bration curve was obtained for 1-μL injections of seven solutions containing 0.0748–299 ng/μL of **7** and a fixed amount of an internal standard, with peak areas for **7** of 70 100 ± 2400 (3.4%) counts/ng. This range permits quantitation of diastereomer ratios of 4000:1. At higher concentrations of **7**, column overloading caused severe deterioration of the base line, whereas smaller quantities gave irreproducible integrations. By proper adjustment of sample concentrations, diastereomer ratios exceeding 2000:1, the value corresponding to 99.9% de, could easily by demonstrated.

(*R*)-(−)-*N*,*S*-Dimethyl-*S*-phenylsulfoximine (1). A mixture of (−)-**2** (0.516 g, 3.33 mmol), 98% formic acid (10 mL), and paraformaldehyde (0.20 g, 6.67 mmol) was heated under argon at 100 °C in an oil bath. Complete reaction, as indicated by GC analysis, required 36 h. After concentration almost to dryness on a hot plate under a stream of argon, the residue was dissolved in 20 mL of 2 M H_2SO_4, and the solution was washed with two 10-mL portions of methylene chloride. The aqueous phase was then basified with 2 M NaOH and extracted with three 20-mL portions of methylene chloride. The latter extracts were dried over $MgSO_4$, filtered, and evaporated, affording 0.510 g of (−)-**1** (3.02 mmol, 91% yield) as a faintly straw-colored oil. This material was greater than 99% homogeneous by capillary GC analysis, and used without purification as described previously:[17] ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 28.8, 44.1, 127.9, 128.7, 132.1, 138.5; mass spectrum (70 eV), *m*/*z* (relative intensity) 171 (2), 170 (5), 169 (M^+, 45), 154 (95), 141 (18), 125 (38), 106 (100), 77 (98). ^1H NMR and IR data were identical with those reported previously for racemic material.[14] A sample of (−)-**1** was subjected to bulb-to-bulb distillation (bath temperature 120–125 °C, 1 mmHg), affording a colorless oil: $[\alpha]^{25}_D$ −135.9° (*c* 4.60, MeOH).[24]

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Registry No. (−)-**1**, 80482-67-3; (±)-**2**, 81162-81-4; (−)-**2**, 60933-65-5; (+)-**2**, 33903-50-3; (−)-**3**, 35963-20-3; (+)-**3**, 3144-16-9; (±)-**4**, 52363-25-4; (−)-**4**, 50896-19-0; (−)-**5**, 116724-94-8; (+)-**5**, 7044-59-9; **6**, 39637-74-6; **7** (isomer 1), 116724-95-9; **7** (isomer 2), 116836-64-7; **8**, 50635-99-9; **9**, 116724-96-0; (−)-**10**, 79896-06-3; **11**, 116724-97-1.

Supplementary Material Available: Experimental procedures for camphenilone resolution and ee determination and for purification of 10-camphorsulfonic acid (2 pages). Ordering information is given on any current masthead page.

Aromatic Bromination Using BrF with No Friedel–Crafts Catalyst

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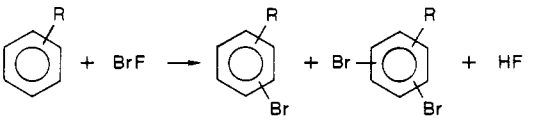
The use of elemental fluorine in organic synthesis has not yet achieved the stage of being a standard procedure, but on the other hand it is not the frightening proposition it used to be until recently. It can serve as a source for fluorine radicals,[1] electrophilic fluorine,[2] and nucleophilic fluorine generated in situ.[3] But elemental fluorine is more than that. Recently, we have shown that it can serve as a vehicle for performing difficult chemical transformations for the preparation of fluorine-free compounds. Thus, for example, one can perform epoxidations,[4] hydroxylation of heterocycles,[5] bromination and chlorination of pyridine derivatives,[6] iodinations,[7] and more. In this study, we report the use of BrF as an electrophilic aromatic bromination agent.

Brominations with bromine of activated rings occur readily, but rings bearing deactivating substituents require large amounts of Friedel–Crafts catalysts, which present both disposal as well as safety problems. The high reaction temperatures required, the yields of which often do not exceed 70–80%, and the loss of one bromine atom through the inevitable generation of HBr are all additional problems. These limitations are magnified when dibromination is the goal of the reaction.

