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Organic Reactions under Solid-State Conditions

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Organic Reactions under Solid-State Conditions

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Manipulatively simple and rapid methods are described for the synthesis of: chiral sulfinate esters from sulfonyl chlorides and sufonic acids; aldehydes and ketones from oximes, alcohols, hydrozones; sulfoxides from sulfides; and disulfides from thiols. The chemical yields are good to excellent and diastereoselectivity is high.

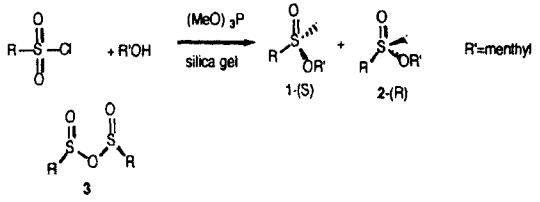
Keywords: Solid-state reactions; microwave irradiation; sulfinate esters; asymmetric reaction; oxidation

Heterogeneous reaction that are facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years. [1-3] The advantage of these methods over conventional homogenous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products and manipulative simplicity.

In continuation of our ongoing program to develop environmentally benign methods using solid supports, [4] we now wish to report some of our results. We have prepared chiral sulfinate esters in high diastreoselectivity with two different methods.

In method 1 we have developed an extremely convenient one-step synthesis of chiral sulfinate ester **1** from readily available sulfonyl chlorides and trimethyl phosphite under solid phase conditions (Scheme I). The process in its entirety involves a simple mixing of sulfonyl chlorides and (-)-menthol with (21%) trimethyl phosphite-silica gel in a mortar and grinding the mixture for the time specified in the table at room temperature. In our best of knowledge this methodology for preparation of chiral sulfinate esters in solid phase conditions has not been reported in literature.

Scheme I



The compounds **1** and **2** have been identified by ^{1}H-NMR analysis, and compound **3** has been formed as an undesired by product (5-10%).

Because of the low reactivity of alkyl sulfonyl chlorides only aromatic sulfonyl chlorides could be converted into the desired products, the results of these efforts are presented in table I. The desired product was usually isolated in good to excellent yield, and excellent diastereoselectivity (Table I).

The ability of silica gel in dry media was demonstrated using toluene-4-sulfonyl chloride with trimethyl phosphite in the absence of silica gel. The toluene-4- sulfonyl chloride was converted to the corresponding ester in less than 10 % yield in more than 40 min.

Table I-Preparation of menthylsulfinate esters 1 and 2

Entry	R	Reaction Period, min	Yield,[a]%	Diastereomer ratio
1	*p*-CH3C6H4	12	86	90:10
2	C6H5	15	78	85:15
3	*p*-CH3OC6H4	10	84	92:8
4	*p*-ClC6H4	18	79	70:30
5	*p*-NO2C6H4	20	75	75:25
6	2-naphthyl	15	88	98:2
7	2-furyl	15	83	85:15
8	*o*-ClC6H4	18	72	78:22
9	*o*-NO2C6H4	20	70	80:20

[a] isolated yield after chromatographic purification.

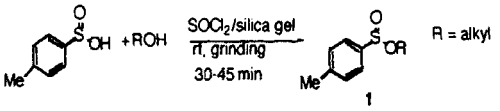
The diastereomer ratio of product as determined by ^{1}H NMR analysis on the crude reaction products, ranged from 70:30 to 98:2 (Table I), the major diastereomer **1** in all cases proved to have a negative sign of rotation. Literature precedent [5] suggests that these compounds have (S) configuration at sulfur. The absolute stereochemistry of **1** was evident from the sign of its optical rotation (-)-S] and ^{1}H NMR when compared that of (-)(s)-menthyl 2-methoxy-1-naphthalensulfinate. [6]

In method 2 we have developed a convenient one-step method for the preparation of sulfinate esters, starting from supported thionyl chloride on silica gel (33 %) with sulfinic acid and aliphatic alcohols under solvent-free conditions. This method would be widely applicable as general method for the synthesis of alkyl sulfinate esters. The process in its entirety involves a simple mixing of *p*-toluenesulfinic acid, supported thionyl chloride on silica gel (33 %) and aliphatic alcohols in a mortar and grinding the mixture for the time specified in the Table II at room temperature. In our best of knowledge this methodology for preparation of chiral sulfinate esters in solid phase conditions has not been reported in literature. This method does not require additional step and excess of thionyl chloride for preparation of sulfinyl chlorides, which are thermally unstable and sensitive to moisture during the reaction, work-up and evaporation

of excess thionyl chloride. This method also does not need any catalysts which can be relatively expensive and can cause problems during purification. [9-11]

