Chem. Pharm. Bull. 28(1) 134—141 (1980)

Novel One-step Preparation of Sulfinic Acid Derivatives from Sulfinic Acid[1]

Mitsuru Furukawa, Tadashi Ohkawara, Yoshihide Noguchi, Masumi Nishikawa, and Masahide Tomimatsu

Faculty of Pharmaceutical Sciences, Kumamoto University[2]

(Received June 21, 1979)

Convenient one-step syntheses of sulfinamides and sulfinate esters from sulfinic acids were achieved by using coupling reagents, such as 2-chloro-1-methylpyridinium iodide, γ-saccharine chloride, N,N′-dicyclohexylcarbodiimide, and diethyl azodicarboxylate and triphenylphosphine. Ammonolysis of sulfinate esters also gave sulfinamides.

Keywords——sulfinic acid; sulfinamide; sulfinate ester; sulfinyl-transfer reagent; coupling reaction; 2-chloro-1-methylpyridinium iodide; γ-saccharine chloride; N,N′-dicyclohexylcarbodiimide; diethyl azodicarboxylate; triphenylphosphine

The most frequently used methods for preparing sulfinate esters[3] and sulfinamides[4] involve sulfinyl transfer with sulfinyl chlorides. In addition, sulfinamides have conventionally been prepared by the treatment of thionylamine with Grignard reagents.[5] Sulfinate esters have been prepared by several methods, including the oxidation of thiols or disulfides with lead (IV) tetraacetate,[6] the reaction of Grignard reagents with dialkyl sulfites,[7] and the condensation of sulfinic acids with alcohols using dicyclohexylcarbodiimide (DCC) as a dehydrating agent.[8] Unfortunately, these methods are of limited applicability and provide low yields owing to the use of unstable precursors and the occurrence of side reactions, with the exception of the last method. More recently, it has been shown by Harpp[9] that N-sulfinylphthalimides possess desirable properties as the sulfinyl transfer agents. They are far more stable than sulfinyl chlorides and react rapidly with nucleophiles such as amines and alcohols, resulting in the formation of the corresponding sulfinyl compounds in high yields. This method, however, is rather laborious and expensive. The processes involve several reaction steps including clean oxidation, for example, of N-sulfenylphthalimides to the N-sulfinyl compounds with *m*-chloroperbenzoic acid. On the other hand, this oxidizing agent has also been reported to oxidize sulfenamides smoothly to sulfonamides.[10]

We report here novel and convenient one-step preparations of sulfinamides and sulfinates, which involve the direct sulfinylation of amines and alcohols with sulfinic acids, using coupling reagents such as 2-chloro-1-methylpyridinium iodide, γ-saccharine chloride, diethyl azodicarboxylate (DEAD) and triphenylphosphine, and DCC. With the exception of the coupling

1) A preliminary communication of a part of this work has appeared in *Synthesis*, **1978**, 441.
2) Location: *5-1 Oe-hon-machi, Kumamoto 862, Japan.*
3) H. Phillips, *J. Chem. Soc.*, **1925**, 2552; I.B. Douglass, *J. Org. Chem.*, **30**, 663 (1965); S.W. Wilt, R.G. Stein, and W.J. Wagner, *J. Org. Chem.*, **32**, 2097 (1967).
4) L.C. Raiford and S.E. Hazlet, *J. Am. Chem. Soc.*, **57**, 2127 (1935); I.B. Douglass and B.S. Farah, *J. Org. Chem.*, **23**, 805 (1958).
5) H. Gilmann and H.L. Morris, *J. Am. Chem. Soc.*, **48**, 2399 (1926); D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959).
6) L. Field, C.B. Hoelzel, and J.M. Locke, *J. Am. Chem. Soc.*, **84**, 847 (1962).
7) M. Mikolajczyk and J. Drabowicz, *Synthesis*, **1974**, 124.
8) Y. Miyaji, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **44**, 862 (1971).
9) D.N. Harpp and T.G. Back, *J. Org. Chem.*, **38**, 4328 (1973).
10) E. Kühle, "The Chemistry of the Sulfenic Acids," George Thiem Verlag, Stuttgart, 1973; R.S. Glass and R.J. Swedo, *Synthesis*, **1977**, 798.

reaction of alcohols with sulfinic acids using DCC,[8] there has been no previous report on the direct use of sulfinic acids as sulfinyl transfer reagents.

