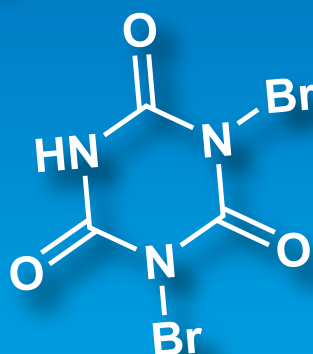
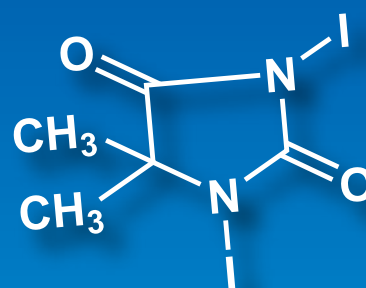
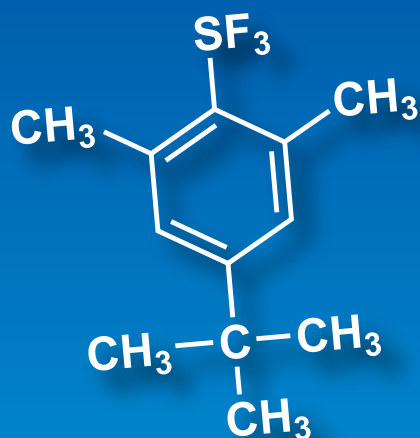


Halogenation Reagents



Fluorinating Agents

Chlorinating Agents

Brominating Agents

Iodinating Agents

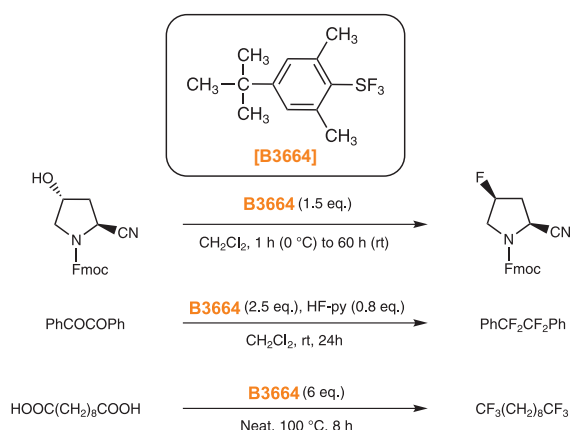
Halogenation Reagents

Halogenation is a basic and fundamental transformation in organic chemistry, and halogenated compounds are of extreme importance as building blocks in organic synthesis.

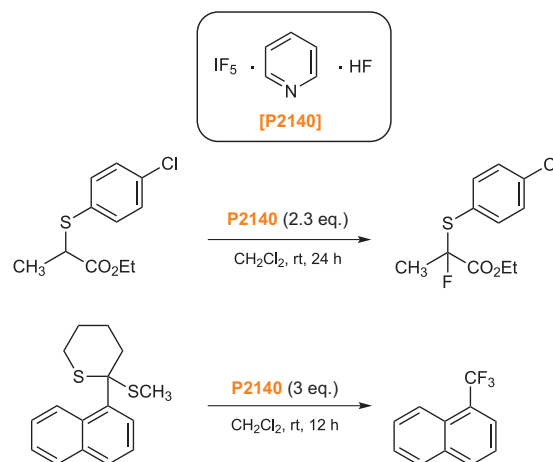
The development of modern coupling reactions, such as the Suzuki-Miyaura and Mizoroki-Heck reactions, have greatly increased the demand for halogenated compounds as starting materials.

On the other hand, introduction of fluorine into a certain position of bioactive compound such as a pharmaceutical and an agricultural chemical may remarkably reduce the toxicity of the compound, or improve the efficiency of medicine. This is due to the structurally mimic and blocking effect characterized by fluorine. In response to this situation, a number of novel halogenation reagents have been developed.