The compounds **1** have been identified by ^{1}H NMR analysis. Because of the low reactivity of aromatic alcohols only aliphatic alcohols could be converted into the desired products, the results of these efforts are presented in table II. The desired product was usually isolated in good to excellent yield, and excellent diastereoselectivity (Table II).

Scheme II

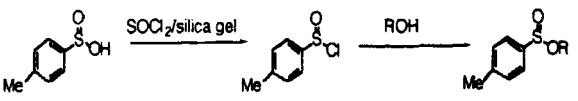


1

The diastereoselectivity of product formation when we used l-menthol, as determined by ^{1}H NMR analysis on the crude reaction products, was 90:10 (Table 1, entry 10); the major diastereomer proved to have a negative sign. Literature precedent suggests that this compound has (S) configuration at sulfur. [5]

we believe that the effect of silica gel is to absorb the thionyl chloride on its surface. The supported thionyl chloride then reacts with sulfinic acid to produce sulfinyl chloride. The alcohol then reacts with sulfinyl chloride to produce sulfinic esters, the proposed mechanism is shown in Scheme III.

Scheme III



In order to evaluate the effect of silica gel in this reaction, several experiments were demonstrated. As shown in table III, when *p*-toluenesulfinic acid with thionyl chloride and ethanol was used in the absence of silica gel, the *p*-toluenesulfinic acid was converted to the corresponding ester in 10 % of yield after 60 min grinding in a mortar at room temperature (Table III, entry 2). The reaction of supported thionyl chloride on silica gel in dichloromethane (2 h,

reflux) was unsuccessful and the *p*-toluenesulfinic acid remained unchanged (entry 3). The reaction of *p*-toluenesulfinic acid and ethanol in the presence of silica gel without thionyl chloride was unsuccessful and the yield of corresponding *p*-toluenesulfinic ester after 80 min grinding in a mortar at 70 °C was only 10 % (entry 4). Similarly when we used thionyl chloride without silica gel for 40 min the condensation proceeded in 25 % yield (entry 5). Only in the case of reaction of reaction of supported thionyl chloride on silica gel with *p*-toluenesulfinic acid and ethanol *p*-toluenesulfinic ester produced in excellent yield (entry 1).

Table II. Preparation of p-toluenesulfinate esters **2.**

Entry	R	Reaction Time (min)	Yield (%)
1	CH_3	30	85
2	CH_3CH_2	40	95
3	$CH_3(CH_2)_2$	40	75
4	$CH_3(CH_2)_3$	40	70
5	$CH_3CH(CH_3)CH_2$	40	75
6	$CH_3(CH_2)_2CH(CH_3)$	40	78
7	cyclohexyl	45	60
8	$C_6H_5CH_2$	35	85
9	$C_6H_5CH_2CH_2$	40	79
10	l-menthyl	45	95
11	$ClCH_2CH_2$	40	75
12	$CH_3(CH_2)_6CH_2$	40	68
13	$CH_3CH_2CH(CH_3)$	40	70
14	$(CH_3)_2CH$	35	75

Table III. Preparation of Ethyl p-Toluenesulfinate Ester.

Entry	Catalyst	Temp (°C)	Time (min)	Solvent	Sulfinate Ester [a] (%)
1	silica gel	rt.	40	none	95
2	none	rt.	60	none	10
3	silica gel	40	120	CH_2Cl_2	0
4	silica gel	70	80	none	10
5	silica gel	rt.	40	none	25

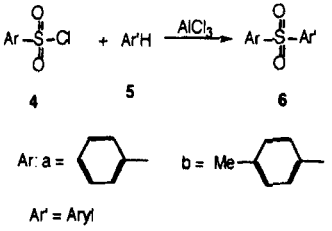
[a]) Evaluated by TLC analysis

we have also find an extremely convenient synthesis of aromatic sulfones from readily available arensulfonyl chloride with aromatic hydrocarbons in the presence of aluminium chloride as catalysts under solid phase conditions (Scheme IV). The process in its entirety involves a simple mixing of sulfonyl chlorides **4** and aromatic hydrocarbons **5** in the presence of aluminium chloride as catalysts in a mortar and grinding the mixture for the time specified in Table IV. The yields of the reactions are high (50-91%) and the reaction times are exceedingly short (2-25 min). To the best of our knowledge this technique for the preparation of aromatic sulfones is completely novel and has not been reported in the literature. The purity of products **6** were determined by ^1H NMR, IR, melting point and TLC analyses.

