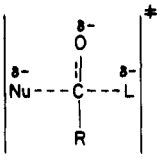
in the "reacting" conformation of the ester oxyanion (eq 9).

Speculations on a Concerted Mechanism of Acyl Group Transfer. Concerted mechanisms of acyl group transfer almost certainly exist where the tetrahedral adduct is too unstable to exist as a discrete molecule. The transition-state geometry for these reactions will be close to that of the tetrahedral structure. "Concerted" in this case does not mean that entering and leaving bonds are equally formed or broken in the transition state but that bond-making and bond-breaking take place in unison. Such a process is called synchronous by Dewar.[18] Another geometry has been neglected for some 20 years, and this involves attack of the nucleophile in a plane with the trigonal ester to give a sort of "square-planar" transition state (**9**). The attacking nucleophile essentially donates



9

its electrons into the antibonding orbital to the breaking C–L bond. The similarity of the central R–C–O grouping to an acylium ion configuration prompted us to enquire of the existence of such a mechanism in the present 4-hydroxybenzoate elimination reactions. The stabilization effected by the 4-oxyanion is sufficient to cause the reaction to proceed via a discrete unsaturated intermediate.[13] That is, the nucleophile and leaving group bonds in structure **9** have zero strength. Electronic factors stabilizing structure **9** will also stabilize either the transition state for the E1cB path or that for the $B_{Ac}2$ mechanism. We tried to disfavor the $B_{Ac}2$ mechanism in a reaction that could not involve the E1cB mechanism by increasing steric requirements for the tetrahedral adduct. Mesitoate hydrolysis in alkali has a β_L which, despite the scatter (Figure 3), is well accommodated by the value expected for $B_{Ac}2$ attack by the hydroxyl ion.[14a] The test for the occurrence of a mechanism involving significant leaving bond cleavage as in **6** is a much more negative β_L than in the $B_{Ac}2$ mechanism. Clearly, in this simple case the amount of steric retardation (structures **6a** and **6b**) caused by the dimethyl groups ortho to the ester is not sufficient to reduce the reactivity of the $B_{Ac}2$ mechanism to a level that allows the "square-planar" one operate. The decrease in reactivity caused by the steric requirements is only about 1000-fold comparing the alkaline hydrolysis rate constants for the 2,4-dinitrophenyl esters of 4-methoxybenzoic acid[13] and 4-methoxy-2,6-dimethylbenzoic acid (Table III).

Acknowledgment. We thank the CNR and Ministero della Pubblica Istruzione (Italy) and NATO (RG 115.80) for support of this work. Part of the work was carried out during tenure of a Ciba-Geigy Senior Fellowship (A.W.).

Registry No. 2,4-Dinitrophenyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, 95741-32-5; 2,4-dinitrophenyl 2,6-dimethyl-4-hydroxybenzoate, 87513-48-2; 2,4-dinitrophenyl 3-methyl-4-hydroxybenzoate, 95741-33-6; 2,4-dinitrophenyl 4-hydroxybenzoate, 83187-56-8; 2,4-dinitrophenyl 3-methoxy-4-hydroxybenzoate, 95741-34-7; 2,4-dinitrophenyl 3-chloro-4-hydroxybenzoate, 95741-35-8; 2,4-dinitrophenyl 3,5-dimethoxy-4-hydroxybenzoate, 95741-36-9; 2,4-dinitrophenyl mesitoate, 95741-37-0; 2,4-dinitro-6-methylphenyl mesitoate, 95741-38-1; 2,6-dinitrophenyl mesitoate, 95741-39-2; 2-chloro-4-nitrophenyl mesitoate, 95741-40-5; 4-chloro-2-nitrophenyl mesitoate, 95741-41-6; 4-nitrophenyl mesitoate, 70076-07-2; 3-nitrophenyl mesitoate, 95741-42-7; 4-chlorophenyl mesitoate, 95741-43-8; 2,4-dinitrophenyl 4-methoxy-2,6-dimethylbenzoate, 87513-49-3; mesitoic acid, 480-63-7; 2,6-dimethyl-4-(benzyloxy)bromobenzene, 95741-44-9; 3,5-dimethyl-4-hydroxybromobenzene, 2374-05-2; benzyl chloride, 100-44-7; 2,6-dimethyl-4-benzyloxybenzoic acid, 95741-45-0; 2,6-dimethyl-4-hydroxybenzoic acid, 75056-97-2; mesitoic anhydride, 5745-51-7.