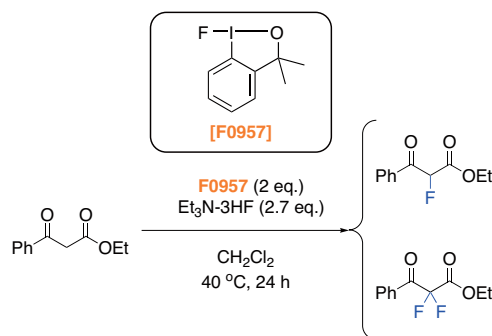
4-*tert*-Butyl-2,6-dimethylphenylsulfur trifluoride (FLUOLEAD™) **[B3664]** is introduced as below: **B3664** is a novel nucleophilic fluorinating agent which was first reported by Umemoto *et al.*¹⁾ Differing from other existing fluorinating agents, such as DAST, **B3664** is a crystalline solid with high thermal stability and less fuming character, which makes it easier to handle. **B3664** fluorinates a hydroxyl or carbonyl group to afford the corresponding fluorinated compounds in good yields.¹⁾



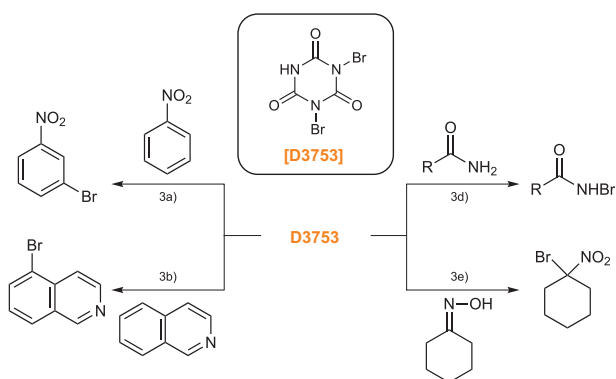
IF_5 -Pyridine-HF (Hara Reagent) **[P2140]** is also a novel fluorinating agent which was first reported by Hara *et al.*²⁾ **P2140** is a crystalline solid reagent with air stability and non-hygroscopicity, and can be used as an alternative reagent to IF_5 which is an unstable liquid in air. **P2140** can be applied to various fluorination reactions of sulfides as follows.



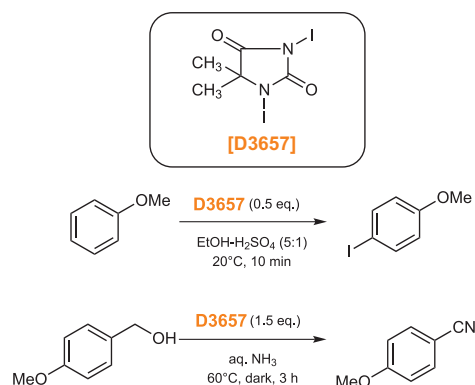
1-Fluoro-3,3-dimethyl-1,2-benziodoxole **[F0957]** is a hypervalent iodine derivative developed by Stuart *et al.*³⁾ **F0957** is stable to air and moisture and used as an electrophilic fluorinating reagent for a α -monofluorination of β -ketoesters in the presence of triethylamine trihydrofluoride.



Dibromoisocyanuric acid (DBI) **[D3753]** which was first reported by Gottardi, is a mild and highly effective brominating agent,^{4a,b,c)} and has superior brominating ability when compared with *N*-bromosuccinimide (NBS), which is frequently used in organic synthesis. For instance, nitrobenzene was converted to 3-bromonitrobenzene in 88% yield with **D3753** in conc. sulfuric acid in 5 min at 20 °C,^{4a)} however, in only 70% yield with NBS in 50% sulfuric acid in 3 h at 85 °C. Thus **D3753** has been widely used as an effective brominating agent.^{4d,e)}



1,3-Diodo-5,5'-dimethylhidantoin (DIH) **[D3657]**, which was first reported by Orazi, is an useful iodinating agent.^{5a)} **D3657** has higher reactivity and selectivity than molecular iodine or *N*-iodosuccinimide (NIS), which are frequently used for iodination reactions. **D3657** reacts smoothly at room temperature with aromatic compounds in the presence of sulfuric acid to give the corresponding iodinate in a high regioselectivity and a high yield.^{5b)} And primary alcohols, and primary, secondary, and tertiary amines can be easily and efficiently converted into the corresponding nitriles in aqueous ammonia using **D3657**.^{5c)} In addition, dimethylhidantoin, which is formed after the reaction, can easily be removed by aqueous extraction.



