Contribution

Study of Ion-supported Reagents for Organic Synthesis: IS-Ph$_3$P, IS-MSO, IS-MS, and IS-DIB

Hideo Togo

Graduate School of Science, Chiba University

1. Introduction

In organic synthesis, most reactions require organic reagents and therefore, after each reaction, the desired product must be purified by column chromatography to remove organic co-products derived from organic reagents. In view of environmentally benign organic synthesis, novel ion-supported reagents, such as ion-supported Ph$_3$P (IS-Ph$_3$P **A** and **B**), ion-supported methyl sulfoxide (IS-MSO **C** and **D**), ion-supported methyl sulfide (IS-MS **E** and **F**), ion-supported (diacetoxyiodo)-benzene (IS-DIB **G** and **H**), and super-DIB (**I**) were developed for easy isolation of desired products from the reaction mixture and reuse of those ion-supported reagents for the same reactions, as shown in Fig. 1. The great advantages of these ion-supported reagents are the simple isolation of the desired products by diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, and their recyclable use for the same reactions through high recovery and efficient regeneration, and therefore those ion-supported reagents are user-friendly and environmentally benign. Experimental procedure for the reaction with ion-supported reagents, isolation of the products, and regeneration and reuse of the ion-supported reagents is shown in Fig. 2

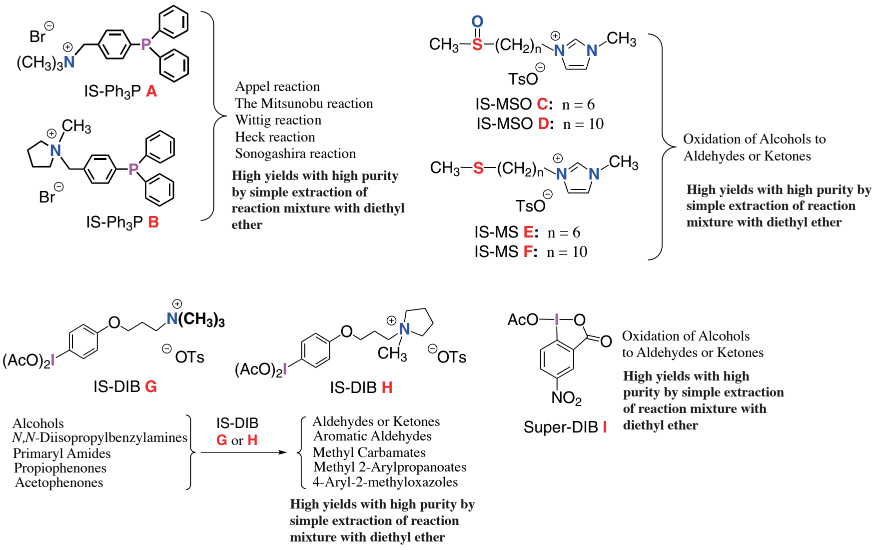


Figure 1. Ion-supported reagents.

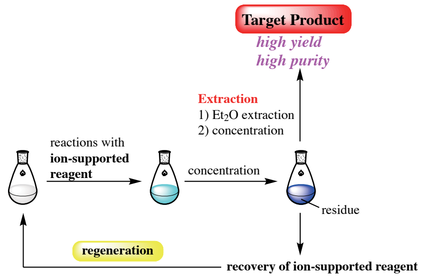


Figure 2. Reaction, recovery, regeneration, and reuse of ion-supported reagents.

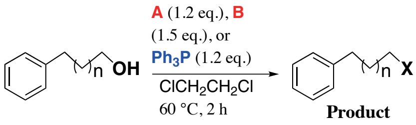
2. Ion-supported Ph$_3$P (IS-Ph$_3$P)

Ph$_3$P is one of the most important reagents for organic synthesis, because it can be used for the halogenation of alcohols with CBr$_4$ or I$_2$ / imidazole (Appel reaction),1) esterification of carboxylic acids with alcohols and diethyl azodicarboxylate (DEAD) (Mitsunobu reaction),2) olefination of aldehydes with phosphonium ylide (Wittig reaction),3) Pd-catalyzed reaction as a ligand (Sonogashira reaction, Mizoroki-Heck reaction),4) *etc*. However, Ph$_3$PO as a co-product is formed in the Appel reaction, the Mitsunobu reaction, and the Wittig reaction, and therefore, it must be removed by column chromatography carefully. Even for the Pd-catalyzed reaction with Ph$_3$P as a ligand, the reaction mixture must be purified by column chromatography.

