative rearrangement of ketones to the esters, TEMPO-mediated oxidation of alcohols to the corresponding aldehydes or ketones, and oxidative dealkylation of *N*-alkylsulfonamides to sulfonamides, and 4-bromo-4′-[(hydroxy)(tosyloxy)-iodo]biphenyl (**A-ii**) and 4,4′-bis[(hydroxy)(tosyloxy)iodo]-biphenyl (**B-ii**) could be used for the α-tosyloxylation of ketones. These trivalent iodine reagents showed the same reactivity as that of *p*-(diacetoxyiodo)toluene (**D-i**) and *p*-[(hydroxy)(tosyloxy)iodo]toluene (**D-ii**). Moreover, after the reactions, the formed iodoarenes are recovered in high yields by simple filtration of the reaction mixture and they can be regenerated and reused for the same reaction. Thus, the present trivalent iodine reagents can be used as simple recyclable reagents, instead of polymer-supported trivalent iodine reagents such as PSDIB or PSHTIB.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were obtained with JEOL-JNM-LA-400, JEOL-JNM-LA-400s, and JEOL-JNM-LA-500 spectrometers. Chemical shifts are expressed in parts per million downfield from tetramethylsilane (TMS) in δ units. Mass spectra were recorded on JEOL-HX-110 and JEOL-JMS-ATII15 spectrometers. Melting points were determined on Yamato melting points apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC. Sonication was performed by Tokyo Rika Kikai AC-70 CO (200 W; 28 kHz) ultrasonic cleaning device.

4.2. Typical procedure for the preparation of iodoarenes

A mixture of 5.2 g of biphenyl, 12.4 g of iodine, 4.7 g of diiodine pentoxide, 10 ml of carbon tetrachloride, and 15 ml of 50% sulfuric acid in 20 ml of nitrobenzene was kept at 90∼100 °C for 48 h. After the reaction, the reaction mixture was poured into methanol (350 ml). The precipitates were collected by filtration (8.1 g, 60% yield).

4.2.1. 4-Bromo-4′-iodobiphenyl. Mp 166–168 °C; IR (KBr) 1470, 1380, 1000, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.29 (2H, d, J=8.5 Hz), 7.41 (2H, d, J=8.5 Hz), 7.56 (2H, d, J=8.5 Hz), 7.76 (2H, d, J=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ=93.43 (q), 121.99 (q), 128.44 (t), 128.72 (t), 132.02 (t), 137.99 (t), 138.96 (q), 139.49 (q).

4.2.2. 4,4′-Diiodobiphenyl. Mp 200–201 °C; IR (KBr) 2360, 1470, 1380, 1000, 800, 460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.28 (4H, d, J=8.5 Hz), 7.76 (4H, d, J=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ=93.49 (q), 128.67 (t), 137.99 (t), 139.54 (q); elemental analysis calcd for $C_{12}H_8I_2$: C 35.50, H 1.99, I 62.51%; found: C 35.58, H 2.03, I 62.56%.

4.2.3. 4,4′-Bis(*p*-iodophenyl)benzene. Mp >280 °C; IR (KBr) 2600, 1480, 1400, 1000, 800, 460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.37 (4H, d, J=8.5 Hz), 7.63 (4H, s), 7.79

(4H, d, J=8.5 Hz); elemental analysis calcd for $C_{18}H_{12}I_2$: C 44.84, H 2.51, I 52.65%; found: C 44.25, H 2.61, I 52.55%.

4.3. Typical procedure for the preparation of (diacetoxyiodo)arenes

A mixture of 4,4′-diiodobiphenyl (1.02 g, 2.5 mmol) and sodium peroxoborate tetrahydrate (3.85 g, 25 mmol) in AcOH (150 ml) was kept at 40–50 °C for 1 h, and then sodium peroxoborate tetrahydrate (3.85 g, 25 mmol) was added again. The mixture was stirred for 24 h at 40–50 °C. After the reaction, water was added and the mixture was extracted with chloroform three times. The organic layer was dried over sodium sulfate. After filtration, removal of the solvent under reduced pressure gave 4,4′-bis(diacetoxyiodo)biphenyl (1.60 g, 99% yield).