Supplementary Material Available: Tables of analytical data and force-field calculations (4 pages). Ordering information is given on any current masthead page.

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Oxidatively Assisted Nucleophilic Substitution of Iodine in Alkyl Iodides by Nucleofugic Anions

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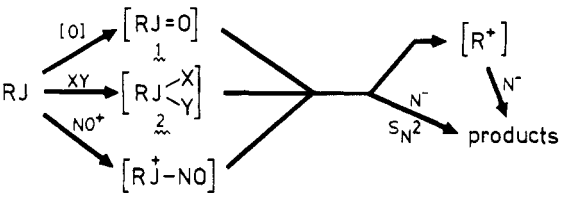
The reaction of alkyl iodides with chlorine or nitronium tetrafluoroborate in the presence of salts of perchloric or substituted sulfonic acids gave alkyl perchlorates or sulfonates as principal products. Some mechanistic aspects of this new reaction are discussed.

The oxidative nucleophilic substitution of iodine in alkyl iodides was first reported in 1905[1] and has received considerable attention in recent literature.[2-15] Effective oxidants for the reaction include Cl_2 and Br_2,[2,3] HNO_3,[4] N_2O_5,[5] $AcONO_2$,[5,6] $NOBF_4$,[7] NO_2BF_4,[8] $K_2Cr_2O_7$,[4a] $KMnO_4$,[4a]

Chart I



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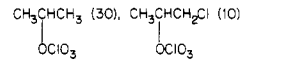
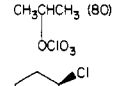
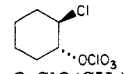
0022-3263/85/1950-1872$01.50/0

Table I. Reaction Conditions and Yields of Products of Deiodination

alkyl iodide	oxidant (molar equiv)[a]	salt (molar equiv)[a]	solvent	temp, °C	time, h	products (yield, %)
CH_3I	Cl_2 (2)	Bu_4NClO_4 (1)	$CDCl_3$	−78	0.1	CH_3ClO_4 (30),[b] CH_3Cl(27)
	H_5IO_6 (2)	Bu_4NClO_4 (1)	$CDCl_3$	40	5	CH_3ClO_4 (30),[b] CH_3OH (40)
	NO_2BF_4 (1.5)	Bu_4NClO_4 (1)	$CDCl_3$	20	15	CH_3ClO_4 (85)[b]
	Cl_2 (2)	Bu_4NOMs (1.5)	$CHCl_3$	−78	0.1	CH_3OMs (36)
	Cl_2 (2)	Bu_4NOTs (1.5)	$CHCl_3$	−78	0.1	CH_3OTs (35)
$C_6H_{13}I$	Cl_2 (2)	$LiClO_4$ (5)	AcOEt	−78	0.1	$C_6H_{13}ClO_4$ (65), $C_6H_{13}Cl$ (13)
	Br_2 (1)	$LiClO_4$ (5)	AcOEt	0	0.5	$C_6H_{13}ClO_4$ (30), $C_6H_{13}Br$ (60)
	m-ClC_6H_4COOOH (1.5)	$LiClO_4$ (5)	AcOEt	0	1	$C_6H_{13}ClO_4$ (40)[c]
	H_5IO_6 (2)	$LiClO_4$ (5)	AcOEt	40	2	$C_6H_{13}ClO_4$ (45), $C_6H_{13}OH$ (22)
	$PhI(OCOCF_3)_2$ (1)	$LiClO_4$ (5)	AcOEt	20	3	$C_6H_{13}ClO_4$ (50), $C_6H_{13}OCOCF_3$ (35)
	PhIOHOTs (1)	$LiClO_4$ (5)	AcOEt	20	2	$C_6H_{13}ClO_4$ (40), $C_6H_{13}OTs$ (5)
	NO_2BF_4 (2)	$LiClO_4$ (5)	AcOEt	20	10	$C_6H_{13}ClO_4$ (92)
	Cl_2 (2)	Bu_4NOTf (1)	CH_2Cl_2	−78	0.1	$C_6H_{13}OTf$ (55), $C_6H_{13}Cl$ (21)
	Cl_2 (2)	Bu_4NOSO_2F (1)	CH_2Cl_2	−78	0.1	$C_6H_{13}OSO_2F$ (47), $C_6H_{13}Cl$ (18)
	Cl_2 (2)	Bu_4NOMs (1)	$CHCl_3$	−78	0.1	$C_6H_{13}OMs$ (25), $C_6H_{13}Cl$ (20)
	Cl_2 (2)	Bu_4NOTs (1)	$CHCl_3$	−78	0.1	$C_6H_{13}OTs$ (28), $C_6H_{13}Cl$ (20)
	Cl_2 (2)	$LiClO_4$ (5)	AcOEt	−78	0.1	
	NO_2BF_4 (1.5)	Bu_4NClO_4 (1)	$CHCl_3$	20	5	
	Cl_2 (2)	$LiClO_4$ (5)	AcOEt	−78	0.1	 (20)[c]
$I(CH_2)_6I$	NO_2BF_4 (3)	$LiClO_4$ (5)	AcOEt	0	5	$O_3ClO(CH_2)_6OClO_3$ (90)
CH_2I_2	NO_2BF_4 (5)	$LiClO_4$ (5)	CH_2Cl_2	20	24	$CH_2(OClO_3)_2$ (96)
$PhCOCH_2I$	NO_2BF_4 (1.5)	$LiClO_4$ (2)	CH_2Cl_2	20	15	$PhCOCH_2OClO_3$ (78)
ICH_2COOH	NO_2BF_4 (1.5)	$LiClO_4$ (2)	CH_2Cl_2	20	24	O_3ClOCH_2COOH (30)
ICH_2COOCH_3	Cl_2 (2)	$LiClO_4$ (5)	AcOEt	−78	0.25	$O_3ClOCH_2COOCH_3$ (35), $ClCH_2COOCH_3$ (60)
	NO_2BF_4 (1.5)	$LiClO_4$ (2)	CH_2Cl_2	20	24	$O_3ClOCH_2COOCH_3$ (92)