2-1. Halogenation of alcohols

IS-Ph$_3$P **A** and **B** are solid, respectively, and IS-Ph$_3$P **A** and **B** are efficient reagents for the bromination and iodination of alcohols with CBr$_4$ and I$_2$ / imidazole, respectively. After the reaction, diethyl ether was added to the reaction mixture to separate the IS-Ph$_3$PO and the oil. After filtration and removal of ether solvent from the filtrate, the corresponding alkyl halides were obtained in high yields with high purity (>90%) in both IS-Ph$_3$P **A** and **B**, without chromatography, by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, as shown in Table 1. Moreover, ion-supported Ph$_3$PO, 4-(diphenylphosphino)benzyltrimethylammonium bromide and *N*-methyl-*N*-[4-(diphenylphosphino)benzyl]-pyrrolidinium bromide, were recovered in over 90% yield. After the *O*-methylation of the recovered ion-supported Ph$_3$PO with dimethyl sulfate and the subsequent reduction with LiAlH$_4$, IS-Ph$_3$P **A** and **B** could be regenerated in high yield, and could be reused for the same halogenation reaction, keeping high yield and high purity of alkyl halides under the same conditions and procedure.5)

Table 1. Halogenation of alcohols.



Bromination: CBr$_4$ (1.1 eq.) and **A**, **B**, or **Ph$_3$P**
Iodination: I$_2$ (1.5 eq.), imidazole (1.5 eq.), KI (5 eq.)

A	Product / %		
	n = 0	n = 1	n = 2
X = Br	86	95, 88^a, 76^b	91
X = I	85	80	80

B	Product / %		
	n = 0	n = 1	n = 2
X = Br	89	95, 93^a, 87^b	97
X = I	83	85	83

Ph$_3$P	Product / %		
	n = 0	n = 1	n = 2
X = Br	72^c	68^c	53^c

[a] Yield of product with the first regenerated **A** or **B**.
[b] Yield of product with the second regenerated **A** or **B**.
[c] Purity of the product after removal of ether from the extracts was 14%~43%. Ph$_3$PO was recovered in 42~44% yield.

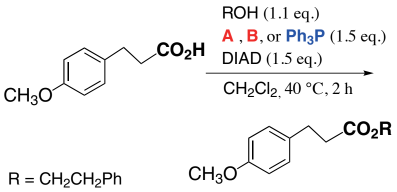
2-2. Mitsunobu reaction

IS-Ph$_3$P **A** and **B** could be also used for esterification of 3-(4'-methoxyphenyl)propanoic acid with 2-phenylethanol and diisopropyl azodicarboxylate (DIAD) in dichloromethane to provide the corresponding 2''-phenylethyl 3-(4'-methoxyphenyl)-propanoate in good yields, as shown in Table 2. After the reaction, diethyl ether was added to the reaction mixture to separate the IS-Ph$_3$PO and the oil. After filtration and removal of ether solvent from the filtrate, the corresponding ester was obtained in high yields with high purity (>90%) in both IS-Ph$_3$P **A** and **B**, respectively, without chromatography. Each IS-Ph$_3$PO was recovered in over 90% yield. Again, after the *O*-methylation of the recovered ion-supported Ph$_3$PO with dimethyl sulfate and the subsequent reduction with LiAlH$_4$, IS-Ph$_3$P **A** and **B** could be regenerated and reused for the same esterification reaction, maintaining good yield with high purity.5) On the other hand, when Ph$_3$P was used for the same esterification of 3-(4'-methoxyphenyl)propanoic acid under the same conditions, Ph$_3$PO was recovered only in 30% yield, together with the ester in 87% yield after purification from ether extracts, as shown in Table 2. This result indicates again IS-Ph$_3$P **A** and **B** are efficiently recyclable reagents for the esterification of carboxylic acids and the purity of ether extracts from the reaction mixture is enough high.

2-3. Wittig reaction

IS-Ph$_3$P **A** and **B** were used for the Wittig reaction. Thus, ion-supported phosphonium salts **A1** and **B1**, which were prepared from the reactions of IS-Ph$_3$P **A** and **B** with ethyl bromoacetate, respectively, reacted with aromatic and aliphatic aldehydes in the presence of K$_2$CO$_3$ to give the corresponding α,β−unsaturated ethyl esters in good yields with high purity by simple filtration of the reaction mixture and subsequent removal of the solvent from the filtrate, as shown in Table 3. Similarly, ion-supported phosphonium salts **A2** and **B2**,

Table 2. Esterification of carboxylic acid.

