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Diphenyl Disulfide and Sodium in NMP as an Efficient Protocol for in Situ Generation of Thiophenolate Anion: Selective Deprotection of Aryl Alkyl Ethers and Alkyl/Aryl Esters under Nonhydrolytic Conditions[†,‡]

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Aryl methyl ethers, methyl esters, aryl esters, and aryl sulfonates are chemoselectively deprotected under nonhydrolytic conditions by treatment with Ph_2S_2 (0.6 equiv) and Na (1.6 equiv) in NMP under reflux or at 90 °C. Quantitative utilization of the ‘PhS’ moiety as the effective nucleophilic species represents conservation of atom economy. Other solvents such as HMPA, DMPU, DMEU, and DMF afforded comparable results. Chloro, nitro, aldehyde, α,α-diketone, and α,β-unsaturated ketone functionalities remain unaffected. The deprotection was found to take place in the order aryl ester > alkyl ester > aryl alkyl ether. Substrates bearing strong electron-withdrawing groups react at a faster rate than those not having such substitution. The differences in rate of reaction has been exploited for selective deprotection for intramolecular competition. An aryl acetate/benzoate is deprotected selectively in preference to a methyl ester or aryl methyl ether. Selective deprotection of a methyl ester is observed in the presence of an aryl alkyl ether.

Deprotection of functional groups[1] is one of the most important and widely carried out synthetic transformations in preparative organic chemistry. In the synthesis of multifunctional molecules often the problem arises that a given functional group has to be deprotected in the presence of others. Of the many functional groups requiring synthetic manipulation involving deprotection, one frequently encounters aryl alkyl ethers, alkyl esters, and phenolic esters due to the ease of formation of aryl alkyl ethers,[2] alkyl esters,[3] and aryl esters.[1] The most strategic approach for deprotection of ethers and esters seems to be the nucleophilic attack on the *O*-alkyl or carbonyl group, and in this regard the sulfur-derived nucleophilic reagents have drawn considerable attention.[4,5] Recently we have developed efficient procedures for the chemoselective deprotection of aryl alkyl ethers,[6] alkyl esters,[7] and aryl esters[8] through the in situ generation of thiolate anion in a ‘demand-based’ fashion. Although excellent selectivity was observed in these procedures, dealing with thiols is alarming because of their radical-generating ability. The susceptibility of thiols to aerial oxidation (to form the corresponding disulfides)[9] is also a potential problem of use of thiols. The lability of the S−S bond makes them a good precursor for generation of the parent thiol. We report herein a SET process for in situ generation of thiophenolate anion from diphenyl disulfide[10] for selective deprotection of aryl alkyl ethers, aryl esters, and aryl sulfonates.

Alkali metal hydrides are known to possess reducing properties[11] and generate alkali selenoates from diorganic diselenides.[12] However, during the attempted demethylation of methyl 2-naphthyl ether with PhS^-Na^+, generated in situ from Ph_2S_2 in the presence of various alkali metal hydrides, only NaH was found to be effective (compare entries 1−6, Table 1). Excellent results are obtained with Li, Na, and K metals in NMP under reflux (entries 7, 8, 12, 13; Table 1). Better results are obtained when the Ph_2S_2 is allowed to react with the reducing agent compared to the case when all of the reactants are added together (entries 2, 7, and 8; Table 1). However, $Na_2S_2O_4$ afforded poor results (entry 17; Table 1) despite its ability to generate thiolate from disulfide.[13] This in situ thiophenolate anion generation protocol was extended for the chemoselective cleavage of various sub-