[a] Equivalent per equivalent of iodide. [b] Established by ^1H NMR. [c] Reaction mixture contains also some unidentified products. [d] Reaction mixture contains also some unidentified chlorides.

Cl_2O_7,[9] $ClOClO_3$,[10] Cl_2O,[11] $(FSO_2O)_2$,[12] $I(CO_2CF_3)_3$,[13] $PhI(CO_2CF_3)_2$,[14] and m-$ClC_6H_4CO_3H$.[15] The alkyl iodides are converted principally into products of either nucleophilic substitution or elimination,[2-15] depending on the structure and reaction conditions. Oxidation of alkyl iodides with m-chloroperoxybenzoic acid has been studied thoroughly[15] because it is a mild and efficient method for deiodination, and it can be considered as a model for the bioactivation of organic halides via halogen oxidation to a hypervalent state.[15b]

The formation of hypervalent organoiodide intermediates, such as alkyliodoso compounds 1,[15] complexes of type RIX_2 2,[2,3] and other derivatives of I^{1+} and I^{3+}, has also been reported.[3-15] Some of the principal pathways are summarized in Chart I. Polyvalent aryl iodine compounds of type 1 or 2 are well-known,[16] but their alkyl analogues are extremely unstable, with rare exceptions,[17] even at low temperatures.[3,15]

The reaction of *tert*-alkyl iodides proceeds via unimolecular formation of carbocationic (or the corresponding ion pair) intermediates.[3] For primary and secondary alkyl iodides both S_N2 and S_N1 processes have been considered.[15] Groups containing hypervalent iodine (e.g., $-IBr_2$[3]) are among the best nucleofugic (leaving) groups.[18] For example, normally unreactive 1-iodonorbornane can be readily transformed into the corresponding bromide via a cationic intermediate.[3]

We have studied the competitive participation of nucleofugic anions, such as ClO_4^-, FSO_3^-, $CF_3SO_3^-$, and TsO^-, in the interception of carbocationic intermediates in the presence of other nucleophiles.[19-21] In such reactions as

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electrophilic addition to olefins,[19] acid-catalyzed epoxide ring opening,[20] and deamination of alkyl amines,[21] these nucleofugic anions, which have been considered as weak nucleophils, compete effectively with such normal nucleophiles as Hal^-, AcO^-, AcOH, in the final step of the reactions.[22]

In preliminary communications,[23] we reported that oxidative deiodination can also be applied to the competitive binding of nucleofugic anions (eq 1). The purpose of the present paper is to discuss these processes in detail and to demonstrate their synthetic potential.