Preparation of Sulfinamides and Sulfinates using 2-Chloro-1-methylpyridinium iodide (Method A)

Recently Mukaiyama has developed a variety of new reactions using 2-chloro-1-methylpyridinium iodide as the activating reagent. We found that the reactions of sulfinic acids with amines and alcohols in the presence of this coupling reagent provided a convenient route for syntheses of sulfinamides and sulfinates. The reactions were carried out by heating a sulfinic acid (**1**) with an equivalent amount of an amine (**4**) or alcohol (**5**) in an inert solvent such as carbon tetrachloride or dichloromethane in the presence of a slight excess of 2-chloro-1-methylpyridinium iodide (**2**) and triethylamine under reflux in a nitrogen atmosphere. Extraction of the reaction mixture with ether and washings with 0.1 N hydrochloric acid and 1% sodium hydrogen carbonate, followed by removal of the solvent and then distillation or recrystallization, provided the sulfinamide (**6**) and sulfinate (**7**) in moderate yields, together with N-methyl-2-pyridone and a small amount of *p*-tolyl *p*-toluenethiolsulfonate as by-products.

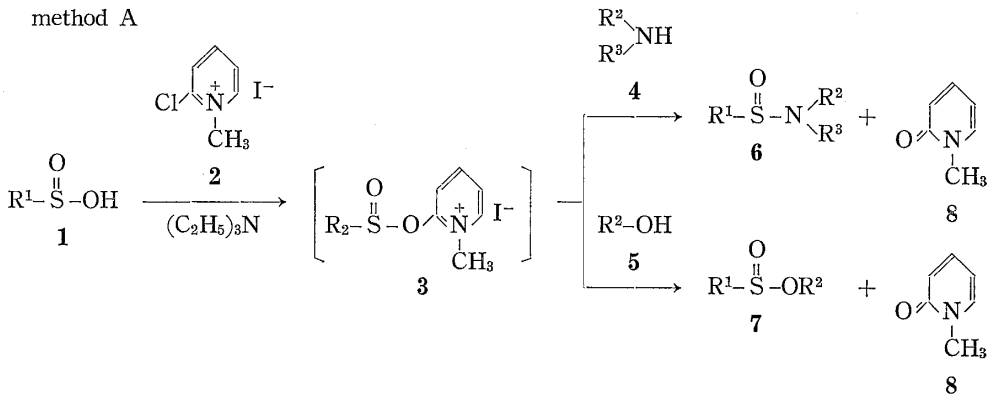


Chart 1

Table I. Preparation of Sulfinamides $R^1-\overset{O}{\overset{\|}{S}}-N\begin{matrix}R^2\\R^3\end{matrix}$

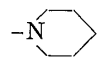
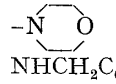
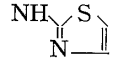
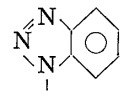
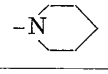
R^1	$-N\begin{matrix}R^2\\R^3\end{matrix}$	mp (°C)	% yield (Reaction time: hr)		
			Method A	Method B	Method D
p-$CH_3C_6H_4$		63— 64	47 (1)	28 (1.5)	36 (12)
p-$CH_3C_6H_4$		114—115	45 (1)	41 (0.75)	44 (12)
p-$CH_3C_6H_4$	$NHCH_2C_6H_5$	80— 81	49 (1)	52 (1.5)	65 (12)
p-$CH_3C_6H_4$	NHC_6H_{45}	117—118	48 (1)	45 (1.3)	56 (12)
p-$CH_3C_6H_4$		169—171	—	46 (17)	—
p-$CH_3C_6H_4$		210—213	—	26 (48)	—
n-$C_{12}H_{25}$	$NHCH_2C_6H_5$	56— 57	39 (1)	—	43 (12)
n-$C_{12}H_{25}$	NHC_6H_5	72— 73	52 (1)	—	65 (12)
C_6H_5		80— 81	—	75 (3)	—