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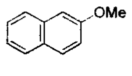
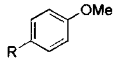
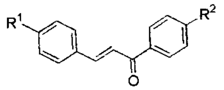
Table 1. Effect of the SET Agent, Solvent, and Temperature on Deprotection of Methyl 2-Naphthyl Ether[a]

entry	SET Agent[b]	solvent	temp (°C)	time (min)	yield (%)[c,d]
1	KH	DMF	reflux	75	[e]
2	NaH	DMF	reflux	75	54 (41)[f]
3	NaH	DMF	reflux	300	73
4	NaH	DMF	80	75	trace
5	NaH	NMP	reflux	30	76
6	LiH	DMF	reflux	45	trace
7	K	NMP	reflux	30	85 (73)[f]
8	K	HMPA	reflux	30	90 (55)[f]
9	K	HMPA	100	60	35
10	K	DMF	reflux	30	54
11	K	DMA	reflux	30	36[g]
12	Na	NMP	reflux	30	93
13	Li	NMP	reflux	30	96
14	K	NMP	reflux	30	75[h]
15	Na	NMP	reflux	30	32[i]
16	Na	DMSO	reflux	30	40
17	$Na_2S_2O_4$	NMP	reflux	30	14
18	KHMDS	NMP	reflux	30	90[j,k]

[a] The diphenyl disulfide (0.6 mol equiv with respect to the ether) was treated with the SET agent at the specified temperature for 15 min before the addition of the ether. [b] Used 1.6 mol equiv. [c] Isolated yield. [d] Except for entries 1 and 11, the unreacted ether could be recovered. [e] An intractable mixture was obtained. [f] The figure in parentheses corresponds to the yield without the prior reaction of the disulfide with the SET agent. [g] An exothermic reaction takes place with the metal and the solvent with the liberation of amine smell. [h] The reaction was carried out with Me_2S_2 instead of Ph_2S_2. [i] The reaction was carried out with $[Et_2NC(=S)S]_2$ instead of Ph_2S_2. [j] The solvent was allowed to react with KHMDS (2 mol equiv with respect to the ether) for 30 min at room temperature followed by 15 min at 90 °C prior to the addition of Ph_2S_2. [k] GCMS of the neutral component of the reaction mixture revealed the presence of thioanisole.

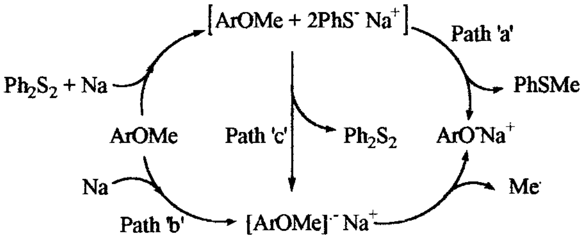
Table 2. Chemoselective Deprotection of Aryl Methyl Ethers[a]

Entry	Ether	Time (min)	Yield (%)[b,c]
1		30	93
			
2	R = Cl	30	100[d]
3	R = COMe	15	90[e]
4	R = CHO	15	92
5	R = COCOPh	15	97
6	R = CN	30	80
7	R = NO_2	30	100
			
8	R^1 = OMe; R^2 = H	30	65
9	R^1 = H; R^2 = OMe	30	79

[a] Reactions were carried out by the treatment of the Ph_2S_2 (0.6 equiv) with Na (1.6 equiv) for 15 min under reflux in NMP followed by the addition of the ether and heating under reflux. [b] Isolated yields. [c] The unreacted ether could be recovered. [d] Phenol was isolated in 84% yield in the absence of the disulfide. [e] Reaction carried out in the absence of disulfide for 30 min resulted in the formation of 1-(4-hydroxyphenyl)ethanol and 1-(4-methoxyphenyl)ethanol in 79 and 13% yields, respectively.

stituted aryl methyl ethers (Table 2). We preferred to employ Na[14] in all of the subsequent studies due to its ease of handling (compared to that of K) and low cost.

Scheme 1



The reaction takes place at a faster rate for substrates bearing electron-withdrawing groups (compare the result of entry 1 with those of entries 2−5, Table 2). Efficient chemoselectivities were observed by the fact that substrates bearing aldehyde or ketone groups do not experience nucleophilic attack at the carbonyl carbon. Substrates bearing an α,β-unsaturated carbonyl group (entries 8 and 9, Table 2) do not undergo Michael type addition[15] or reduction[16] although thiolate anions are known to possess single electron transfer (SET) properties.[17]

The reaction may be thought to take place through (a) a nucleophilic attack of PhS^-, generated in situ from Ph_2S_2, on the *O*-Me (Scheme 1, path a); (b) a direct reductive cleavage[18] (Scheme 1, path b); or (c) a SET from the PhS^- [17] (Scheme 1, Path c).