4.3.1. 4-Bromo-4′-(diacetoxyiodo)biphenyl. Mp (decomp.) 171 °C; IR (KBr) 2400–2300, 1560, 1410, 1000, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.03 (6H, s), 7.45 (2H, d, J=8.5 Hz), 7.62 (2H, d, J=8.5 Hz), 7.65 (2H, d, J=8.5 Hz), 8.15 (2H, d, J=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ=20.52 (p), 120.54 (q), 123.23 (q), 128.99 (t), 129.49 (t), 132.39 (t), 135.68 (t), 138.15 (q), 143.84 (q), 176.61 (q); elemental analysis calcd for $C_{16}H_{14}BrIO_4$: C 40.28, H 2.96%; found: C 40.25, H 3.06%.

4.3.2. 4,4′-Bis(diacetoxyiodo)biphenyl. Mp (decomp.) 176–177 °C; IR (KBr) 2360, 1580, 1410, 1000, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.04 (12H, s), 7.67 (4H, d, J=8.5 Hz), 8.20 (4H, d, J=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ=20.52 (p), 121.42 (q), 129.89 (t), 135.76 (t), 142.90 (q), 176.65 (q); elemental analysis calcd for $C_{20}H_{20}I_2O_8\cdot H_2O$: C 36.39, H 3.36, I 38.44%; found: C 36.32, H 3.27, I 38.49%.

4.4. Preparation of 1,4-bis(4-diacetoxyiodophenyl)-benzene

To a stirred solution of 4,4′-bis(*p*-iodophenyl)benzene (0.96 g, 2 mmol) in a mixture of $CHCl_3$ (300 ml) and AcOH (40 ml) was added *m*CPBA (2.08 g, 12 mmol) at room temperature. The reaction mixture was stirred for 24 h under the same reaction conditions. The resultant slightly clouded solution was filtered to give a clear solution. Chloroform of the filtrate was removed under reduced pressure and then hexane was added to the residue and stirred for 8 h to precipitate 1,4-bis(4-diacetoxyiodophenyl)benzene. After filtration, the crude product was washed with hexane and Et_2O several times, and dried in vacuo to give 1,4-bis(4-diacetoxyiodophenyl)benzene (1.41 g, 98% yield).

4.4.1. 1,4-Bis(4-diacetoxyiodophenyl)benzene. Mp (decomp.) 214 °C; IR (KBr) 2360, 1560, 1390, 1000, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.04 (12H, s), 7.71 (4H, s), 7.73 (4H, d, J=8.5 Hz), 8.19 (4H, d, J=8.5 Hz); elemental analysis calcd for $C_{26}H_{24}I_2O_8\cdot 3CH_3COOH$: C 42.78, H 4.04, I 28.25%; found: C 42.67, H 4.24, I 28.30%.

4.5. Typical procedure for the preparation of [hydroxy(tosyloxy)iodo]arenes

To a mixture of 4,4′-diiodobiphenyl (2.03 g, 5 mmol) and *p*-toluenesulfonic acid monohydrate (2.00 g, 11 mmol) in chloroform (60 ml) was added *m*CPBA (2.10 g, 11 mmol). The obtained mixture was stirred for 4 h at room temperature under an argon atmosphere. After the reaction, diethyl ether (20 ml) was added to the reaction mixture, and the obtained mixture was filtered and the solids were washed with diethyl ether to provide 4,4′-bis[(hydroxy)(tosyloxy)iodo]biphenyl (3.32 g, 85% yield).

4.5.1. 4-Bromo-4′-[(hydroxy)(tosyloxy)iodo]biphenyl. Mp (decomp.) 98–100 °C; IR (KBr) 3700–3200, 1480, 1390, 1190, 1130, 1040, 1000, 800, 600 cm^{-1}; ^1H NMR ($CDCl_3$+3 drops of CF_3CO_2H) δ=2.45 (3H, s), 7.35 (2H, d, J=8.2 Hz), 7.48 (2H, d, J=8.7 Hz), 7.66 (2H, d, J=8.7 Hz), 7.73 (2H, d, J=8.2 Hz), 7.77 (2H, d, J=8.7 Hz), 8.29 (2H, d, J=8.7 Hz); elemental analysis calcd for $C_{19}H_{16}BrIO_4S$: C 41.70, H 2.95%; found: C 41.54, H 3.06%.

4.5.2. 4,4′-Bis[(hydroxy)(tosyloxy)iodo]biphenyl. Mp (decomp.) 104 °C; IR (KBr) 3700–3200, 1470, 1190, 1130, 1040, 800, 600 cm^{-1}; ^1H NMR ($CDCl_3$+3 drops of CF_3CO_2H) δ=2.45 (6H, s), 7.33 (4H, d, J=8.2 Hz), 7.72 (4H, d, J=8.2 Hz), 7.81 (4H, d, J=8.7 Hz), 8.37 (4H, d, J=8.7 Hz); elemental analysis calcd for $C_{26}H_{24}I_2O_8S_2\cdot H_2O$: C 39.01, H 3.27%; found: C 39.31, H 3.16%.