The substitution effect has been studied in these reactions (Table IV). According to data listed in Table IV, it is clear that electron donating groups will increased the reaction rate as well as reaction yields (Table IV, entries 1-12). On the other hand electron withdrawing groups will decreased yields and increased reaction time (Table IV, entries 13-18). When more than one moderate electron withdrawing groups or one strong withdrawing group are on the aromatic hydrocarbon **5** the reaction does not take place at all, even at 80 °C after 30 min grinding of the reaction mixture (Table IV, entries 20-21). When a group such as

N,N-dimethylamine was located on the aromatic hydrocarbon **5**, Although this group is an excellent electron releasing group, but the reaction does not occur at all, even at 80 °C after 30 min grinding of the reaction mixture (Table IV, entry 22). This could be explained in terms of complex formation between this group and aluminium chloride which retards the reaction.

Scheme IV



6a Ar = p-$CH_3C_6H_4$, Ar'H = benzene, **6b** Ar = p-$CH_3C_6H_4$, Ar'H = toluene

6c Ar = p-$CH_3C_6H_4$, Ar'H = ethylbenzene, **6d** Ar = p-$CH_3C_6H_4$, Ar'H = biphenyl

6e Ar = p-$CH_3C_6H_4$, Ar'H = o-xylene, **6f** Ar = p-$CH_3C_6H_4$, Ar'H = p-xylene

6g Ar = C_6H_5, Ar'H = benzene, **6h** Ar = C_6H_5, Ar'H = toluene

6i Ar = C_6H_5, Ar'H = ethylbenzene, **6k** Ar = C_6H_5, Ar'H = biphenyl

6l Ar = C_6H_5, Ar'H = p-xylene, **6m** Ar = C_6H_5, Ar'H = o-xylene

6n Ar = C_6H_5, Ar'H = m-xylene, **6o** Ar = , Ar'H = 3-bromotoluene

6p Ar = p-$Ch_3C_6H_4$, Ar'H = 3-bromotoluene, **6q** Ar=p-$Ch_3C_6H_4$, Ar'H = chlorobenzene

6r Ar = p-$Ch_3C_6H_4$, Ar'H = bromobenzene, **6s** Ar = C_6H_5, Ar'H = bromobenzene

6t Ar = p-$Ch_3C_6H_4$, Ar'H = 4-bromotoluene, **6u** Ar = C_6H_5, Ar'H = 3-bromotoluene

6v Ar=p-$Ch_3C_6H_4$, Ar'H=nitrobenzene, **6w** Ar=p-$Ch_3C_6H_4$, Ar'H=2,4-dibromobenzene