The main role of any catalyst in aromatic electrophilic bromination is to polarize the reagent in such a way that the bromine atom will be as positive as possible, usually using metals with empty low energy D orbitals. Many other sources for positive bromine, such as NaOBr, are not very soluble in organic solvents and therefore of little use. We have searched for a simple and yet soluble molecule in which the bromine is highly polarized by being attached to a strongly electronegative moiety. Since fluorine is the most electronegative element, BrF seemed to be an ideal candidate.

Bromine monofluoride has been the subject of several studies conducted by inorganic chemists. It could not be obtained in a pure form, but Naumann successfully isolated and fully characterized its complex with pyridine.[9] A mixture of Br_2 and BrF_3 has also been used on several occasions for adding the elements of Br and F to various olefins.[10] We adopted a different approach. Passing fluorine through a cold suspension of bromine in trichlorofluoromethane resulted in the formation of BrF but, because of its tendency to disproportionate to BrF_3 and Br_2, we did not attempt purification or isolation but used it directly for organic synthesis. Thus, BrF adds to many types of double bonds[8] as well as acetylenes[3a] to produce the corresponding adducts in good yields.

We report here the use of BrF for electrophilic bromination and dibromination of a broad spectrum of aromatic compounds.[11] The method is general, addition of catalyst is not required,[12] and it offers excellent yields, short reaction times, and very mild conditions, thus reducing or completely eliminating most of the problems associated with present methods.



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(12) It is possible that the HF present in the reaction mixture has a similar effect on the BrF as does the added EtOH, forming a potential highly ionic specie—$Br^+HF_2^-$.

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When a slight excess of BrF reacted with toluene, even at −75 °C, rapid disappearance of starting material was observed, but a mixture of many products was obtained. Eventually, we found that, as with other reactions of BrF,[3a,8] the addition of a small amount of ethanol has a marked taming effect on the reagent and most of the radical reactions were suppressed. Thus, toluene was converted almost quantitatively to a mixture of 2- and 4-bromotoluene in a 1:1 ratio. Apart from supplying the polar environment conducive to ionic type reactions, ethanol or similar soluble protic solvents also solvates the fluorine in BrF, thus lowering its reactivity. Using a 2-fold excess of BrF afforded 2,4-dibromotoluene in good yield. *p*-Xylene and anisole also gave mono- and dibrominated products, while with compounds in which the ortho position was less accessible, e.g. *tert*-butylbenzene, phenyl acetate, and bromobenzene, only the *p*-bromo derivatives were obtained in yields exceeding 90%.

The full advantage of BrF as an electrophilic brominating agent comes to light with deactivated aromatic rings. After a 5-min reaction at −40 °C, acetophenone was fully converted to 3-bromoacetophenone. With the less sterically demanding benzonitrile, the yield of the 3-bromo derivative dropped to 80%, since an additional 10% of the 2-bromobenzonitrile was also obtained. Even with this deactivated ring, a 1-h reaction with an excess of BrF was sufficient to produce 2,5-dibromobenzonitrile in greater than 80% yield, without the assistance of any Friedel–Crafts catalyst. It is instructive to compare these conditions with those reported in the literature[13] (3.5 mol/equiv $AlCl_3$, high temperature, 6 h) to appreciate the ease of bromination with BrF. Although quite reactive, this reagent is not a strong oxidizer and it reacted with benzaldehyde to give 3-bromobenzaldehyde in 95% yield. Dibromination with excess reagent also did not affect the aldehyde moiety and, after 50 min, 2,5-dibromobenzaldehyde was obtained in 90% yield. The spectral data of this compound is in excellent agreement with the proposed structure but, since its preparation has been reported only once before by amidomethylation of *p*-dibromobenzene and no physical data were reported,[14] it was also identified by oxidation to 2,5-dibromobenzoic acid.[13] Similar behavior was found with ethyl benzoate and nitrobenzene. Both were monobrominated at the meta position in practically quantitative yields in a matter of 2 h. They too could be dibrominated to the corresponding 2,5-dibromo derivatives.