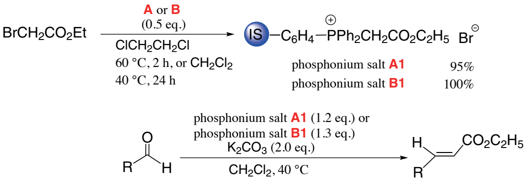


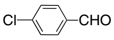
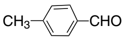
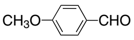
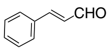
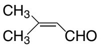
	Yield of Ester / %		
Reuse	0	1	2
A	84	79^a	70^b
B	87	80^a	77^b
Ph$_3$P	87^c	-	-

[a] Yield of ester with the first regenerated **A** or **B**.
[b] Yield of ester with the second regenerated **A** or **B**.
[c] Ph$_3$PO was recovered in 30% yield.

which were prepared from the reactions of IS-Ph_3P **A** and **B** with *p*-methylbenzyl bromide, respectively, reacted with aromatic and aliphatic aldehydes in the presence of NaH to provide the corresponding *p*-methylstyrene derivatives in good yields with high purity by simple filtration of the reaction mixture and the subsequent removal of the solvent from the filtrate. In both reactions, the co-product, ion-supported Ph_3PO, could be obtained quantitatively by simple filtration, and was converted into the corresponding IS-Ph_3P **A** and **B** again in high yields using dimethyl sulfate, followed by the reduction with $LiAlH_4$. Recovered and regenerated IS-Ph_3P **A** and **B** could be reused for the same Wittig reaction while maintaining good yields of ethyl (*E*)-3-(4'-chlorophenyl)-2-propenoate and 1-(4'-chlorophenyl)-2-(4''-methylphenyl)ethene with high purity by simple filtration and removal of the solvent from the filtrate, as shown in Tables 3 and 4, respectively.[6)]

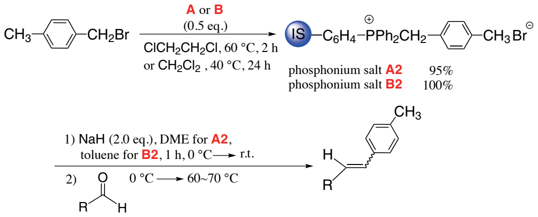
Table 3. Wittig reaction with IS-Ph_3P **A** and **B**.

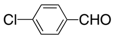
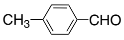
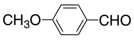
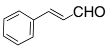
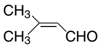


Substrate	**A** α,β–Unsaturated Ester				**B** α,β–Unsaturated Ester			
	Time (h)	Yield (%)[a]	Purity (%)[b]	*E*:*Z*	Time (h)	Yield (%)[a]	Purity (%)[b]	*E*:*Z*
	8	94	97	96:4	8	98	98	94:6
	8[c]	95	97	96:4	8[c]	95	90	96:4
	8[d]	92	97	96:4	8[d]	91	90	96:4
	8[e]	99	43	96:4				
	10	95	98	97:3	8	96	90	96:4
	50	98	97	96:4	24	91	90	95:5
$CH_3(CH_2)_6CHO$	24	100	97	97:3	20	90	86	93:7
	24	93	89	90:10	20	92	95	92:8
	24	92	90	95:5	16	88	80	94:6

[a] Isolated yield of *E* and *Z* alkenes. Ion-supported Ph_3PO was recovered in 92%~100% yields.
[b] Purity of product after removal of solvent from the extracts.
[c] The first regenerated IS-Ph_3P **A** or **B** was used.
[d] The second regenerated IS-Ph_3P **A** or **B** was used.
[e] **Ph_3P** was used instead of IS-Ph_3P **A** or **B**, and Ph_3PO was recovered in 50% yield.

Table 4. Wittig reaction with IS-Ph_3P **A** and **B**.