6x Ar = p-$Ch_3C_6H_4$, Ar'H = *N,N*-dimethylaniline

Table IV. Reaction of arensulfonyl chloride with aromatic hydrocarbons

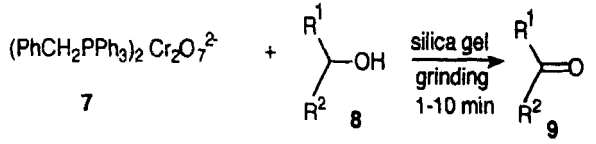
Products **6**[a]	Reaction Time(min)	Yield (%)[b]	mp°C (lit. [7, 8])
4-$MeC_6H_4SO_2C_6H_5$ (**6a**)	10	65	117-119 (125)
4-$MeC_6H_4SO_2C_6H_4Me$-4 (**6b**)	15	68	153-155 (156)
4-$MeC_6H_4SO_2C_6H_4Et$-4 (**6c**)	10	77	104-106 (109-110)
4-$MeC_6H_4SO_2C_6H_4Ph$-4 (**6d**)	5	75	198-203 (-)
4-$MeC_6H_4SO_2C_6H_3(Me)_2$-3,4 (**6e**)	10	83	127-129 (130-131)
4-$MeC_6H_4SO_2C_6H_3(Me)_2$-2,5 (**6f**)	10	81	105-108 (108-110)
$C_6H_5SO_2C_6H_5$ (**6g**)	8	63	119-121 (125)
$C_6H_5SO_2C_6H_5$ (**6h**)	6	69	117-119 (125)
$C_6H_5SO_2C_6H_4Et$-4 (**6i**)	3	57	88-91 (93-93.5)
$C_6H_5SO_2C_6H_4Ph$-4 (**6j**)	4	91	143-146 (148)
$C_6H_5SO_2C_6H_3(Me)_2$-2,5 (**6k**)	3	50	107-110 (-)
$C_6H_5SO_2C_6H_3(Me)_2$-3,4 (**6l**)	2	71	108-112 (-)
$C_6H_5SO_2C_6H_3(Me)_2$-2,4 (**6m**)	5	46	79-82 (87)
4-$MeC_6H_4SO_2C_6H_3$-2-Me-4-Br(**6n**)	12	56	-
4-$MeC_6H_4SO_2C_6H_3$-2-Br-4-Me (**6o**)			
4-$MeC_6H_4SO_2C_6H_4Cl$-4 (**6p**)	25	52	118-121 (123-124)
4-$MeC_6H_4SO_2C_6H_4Br$-4 (**6q**)	15	73	130-134 (134-135)
$C_6H_5SO_2C_6H_4Br$-4 (**6r**)	5	51	98-103 (108-108.5)
4-$MeC_6H_4SO_2C_6H_3$-2-Me-5-Br (**6s**)	10	84	-
4-$MeC_6H_4SO_2C_6H_3$-2-Br-5-Me			
$C_6H_5SO_2C_6H_3$-2-Me-4-Br (**6t**)	5	60	-
$C_6H_5SO_2C_6H_3$-2-Br-4-Me			
- (**6u**)	30	0	-
- (**6v**)	30	0	-
- (**6w**)	30	0	-

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product.

we also wish to report an extremely convenient method for oxidation of organic compounds with supported benzyltriphenylphosphonium dichromate ($(PhCH_2PPh_3)_2\ Cr_2O_7$) on silica gel under solid phase conditions (Scheme I).

The oxidation of alcohols with **7** proceeds well in solid-phase conditions. Benzylic alcohols **8** are oxidised to the corresponding carbonyl compounds in high yields (Table V); allylic alcohols have also been selectively oxidised to α, β-unsaturated carbonyl compounds without cleavage of the carbon-carbon double bonds; α-hydroxy ketone was converted to α-diketone in excellent yield (Table V). Because of the low reactivity of aliphatic alcohols only benzylic and allylic alcohols could be converted into the corresponding carbonyl compounds. In contrast, oxidation of allylic alcohols with manganese dioxide require a large excess of this reagent and long reaction times. The process in its entirety involves a simple mixing of supported benzyltriphenylphosphonium dichromate ($(PhCH_2PPh_3)_2\ Cr_2O_7$) on silica gel and alcohols **8** in a mortar (Scheme V) and grinding the mixture for the time specified in Table V at room temperature. The yields of the reactions are excellent (90-100 %) and the reaction times are exceedingly short (1-10 min). The compounds **9** were characterized by ^1H NMR and IR.

Scheme V



We also found that the reaction of **7** with oximes **10** and substituted hydrazones **11** in the same condition gave the corresponding carbonyl compounds (Scheme VI). No further oxidation to their carboxylic acids was observed (Tables VI and VII). The mechanism of the product formation is not readily clear at this time.

Table V. Oxidation of alcohols 8 to Carbonyl Compounds 9. [a]