The isolation/detection of thioanisole in the neutral component (see Experimental Section) of the reaction mixture provided evidence in favor of the nucleophilic cleavage (path a). The possibility of electron-transfer-induced reductive demethylation[18] (path b) may be ruled out due to the better susceptibility of the S−S bond to reductive cleavage than that of the ether (cf. entries 2, 3; Table 2). Demethylation mediated through SET from PhS^- (path c) also appears unlikely, as the reaction rate is dependent on the nature of the relative leaving group ability of the phenolate anion (entries 1−5, Table 2), reinforcing the concept of nucleophilic attack. Moreover, during the demethylation of 4-nitroveratrole via photochemically induced SET process,[19] the regioselective outcome does not correspond to the leaving group ability of the phenolate anion, and the dealkylation of quaternary ammonium salts,[20] which has been mentioned to occur through a SET process from PhS^-, involves a positively charged substrate as in the case of photochemically induced dealkylation.

Since enolates are known to possess the SET property,[21] an alternative path to generate the PhS^- by the reaction of Ph_2S_2 with the enolate of NMP is also possible. Thus the reaction of preformed enolate of NMP, obtained by the reaction of NMP with KHMDS, also resulted in ether cleavage (entry 18, Table 1). The detection of thioanisole (GCMS) and the lack of formation of any heptamethyldisilazane in the reaction mixture is indica-

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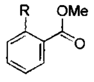
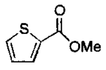
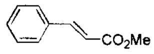
Table 3. Chemoselective Deprotection of Alkyl Esters[a]

Entry	Ester	Yield (%)[b,c]
		
1	R = H	100 (83)[d,e,f]
2	R = Cl	100
3	$R = NO_2$	70
4		100
5		70[g]

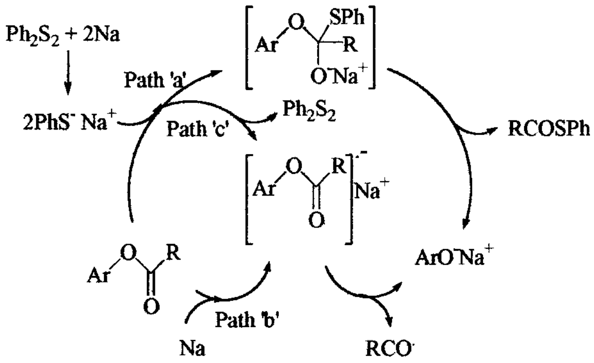
[a] Reactions were carried out by the treatment of the Ph_2S_2 (0.6 equiv) with Na (1.6 equiv) for 15 min at 90 °C in NMP followed by the addition of the ester and heating at 90 °C for another 15 min. [b] Isolated yields. [c] The unreacted ester could be recovered. [d] The figure in parentheses is the corresponding yield under reflux. [e] A 40% yield of the product was obtained in carrying out the reaction at room temperature for 7 h. [f] The ester remains unchanged under the treatment in the absence of the sulfide. [g] A 10:1 mixture of cinnamic acid and dihydrocinnamic acid.

Table 4. The Effect of Disulfide (R_2S_2) and Solvent on Deprotection of 2-Naphthyl Benzoate[a]

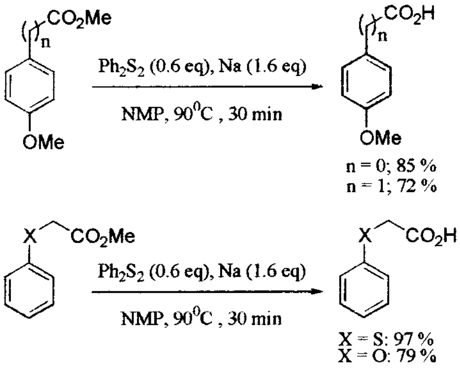
entry	R	solvent	time (min)	yield (%)[b,c]
1	Ph	NMP	30	95[d]
2	Ph	NMP	15	100
3	Ph	DMPU	15	100
4	Ph	DMEU	15	100
5	Ph	sulfolane	15	62.5
6	Ph	NMP	60	30[e]
7	–	NMP	30	trace[f]
8	$2\text{-}NH_2\text{-}C_6H_4$	NMP	15	100
9	Me	NMP	30	trace