TCl offers a variety of halogenation reagents other than the two items above. All the products are listed below.

References

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- 2) a) S. Hara, M. Monoi, R. Umemura, C. Fuse, *Tetrahedron* **2012**, *68*, 10145.
b) M. Kunigami, S. Hara, *J. Fluorine Chem.* **2014**, *167*, 101.
c) T. Inoue, C. Fuse, S. Hara, *J. Fluorine Chem.* **2015**, *179*, 48.
d) M. Kunigami, S. Hara, *Carbohydr. Res.* **2015**, *417*, 78.
- 3) G. C. Geary, E. G. Hope, K. Singh, A. M. Stuart, *Chem. Commun.* **2013**, *49*, 9263.
- 4) a) W. Gottardi, *Monatsh. Chem.* **1968**, *99*, 815.
b) W. D. Brown, A. H. Goulliaev, *Synthesis* **2002**, 83.
c) S. C. Virgil, in *Encyclopedia of Reagents for Organic Synthesis*, ed. by L. A. Paquette, John Wiley & Sons, Chichester, **2001**, pp. 1560-1561.
d) Z. P. Demko, M. Bartsch, K. B. Sharpless, *Org. Lett.* **2000**, *2*, 2221.
e) T. R. Walters, W. W. Zajac Jr., J. M. Woods, *J. Org. Chem.* **1991**, *56*, 316.
- 5) a) O. O. Orazi, R. A. Corral, H. E. Bertorello, *J. Org. Chem.* **1965**, *30*, 1101.
b) V. K. Chaikovskii, V. D. Filimonov, A. A. Funk, V. I. Skorokhodov, V. D. Ogorodnikov, *Russ. J. Org. Chem.* **2007**, *43*, 1291.
c) S. Iida, H. Togo, *Tetrahedron* **2007**, *63*, 8274.

Fluorinating Agents

 Nucleophilic
Fluorinating
Agents

P1888	500g	C2204	10g 25g 100g
KHF_2		CsF	
Potassium Hydrogenfluoride CAS RN: 7789-29-9		Cesium Fluoride CAS RN: 13400-13-0	

T2754	5g 25g	T1037	25g 100g	T1339	25g 100g 500g	T1338	25mL 100mL 500mL	T2022	10g
								$(\text{CH}_3\text{CH}_2)_3\text{N} \cdot 3\text{HF}$	
Tetramethylammonium Fluoride Tetrahydrate CAS RN: 17787-40-5		Tetrabutylammonium Fluoride Hydrate CAS RN: 22206-57-1		Tetrabutylammonium Fluoride (70-75% in Water) CAS RN: 429-41-4		Tetrabutylammonium Fluoride (ca. 1mol/L in Tetrahydrofuran) CAS RN: 429-41-4		Triethylamine Trihydrofluoride CAS RN: 73602-61-6	

D5272	1g 5g	P2140	1g 5g	T2026	10g	T2027	10g	T1295	5g 25g
		$\text{IF}_5 \cdot \text{C}_5\text{H}_5 \cdot \text{HF}$		$(\text{CH}_3\text{CH}_2)_4\text{NF} \cdot 3\text{HF}$		$(\text{CH}_3\text{CH}_2)_4\text{NF} \cdot 4\text{HF}$			
DMPU-HF Reagent (HF 65%) CAS RN: 287966-55-6		IF ₅ -Pyridine-HF CAS RN: 2243786-10-7		Tetraethylammonium Fluoride Trihydrofluoride CAS RN: 42539-97-9		Tetraethylammonium Fluoride Tetrahydrofluoride CAS RN: 145826-81-9		Tetrabutylammonium Bifluoride CAS RN: 23868-34-0	