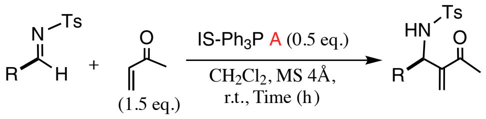
Substrate	**A** Styrene Derivative				**B** Styrene Derivative			
	Time (h)	Yield (%)[a]	Purity (%)[b]	*E*:*Z*	Time (h)	Yield (%)[a]	Purity (%)[b]	*E*:*Z*
	8	95	95	75:25	9	91	90	75:25
	8[c]	94	95	75:25	9[c]	90	85	75:25
	8[d]	92	95	75:25	9[d]	90	81	75:25
	9[e]	90	46	50:50				
	10	95	95	75:25	9	100	90	78:28
	50	91	96	79:21	24	90	95	81:19
$CH_3(CH_2)_6CHO$	24[f]	86	91	71:29	24[f]	77	70	74:26
	24	91	94	90:10	24	82	90	84:16
	24[f]	71	64	78:22	24[f]	85	56	71:29

[a] Isolated yield of *E* and *Z* alkenes. Ion-supported Ph_3PO was recovered in 93%~100% yields.
[b] Purity of product after removal of solvent from the extracts .
[c] The first regenerated IS-Ph_3P **A** or **B** was used.
[d] The second regenerated IS-Ph_3P **A** or **B** was used.
[e] **Ph_3P** was used instead of IS-Ph_3P **A** or **B**, and Ph_3PO was recovered in 46% yield.

2-4. *aza*-Morita-Baylis-Hillman reaction

Various *N*-tosyl arylimines reacted with methyl vinyl ketone in the presence of IS-Ph_3P **A** and **B** to give adducts, *N*-(2'-methylene-3'-oxo-1'-arylbutyl)-4-methylbenzenesulfonamides, in good yields with high purity by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, as shown in Table 5 and 6. Moreover, IS-Ph_3P **A** and **B** could be repeatedly used for the same reaction to provide the corresponding adducts while maintaining good yields with high purity.[7)]

Table 5. *aza*-Morita-Baylis-Hillman Reaction with IS-Ph_3P **A**.



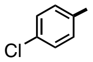
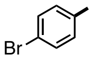
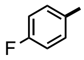
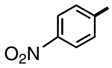
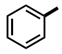
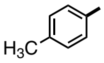
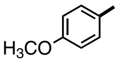
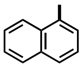
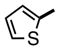
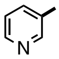
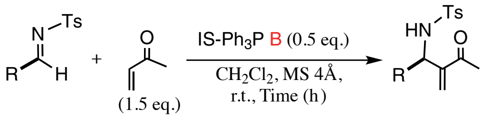
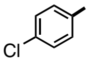
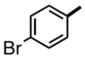
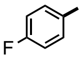
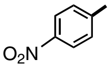
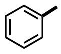
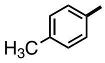
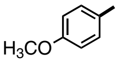
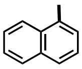
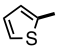
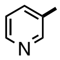
R	Time (h)	Yield (%)	Purity (%)
	24	100	92
	24	95	91
	5	97	94
	3	94	90
	24	96	97
	24	94	95
	24	87	90
	48	74	86
	50	80	85
	48	60	80

Table 6. *aza*-Morita-Baylis-Hillman Reaction with IS-Ph_3P **B**.



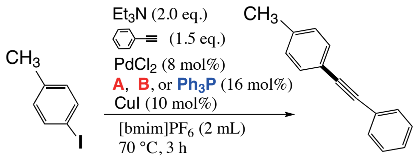
R	Time (h)	Yield (%)	Purity (%)
	24	95	99
	24	94	90
	5	100	95
	3	92	93
	24	97	99
	24	95	92
	24	90	90
	48	66	50
	50	85	80
	48	62	78

2-5. Sonogashira reaction

Ionic liquid reaction media containing $Pd(OAc)_2$ or $PdCl_2$ and IS-Ph_3P **A** and **B** as catalysts could be used and reused for the Sonogashira reaction and the Mizoroki-Heck reaction maintaining high yields of products, using iodotoluene with phenylacetylene and methyl acrylate, respectively. The Sonogashira reaction with IS-Ph_3P **A** and **B** are shown in Table 7.[5)]

Today, IS-Ph_3P **B** is commercially available from Tokyo Chemical Industry Co., Ltd.

Table 7. Sonogashira reaction.



Reuse	Yield of product / %		
	A	**B**	**Ph_3P**
0	100^{a}	100^{a}	91^{b}
1^{c}	100^{a}	100^{a}	92^{b}
2^{c}	97^{a}	100^{a}	99^{b}
3^{c}	100^{a}	100^{a}	76^{b}
4^{c}	100^{a}	100^{a}	41
5^{c}	96^{a}	90^{a}	18
6^{c}	96^{a}	95^{a}	-
7^{c}	100^{a}	94^{a}	-

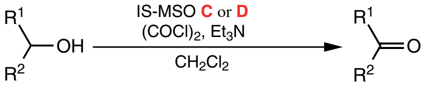
[a] Yield of product. Purity of the product after removal of ether from the extracts was 95~85%.
[b] Yield of product. Each ether extract contains 2~3% of Ph_3P.
[c] Only iodotoluene, phenylacetylene, and Et_3N were added.