$$RJ + LiClO_4 \xrightarrow{[oxidant]} ROClO_3 \qquad (1)$$

Results and Discussion

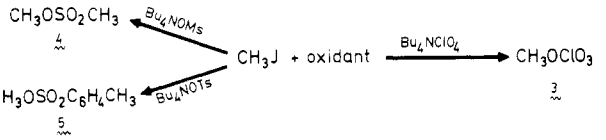
The reactions investigated are represented by eq 2, where Y^- is the nucleofugic anion. The study included

$$RJ + M^+Y^- \xrightarrow{[oxidant]} RY \qquad (2)$$

$Y = ClO_4$; CF_3SO_3; FSO_3; TsO; MsO;

primary mono- and diiodoalkanes, secondary alkyl iodides, and compounds of the structure ICH_2COR. Oxidants used included Cl_2, Br_2, m-$ClC_6H_4CO_3H$, H_5IO_6, NO_2BF_4, $PhI(OCOCF_3)_2$,[14] and PhI(OH)OTs.[24] The choice of salts containing nucleofugic anions was dictated by their solubility in common organic solvents, and we found that $LiClO_4$ and tetrabutylammonium sulfonates met this requirement. Reaction products were isolated and purified chromatographically, and identified by their ^1H NMR spectra. Experimental details and the yields of products are summarized in Table I.

Reactions of Methyl and *n*-Hexyl Iodides. These two primary alkyl iodides were used to study the effectiveness of different oxidants and various reaction conditions. Reactions of CH_3I with a number of oxidants in the presence of tetrabutylammonium salts of perchloric and sulfonic acids gave methyl perchlorate (**3**) or methyl sulfonates **4** or **5**. The reaction initiated with H_5IO_6 required rather high temperatures (40–50 °C) and gave a mixture of **3** and methanol (4:1). The reaction with Cl_2 proceeded quite rapidly at −78 °C but gave methyl chloride in addition to **3** (1:1). The best yield (85%) of **3** was obtained with NO_2BF_4 as the oxidant; the reaction proceeded at room temperature but required 10–15 h for completion.

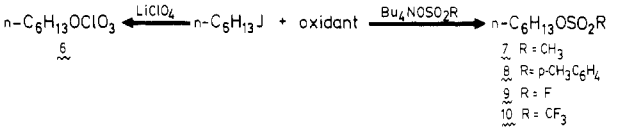


The best yields of *n*-hexyl perchlorate (**6**, 60–90%) from *n*-hexyl iodide were also obtained with Cl_2 or NO_2BF_4. The reaction with Cl_2 proceeded rapidly, but **6** was accompanied by 1-chlorohexane. The reaction with NO_2BF_4 required a relatively long time but gave pure **6** in a 92% yield.

In view of these results, only Cl_2 or NO_2BF_4 was used as the oxidant in the reactions of the other alkyl iodides.

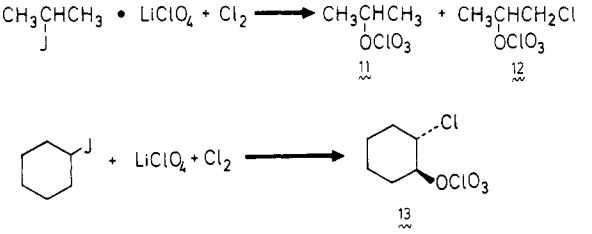
In contrast to our observations, a recent study[15a] of the deiodination of 1-iodooctane by m-$ClC_6H_4CO_3H$ in the presence of $LiClO_4$ did not report formation of *n*-octyl perchlorate.

Reactions of 1-iodohexane assisted with Cl_2 in the presence of tetrabutylammonium salts of methanesulfonic,



p-toluenesulfonic, fluorosulfonic, and triflic acids gave the corresponding sulfonates **7**–**10**. The formation of fluorosulfonate **9** and triflate **10** is remarkable because of the powerful nucleofugic nature of the corresponding anions.[18]

Reactions of Secondary Alkyl Iodides. The oxidative deiodination of 2-iodopropane assisted by Cl_2 gave the two perchlorates **11** and **12** (3:1). Perchlorate **11** is the product of a normal substitution reaction. The formation of **12** can

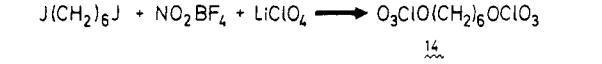


be explained by an initial elimination reaction to give propylene, which then undergoes electrophilic chlorperchloration; the latter reaction has been reported in our previous publications.[19]