T1635	5g 25g	F0225	5g 25g	D1868	5g 25g 100g	M1573	1g 5g	H0598	25g 100g 500g
								$\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{F})_2\text{CHFCF}_3$	
Tetrabutylammonium Dihydrogen Trifluoride CAS RN: 99337-56-1		2-Fluoro-1-methylpyridinium <i>p</i> -Toluenesulfonate CAS RN: 58086-67-2		DAST CAS RN: 38078-09-0		Morph-DAST CAS RN: 51010-74-3		Ishikawa's Reagent CAS RN: 309-88-6	

B3664	1g 5g	P2398	5g	P2465	1g 5g	T1909	5g 25g	T1592	1g 5g
FLUOLEAD™ CAS RN: 947725-04-4		PyFluor CAS RN: 878376-35-3		Pyrimidine-2-sulfonyl Fluoride CAS RN: 35762-87-9		Tetrabutylammonium Difluorotriphenylsilicate CAS RN: 163931-61-1		Tetrabutylammonium Difluorotriphenylstannate CAS RN: 139353-88-1	

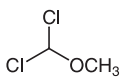
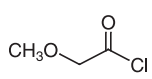
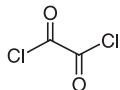
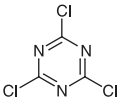
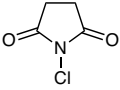
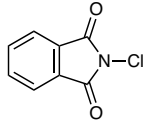
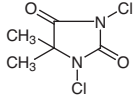
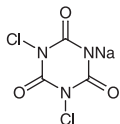
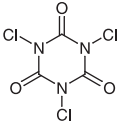
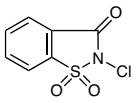

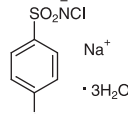
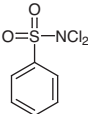
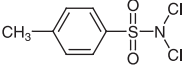
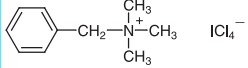
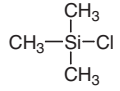
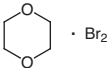

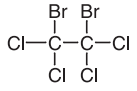
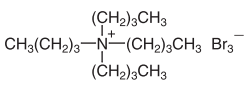
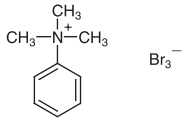
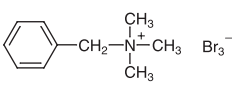
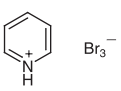
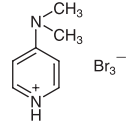
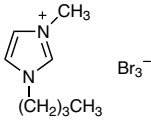
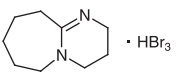
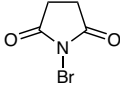
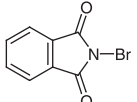
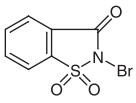
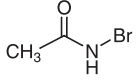
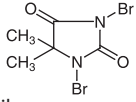
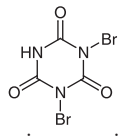
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AlkylFluor™ CAS RN: 2043361-32-4		PhenoFluor™ Mix CAS RN: 1648825-53-9				1-Fluoropyridinium Trifluoromethanesulfonate CAS RN: 107263-95-6		1-Fluoro-2,4,6-trimethylpyridinium Tetrafluoroborate CAS RN: 109705-14-8	

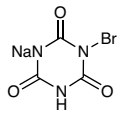
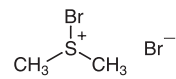
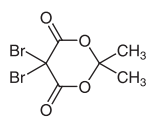
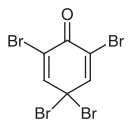
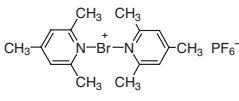
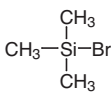