Table II. Preparation of Sulfinates $R^1-\overset{O}{\overset{\|}{S}}-OR^2$

R^1	R^2	bp °C (mmHg)	% yield (Reaction time: hr) Method A	Method B	Method C	Method F
p-$CH_3C_6H_4$	C_2H_5	96 (2.0)	76 (3)	59	36 (5)	43 (3)
p-$CH_3C_6H_4$	n-C_4H_9	104 (1.5)	75 (3)	69	31 (5)	47 (3)
p-$CH_3C_6H_4$	$tert$-C_4H_9	98 (2.0)	0 (3) [a]	39	0 (5) [b]	42 (3)
p-$CH_3C_6H_4$	n-C_8H_{17}	152 (2.0)	60 (3)	58	39 (5)	49 (3)
p-$CH_3C_6H_4$	CH_2=$CHCH_2$	114 (2.0)	52 (3)	57	32 (5)	51 (3)
p-$CH_3C_6H_4$	$C_6H_5CH_2$	161 (2.5)	65 (3)	25	35 (5)	43 (3)
p-$CH_3C_6H_4$	l-Menthyl	105—106 [c]	35 (3) [d]	24 [e]	27 (5) [f]	23 (3) [g]
n-$C_{12}H_{25}$	C_2H_5	134 (2.5)	62 (3)	—	33 (5)	58 (3)
p-$CH_3C_6H_4$	n-C_6H_{13}	139 (1.0)	—	69	—	—
p-$CH_3C_6H_4$	$CH{\equiv}CCH_2$	135 (2.0)	—	57	—	—

a) An 82% yield of p-tolyl p-toluenethiolsulfonate was obtained.
b) A 31% yield of p-tolyl p-toluenethiolsulfonate was obtained.
c) mp (°C).
d) $[\alpha]_D^{15}$ −198.7° (c=1.9, acetone).
e) $[\alpha]_D^{15}$ −196.0° (c=1.9, acetone).
f) $[\alpha]_D^{15}$ −190.4° (c=2.5, acetone).
g) $[\alpha]_D^{15}$ −196.8° (c=1.9, acetone).

This reactions appears to involve the initial formation of the activated sulfinate ester intermediate (**3**), followed by nucleophilic attacks of **4** and **5** at the sulfinyl sulfur atom activated by the positive quaternary ammonium group. All the compounds **6** and **7** obtained are listed in Tables I and II, respectively.

It is interesting to note that aniline, an aromatic amine, is sufficiently nucleophilic to generate sulfinanilides in about 50% yield, while phenol, an aromatic alcohol, and the bulky *tert*-butyl alcohol are not nucleophilic. The reaction of p-toluenesulfinic acid with *tert*-butyl alcohol and phenol, for example, unexpectedly gave p-tolyl p-toluenethiolsulfonate in 82% and 24% yields, respectively, with no formation of the expected p-toluenesulfinates. It seems that thiolsulfonate may be formed by the preferential attack of sulfinic acid rather than *tert*-butyl alcohol or phenol on the intermediate ester (**3**).

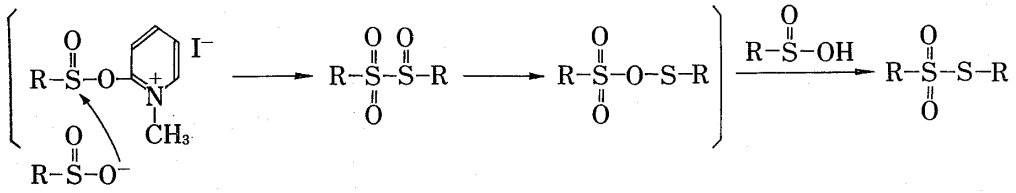


Chart 2

A similar disproportionation of sulfinic acid to thiolsulfonate was reported in detail by Kice.[11] The formation of at least a trace of thiolsulfonate was observed in all cases here.

Preparation of Sulfinamides and Sulfinates using γ-Saccharine Chloride (Method B)

We found that γ-saccharine chloride (**9**) was also effective as a readily available coupling reagent. The preparation of sulfinamides (**6**) was successfully achieved by stirring a solution of equivalent amounts of sulfinic acid (**1**) and amine (**4**) in dichloromethane with a slight excess of γ-saccharine chloride (**9**) and triethylamine at room temperature under a nitrogen

11) J.L. Kice and K.W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962); *J. Org. Chem.*, **29**, 1162 (1963).

atmosphere. Extraction of the reaction mixture with diethyl ether, washings with 0.1 N hydrochloric acid and then 1% aqueous sodium hydrogen carbonate, removal of the solvent, and finally recrystallization afforded the desired **6** in 26—75% yields. Sulfinates (**7**) were also prepared analogously by using the alcohols (**5**) instead of **4** under similar conditions (21—95% yields). In these reactions *p*-tolyl *p*-toluenethiolsulfonate was obtained as a by-product in low yield.