[a] Reactions were carried out by the treatment of the R_2S_2 (0.6 equiv) with Na (1.6 equiv) for 15 min at 90 °C in NMP followed by the addition of the ester and heating at 90 °C. [b] Isolated yield. [c] The unreacted ester could be recovered. [d] Quantitative yield under reflux for 30 min. [e] The recation was carried out with 15 mol % of Ph_2S_2. [f] The reaction was carried out in absence of any disulfide.

Scheme 2



Scheme 3



tive of the involvement of thiophenolate anion as the effective nucleophile. It is interesting to note that the competitive sulfenylation does not take place (as evidenced by excellent results exemplifying atom economy[22]) despite the known electrophilic property of disulfides.[23]

The isolation/detection of thioanisole in the neutral component (see Experimental Section) of the reaction mixture obtained during the reaction with methyl benzoate suggests that deprotection of the alkyl ester takes place via *O*-alkyl cleavage. We extended this nucleophilic *O*-Me cleavage to other methyl ester substrates (Table 3). As expected, due to the better leaving group property of the carboxylate anion compared to that of the phenolate anion, the ester cleavage took place at a faster rate at a lower temperature. Excellent chemoselectivity was observed in that no competitive aromatic nucleophilic substitution of the chloro[24] (entry 2, Table 3) or nitro group[25] (entry 3, Table 3) or reduction of the nitro group[26] (entry 3, Table 3) occurred. The absence of any competitive reduction of the ester[27] and acyloin condensation[28] further demonstrates the chemoselectivity.

Systematic studies were carried out with 2-naphthyl benzoate to delineate the effect of solvent, temperature, and the disulfide while extending this in situ thiolate anion generation protocol for deprotection of phenolic esters (Table 4). Deprotection is best carried out by the treatment of the aryl ester with diphenyl disulfide or di-2-aminophenyl disulfide in the presence of sodium metal in NMP at 90 °C. Other dipolar aprotic solvents such as DMPU and DMEU are equally effective, but sulfolane gave an inferior result. The inefficiency of Me_2S_2 (entry 9, Table 4) may be due to the poor leaving group property of the alkanethiolate anion after initial electron capture from the metal under milder conditions (compare with entry 14, Table 1).[29] The reaction is believed to take place through nucleophilic attack on the ester carbonyl by PhS^- following a tetrahedral mechanism, as indicated by the formation of PhSCOR (path a, Scheme 3). The involvement of the radical anion intermediate arising out of the direct electron transfer from the metal (path b, Scheme 3) is unlikely due to the better electron capture capability of the disulfide and as no deprotection could be observed in the absence of the disulfide (entry 7, Table 4). Furthermore, the lack of detection (GCMS) of PhCHO, PhCOCOPh, or PhCOCH(OH)Ph that might have re-

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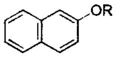
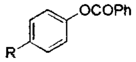
Table 5. Chemoselective Deprotection of Phenolic Esters[a]

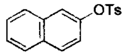
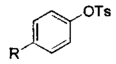
Entry	Ester	Time (min)	Yield (%)[b,c]
			
1	R = COMe	30	95
2	R = COMe	15	88
3	R = COPh	15	100
4	R = Bu^t	45	51
			
5	R = Cl	30	84
6	R = COMe	15	90
7	R = CHO	15	95
8	R = CN	15	84
9	R = NO_2	15	100

[a] Reactions were carried out by the treatment of the Ph_2S_2 (0.6 equiv) with Na (1.6 equiv) for 15 min at 90 °C in NMP followed by addition of the ester and heating at 90 °C. [b] Isolated yields. [c] The unreacted ester could be recovered.