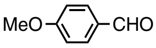
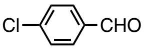
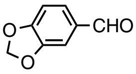
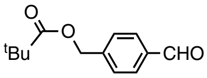
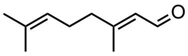
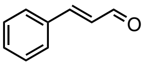
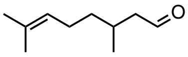
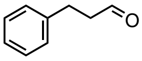
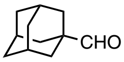
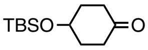
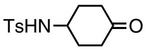
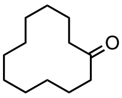
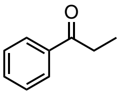
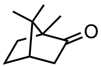
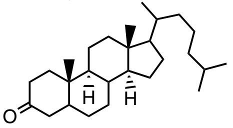
3. Ion-supported Methyl Sulfoxide (IS-MSO) and Ion-supported Methyl Sulfide (IS-MS)

The Swern oxidation[8)] of various benzylic and allylic alcohols, primary alcohols, and secondary alcohols with IS-MSO **C** or **D**, and oxalyl chloride in the presence of triethylamine in dichloromethane, followed by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, gave the corresponding aldehydes and ketones, respectively, in good yields with high purity, as shown in Table 8.[9)] Here, IS-MSO **C** is odorless viscous oil and IS-MSO **D** is a odorless solid. On the other hand, IS-MS **E** and **F** are odorless solid, respectively. The Corey-Kim oxidation[10)] of various benzylic and allylic alcohols, primary alcohols, and secondary alcohols with IS-MS **E** or **F**, and *N*-chlorosuccinimide in the presence of triethylamine in dichloromethane, followed by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, furnished the corresponding aldehydes and ketones, respectively, in good yields with high purity, as shown in Table 9.[11)] Both reactions did not produce any unpleasant odor at all. In the Swern oxidation, ion-supported methyl sulfides were recovered in high yields and could be re-oxidized to produce IS-MSO **C** and **D** with hydrogen peroxide, for reuse in the same oxidation. In the Corey-Kim oxidation, IS-MS **E** and **F** were recovered in high yields and could be also reused for the same oxidation.

Today, IS-MSO **C** and IS-MS **E** is commercially available from Tokyo Chemical Industry Co., Ltd.

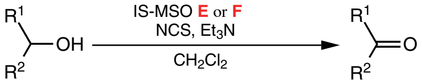
Table 8. Swern oxidation with IS-MSO **C** and **D**.

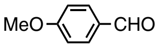
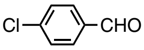
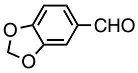
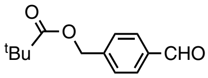
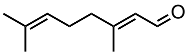
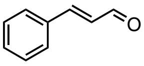
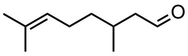
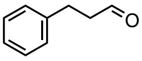
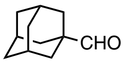
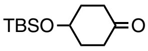
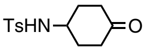
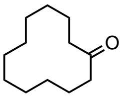
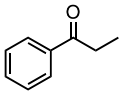
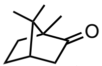
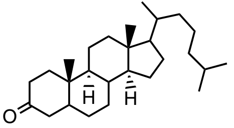


IS-MSO **C** or **D**	Product	Yield	Purity
C **D**		92 98	99 98
C **D**		84 84	88 96
C **C**[a] **D** **D**[a]		99 95 94 84	98 99 89 99
C **D**		93 86	99 99
C **D**		99 94	99 94
C **D**		99 92	98 93
C **D**		83 89	82 99
C **D**		85 92	85 99
C **D**		78 90	90 99
C **D**		96 95	99 99
C **D**		99 99	99 99
C **D**		99 91	99 99
C **D**		99 91	99 99
C **D**		99 92	99 99
C **D**		88 99	99 99

[a] Ion-supported methyl sulfide that was recovered and regenerated, was reused.

Table 9. Corey-Kim oxidation with IS-MS **E** and **F**.