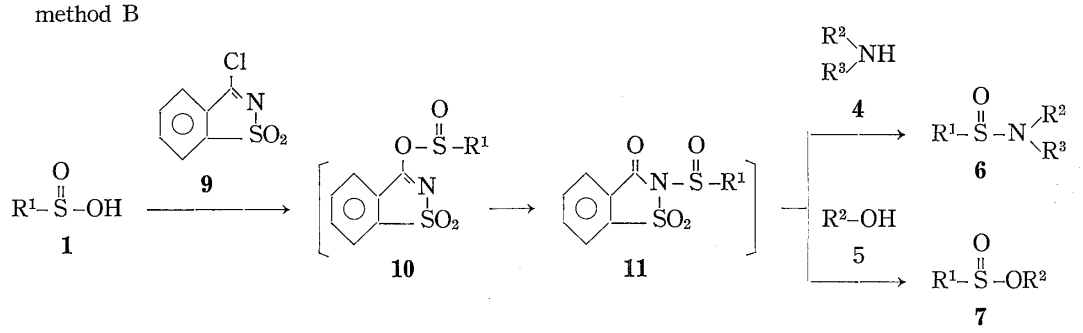


Chart 3

The reaction may involve the initial formation of the intermediate ester form (**10**) followed by conversion into the amide form (**11**) by O→N migration of the sulfinyl group, followed by the nucleophilic attack of **4** or **5** at the sulfinyl group (the electrophilic character is enhanced by the adjacent carbonyl and sulfonyl groups) to afford **6** and **7**, respectively, together with saccharine and a small amount of *p*-tolyl *p*-toluenethiolsulfonate as by-products.

In fact, the intermediate product (**11**) was isolated from the reaction mixture and exhibited absorption assignable to the carbonyl group at 1720 cm^{-1} in the infrared (IR) spectrum. These results suggest that the amide form (**11**) is more likely for the intermediate. All the compounds obtained by this procedure are summarized in Tables I and II.

Analogously to the case of 2-chloro-1-methylpyridinium iodide, this procedure gave the desired sulfinamides with aromatic amines such as aniline, 2-aminothiazole and benzotriazole, and gave thiolsulfonates with aromatic alcohols such as phenol, picric acid and 2-hydroxypyridine, in high yields, but without formation of the desired sulfinates.

Preparation of Sulfinates using DEAD and Triphenylphosphine (Method C)

It has been known for a number of years that oxidative–reductive dehydrative coupling of certain compounds occurs in the presence of DEAD and triphenylphosphine. These reagents have been utilized in the synthesis of carboxylic esters,[12] carbodiimides,[13] ketenimines,[14] isonitriles,[15] amines,[16] sterol esters,[17] *o*-(N-phenylcarbamoyl) hydroxamates,[18] benzoylated diols,[19] aryl alkyl ethers,[20] lactones,[21] nitriles,[22] carbamates[23] and heterocyclic

12) O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Jpn.*, **40**, 2380 (1967).
13) O. Mitsunobu, K. Kato, and F. Kakase, *Tetrahedron Lett.*, **1969**, 2473; O. Mitsunobu, K. Kato, and M. Tomari, *Tetrahedron*, **26**, 5731 (1970).
14) O. Mitsunobu, K. Kato, and M. Wada, *Bull. Chem. Soc. Jpn.*, **44**, 1362 (1971).
15) B. Beiyer, E. Von Hinrichs, and I. Ugi, *Angew. Chem. Int. Ed. Engl.*, **11**, 929 (1972).
16) O. Mitsunobu, M. Wada, and T. Sano, *J. Am. Chem. Soc.*, **94**, 679 (1972).
17) A.K. Bose, B. Lal, W.A. Hoffman III, and M.S. Manhas, *Tetrahedron Lett.*, **1973**, 1619.
18) S. Mittner, S. Grinberg, and I. Kartoon, *Tetrahedron Lett.*, **1974**, 1965.
19) O. Mitsunobu, J. Kimura, K. Siizumi, and N. Yanagida, *Bull. Chem. Soc. Jpn.*, **49**, 510 (1976).
20) M.S. Manhas, W.A. Hoffman, F. Lal, and A.K. Bose, *J. Chem. Soc., Perkin I*, **1975**, 461; S. Bittner, and Y. Assaf, *Chem. Ind.* (London), **1975**, 281.
21) T. Kurihara, Y. Nakajima, and O. Mitsunobu, *Tetrahedron Lett.*, **1976**, 2455; P. Bakuzis, M.L.F. Bakuzis, and T.F. Weingartner, *Tetrahedron Lett.*, **1978**, 2371.
22) M.D. Dowle, *Chem. Comm.*, **1977**, 220.
23) E. Grochowski and J. Jurczak, *J. Org. Chem.*, **43**, 2541 (1978).