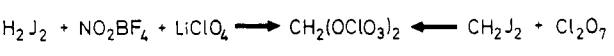
Analogous reaction of iodocyclohexane with $Cl_2 + LiClO_4$ gave a complex mixture containing at least three perchlorates (TLC data); however, we were able to isolate perchlorate **13** by chromatography in 20% yield. Compound **13** is identical with one previously obtained by the chloroperchloration of cyclohexene.[19c] The deiodination of 1-iodocyclohexane in the presence of m-$ClC_6H_4CO_3H$ has been reported to give almost exclusive elimination.[15]

The reaction of 2-iodopropane with $NO_2BF_4 + LiClO_4$ proceeded smoothly to give perchlorate **11** exclusively in an 80% yield. In contrast, the reaction of iodocyclohexane with NO_2BF_4 and $LiClO_4$ gave a complex mixture containing several perchlorates (TLC data).[25]

Reactions of Diiodides. Treatment of 1,6-diiodohexane with $NO_2BF_4 + LiClO_4$ yielded the corresponding bis-perchlorate **14** in 90% yield, and reaction of methylene



iodide with the same reagents gave bis-perchlorate **15** in 96% yield. The latter compound is an *explosive*, colorless liquid that fumes in moist air with the production of a formaldehyde-like odor. Perchlorate **15** was also obtained from CH_2I_2 and Cl_2O_7 but in only 10% yield.



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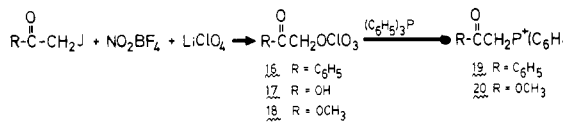
(25) One of these products is *cis*-1,2-bis(perchloryloxy)cyclohexane, identical with an authentic sample,[24b] and the others are unstable isomeric nitrocyclohexyl perchlorates.[19c] The reaction mixture also contains other unidentified products.

Reactions of ICH_2COR. Iodoacetophenone reacted smoothly with NO_2BF_4 + $LiClO_4$ to give the unstable perchlorate **16**, which is very sensitive to moisture. However, we could isolate it in pure form by chromatography to obtain its IR and ^1H NMR spectra. Iodoacetic acid and its methyl ester react with NO_2BF_4 + $LiClO_4$ to give the corresponding perchlorates **17** and **18**. The compounds



16 and **18** were additionally identified as their triphenylphosphonium salts **19** and **20**. Perchlorate **17** is quite unstable at room temperature, but we could record its IR and ^1H NMR spectra. In contrast, perchlorate **18** is the most stable of all our products; it does not decompose up to 200 °C but explodes at higher temperatures or upon striking.

Conclusion

Oxidative deiodination of alkyl iodides in the presence of salts containing nucleofugic anions is a convenient method for the synthesis of alkyl perchlorates and sulfonates. This synthesis of alkyl perchlorates uses the relatively safe reagent $LiClO_4$ instead of explosive and dangerous reagents such as $AgClO_4$,[26] $HClO_4$,[26] or Cl_2O_7.[26,27]

Caution. Alkyl perchlorates are inherently unstable and potentially explosive. All work with them should be conducted behind a strong shield, and they should never be isolated in greater than milligram quantities.

Experimental Section

General Methods. ^1H NMR spectra were recorded in the indicated solvents in Varian ST-60 or JEOL XL-100 spectrometers. Tetramethylsilane was used as an internal standard and the chemical shifts are presented in δ values. IR spectra were determined on thin films or CCl_4 solutions on a UR-10 spectrophotometer. Analytical TLC was performed by using plates with a fixed silica gel layer; the perchlorates and sulfonates were identified by heating the TLC plate to induce a characteristic decomposition with formation of a black spot.[19a-c] The preparative separation was performed by column chromatography on silica gel 40/100. Solvents were dried by usual methods before use.

Caution: The following small-scale procedures for preparation of covalent perchlorates have proved innocuous, but caution is still strongly advised.

Reactions of Methyl Iodide with Oxidants in the Presence of Bu_4NClO_4. A solution of methyl iodide (0.07 g, 0.5 mmol) and Bu_4NClO_4 (0.17 g, 0.5 mmol) in $CDCl_3$ (0.5 mL) was treated with the oxidant, (see Table I). The volatile products were distilled off together with the solvent (bp of CH_3OClO_3 is 52 °C[26]), and the yields of products were determined by NMR using the internal standard CH_2Cl_2. Methyl perchlorate (**3**):[27] IR ($CDCl_3$) 1280, 1250, 1045, 965 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 4.25 (s).