IS-MSO **E** or **F**	Product	Yield	Purity
E **F**		97 83	99 84
E **F**		85 81	96 95
E **F**		93 81	97 94
E **F**		89 88	96 99
E **F**		82 74	94 99
E **F**		94 75	96 78
E **F**		80 90	99 80
E **F**		94 92	97 91
E **F**		92 87	98 99
E **F**		86 86	86 99
E **F**		85 78	99 99
E **F**		99 83	99 99
E **F**		99 88	98 99
E **E**[a] **F** **F**[a]		99 90 85 84	99 99 99 97
E **F**		88 90	99 99

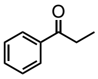
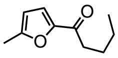
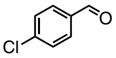
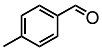
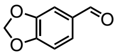
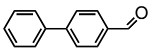
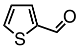
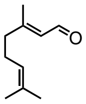
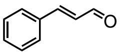
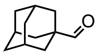
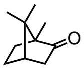
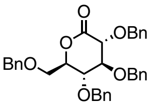
[a] Ion-supported methyl sulfide that was recovered, was reused.

4. Ion-supported (Diacetoxyiodo)benzene (IS-DIB)

Recently, oxidation of alcohols with (diacetoxyiodo)-benzene (DIB) in the presence of 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) at room temperature has become very popular,12) due to the mild metal-free oxidation of alcohols. The oxidation of secondary alcohols and primary alcohols with IS-DIB **G** and **H** in the presence of a catalytic amount of TEMPO in dichloromethane at room temperature proceeded efficiently to provide the corresponding ketones and aldehydes, respectively, in good yields with high purity by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, as shown in Table 10. Oxidative reaction of *p*-substituted *N*,*N*-diisopropylbenzylamines with IS-DIB **G** and **H** was also carried out to generate the corresponding aromatic aldehydes in good yields with high purity by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, as shown in Table 11. In addition, the Hofmann reaction of primary amides in methanol under basic conditions and oxidative 1,2-rearrangement reaction of propiophenones in trimethyl orthoformate under acidic conditions with IS-DIB **G** and **H** provided the corresponding methyl carbamates and methyl 2-arylpropanoates, respectively, in good yields with high purity again, by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent, as shown in Table 12 and Table 13. Moreover, treatment of *p*-substituted acetophenones with IS-DIB **G** and **H** in the presence of trifluoromethanesulfonic acid in acetonitirle generated the corresponding 5-aryl-2-methyloxazoles in good yields with high purity, as shown in Table 14. In those five reactions, the products were obtained in good yields with high purity by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent from the extract. Moreover, ion-supported iodobenzenes, which were co-products derived from IS-DIB **G** and **H** in the present oxidative reactions, were recovered in good yields and could be re-oxidized to IS-DIB **G** and **H** by the reaction with *m*-chloroperoxybenzoic acid (*m*CPBA)13) and regenerated IS-DIB **G** and **H** could be reused for the same oxidative reactions.14) On the other hand, when DIB was used for these reactions under the same conditions and procedure, the corresponding products were obtained in good yields, however, the purity of the products was less than 50% due to the presence of iodobenzene, as shown in Tables 10~14.

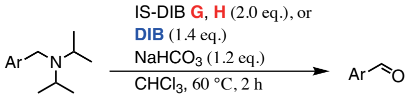
Table 10. Oxidation of alcohols with IS-DIB **G** and **H**.

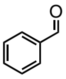
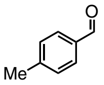
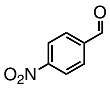
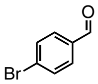
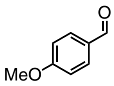
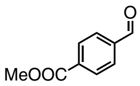
$$\textbf{Alcohol} \xrightarrow[\text{CH}_2\text{Cl}_2\text{ (0.25 M), r.t., Time (h)}]{\text{IS-DIB G, H or DIB (1.5 eq.), TEMPO (10 mol\%)}} \textbf{Aldehyde or Ketone}$$

IS-DIB **G**, **H**, or **DIB**	Aldehyde or Ketone Time (h), Yield (%), [Purity (%)]	
		
IS-DIB **G** IS-DIB **H**	8, 97, [97] 4.5, 99, [99]	9, 99, [99] 10.5, 93, [98]
		
IS-DIB **G** IS-DIB **H**	6, 98, [99] 2, 98, [99]	4, 98, [99] 1.5, 98, [99]
		
IS-DIB **G** IS-DIB **H**	8, 95, [92] 3.5, 97, [99]	6, 98, [98] 6, 99, [99]
		
IS-DIB **G** IS-DIB **H** **DIB**	6, 99, [99] 3, 99, [99] 1.5, 99, [48]	2, 99, [98] 1.5, 94, [99]
		
IS-DIB **G** IS-DIB **H** IS-DIB **A**[a] IS-DIB **B**[a]	4, 98, [99] 2, 98, [99] 4, 99, [98] 2, 99, [99]	18, 91, [88] 12, 84, [83]
		
IS-DIB **G** IS-DIB **H** **DIB**	12, 99, [99] 6, 95, [99] 4.5, 99, [48]	6, 94, [94] 5, 99, [99] 1.5, 97, [48]

[a] Recovered and regenerated IS-DIB was used.