compounds.[24] In the present study, convenient preparation of sulfinates was also achieved by using these coupling reagents. The reaction was carried out by adding equivalent amount of **1** and alcohols (**5**) to a mixture of DEAD (**12**) and triphenylphosphine (**13**) in benzene at room temperature. Removal of the solvent, followed by extraction with *n*-hexane and then by silica gel chromatography, provided comparatively pure sulfinates in 27—40% yields, with small amounts of *p*-tolyl *p*-toluenethiolsulfonate and di-*p*-tolyl disulfide. It is of interest that, when alcohols were added to the mixture of **12** and **13** prior to the addition of sulfinic acids, a decrease in the yields of the sulfinates was observed.

This reaction appears to proceed through the initial formation of the phosphine azo intermediate (**14**) previously described by Morrison.[25] The betaine interacts with sulfinic acids to form the adduct (**15**) or the corresponding salt (**16**). The attack of alcohol on the intermediate forms the sulfinates (**7**), triphenylphosphine oxide (**18**) and diethoxycarbonylhydrazine (**17**).

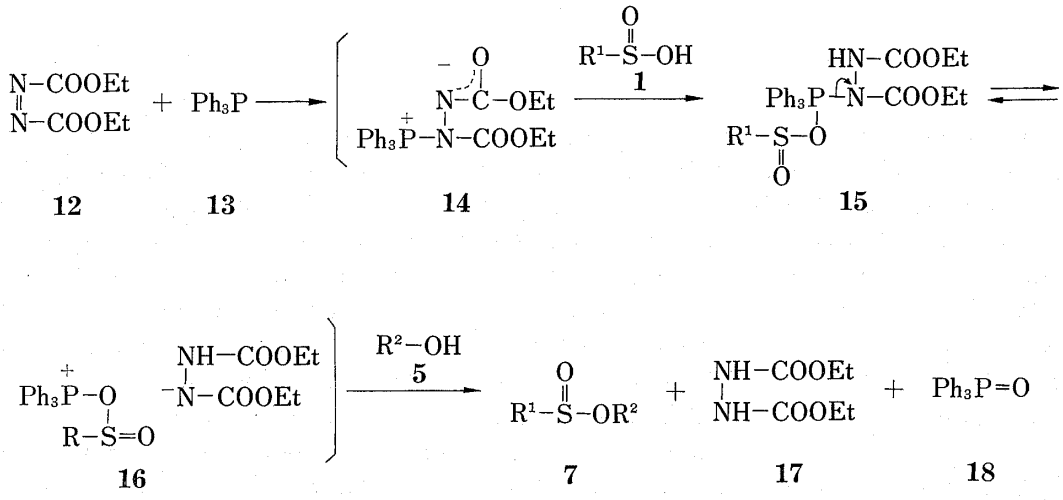


Chart 4

Unfortunately, this procedure could not be extended to the preparation of sulfinamides, because of the extreme difficulty in separating the resulting sulfinamides from the by-product diethoxycarbonylhydrazine. The sulfinates prepared by this method are listed in Table II.

Preparation of Sulfinamides using DCC (Method D)

Sulfinates can be obtained in high yields by the coupling reaction of sulfinic acids with alcohols using DCC.[8] We found that this simple one-step procedure was effective for the preparation of sulfinamides. The reaction was carried out by stirring equivalent amounts of sulfinic acids (**1**) and amines (**4**) in dioxane in the presence of a slight excess of DCC at room temperature overnight. Removal of dicyclohexylurea from the reaction mixture by filtration, followed by removal of the solvent by evaporation, provided the corresponding sulfinamides (**6**) in 36—65% yields after recrystallization; small amounts of *p*-tolyl *p*-toluenethiolsulfonate were also obtained.