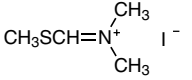
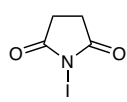
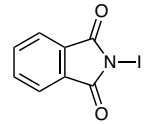
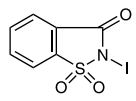
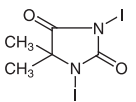
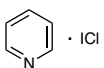
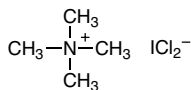
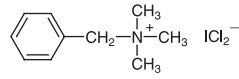
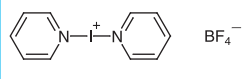
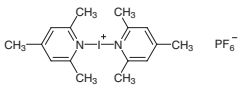
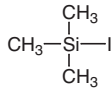
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						$\text{IF}_5 \cdot \text{C}_5\text{H}_5 \cdot \text{HF}$			
1,1'-Difluoro-2,2'-bipyridinium Bis(tetrafluoroborate) CAS RN: 178439-26-4		N-Fluorobenzenesulfonylimide CAS RN: 133745-75-2		F-TEDA-BF ₄ CAS RN: 140681-55-6		IF ₅ -Pyridine-HF CAS RN: 2243786-10-7		1-Fluoro-3,3-dimethyl-1,2-benziodoxole CAS RN: 1391728-13-4	

Chlorinating Agents

Thionyl Chloride CAS RN: 7719-09-7

T2040	500mL	T2048	500mL	M0094	25g 500g
Thionyl Chloride CAS RN: 7719-09-7		Thionyl Chloride (ca. 1mol/L in Dichloromethane) CAS RN: 7719-09-7		Methanesulfonyl Chloride CAS RN: 124-63-0	

T0611 5g 25g $\text{CCl}_3\text{SO}_2\text{Cl}$ Trichloromethanesulfonyl Chloride CAS RN: 2547-61-7	H0362 25g $(\text{CH}_3)_3\text{COCl}$ tert-Butyl Hypochlorite CAS RN: 507-40-4	D1645 25g 250g  Dichloromethyl Methyl Ether CAS RN: 4885-02-3	M0970 25g 100g 500g  Methoxyacetyl Chloride CAS RN: 38870-89-2	O0082 25g 100g 500g  Oxalyl Chloride CAS RN: 79-37-8
C0460 25g 500g  Cyanuric Chloride CAS RN: 108-77-0	C0291 25g 100g 500g  N-Chlorosuccinimide (= NCS) CAS RN: 128-09-6	C0802 25g 500g  N-Chlorophthalimide CAS RN: 3481-09-2	D1783 25g 100g 500g  1,3-Dichloro-5,5-dimethylhydantoin CAS RN: 118-52-5	D1003 25g 500g  Sodium Dichloroisocyanurate CAS RN: 2893-78-9
T0620 25g 500g  Trichloroisocyanuric Acid CAS RN: 87-90-1	C1674 5g 25g  N-Chlorosaccharin CAS RN: 14070-51-0	C0075 25g 100g 500g  Chloramine B Hydrate CAS RN: 127-52-6	C0076 25g 500g  Chloramine T Trihydrate CAS RN: 7080-50-4	D0317 5g 25g  Dichloramine B CAS RN: 473-29-0
D0318 25g 100g 500g  Dichloramine T CAS RN: 473-34-7	B1543 5g  Benzyltrimethylammonium Tetrachloroiodate CAS RN: 121309-88-4	C0306 25mL 100mL 500mL  Trimethylsilyl Chloride CAS RN: 75-77-4		
<h2>Brominating Agents</h2>		B2414 90g 500g Br_2 Bromine CAS RN: 7726-95-6	B2719 5g 25g  Bromine - 1,4-Dioxane Complex CAS RN: 15481-39-7	B0662 25g 500g  Bromotrichloromethane CAS RN: 75-62-7
D1987 25g  1,2-Dibromo- 1,1,2,2-tetrachloroethane CAS RN: 630-25-1	T0038 25g 100g 500g CBr_4 Carbon Tetrabromide CAS RN: 558-13-4	T1284 25g 100g 500g  Tetrabutylammonium Tribromide CAS RN: 38932-80-8	P0928 25g 500g  Trimethylphenylammonium Tribromide CAS RN: 4207-56-1	T1382 5g 25g  Benzyltrimethylammonium Tribromide CAS RN: 111865-47-5
P0825 25g 100g 500g  Pyridinium Bromide Perbromide CAS RN: 39416-48-3	D1787 5g 25g  4-Dimethylaminopyridinium Bromide Perbromide CAS RN: 92976-81-3	B3596 5g  1-Butyl-3-methylimidazolium Tribromide CAS RN: 820965-08-0	D3976 5g  1,8-Diazabicyclo[5.4.0]- 7-undecene Hydrogen Tribromide CAS RN: 138666-59-8	B0656 25g 100g 500g  N-Bromosuccinimide (= NBS) CAS RN: 128-08-5
B1697 5g 25g  N-Bromophthalimide CAS RN: 2439-85-2	B2152 5g 25g  N-Bromosaccharin CAS RN: 35812-01-2	B0530 5g 25g  N-Bromoacetamide CAS RN: 79-15-2	D1265 25g 500g  1,3-Dibromo-5,5-dimethylhydantoin CAS RN: 77-48-5	D3753 5g 25g  Dibromoisocyanuric Acid (= DBI) CAS RN: 15114-43-9