Cmpd	R^1	R^2	Time (min)	Yield[b] (%)	mp °C or bp °C/torr (lit. 9-11)
8a	C_6H_4	H	3	100	179/760 (178)
8b	4-$NO_2C_6H_4$	H	5	92	104 (104-105
8c	3,4-$(MeO)_2C_6H_3$	H	10	95	82 (81-83
8d	4-PhC_6H_4	Me	5	99	117-119 (117-119)
8e	2-pyridyl	C_6H_5	5	98	84/760 (83-85)
8f	C_6H_5	Me	5	100	119/760 (118-121)
8g	4-$MeOC_6H_4$	H	1	100	35-37 (35-37)
8h	2-$MeOC_6H_4$	H	5	100	47 (47-47-49)
8i	C_6H_5	C_6H_5	10	90	102/760 (100-103)
8j	3-$MeOC_6H_4$	H	5	93	45 (45-47)
8k	4-ClC_6H_4	H	3	94	196/760 (195-198)
8l	2-ClC_6H_4	H	4	96	212/760 (212-214)
8m	C_6H_5	$C_6H_5CH_2$	5	96	54 (54-55)
8n	4-BrC_6H_4	Me	10	91	49-50 (49-51)
8o	4-ClC_6H_4	Me	5	94	232/760 (232-234)
8p	C_6H_5	C_6H_5CO	5	95	95 (94-96)
8q	2,3-$(MeO)_2C_6H_3$	H	7	98	49-52 (49-53)
8r	C_6H_4CH=CH	C_6H_5	5	95	54-57 (54-57)
8s	C_6H_4CH=CH	Me	8	92	39 (39-40)
8t	4-$NO_2C_6H_4CH$=CH	H	10	96	138-142 (139-142)
8u	C_6H_4CH=CH	H	10	90	127/760 (125-128)

[a] Confirmed by comparison with authentic sample (IR, TLC and NMR). [b] Yield of isolated pure product.

Scheme VI

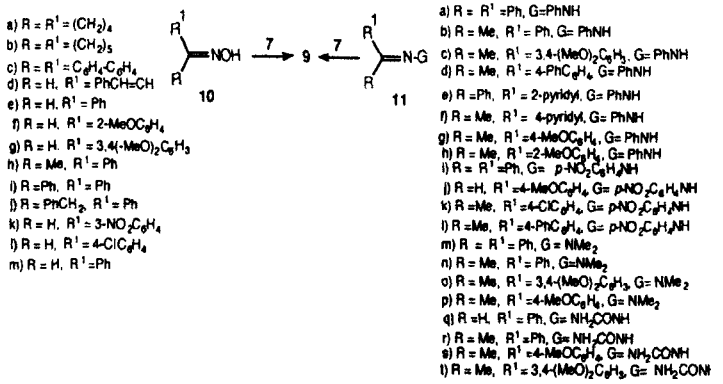


Table VI. Conversion of 10 to Carbonyl Compound 9.

Starting Material	Product [a]	Reaction Time (min)	Yield [b] (%)	mp °C or bp °C/torr (lit. [12, 13, 14])
9a	10a	5	92	127-130/760 (127-130)
9b	10b	4	96	154-156/760 (154-156
9c	10c	4	96	177/760 (179)
9d	10d	7	93	240/760 (240)
9e	10e	5	96	42-44 (41-44)
9f	10f	4	100	204/760 (203)
49g	10g	5	100	49-52 (50-52)
9h	10h	4	97	55-57 (55-57)
9i	10i	10	97	58-60 (58-60)
9j	10j	5	98	80-83 (80-83)
9k	10k	6	95	232/760 (234)
9l	10l	5	98	117-119 (117-118)
9m	10m	8	94	126/760 (125-128)

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product.

Table VII. Conversion of 11 to Carbonyl Compounds 9. [a]

Starting Material	Product [a]	Reaction Time (min)	Yield [b] (%)	mp °C or bp °C/torr (lit. [9-10])
11a	9a	10	92	48 (47-49)
11b	9b	4	98	82-85/760 (83-85)
11c	9c	10	95	48 (47-50)
11d	9d	8	94	118 (117-119)
11e	9e	10	98	42 (41-43)
11f	9f	10	93	78/760 (76-79)
11g	9g	7	98	38 (37-39)
11h	9h	10	94	244-249/760 (245-248)
11i	9i	10	92	49 (47-49)
11j	9j	10	90	120/760 (118-121)
11k	9k	15	95	232/760 (232)
11l	9l	15	94	118-120 (117-119)
11m	9m	8	96	48 (47-49)
11n	9n	8	98	84/760 (83-85)
11o	9o	10	100	48-49 (47-50)
11p	9p	15	95	37-39 (37-39)
11q	9q	10	97	178-190/760 (177-179)
11r	9r	10	92	84-85 (83-85)
11s	9s	15	95	38 (37-39)
11t	9t	15	80	47-49 (47-50)

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product.