Reaction of Methylene Iodide with NO_2BF_4 and $LiClO_4$. A mixture of methylene iodide (0.13 g, 0.5 mmol), NO_2BF_4 (0.33 g, 2.5 mmol), and $LiClO_4$ (0.27 g, 2.5 mmol) in CH_2Cl_2 (5 mL) was stirred for 24 h and then was diluted with CCl_4 (50 mL) and filtered through silica gel. Evaporation of the solvent gave 0.1 g (96%) of oily methylene diperchlorate (**15**): R_f 0.6 (ethyl acetate–hexane, 1:3); decomposition at 120 °C (expl); IR 1290, 1260, 1045 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 6.3 (s).

Reaction of Methylene Iodide with Cl_2O_7. Methylene iodide (0.27 g, 1 mmol) was added to 10 mL of a 0.3 M solution of Cl_2O_7 in CCl_4[27] at 0 °C. The mixture was stirred for 1 h and filtered through silica gel. Removal of the solvent gave 0.028 g (13%) of methylene diperchlorate.

General Procedure for Oxidative Deiodination of Alkyl Iodides in the Presence of Salts. The oxidant (1.5 mmol) was added to a solution of alkyl iodide (1 mmol) and salt (1–5 mmol of $LiClO_4$ or 1–1.5 mmol of Bu_4NOTs, Bu_4NOMs, Bu_4NOMs, Bu_4NOTf, Bu_4NOSO_2F) in 5 mL of organic solvent (Table I). The mixture was stirred for the indicated time, then poured into ice water (10 mL), and extracted with $CHCl_3$ (3 × 10 mL). The extract was washed with a cold solution of $Na_2S_2O_3$ (10 mL), dried with Na_2SO_4, and concentrated. The products were separated by column chromatography. The esters of sulfonic acids were additionally purified by distillation. The yields of products are given in Table I.

Methyl mesylate (4):[28] oil; R_f 0.2 (ethyl acetate–hexane, 1:3); bp 66–70 °C (2 mm); IR 1360, 1195, 990 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.0 (s, 3 H, CH_3O), 3.0 (s, 3 H, CH_3S).

Methyl tosylate (5):[29] oil; R_f 0.4 (ethyl acetate–hexane, 1:3); bp 125 °C (2 mm); IR 1365, 1190, 980 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 7.6 (m, 4 H, C_6H_4), 3.9 (s, 3 H, CH_3O), 2.3 (s, 3 H, CH_3).

***n*-Hexyl perchlorate (6):**[27] explosive oil; R_f 0.6 (hexane); IR 1270, 1245, 1045 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.5 (t, 2 H, J = 6.5 Hz, CH_2OClO_3), 2.1–1.0 (m, 11 H).

***n*-Hexyl mesylate (7):**[30] oil; R_f 0.46 (ethyl acetate–hexane, 1:6); bp 85–90 °C (2 mm); IR 1360, 1195, 990 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.2 (t, 2 H, J = 6 Hz, CH_2OMs), 3.0 (s, 3 H, CH_3), 1.8–0.8 (m, 11 H).

***n*-Hexyl tosylate (8):**[31] oil; R_f 0.33 (ethyl acetate–hexane, 1:10); bp 197 °C (2 mm); IR 1365, 1190, 985 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 7.6 (m, 4 H, C_6H_4), 4.0 (t, 2 H, J = 6 Hz, CH_2OTs), 2.4 (s, 3 H, CH_3), 1.8–0.8 (m, 11 H).

***n*-Hexyl fluorosulfonate (9):** oil; R_f 0.46 (ethyl acetate–hexane, 1:6), bp 48–49 °C (1 mm); IR 1430, 1225, 960, 790 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.5 (t, 2 H, J = 6 Hz, CH_2OSO_2F), 2.0–0.9 (m, 11 H).

***n*-Hexyl triflate (10):** oil; R_f 0.4 (hexane), bp 64–65 °C (1 mm); IR 1390, 1225, 1150, 1120 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.5 (t, 2 H, J = 6 Hz, CH_2OTf), 2.9–0.9 (m, 11 H).