B2148 25g  Monosodium Bromoisocyanurate CAS RN: 164918-61-0	B2553 100mL BBr_3 Boron Tribromide (17% in Dichloromethane, ca. 1mol/L) CAS RN: 10294-33-4	P1743 300g PBr_3 Phosphorus Tribromide CAS RN: 7789-60-8	B3311 5g 25g  Bromodimethylsulfonium Bromide CAS RN: 50450-21-0	D1710 5g 25g  5,5-Dibromomeldrum's Acid CAS RN: 66131-14-4
T1235 5g 25g  2,4,4,6-Tetrabromo-2,5-cyclohexadienone CAS RN: 20244-61-5	B2358 1g 5g  Bis(2,4,6-trimethylpyridine)-bromonium Hexafluorophosphate CAS RN: 188944-77-6	B1087 5mL 25mL 250mL  Trimethylsilyl Bromide CAS RN: 2857-97-8		
<h1>Iodinating Agents</h1>				
I0604 25g 500g I_2 Iodine CAS RN: 7553-56-2	H1221 300mL HI Hydriodic Acid (57%) CAS RN: 10034-85-2	C0936 10g  Carbon Tetraiodide CAS RN: 507-25-5		
C1190 1g 5g $\text{ICH}_2\text{CH}_2\text{Cl}$ 1-Chloro-2-iodoethane CAS RN: 624-70-4	D4340 5g 25g  <i>N,N</i> -Dimethyl- <i>N</i> -(methylsulfanylmethylene)-ammonium iodide CAS RN: 29085-13-0	I0074 5g 25g 100g  <i>N</i> -Iodosuccinimide (= NIS) CAS RN: 516-12-1	I1052 5g 25g  <i>N</i> -Iodophthalimide CAS RN: 20919-42-0	I0784 5g  <i>N</i> -Iodosaccharin CAS RN: 86340-94-5
D3657 5g 25g  1,3-Diiodo-5,5-dimethylhydantoin (= DIH) CAS RN: 2232-12-4	P2086 1g 5g  Pyridine Iodine Monochloride CAS RN: 6443-90-9	T2717 5g  Tetramethylammonium Dichloroiodate CAS RN: 1838-41-1	B1604 5g 25g  Benzyltrimethylammonium Dichloroiodate CAS RN: 114971-52-7	B2539 1g  Bis(pyridine)iodonium Tetrafluoroborate CAS RN: 15656-28-7
B2359 1g 5g  Bis(2,4,6-trimethylpyridine)iodonium Hexafluorophosphate CAS RN: 113119-46-3	I0308 5g 25g  Trimethylsilyl Iodide CAS RN: 16029-98-4			

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