The mildness of the reagent has been shown by the oxidation of thiols **12** to their disulfides **13** in excellent yields (Table VIII). This reagent is able to oxidise sulfides **14** to the corresponding sulfoxides **15** in high yield. No further oxidation to their sulfones was observed (Table IX).

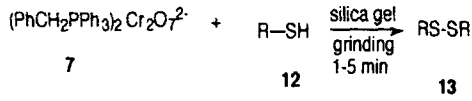


Table VIII. Oxidation of Thiols 12 to Disulfides 13

Entry	R	Reaction Time (min)	Yield (%) a, b	mp °C or bp °C/torr (lit. 10a, 14)
1	phenyl	1	98	58-60 (58-60)
2	4-nitrophenyl	3	87	184-186 (184-186)
3	2-pyridyl	3	92	56-58 (56-58)
4	2-benzimidazoyl	5	86	144-145 (142-145)
5	2-furyl	2	95	118-120/0.8 (112-115/0.5)

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product.

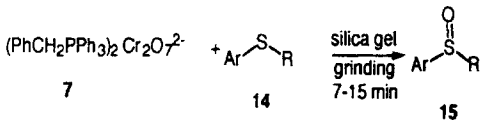
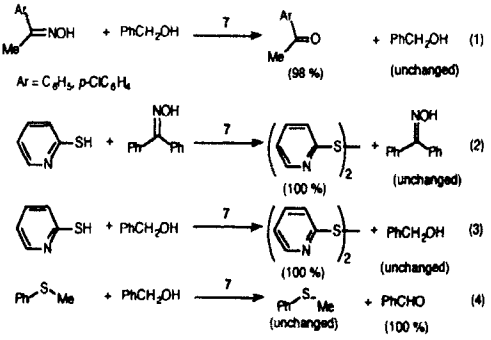


Table IX. Oxidation of Sulfides 14 to Sulfoxides 15.

Entry	Ar	R	Reaction Time (min)	Yield (%) a, b	mp °C or bp °C/torr (lit. 9)
1	benzyl	benzyl	9	93	134-136 (133-135)
2	phenyl	benzyl	7	97	120-122 (122-124)
3	4-nitrophenyl	phenyl	15	90	107-108 (107-108)
4	benzyl	n-butyl	10	96	63-64 (62-63)
5	phenyl	methyl	10	93	124-126/0.8 (139-141/14)
6	phnyl	n-butyl	10	92	103-105 (102-104)

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product.

Another noteworthy advantage of the reagent lies in its ability to afford exclusively carbonyl compounds in the presence of other oxidizable functions (alcohols and double bonds) . When we retreated an equimolar amount of oxime (**10l** or **19h**) with **7** in the presence of benzyl alcohol, only the oxime was selectively oxidised (eq. 1); the hydroxyl groups or C=NOH groups of α,β-unsaturated alcohols or α,β-unsaturated oximes were selectively oxidised to the corresponding carbonyl compounds; the double bonds remained intact (Table VI, oxime **10d** and Table V, alcohols **8r-8u**). In order to evaluate the selectivity of reagent **7**, the competitive reactions shown in eqs. 1-4 were carried out. We retreated an equimolar amount of acetophenoneoxime in the presence of 2-mercaptopyridine; only 2-mercaptopyridine was selectively oxidised (eq. 2). Treatment of a mixture of benzyl alcohol and 2-mercaptopyridine with the reagent **7**, resulted exclusively in the oxidation of 2-mercaptopyridine (eq. 3). In eventually treatment with reagent **7** on benzyl alcohol in the presence of thioanidole, showed only benzyl alcohol was oxidised (eq. 4).



Experimental Section

All products were identified by comparison with an authentic sample (IR, NMR, mp). All mps. were taken on a Gallenkamp melting apparatus and are uncorrected. Elemental analysis was performed by Research Institute of Petroleum Industry, Tehran, I. R. Iran. ^{1}H NMR spectra were recorded on a Varian EM-390 NMR Spectrometer operating at 90 MHz, or a Varian Unity 400 Fourier Transform NMR Spectrometer operating at 400 MHz. The

spectra were measured in $CDCl_3$ unless otherwise stated, relative to TMS (0.00 ppm). Optical rotations were recorded with a JASCO, DIP-370, Digital Polarimeter.