2-Propyl perchlorate (11):[27] explosive oil; R_f 0.4 (hexane); IR 1275, 1240, 1115, 1035 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.2 (m, 1 H, $CHOClO_3$), 1.4 (d, 6 H, J = 7 Hz, 2 CH_3).

1-Chloro-2-propyl perchlorate (12):[32] explosive oil; R_f 0.2 (hexane); IR 1265, 1230, 1005 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.2 (m, 1 H, $CHOClO_3$), 3.7 (d, 2 H, J = 7 Hz, CH_2Cl), 1.6 (d, 3 H, J = 7 Hz, CH_3).

***trans*-2-Chlorocyclohexyl perchlorate (13):**[19c] explosive oil; R_f 0.55 (ethyl acetate–hexane, 1:4); decomposition at 120 °C; IR 1290, 1275, 1250, 1035 cm^{-1}; ^1H NMR (100 MHz, CCl_4) 4.9 (m, 1 H, $w_{1/2}$ = 17.5 Hz, $HCOClO_3$); 4.05 (m, 1 H, $w_{1/2}$ = 18 Hz, HCCl), 2.6–1.2 (m, 8 H).

1,6-Hexanediyl diperchlorate (14): explosive oil; R_f 0.1 (hexane); decomposition at 100 °C (expl); IR 1270, 1240, 1040 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.7 (t, 4 H, J = 7 Hz, 2 CH_2OClO_3), 2.0–1.3 (m, 8 H, 4 CH_2).

(Phenylcarbonyl)methyl perchlorate (16): unstable oil; R_f 0.2 (ethyl acetate–hexane, 1:8); IR 1700, 1580, 1290, 1260, 1210, 1050 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 8.1–7.5 (m, 5 H, C_6H_5), 5.7 (s, 2 H, CH_2OClO_3).

Carboxymethyl perchlorate (17): unstable needles; R_f 0.1 (ethyl acetate–hexane, 1:3); mp 68–70 °C dec; IR 1710, 1260, 1240, 1090, 1045 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 5.05 (s, CH_2).

Carbomethoxymethyl perchlorate (18): explosive oil; R_f 0.4 (ethyl acetate–hexane, 1:3); decomposition with explosion at 200–210 °C; IR 1763, 1280, 1250, 1240, 1225, 1050, 1020 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.0 (s, 2 H, CH_2), 3.75 (s, 3 H, CH_3).

Preparation of Triphenylphosphonium Salts from Perchlorates 16 and 18. The perchlorate **16** or **18** (0.5 mmol) in dry $CHCl_3$ (2 mL) was added dropwise to a solution of triphenylphosphine (0.25 g, 1 mmol) in $CHCl_3$ (2 mL) at 0 °C. The mixture

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was allowed to warm to room temperature and kept at that temperature for 2 h. The solvent was evaporated and the residue washed with ether (2 × 5 mL) to remove excess triphenylphosphine. Crystallization of the residue from the ethyl acetate–ether mixture gave triphenylphosphonium salt **19** or **20** in a yield 80–90%.

[(Phenylcarbonyl)methyl]triphenylphosphonium perchlorate (19): mp 224–225 °C; IR 1680, 1600, 1440, 1090, 980 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 7.9–7.5 (m, 20 H, 4 C_6H_5), 5.4 (m, 2 H, CH_2P^+). Anal. Calcd for $C_{26}H_{22}ClO_5P$: C, 64.94; H, 4.61. Found: C, 64.65; H, 4.60.

(Carbomethoxymethyl)triphenylphosphonium perchlorate (20): mp 155–159 °C; IR 1690, 1435, 1090, 980 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 7.9–7.5 (m, 15 H, 3 C_6H_5), 5.2 (m, 2 H, CH_2P^+), 3.9 (s, 3 H, CH_3O). Anal. Calcd for $C_{21}H_{20}ClO_6P$: C, 58.01; H, 4.64. Found: C, 57.95; H, 4.66.