sulted from PhCO• through hydrogen abstraction, radical coupling, or acyloin condensation, respectively, is indicative that the reaction does not proceed via the formation of the radical anion intermediate. The radical anion formation involving SET from PhS^- (path c, Scheme 2) also failed to gain importance, as it would have implicated the cleavage to be operative with catalytic amounts of the disulfide (entry 6, Table 4).[30] Various aryl esters were subjected to deprotection (Table 5). Although aryl acetates and benzoates are effectively deprotected, the deprotection of the corresponding pivalate provides an inferior result (compare entries 1–3 with 4; Table 5).

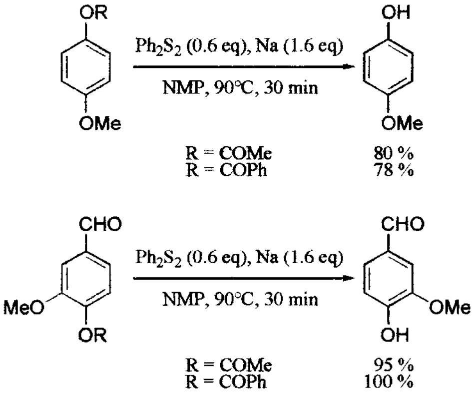
Sulfonates of various phenols were subjected to deprotection (Table 6). Reactions with 2-naphthyl tosylate reveals that the reaction could be carried out either under reflux for 0.5 h or at 90 °C for 2 h. No competitive aromatic nucleophilic substitution[31] was observed for substrates bearing strong electron-withdrawing groups (entries 5–7, Table 6). However, for substrates bearing a chlorine atom or cyano group, dehalogenation/decyanation took place along with deprotection under reflux.

Table 6. Chemoselective Deprotection of the *p*-Toluenesulfonate Ester of Phenols[a]

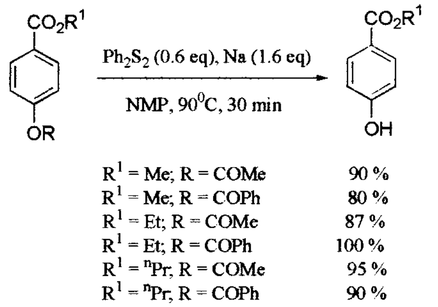
Entry	Ester	Time (min)	Yield (%)[b,c]
			
1		15	30
2		60	67
3		120	75
4		30	86[d]
			
5	R = Cl	120	90[e,f]
6	R = CN	60	72[f]
7	R = NO_2	120	73

[a] Reactions were carried out by the treatment of the Ph_2S_2 (0.6 equiv) with Na (1.6 equiv) for 15 min at 90 °C in NMP followed by addition of the ester and heating at 90 °C. [b] Isolated yields. [c] The unreacted ester could be recovered. [d] Reaction was carried out under reflux. [e] Dehalogenated product was formed in 6% yield. [f] Phenol was formed in quantitative yield when all the reactants were added together and heated under reflux for 30 min.

Scheme 4



Scheme 5



The distinct differences in the rates of reaction of deprotection of ethers and alkyl/aryl esters encouraged us to extend this methodology for selective deprotection of aryl alkyl ethers in the presence of alkyl (Scheme 3) and aryl (Scheme 4) esters, and alkyl esters in the presence of aryl esters (Scheme 5) during intramolecular competition studies. Selective cleavage of the methyl ester was observed in excellent yields when methyl 4-methoxyphenylacetate, methyl 4-methoxybenzoate, methyl phenoxyacetate, and methyl thiophenoxyacetate were reacted separately (Scheme 3). Reactions with 4-methoxyphenyl acetate, 4-methoxyphenyl benzoate, 4-acetoxy-3-methoxybenzaldehyde, and 4-benzoyloxy-3-methoxybenzaldehyde exhibited excellent selectivity for deprotection of the acetate or benzoate functionality without any noticeable demethylation (Scheme 4). Similarly, during the reactions with methyl 4-acetoxybenzoate, methyl 4-benzoyloxybenzoate, ethyl 4-acetoxybenzoate, ethyl 4-benzoyloxybenzoate, propyl 4-acetoxybenzoate, and propyl 4-benzoyloxybenzoate, complete chemoselectivity was observed in favor of deprotection of the acetoxy or benzoyloxy groups (Scheme 5).