4.6. Typical procedure for the conversion of arylketones to esters

Sulfuric acid (2 mmol) was added dropwise to a solution of 4,4′-bis(diacetoxyiodo)biphenyl (0.6 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. Hexane was then added to the solution, and the formed 4,4′-diiodobiphenyl was removed by filtration. The filtrate was poured into water (10 ml), extracted with ether, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was poured into methanol (5 ml). Once again 4,4′-diiodobiphenyl was removed by filtration. The filtrate was evaporated under reduced pressure and the residue was purified by preparative TLC on silica gel (85% yield).

4.6.1. Methyl 2-phenylpropanoate. Bp 65 °C/2.5 mmHg (lit.[14] 104–105 °C/18 mmHg); IR (neat) 2980, 1740, 1600, 1495, 1455, 1210, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (3H, d, J=7.2 Hz), 3.66 (3H, s), 3.73 (1H, q, J=7.2 Hz), 7.23–7.35 (5H, m).

4.6.2. Methyl 2-(4-methylphenyl)propanoate. IR (neat) 2955, 1740, 1515, 1460, 1205, 1165 cm^{-1}; ^1H 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).

4.6.3. Methyl 2-(4-methoxyphenyl)propanoate. IR (neat) 2980, 2960, 2840, 1740, 1340 cm^{-1}; ^1H 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).

4.6.4. Methyl 2-(4-fluorophenyl)propanoate. IR (neat) 2980, 2960, 1740, 1320 cm^{-1}; ^1H 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).

4.7. Typical procedure for the oxidation of alcohols to aldehydes or ketones

4,4′-Bis(diacetoxyiodo)biphenyl (0.3 mmol) was added to a solution of cinnamyl alcohol (0.5 mmol) and TEMPO (7.8 mg, 0.05 mmol) in $CHCl_3$ (1 ml), and the mixture was stirred at room temperature for 2 h. Then, hexane was added and the mixture was filtered to remove the formed 4,4′-diiodobiphenyl. After removal of the solvent from the filtrate, the residue was poured into methanol (5 ml). Once again 4,4′-diiodobiphenyl was removed by filtration. After removal of the solvent from the filtrate, the corresponding carbonyl compound was obtained.

All aldehydes and ketones mentioned in this work are commercially available, and all compounds were identified with the authentic samples.

4.8. Typical procedure for the oxidative dealkylation of *N*-alkylsulfonamides

4,4′-Bis(diacetoxyiodo)biphenyl (0.75 mmol) and iodine (0.5 mmol) were added to a solution of *N*-ethyl-benzylsulfonamide (0.5 mmol) in 1,2-dichloroethane (7 ml). The mixture was stirred preliminarily for 10 min under dark conditions, and then irradiated with an ultrasonic cleaning bath (200 W; 28 kHz or 100 W; 28, 45, and 100 kHz) for 3 h under an argon atmosphere in the range of 30–40 °C. After the reaction, the mixture was poured into ethyl acetate and washed with aq sodium sulfite (Na_2SO_3) solution and subsequently washed with water. The organic layer was dried over sodium sulfate (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was poured into methanol (5 ml). The mixture was filtered to remove the formed 4,4′-diiodobiphenyl. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel preparative TLC using a mixture of hexane and ethyl acetate (2:1) as an eluant.

4.8.1. Benzylsulfonamide. Mp 99–100 °C (lit.[15] 101–102 °C); IR (KBr) 3380, 3320, 1325, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.30 (2H, s), 4.72 (2H, br s), 7.37–7.44 (5H, m); MS (EI) found: M^+=171.

4.8.2. 5-Bromo-2-methylbenzenesulfonamide. Mp 163.0–164.5 °C (lit.[16] 164.0–165.0 °C); IR (KBr) 3400, 3295, 1295, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.63 (3H, s), 4.92 (2H, br s), 7.21 (1H, d, J=8.0 Hz), 7.58 (1H, dd, J=8.2 and 2.2 Hz), 8.15 (1H, d, J=2.2 Hz); MS (EI) found: M^+= 249, 251.

Benzenesulfonamide was identified with commercially available authentic compound.