Registry No. **3**, 17043-56-0; **4**, 66-27-3; **5**, 80-48-8; **6**, 52936-24-0; **7**, 16156-50-6; **8**, 3839-35-8; **9**, 13001-92-8; **10**, 53059-88-4; **11**, 52936-33-1; **12**, 58426-27-0; **13**, 81971-84-8; **14**, 95407-64-0; **15**, 88504-82-9; **16**, 95407-65-1; **17**, 95407-66-2; **18**, 95407-67-3; **19**, 95407-68-4; **20**, 39720-64-4; CH_3I, 74-88-4; $C_6H_{13}I$, 638-45-9; CH_3CHICH_3, 75-30-9; c-$C_6H_{11}I$, 626-62-0; $I(CH_2)_6I$, 629-09-4; CH_2I_2, 75-11-6; $PhCOCH_2I$, 4636-16-2; ICH_2COOH, 64-69-7; ICH_2COOCH_3, 5199-50-8; Cl_2, 7782-50-5; H_5IO_6, 10450-60-9; NO_2BF_4, 13826-86-3; Br_2, 7726-95-6; m-ClC_6H_4COOOH, 937-14-4; $PhI(OCOCF_3)_2$, 2712-78-9; PhIOHOTs, 27126-76-7; Bu_4NClO_4, 1923-70-2; Bu_4NOMs, 65411-49-6; Bu_4NOTs, 7182-86-7; $LiClO_4$, 7791-03-9; Bu_4NOTf, 35895-70-6; Bu_4NOSO_2F, 88504-81-8; Cl_2O_7, 12015-53-1; PPh_3, 603-35-0.

Aromatic Fluoroalkoxylation via Direct Displacement of a Nitro or Fluoro Group

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Nitro- and fluorobenzenes substituted with a range of electron-withdrawing groups readily undergo fluoroalkoxylation via direct displacement of the nitro or fluoro group. A number of compounds, which cannot be usefully prepared by direct displacement of a chloro group and which are otherwise inaccessible, have been synthesized. Yields and reaction conditions are comparable to those reported by other workers for reactions involving strong nucleophiles.

The nucleophilic displacement of a nitro group from a singly activated aromatic substrate has been effectively used with a variety of strong nucleophiles under dipolar aprotic solvent conditions. For example, at room temperature in DMF, Me_2SO, or HMPA, hydroxy or alkoxyl anions,[1-4] thiol anions,[1,5,6] sulfinate anions,[1] and oximate anions[7] effect a synthetically useful displacement of a nitro group from carbonyl,[1-3,6,7] nitro,[1,7] cyano,[1,4,5,7] sulfone,[1] and aryl[7] activated substrates. Each of these procedures are formal, "one-pot" displacements of the nitro group and represent transformations which, in general, occur more readily compared to the corresponding chloro leaving group substrates. Similarly, as we[8] and others[9] have previously demonstrated, fluoro is comparable to nitro in leaving group ability in an SnAr reaction.

In connection with our interest in aromatic fluoroalkoxylation via direct aromatic nucleophilic substitution,[10,11] we have recently reported[8] that certain fluoroalkoxide anions react in dipolar aprotic solvents with activated aryl and heteroaryl chlorides at temperatures of 90–150 °C to produce the corresponding fluoroalkyl ethers. While a number of dipolar aprotic solvent promote the reaction (HMPA, DMF, Me_2SO, and 1-methyl-2-pyrrolidinone), HMPA provided the most consistent set of reactive conditions. As expected, cyano and nitro groups were particularly effective activators and provided virtually quantitative, isolated yields of ortho- and para-substituted products with 2,2,2-trifluoroethoxide ion as the nucleophile and extremely good (~80%) yields of the corresponding meta-substituted products. The trifluoromethyl, phenylcarbonyl, and phenylsulfonyl groups proved to be sufficiently activating so as to provide modest to fair yields (30–60%) of the corresponding (2,2,2-trifluoroethoxy)-benzenes; however, chloro-, aldehydo-, carbomethoxy-, and amido-substituted chlorobenzenes provided either no reaction or only traces of product. Additionally, with 4-chlorobenzonitrile as substrate, tertiary fluoroalkoxide ions (e.g., $^-OC(CH_3)_2CF_3$) and fluoroalkoxide ions containing more than four fluorines promote little, if any, direct fluoroalkoxylation; even the four fluorine nucleophile $^-OCH_2CF_2CF_2H$ gave only a modest yield (~40%) of fluoroalkoxylated product when reacted with 4-chlorobenzonitrile at 200 °C.

Because of our interest in extending the general synthetic usefulness of direct aromatic nucleophilic fluoroalkoxylation, we felt it would be of value to examine the reaction of a set of substrates containing a potentially more reactive leaving group than chloro. Thus, a range of monosubstituted nitrobenzenes or fluorobenzenes have been investigated.

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