In conclusion, we have described herein an extremely efficient protocol for in situ generation of thiolate anion for chemoselective deprotection of aryl alkyl ethers, aryl esters, and aryl sulfonates following the conservation of atom economy. The deprotection was found to take place in the order aryl ester > alkyl ester > aryl sulfonates. Substrates bearing a strong electron-withdrawing sub-

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stituent react at a faster rate than those having no such substitution. Excellent selectivity has been achieved in the deprotection of methyl esters over aryl methyl ethers, aryl esters over aryl alkyl ethers, and aryl esters over alkyl esters during intramolecular competitions.

Experimental Section

General. The aryl methyl ethers, alkyl esters, and aryl esters were either available commercially or prepared by standard procedures.[1−3] Solvents were distilled before use. DMPU, DMEU, HMPA, sulfolane, Ph_2S_2, $(2\text{-}NH_2\text{-}C_6H_4)_2S_2$, Me_2S_2, $[Et_2NC({=}S)S]_2$, Li, LiH, $KOBu^t$, and KH were purchased from Aldrich. DMF, NMP, Na, K, and NaH were purchased from S. d. fine chemicals, India.

General Procedure for Deprotection. Representative Procedure for Deprotection of Aryl Alkyl Ethers. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) under reflux for 15 min under N_2. 2-Methoxynaphthalene (395.4 mg, 2.5 mmol) in NMP (3 mL) was added, and the mixture was heated under reflux for 30 min. The cooled reaction mixture was made alkaline with 5% aqueous NaOH (25 mL) and extracted with Et_2O (3 × 15 mL) to separate any neutral component (GCMS of these combined ethereal extracts showed the presence of PhSMe). The aqueous part was acidified in the cold (ice bath) with 6 N HCl and extracted with Et_2O (3 × 15 mL). The combined Et_2O extracts were washed with brine (15 mL), dried (Na_2SO_4), and concentrated under vacuo to afford a brown solid which on passing through a column of silica gel (230−400, 1 g) and elution with 5% EtOAc−hexane (200 mL) afforded the product (340 mg, 93%) which was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of 2-naphthol.

Representative Procedure for Deprotection of Alkyl Esters. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) at 90 °C for 15 min under N_2. Methyl benzoate (340.4 mg, 2.5 mmol, 0.31 mL) in NMP (3 mL) was added, and the mixture was heated at 90 °C for 15 min. The cooled reaction mixture was made alkaline with saturated aqueous $NaHCO_3$ (25 mL) and extracted with Et_2O (3 × 15 mL) to separate any neutral component (GCMS of these combined ethereal extracts showed the presence of PhSMe). The aqueous part was acidified in the cold (ice bath) with 6 N HCl and extracted with Et_2O (3 × 15 mL). The combined Et_2O extracts were washed with brine (15 mL), dried (Na_2SO_4), and concentrated under vacuo to afford a light yellow solid which on crystallization (5% EtOAc−hexane) afforded the product (305 mg, 100%) which was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of benzoic acid.

Representative Procedure for Deprotection of Aryl Ester. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) at 90 °C for 15 min under N_2. 2-Naphthyl benzoate (620 mg. 2.5 mmol) in NMP (3 mL) was added, and the mixture was heated at 90 °C for 15 min. The cooled reaction mixture was made alkaline with 5% aqueous NaOH (25 mL) and extracted with Et_2O (3 × 15 mL) to separate any neutral component (GCMS of these combined ethereal extracts showed the presence of PhSCOPh). The aqueous part was acidified in the cold (ice bath) with 6 N HCl and extracted with Et_2O (3 × 15 mL). The combined Et_2O extracts were washed with saturated aqueous $NaHCO_3$ (2 × 15 mL), to separate any benzoic acid formed as a result of partial hydrolysis of PhSCOPh, and brine (15 mL), dried (Na_2SO_4), and concentrated under vacuo to afford a brown solid which on passing through a column of silica gel (230−400, 1 g) and elution with 5% EtOAc−hexane (200 mL) afforded the product (360 mg, 100%) which was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of 2-naphthol.