4.9. Typical procedure for the α-tosyloxylation of ketones

4,4′-Bis[(hydroxy)(tosyloxy)iodo]biphenyl (0.3 mmol) was added to a solution of acetophenone (0.5 mmol) in acetonitrile (3 ml). The mixture was refluxed for 4 h under an argon atmosphere, and then the reaction mixture was poured into methanol (5 ml). The mixture was filtered to remove 4,4′-diiodobiphenyl. After removal of the solvent under reduced pressure, the residue was poured into methanol (5 ml). The mixture was filtered to remove the formed 4,4′-diiodobiphenyl. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel by column chromatography.

4.9.1. α-Tosyloxyacetophenone. Mp 90 °C (lit.[13c] 90–91 °C); IR (KBr) 1715, 1360, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (3H, s), 5.27 (2H, s), 7.35 (2H, d, J=8.5 Hz), 7.47 (2H, t, J=8.2 Hz), 7.61 (1H, t, J=8.2 Hz), 7.85 (4H, m).

4.9.2. α-Tosyloxy-*p*-methylacetophenone. Mp 80 °C (lit.[13c] 82–83 °C); IR (KBr) 1700, 1350, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.41 (3H, s), 2.45 (3H, s), 5.24 (2H, s), 7.26 (2H, d, J=8.1 Hz), 7.35 (2H, d, J=8.2 Hz), 7.74 (2H, d, J=8.1 Hz), 7.86 (2H, d, J=8.2 Hz).

4.9.3. α-Tosyloxy-*p*-chloroacetophenone. Mp 122 °C (lit.[13c] 125 °C); IR (KBr) 1710, 1360, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.46 (3H, s), 5.21 (3H, s), 7.35 (2H, d, J=8.4 Hz), 7.45 (2H, d, J=8.6 Hz), 7.80 (2H, d, J= 8.6 Hz), 7.84 (2H, d, J=8.4 Hz).

4.9.4. α-Tosyloxy-*p*-nitroacetophenone. Mp 139–140 °C (lit.[13c] 139 °C); IR (KBr) 1710, 1340, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.47 (3H, s), 5.25 (2H, s), 7.37 (2H, d, J=8.3 Hz), 7.83 (2H, d, J=8.3 Hz), 8.02–8.05 (2H, m), 8.31–8.35 (2H, m).

4.9.5. α-Tosyloxypropiophenone. Mp 68 °C (lit.[13c] 68–69 °C); IR (KBr) 1700, 1370, 1170, 830, 760, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.60 (3H, d, J=7.0 Hz), 2.41 (3H, s), 5.79 (1H, q, J=7.0 Hz), 7.29 (2H, d, J=8.1 Hz), 7.46 (2H, t, J=7.2 Hz), 7.60 (1H, t, J=7.2 Hz), 7.75 (2H, d, J= 7.2 Hz), 7.88 (2H, d, J=8.1 Hz).

4.9.6. α-Tosyloxy-*p*-methylpropiophenone. Mp 88–89 °C; IR (KBr) 1690, 1360, 1180, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.56 (3H, d, J=7.0 Hz), 2.41 (3H, s), 2.42 (3H, s), 5.77 (1H, q, J=7.0 Hz), 7.23 (4H, m), 7.73 (4H, m); ^{13}C NMR ($CDCl_3$) δ=18.78 (p), 21.63 (p), 21.72 (p), 77.32 (t), 127.92 (t), 128.86 (t), 129.44 (t), 129.72 (t), 131.14 (q), 133.53 (q), 144.89 (q), 144.93 (q), 194.29 (q); HRMS (FAB) obsd: M+H=319.1004, calcd for $C_{10}H_{12}O$: M+H=319.1007.

4.9.7. α-Tosyloxyoctyl phenyl ketone. Mp 59–60 °C; IR (KBr) 1700, 1340, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (3H, t, J=7.0 Hz), 1.20–1.43 (10H, m), 1.84–1.91 (2H, m), 2.40 (3H, s), 5.59 (1H, dd, J=8.2 and 4.8 Hz), 7.24 (2H, d, J=8.0 Hz), 7.43–7.47 (2H, m), 7.56–7.60 (1H, m), 7.73–7.77 (2H, m), 7.84–7.86 (2H, m); ^{13}C NMR ($CDCl_3$) δ=14.01 (p), 21.60 (p), 22.53 (s), 24.95 (s), 28.74 (s), 28.87 (s), 31.58 (s), 32.66 (s), 81.37 (t), 128.00 (t), 128.61 (t), 128.69 (t), 133.12 (q), 133.72 (t), 133.98 (q), 144.92 (q), 1955.02 (q); elemental analysis calcd for $C_{22}H_{28}O_4S$: C 68.01, H 7.43%; found: C 68.01, H 7.26%.