Formation of Sulfinamides (6) and Sulfinates(7) (Method E and F)

Two procedures for the transformation of **7** into **6** were examined (Method E). One is the reaction of **7** with amines (**4**) in the presence of sodium hydride as a catalyst, and the other is the use of bifunctional catalysts. When methyl *p*-toluenesulfinate was heated with

24) J.T. Carlock and M.P. Mack, *Tetrahedron Lett.*, **1978**, 5153.
25) D.C. Morrison, *J. Org. Chem.*, **23**, 1072 (1958).

method D

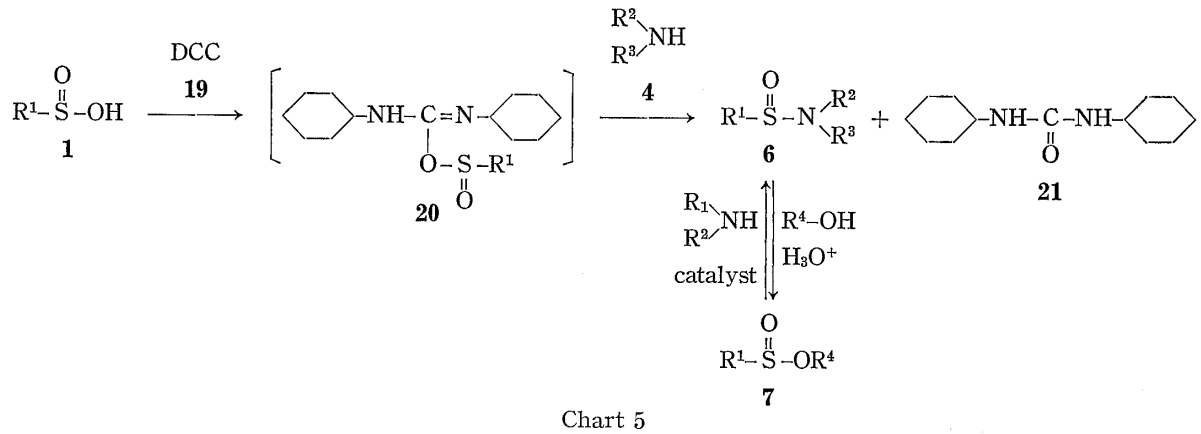
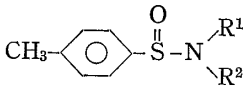
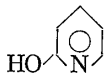
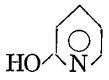
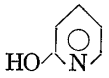
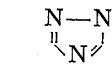
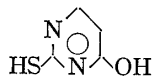
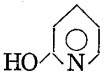
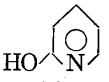
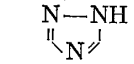
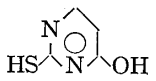
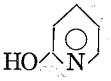


Chart 5

TABLE III. *p*-Toluenesulfinamides obtained from Methyl *p*-Toluene Sulfinate using Catalysts



$-N\begin{matrix}R^1\\R^2\end{matrix}$	Catalyst	Solvent	Reaction time (hr)	Yield (%)
	None	CH_3CN	48	7
	NaH	Dioxane	4	70
		CH_3CN	24	37
		$CHCl_3$	24	27
		DMF (70—80°)	23	11
		CH_3CN	12	53
		CH_3CN	12	36
$NHCH_2C_6H_5$	None	CH_3CN	48	7
$NHCH_2C_6H_5$	NaH	THF	4	49
$NHCH_2C_6H_4$		CH_3CN	7	20
$NHCH_2C_6H_5$		Benzene	20	0
$NHCH_2C_6H_5$		CH_3CN	18	63
$NHCH_2C_6H_5$		CH_3CN	18	37
NHC_6H_5	None	CH_3CN	48	0
NHC_6H_5	NaH	CH_3CN	5	82
NHC_6H_5		CH_3CN	12	11
	NaH	Dioxane	5	65

one equivalent of **4** in the presence of one equivalent of sodium hydride in dioxane or tetrahydrofuran (THF) for 4—5 hr under a nitrogen atmosphere, the corresponding **6** was obtained in 40—82% yield, together with a small amount of *p*-tolyl *p*-toluenethiolsulfonate.