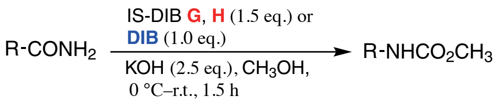
Table 11. Oxidation of *N*,*N*-diisopropylbenzylamines with IS-DIB **G** and **H**.

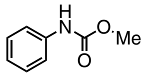
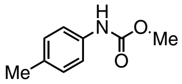
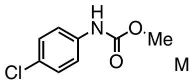
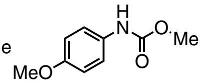
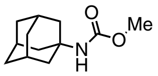
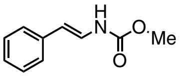


IS-DIB **G**, **H**, or **DIB**	Aldehyde Yield (%), [Purity (%)]	
		
IS-DIB **G** IS-DIB **H** **DIB** IS-DIB **G**[a] IS-DIB **H**[a]	94, [99] 97, [98] 82, [33] 95, [97] 96, [94]	94, [99] 93, [97] 87, [45]
		
IS-DIB **G** IS-DIB **H** **DIB**	92, [99] 93, [98] 88, [45]	91, [99] 92, [97] 87, [40]
		
IS-DIB **G** IS-DIB **H** **DIB**	93, [98] 92, [98] 86, [42]	87, [86] 88, [87] 81, [33]

[a] Recovered and regenerated IS-DIB was used.

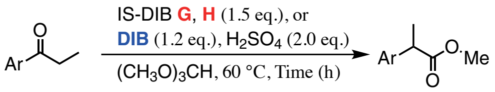
Table 12. Hofmann reaction with IS-DIB **G** and **H**.



IS-DIB G, H, or DIB	Methyl carbamate Yield (%), [Purity (%)]	
		
IS-DIB G	99, [99]	97, [98]
IS-DIB H	99, [99]	98, [99]
DIB	99, [68]	99, [70]
IS-DIB G[a]	99, [99]	
IS-DIB H[a]	99, [99]	
		
IS-DIB G	99, [99]	98, [98]
IS-DIB H	97, [99]	97, [98]
DIB	98, [67]	98, [66]
		
IS-DIB G	99, [99]	97, [99]
IS-DIB H	99, [99]	96, [97]
DIB	99, [65]	98, [66]

[a] Recovered and regenerated IS-DIB was used.

Table 13. Oxidative reaction of propiophenones with IS-DIB **G** and **H**.



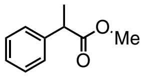
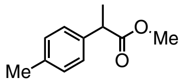
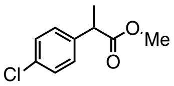
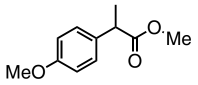
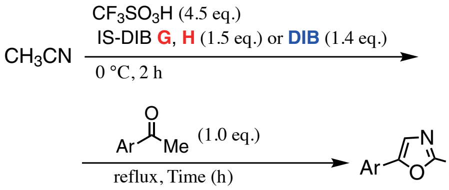
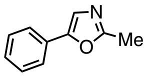
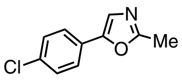
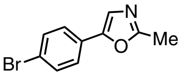
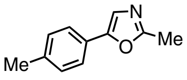
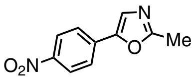
IS-DIB G, H, or DIB	Methyl ester Time (h), Yield (%), [Purity (%)]	
		
IS-DIB G	3, 95, [95]	3, 98, [99]
IS-DIB H	3, 99, [99]	3, 94, [97]
DIB	2, 94, [52]	2, 95, [47]
IS-DIB G[a]	3, 97, [97]	3, 94, [96]
IS-DIB H[a]	3, 96, [96]	3, 94, [97]
		
IS-DIB G	5, 96, [99]	3, 99, [99]
IS-DIB H	5, 95, [98]	3, 95, [97]

Table 14. Formation of oxazoles with IS-DIB **G** and **H**.