4.9.8. α-Tosyloxy-6-undecanone. Mp 72 °C; ^1H NMR ($CDCl_3$) δ=0.70–0.80 (3H, m), 0.86–0.89 (3H, m),

1.09–1.75 (14H, m), 2.46 (3H, s), 2.49–2.53 (2H, m), 4.64 (1H, dd, J=8.0 and 4.6 Hz), 7.36 (2H, d, J=8.0 Hz), 7.79–7.82 (2H, m); ^{13}C NMR ($CDCl_3$) δ=13.64 (p), 13.89 (p), 21.70 (p), 21.99 (s), 22.45 (s), 22.50 (s), 26.63 (s), 31.25 (s), 31.50 (s), 38.20 (s), 84.94 (t), 128.72 (t), 130.67 (t), 133.80 (q), 146.13 (q), 208.63 (q); elemental analysis calcd for $C_{18}H_{28}O_4S$: C 63.50, H 8.29% found: C 63.40, H 8.50%.

4.9.9. α-Tosyloxy-2,4-pentadione. Mainly enol tautomer; mp 82 °C (lit.[13b] 82–83 °C); IR (KBr) 3060, 1600, 1370, 1200, 1180, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.96 (6H, s), 2.49 (3H, s), 7.40 (2H, d, J=8.1 Hz), 7.83 (2H, d, J=8.1 Hz), 14.80 (1H, s).