Representative Procedure for Deprotection of Aryl Sulfonate Esters. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) at 90 °C for 15 min under N_2. 2-Naphthyl tosylate (745 mg. 2.5 mmol) in NMP (3 mL) was added, and the mixture was heated at 90 °C for 2 h. The cooled reaction mixture was made alkaline with 5% aqueous NaOH (25 mL) and extracted with Et_2O (3 × 15 mL) to separate any neutral component (GCMS of these combined ethereal extracts showed the presence of PhSTs). The aqueous part was acidified in the cold (ice bath) with 6 N HCl and extracted with Et_2O (3 × 15 mL). The combined Et_2O extracts were washed with brine (15 mL), dried (Na_2SO_4), and concentrated under vacuo to afford a brown solid which on passing through a column of silica gel (230−400, 1 g) and elution with 5% EtOAc−hexane (200 mL) afforded the product (360 mg, 100%) which was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of 2-naphthol.

Selective Deprotection in Intramolecular Competition. Selective Deprotection of Methyl Esters in Intramolecular Competition between Methyl Esters and Aryl Alkyl Thioethers. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) at 90 °C for 15 min under N_2. Methyl thiophenoxyaceate (455 mg. 2.5 mmol) in NMP (3 mL) was added, and the mixture was heated at 90 °C for 15 min. The cooled reaction mixture was made alkaline with saturated aqueous $NaHCO_3$ (25 mL) and extracted with Et_2O (3 × 15 mL) to separate any neutral component (GCMS of these combined ethereal extracts showed the presence of PhSMe). The aqueous part was acidified in the cold (ice bath) with 6 N HCl and extracted with Et_2O (3 × 15 mL). The combined Et_2O extracts were washed with brine (15 mL), dried (Na_2SO_4), and concentrated under vacuo to afford a light yellow solid which on passing through a column of silica gel (60−120, 10 g) and elution with 10% EtOAc−hexane afforded the product (400 mg, 97%) which was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of thiophenoxyacetic acid.

Selective Deprotection of Phenolic Esters in Intramolecular Competition between Phenolic Esters and Aryl Alkyl Ethers. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) at 90 °C for 15 min under N_2. 3-Methoxy-4-benzoyloxybenzaldehyde (640 mg. 2.5 mmol) in NMP (3 mL) was added, and the mixture was heated at 90 °C for 15 min. After the usual workup and purification, the phenolic product was isolated (380 mg, 100%) and was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of vanillin. Deprotection of the corresponding acetate in an analogous manner resulted in a 95% yield of vanillin. No cleavage of the methyl ether was observed in either occasion.

Selective Deprotection of Aryl Esters in Intramolecular Competition between Alkyl and Aryl Esters. The magnetically stirred solution of Ph_2S_2 (327 mg, 1.5 mmol) in NMP (2 mL) was treated with Na (92.00 mg, 4.0 mmol) at 90 °C for 15 min under N_2. Methyl 4-acetoxybenzoate (485 mg, 2.5 mmol) in NMP (3 mL) was added and the mixture was heated at 90 °C for 15 min. After the usual workup and purification, the phenolic product **2** was isolated (342 mg, 90%) and was in full agreement with mp and spectral data (IR, ^1H NMR, and GCMS) of an authentic sample of methyl 4-hydroxybenzoate. Deprotection of methyl 4-benzoyloxybenzoate, ethyl 4-acetoxybenzoate, ethyl 4-benzoyloxybenzoate, propyl 4-acetoxybenzoate, and propyl 4-benzoyloxybenzoate in an analogous manner resulted the corresponding phenolic esters in 80, 87, 100, 95, and 90% yields, respectively. No appreciable amount of alkyl ester cleavage could be detected in each occasion.

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