The reaction also proceeded smoothly with aromatic compounds possessing both an electron-withdrawing and an electron-donating group. Methyl 4-methylbenzoate and 4-methylnitrobenzene reacted with a slight excess of BrF at −40 °C for about an hour and were converted almost quantitatively to the corresponding 3-bromo derivatives. The power of this reagent is perhaps best demonstrated by the bromination of dinitrobenzene. Previously, direct bromination was achieved in moderate yield by using silver trifluoromethanesulfonate, bromine, and concentrated sulfuric acid for 16 h at 90 °C.[15] In our case, a straightforward reaction for 45 min at −45 °C sufficed to produce 3,5-dinitrobromobenzene in excellent yield.

In conclusion, we have shown that fluorine, which can be used for electrophilic aromatic fluorinations,[16] can also be used for electrophilic aromatic brominations. The regiospecificity of the bromination does not differ much from other aromatic electrophilic bromination methods, but the ease and the efficiency of the method, which does not require any catalyst, can hardly be matched.

Table I

starting material	product (yield, %)	molar equiv BrF:subst	react time (min)
$C_6H_5CH_3$	*o*-$CH_3C_6H_4Br$ (47) *p*-$CH_3C_6H_4Br$ (47)	1.1	10
$C_6H_5CH_3$	2,4-$Br_2C_6H_3CH_3$ (80)	2.1	20
p-$(CH_3)_2C_6H_4$	2,5-$(CH_3)_2C_6H_3Br$ (90)	1.1	5
p-$(CH_3)_2C_6H_4$	1,4-$Br_2C_6H_2$-2,5-$(CH_3)_2$ (70)	2.1	5
t-BuC_6H_5	*p*-*t*-BuC_6H_4Br (89)	1.1	5
$MeOC_6H_5$	*o*-$MeOC_6H_4Br$ (18) *p*-$MeOC_6H_4Br$ (76)	1.1	5
$MeOC_6H_5$	2,4-$Br_2C_6H_3OMe$ (65)[18]	2.1	5
$AcOC_6H_5$	*p*-$AcOC_6H_4Br$ (95)	1.1	15
AcC_6H_5	*m*-AcC_6H_4Br (92)	1.1	5
BrC_6H_5	*p*-BrC_6H_4Br (100)	1.4	30
NCC_6H_5	*m*-NCC_6H_4Br (81) *o*-NCC_6H_4Br (10)	1.45	15
NCC_6H_5	2.5-$Br_2C_6H_4CN$ (82)[13]	4	60
$OHCC_6H_5$	*m*-$OHCC_6H_4Br$ (94) 2,5-$Br_2C_6H_3CHO$ (5)	1.45	5
$OHCC_6H_5$	2,5-$Br_2C_6H_3CHO$ (90)[a] *m*-$OHCC_6H_4Br$ (5)	3	50
$EtOOCC_6H_5$	*m*-$EtOOCC_6H_4Br$ (95) 2,5-$Br_2C_6H_3COOEt$ (5)	1.5	120
$EtOOCC_6H_5$	2,5-$Br_2C_6H_3COOEt$ (72)[b]	4	30
$O_2NC_6H_5$	*m*-$O_2NC_6H_4Br$ (95)	1.7	120
$O_2NC_6H_5$	2,5-$Br_2C_6H_3NO_2$ (70)	4.5	45
p-$MeC_6H_4NO_2$	2-Me-5-$O_2NC_6H_3Br$ (98)	1.4	60
p-MeC_6H_4COOMe	3-Br-4-Me-C_6H_3COOMe (95)[c]	1.4	40
m-$(NO_2)_2C_6H_4$	3,5-$(O_2N)_2C_6H_3Br$ (93)[d]	7	45

[a] mp 74–75 °C; ^1H NMR 10.25 (1 H, s), 8.0–7.5 ppm (3 H, Ar); see also ref 14. [b] ^1H NMR 8.2–7.13 (3 H, Ar), 4.32 (2 H, q, J = 7.5 Hz), 1.38 ppm (3 H, t, J = 7.5 Hz); the compound was also identified through hydrolysis to the corresponding acid, mp 154 °C (ref 13). [c] The identification of this compound was completed by saponification to the known commercial acid. [d] mp 75–76 °C; ^1H NMR was identical with the one reported in the literature (ref 19).

Experimental Section

^1H NMR spectra were recorded with a Bruker WH-360 spectrometer at 360 MHz with $CDCl_3$ as a solvent and Me_4Si as internal standard. Mass spectra were measured with a Du Pont 21-491B spectrometer. IR spectra were recorded on a Perkin-Elmer 177 spectrometer.