General procedure for preparation of Sulfinate esters 1 and 2, Method 1:. A mortar was charged with the menthol (1 mmol, 0.16 g), sulfonyl chloride (1.5 mmol), trimethyl phosphite (1 mmol, 0.27 g) and silica gel [15] (1 g). The reaction mixture was ground with a pestle in the mortar. When TLC shows no remaining sulfonyl chloride, the reaction mixture was poured into a mixture of ether (20 ml) and 1 N HCl (5 ml). The organic layer was washed with saturated NaHCO3 and saturated NaCl, dried (MgSO4), and concentrated to oil using a rotary evaporator. Purification by flash chromatography on silica gel using a mixture of n-hexane/ethyl acetate (85/15) as eluent affords the pure product as a mixture of diastereomers, which in many cases can be separated by recrystalization from acetone.

Method 2: A mortar was charged with 33% supported thionyl chloride on silica gel (0.45 g, 1.3 mmol thionyl chloride on 0.90 g silica gel), *p*-toluenesulfinic acid (0.16 g, 1 mmol), and the mixture was ground with a pestle for 1 min, then alcohol (1 mmol) was added to the mixture. The reaction mixture was ground for the time specified in table 1. When TLC showed no remaining *p*-toluenesulfinic acid, the reaction mixture was poured into a mixture of ether (20 ml) and H_2O (5 ml). The ethereal layer was washed with saturated $NaHCO_3$ (15 ml), dried ($CaCl_2$), and evaporated to dryness using a rotary evaporator to give pure product.

Preparation of sulfone 6: A mortar was charged with the sulfonyl chloride (2 mmol), and powdered anhydrous aluminium chloride (0.21 g, 2 mmol) under efficient hood. The reaction mixture was ground with a pestle in the mortar for 1, then aromatic hydrocarbon (2 mmol) was added to the reaction mixture. The reaction mixture was ground till TLC shows no remaining sulfonyl chloride, the reaction mixture was extracted with ether (2x20 ml). The solvent was evaporated under reduced pressure at room

temperature and the crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (90:10) as eluent.

Preparation of Benzyltriphenylphosphonium Dichromate 7.

To an aqueous solution of benzyltriphenylphosphonium chloride (8.55 g, 22 mmol, 75 ml H_2O), was added a solution of chromium (VI) oxide (11 g, 11 mmol) in HCl 3 N (220 ml). The reaction mixture was stirred at room temperature for 15 min. The resulting orange solid products was collected, washed with water (20 ml) and dried in a desiccator under vacuum over calcium chloride, yield 9.43 g (10.34 mmol, 94 %) of (1), mp 210-212 °C. ^1H NMR: δ 7.93-6.87 (m, 20 H), 4.7 (d, J=25.6 Hz, C$\underline{H}_2$-P). ^{13}C NMR: δ 133.50, 133.20, 130.20, 129.60, 129.40, 128.10, 127.70, 127.2, 117.30 (d, J=85.5 Hz, P-$\underline{C}H_2$). IR (KBr): 1298, 1269, 1098, 1060, 700, 658, 590, 546 cm^{-1}. Found: C, 69.60; H, 50.20; Cr, 11.90 %. Calcd for $C_{50}H_{44}Cr_2O_7$: C, 69.70; H, 5.15; Cr, 12.08 %.

Oxidation of 8 to 9 or 12, and 14 to 13 and 15: A mortar was charged with alcohol 8, thiol (12 or sulfide 14 (1 mmol) and a supported oxidant 7 on silica gel (prepared from 1 mmol, 0.91 g of oxidant and 0.3 g silica gel). The mixture was grinding with a pestle until TLC showed complete disappearance of starting material. The mixture was then extracted with acetone (2x10 ml). Evaporation of the solvent gave the products.

Conversion of 10 or 11 to 9: A mortar was charged with oxime 10 or hydrazone or semicarbazone derivatives 11 (1 mmol) and a supported oxidant 7 on silica gel (prepared from 1 mmol, 0.91 g of oxidant and 0.3 g silica gel). The mixture was grinding with a pestle until TLC showed complete disappearance of starting material. The mixture was then extracted with acetone (2x10 ml). Evaporation of the solvent gave the products.

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