IS-DIB G,H, or DIB	Oxazole Time (h), Yield (%), [Purity (%)]	
		
IS-DIB G	5, 93, [95]	5, 92, [93]
IS-DIB H	5, 92, [96]	5, 91, [92]
DIB	3, 91, [38]	3, 94, [40]
IS-DIB G[a]	5, 92, [94]	
IS-DIB H[a]	5, 92, [95]	
		
IS-DIB G	5, 94, [94]	7, 92, [94]
IS-DIB H	5, 93, [93]	7, 90, [90]
DIB	3, 92, [39]	6, 92, [41]
		
IS-DIB G	5, 94, [95]	
IS-DIB H	5, 93, [93]	
DIB	3, 97, [42]	

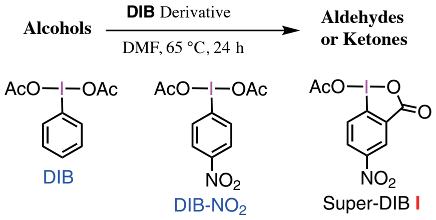
[a] Recovered and regenerated IS-DIB was used.

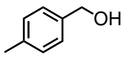
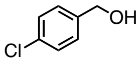
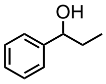
5. Super-DIB

DMP (Dess-Martin Periodinane) [I(V)] is one of the most excellent reagents for the oxidation of alcohols to aldehydes or ketones.[15)] However, it is explosive and therefore, it is very difficult to carry out the oxidation of alcohols with DMP in large preparative scale. To break through this problem, super-DIB **I** [I(III)] was prepared and the oxidation of alcohols was carried out to give the corresponding aromatic aldehydes and ketones in good yields with high purity, as shown in Table 15.[16)] After the reaction, water was added to the reaction mixture, and the product could be obtained by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent. *p*-Nitro-*o*-iodobenzoic acid, co-product, could be also extracted and recovered by chloroform in high yield from the water by acidification. Super-DIB **I** could be regenerated by the treatment with *m*CPBA in acetic acid[13)] and could be reused for the same reactions to give the product in good yield with high purity.

Now, Super-DIB **I** is under way as a commercially available reagent in Tokyo Chemical Industry Co., Ltd.

Table 15. Oxidation of alcohols with Super-DIB **I**.



Alcohol	**DIB** Derivative	Aldehyde or Ketone Yield (%)	[Purity (%)]
	**DIB** (2.0 eq.)	16	[3]
	DIB-NO$_2$ (2.0 eq.)	35	[14]
	Super-DIB **I** (2.0 eq.)	97	[98]
	**DIB** (2.0 eq.)	23	[8]
	DIB-NO$_2$ (2.0 eq.)	35	[15]
	Super-DIB **I** (2.0 eq.)	87	[86]
	**DIB** (2.0 eq.)	20	[5]
	DIB-NO$_2$ (2.0 eq.)	31	[12]
	Super-DIB **I** (2.0 eq.)	87	[86]

Acknowledgement

Financial support in the form of a Grant-in–Aid for Scientific Research (No. 23655142, 20550033) from the Ministry of Education, Culture, Sports, Science, and Technology in Japan, Futaba Memorial Foundation, and Iodine Research Project in Chiba University is gratefully acknowledged.

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Introduction of the author :

Hideo Togo
Professor of Organic Chemistry Division, Graduate School of Science, Chiba University, Japan

Hideo Togo was born in Ibaraki in 1956. He completed his doctoral thesis in 1983, at Tsukuba University. Then, he became a post-doctoral fellow at University of Lausanne in Switzerland, and ICSN (Professor Sir, Derek H. R. Barton) of CNRS in France. He became a research associate in Chiba University in 1989, an associate professor in 1994, and a full professor in 2005. His research interests are organic iodine chemistry and radical chemistry, and green chemistry.

TCI Related Compounds

M2103	IS-Ph$_3$P (**B**) [=1-Methyl-1-[4-(diphenylphosphino)benzyl]pyrrolidinium Bromide]	1g
M2274	IS-MSO (**C**) [=1-Methyl-3-[6-(methylsulfinyl)hexyl]imidazolium *p*-Toluenesulfonate]	1g, 5g
M2321	IS-MS (**E**) [=1-Methyl-3-[6-(methylthio)hexyl]imidazolium *p*-Toluenesulfonate]	1g, 5g