General Fluorination Procedure. A description of the setup and the procedure for working with elemental fluorine has previously been described.[17] It should, however, be remembered that the reactions described herein should be conducted with care since F_2 is a strong oxidant. If elementary precautions are taken, however, work with fluorine and its derivatives is safe and relatively simple and, so far in the past, we have never had an accident while working with it.

Preparation and Reaction of BrF. For preparation, behavior, and properties of BrF in general, see ref 8. For brominations of the compounds in Table I, the following procedure was used. A suspension of 1.5 mL of Br_2 (about 30 mmol) in 100 mL of $CFCl_3$ was prepared at −78 °C. Nitrogen-diluted (10%) F_2 was

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bubbled through the suspension until the red color of Br_2 disappeared and was replaced by a pale yellow suspension of BrF. From previous work and from independent experiments with olefins, it was concluded that the yield of BrF is practically quantitative in respect to both bromine and fluorine. The amount of ethanol which was then added depended on the substrate to be brominated or dibrominated. For best results with activated aromatic rings, the ratio of EtOH:BrF should be kept around 3, while for monobromination of deactivated compounds this ratio was lowered to 2. For dibromination of the latter type of compounds, it was further lowered to 1 to 1.5 and, with the most difficult case of 1,3-dinitrobenzene, this ratio was only 0.66. In all cases, the addition of the EtOH dissolved the BrF, forming a clear reddish solution. The aromatic substrate (26–27 mmol) was dissolved in a minimum amount of precooled $CHCl_3$ and added in one portion to the reaction vessel. The reaction mixture with the activated compounds was kept at −78 °C, while with the deactivated ones at −40 °C. The reactions were monitored by GC and stopped when practically full conversion was achieved. The mixture was then poured into dilute thiosulfate solution and the organic layer was washed with water and $NaHCO_3$ until neutral, dried over $MgSO_4$, and evaporated. For products commercially available, a direct comparison with authentic samples was made. For compounds which are only described in the literature, all the physical and spectral properties were in complete agreement with the structure and the data published.

Registry No. BrF, 59680-92-1; $C_6H_5CH_3$, 108-88-3; *p*-$(CH_3)_2C_6H_4$, 106-42-3; *t*-BuC_6H_5, 98-06-6; $MeOC_6H_5$, 100-66-3; $AcOC_6H_5$, 122-79-2; AcC_6H_5, 98-86-2; BrC_6H_5, 108-86-1; NCC_6H_5, 100-47-0; $OHCC_6H_5$, 100-52-7; $EtOOCC_6H_5$, 93-89-0; $O_2NC_6H_5$, 98-95-3; *p*-$MeC_6H_4NO_2$, 99-99-0; *p*-MeC_6H_4COOMe, 99-75-2; *m*-$(NO_2)_2C_6H_4$, 99-65-0; *o*-$CH_3C_6H_4Br$, 95-46-5; *p*-$CH_3C_6H_4Br$, 106-38-7; 2,4-$Br_2C_6H_3CH_3$, 31543-75-6; 2,5-$(CH_3)_2C_6H_3Br$, 553-94-6; 1,4-$Br_2C_6H_2$-2,5-$(CH_3)_2$, 1074-24-4; *p*-*t*-BuC_6H_4Br, 3972-65-4; *o*-$MeOC_6H_4Br$, 578-57-4; *p*-$MeOC_6H_4Br$, 104-92-7; 2,4-$Br_2C_6H_3OMe$, 21702-84-1; *p*-$AcOC_6H_4Br$, 1927-95-3; *m*-AcC_6H_4Br, 2142-63-4; *p*-BrC_6H_4Br, 106-37-6; *m*-NCC_6H_4Br, 6952-59-6; *o*-NCC_6H_4Br, 2042-37-7; 2,5-$Br_2C_6H_4CN$, 57381-41-6; *m*-$OHCC_6H_4Br$, 591-20-8; 2,5-$Br_2C_6H_3CHO$, 74553-29-0; *m*-$EtOOCC_6H_4Br$, 24398-88-7; 2,5-$Br_2C_6H_3COOEt$, 76008-76-9; *m*-$O_2NC_6H_4Br$, 585-79-5; 2,5-$Br_2C_6H_3NO_2$, 3460-18-2; 2-Me-5-$O_2NC_6H_3Br$, 7745-93-9; 3-Br-4-Me-C_6H_3COOMe, 104901-43-1; 3,5-$(O_2N)_2C_6H_3Br$, 18242-39-2; Br_2, 7726-95-6; 2,5-$Br_2C_6H_3COOH$, 610-71-9; 3-Br-4-Me-C_6H_3COOH, 7697-26-9.