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References and notes

1. Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic: San Diego, 1997.
2. For reviews, see: (a) Ochiai, M. *Rev. Heteroatom Chem.* **1989**, *2*, 92; (b) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431; (c) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365; (d) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274; (e) Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221; (f) Kitamura, T. *Yuki Gosei Kagaku Kyokaishi* **1995**, *53*, 893; (g) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123; (h) Umemoto, T. *Chem. Rev.* **1996**, *96*, 1757; (i) Kita, Y.; Takada, T.; Tohma, H. *Pure Appl. Chem.* **1996**, *68*, 627; (j) Togo, H.; Hoshina, Y.; Nogami, G.; Yokoyama, M. *Yuki Gosei Kagaku Kyokaishi* **1997**, *55*, 90; (k) Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179; (l) Zhdankin, V. V. *Rev. Heteroatom Chem.* **1997**, *17*, 133; (m) Muraki, T.; Togo, H.; Yokoyama, M. *Rev. Heteroatom Chem.* **1997**, *17*, 213; (n) Kitamura, T.; Fujiwara, Y. *Org. Prep. Proced. Int.* **1997**, *29*, 409; (o) Varvoglis, A.; Spyroudis, S. *Synlett* **1998**, 221; (p) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927; (q) Moriarty, R. M.; Prakash, O. *Adv. Heterocycl. Chem.* **1998**, *69*, 1; (r) Kita, Y.; Egi, M.; Takada, T.; Tohma, H. *Synthesis* **1999**, 885; (s) Wirth, T.; Hirt, U. H. *Synthesis* **1999**, 1271; (t) Ochiai, M.; Kitagawa, Y. *Yuki Gosei Kagaku Kyokaishi* **2000**, *58*, 1048; (u) Togo, H.; Katohgi, M. *Synlett* **2001**, 565; (v) Wirth, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2812; (w) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523; (x) Togo, H.; Sakuratani, K. *Synlett* **2002**, 1966; (y) Tohma, H.; Kita, Y. *Adv. Synth. Catal.* **2004**, *346*, 111; (z) Tohma, H.; Kita, Y. *Yuki Gosei Kagaku Kyokaishi* **2004**, *62*, 116.
3. For reviews, see: (a) Kirschning, A.; Monenschein, H.; Wittenberg, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 650; (b) Togo, H.; Sakuratani, K. *Synlett* **2002**, 1966 and references cited therein. For recent papers, see: (c) Tohma, H.; Maegawa, T.; Kita, Y. *Synlett* **2003**, 723; (d) Tashino, Y.; Togo, H. *Synlett* **2004**, 2010; (e) Ueno, M.; Togo, H. *Synthesis* **2004**, 2673; (f) Chen, J.; Huang, X. *Synlett* **2004**, 552; (g) Chen, J.; Huang, X. *Synthesis* **2004**, 1577; (h) Chen, J.; Huang, X. *Synthesis* **2004**, 2459; (i) Marinescu, L. G.; Pedersen, C. M.; Bols, M. *Tetrahedron* **2005**, *61*, 123; (j) Teduka, T.; Togo, H. *Synlett* **2005**, 923; (k) Chung, W.; Kim, D.; Lee, Y. *Synlett* **2005**, 2175; (l) But, T. Y. S.; Tashino, Y.; Togo, H.; Toy, P. H. *Org. Biomol. Chem.* **2005**, *3*, 970; (m) Herrerias, C. I.; Zhang, T. Y.; Li, C. *Tetrahedron Lett.* **2006**, *47*, 13; (n) Ladziata, U.; Willging, J.; Zhdankin, V. V. *Org. Lett.* **2006**, *8*, 167.
4. (a) Tohma, H.; Maruyama, A.; Maeda, A.; Maegawa, T.; Dohi, T.; Shiro, M.; Morita, T.; Kita, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3595; (b) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Shiro, M.; Kita, Y. *Chem. Commun.* **2005**, 2205.
5. Recently, synthetic use of 4,4′-bis(dichloroiodo)biphenyl as a recyclable reagent was reported, see: Yusubov, M. S.; Drygunova, L. A.; Zhdankin, V. V. *Synthesis* **2004**, 2289.
6. Stapp, P. R. U.S. Patent 422,1927, 1980.
7. McKillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299.
8. Yamamoto, Y.; Togo, H. *Synlett* **2005**, 2486.
9. Togo, H.; Abe, S.; Nogami, G.; Yokoyama, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2351.
10. (a) De Mico, A.; Margarita, R.; Parlanti, L.; Vescovi, A.; Piancatelli, G. *J. Org. Chem.* **1997**, *62*, 6974; (b) Sakuratani, K.; Togo, H. *Synthesis* **2003**, 21.
11. (a) Katohgi, M.; Yokoyama, M.; Togo, H. *Synlett* **2000**, 1055; (b) Katohgi, M.; Togo, M. *Tetrahedron* **2001**, *57*, 7481.
12. For reviews, see: (a) Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89; (b) Prakash, O.; Saini, N.; Sharma, P. K. *Heterocycles* **1994**, *38*, 409. For papers, see: (c) Neilands, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 885; (d) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Bertram, A. F. *J. Org. Chem.* **1976**, *41*, 3609; (e) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476; (f) Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1543; (g) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487; (h) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101; (i) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, *31*, 201; (j) Tuncay, A.; Dustman, J. A.; Fisher, G.; Tuncay, C. I. *Tetrahedron Lett.* **1992**, *33*, 7647; (k) Moriarty, R. M.; Vaid, B. K.; Duncan, M. P.; Levy, S. G.; Prakash, O.; Goyal, S. *Synthesis* **1992**, 845; (l) Prakash, O.; Goyal, S. *Synthesis* **1992**, 629; (m) Prakash, O.; Rani, N.; Goyal, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 707; (n) Varma, R. S.; Kumar, D.; Liesen, P. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4093; (o) Muraki, T.; Togo, H.; Yokoyama, M. *J. Org. Chem.* **1999**, *64*, 2883; (p) Lee, J. C.; Choi, J.-H. *Synlett* **2001**, 234; (q) Nabana, T.; Togo, H. *J. Org. Chem.* **2002**, *67*, 4362; (r) Misu, Y.; Togo, H. *Org. Biomol. Chem.* **2003**, *1*, 1342; (s) Sakuratani, K.; Togo, H. *ARKIVOC* **2003**, 11.
13. (a) Abe, S.; Sakuratani, K.; Togo, H. *Synlett* **2001**, 22; (b) Abe, S.; Sakuratani, K.; Togo, H. *J. Org. Chem.* **2001**, *66*, 6174; (c) Ueno, M.; Nabana, T.; Togo, H. *J. Org. Chem.* **2003**, *68*, 6424.
14. (a) Tamura, Y.; Yakura, T.; Shirouchi, Y.; Haruta, J. *Chem. Pharm. Bull.* **1985**, *33*, 1097; (b) Tamura, Y.; Shirouchi, Y.; Haruta, J. *Synthesis* **1984**, 231.
15. Graham, S. L.; Scholz, T. H. *Synthesis* **1986**, 1031.
16. Huntress, E. H.; Carten, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 511.