Facile Diacylation of Glycidyl Tosylate. Chiral Synthesis of Symmetric-Chain Glycerophospholipids

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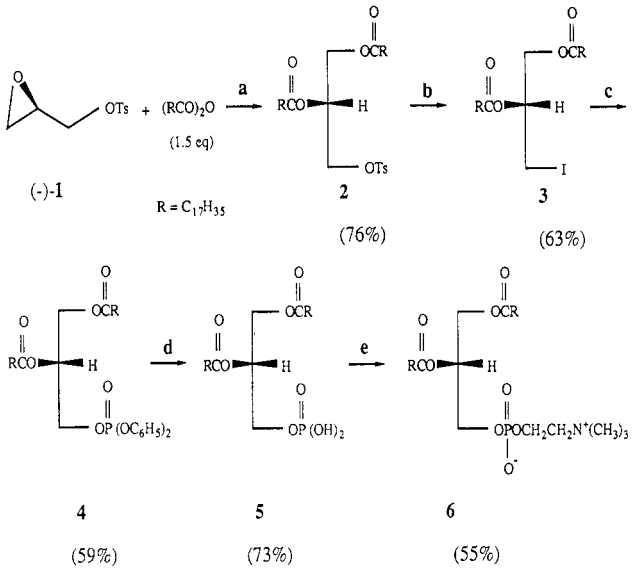
The chemical synthesis of optically active phospholipids involves the extensive use of protecting groups and requires considerable expertise in synthetic lipid chemistry. For example, the synthesis of enantiomerically pure mixed-chain glycerophospholipids from 1,2-isopropylidene-*sn*-3-glycerol or 2,3-isopropylidene-*sn*-1-glycerol entails the use of three protecting groups.[1] Since chiral epoxides have been found to be valuable intermediates in the synthesis of many optically active natural products, we have sought to prepare the natural 1,2-diacyl-*sn*-3-glycerophosphocholines by Lewis acid catalyzed ring opening of chiral epoxides. Conversion of racemic glycidol to racemic ester-linked glycerols has been reported,[2] and optically active glycidol was used as the precursor of triacylglycerols.[3] The preparation of a monoacylglycerol from optically active glycidol in the presence of titanium(IV) isopropoxide was reported during the course of our investigations; titanium-assisted nucleophilic epoxide opening with stearic acid gave glycidyl stearate in low yield.[4]

Scheme I[a]



[a] (a) BF_3·Et_2O, CH_2Cl_2, 40 °C, 2 h; (b) NaI (excess), acetone, reflux, 24 h; (c) $AgOP(O)(OPh)_2$, benzene, 80 °C, 4 h; (d) H_2/PtO_2, cyclohexane–HOAc, 1:1, 4 h; (d) $HOCH_2CH_2N^+(CH_3)_3$ OTs^-, Cl_3C-CN, Py, 50 °C, 48 h.

We report here an efficient enantiospecific synthesis of 1,2-diacyl-*sn*-3-glycerophosphocholines from (*R*)-(−)-glycidyl tosylate (1). The synthetic usefulness of the tosyl derivative of glycidol is demonstrated by (a) facile diacylation in the presence of BF_3 etherate, and (b) conversion of the 3-tosyl group into the 3-phosphocholine moiety, with retention of configuration at C-2 in both steps. Since allyl alcohol is readily converted to either (*R*)- or (*S*)-glycidyl tosylate by asymmetric epoxidation and in situ derivatization,[5] the procedures described here are also applicable to the preparation of phospholipids with the *sn*-1 configuration.

The attachment of two identical fatty acid ester linkages simultaneously to *sn*-glycero-3-phosphocholine or its $CdCl_2$ complex, to give symmetric-chain diacylphosphocholines, has been achieved by well-known methods.[6] In the absence of efficient catalysts, these methods suffer from the need to use severe reaction conditions such as high temperature and long times to obtain a homogeneous mixture

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