As bifunctional catalysts, 2-hydroxypyridine, 4H-1,2,4-triazole and 2-thiouracil were employed. The similar synthesis of amides from carboxylic esters using these bifunctional catalysts was described by Beyerman[26] in the field of peptide synthesis. The synthesis of **6** was successfully carried out by heating equivalent amounts of methyl *p*-toluenesulfinate, **4** and the catalyst in a solvent such as acetonitrile, chloroform or dimethylformamide (DMF) to give the corresponding *p*-toluenesulfinamides in 11—63% yields (Chart 5) together with a small amount of *p*-tolyl *p*-toluenethiolsulfonate. These results are summarized in Table III.

As shown in Table III, the yield of **6** is extremely low in the absence of the catalyst, and it seems clear that these catalysts promote the reactions. Among the bifunctional catalysts, the best result was obtained with 4H-1,2,4-triazole. The reaction presumably proceeds through the following transition state, in which hydrogen bonds between the reactants and catalyst participate.

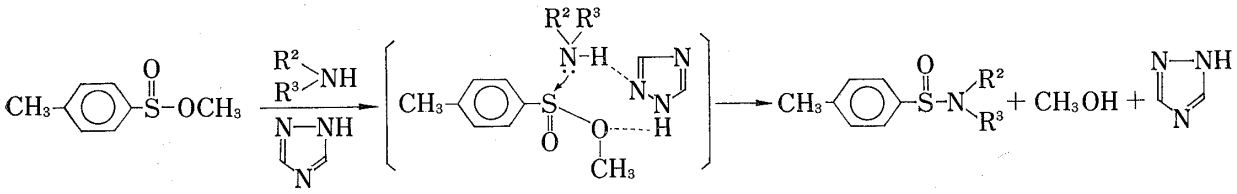


Chart 6

Recently, the alcoholysis of sulfinamides (**6**) to sulfinates (**7**) was reported to occur readily with simple alcohols in the presence of two equivalents of strong acids at 0 °C or at room temperature in excellent yields.[27] In this study, alcoholysis with several alcohols, including sterically bulky alcohols, was examined, using N-benzylsulfinamides (Method F).

The reactions were successfully carried out by heating a solution of equivalent amounts of N-benzylsulfinamides and alcohols (**5**) in benzene containing one equivalent of sulfuric acid. Washings with 1 N hydrochloric acid, 1% aqueous sodium hydrogen carbonate and water, followed by removal of the solvent and distillation or recrystallization, provided the desired **7** in 23—58% yields, together with small amounts of *p*-tolyl *p*-toluenethiolsulfonate. These results are summarized in Tables I and II. It is interesting to note that this method can provide **7** having sterically bulky groups. For example, *tert*-butyl *p*-toluenesulfinate was obtained in 42% yield.

Experimental[28]

Preparation of Sulfinamides (6) and Sulfinates (7). General Procedure——Method A: Using 2-Chloro-1-methylpyridinium Iodide (**2**): Powdered **2** (2.4 mmol) was added with stirring to a solution of sulfinic acid (**1**) (2 mmol), amine (**4**) (2 mmol) or alcohol (**5**) (2 mmol), and triethylamine (4.8 mmol) in dichloromethane (20 ml) at room temperature. The solution was refluxed with stirring for 1 hr under a nitrogen atmosphere, and after cooling, ether (40 ml) was poured into the solution. The mixture was washed with 1% aqueous $NaHCO_3$ (40 ml) and H_2O (40 ml) twice each, and then dried over Na_2SO_4. After removal of the solvent by evaporation, the residue was purified by recrystallization from MeOH or AcOEt in the case of **6**, and by distillation or recrystallization from acetone and H_2O (9: 1) in the case of **7**.

26) H.C. Beyerman and W. Waasen, *Proc. Chem. Soc.*, **1963**, 266.
27) M. Mikolajczyk, J. Drabowicz, and B. Bujnicki, *J. Chem. Soc., Chem. Comm.*, **1976**, 568.
28) All melting points are uncorrected. IR spectra were measured on a Jasco IRA-1 grating infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were taken on a JEOL C-60H high resolution NMR instrument at 60 MHz. Mass spectra (MS) were determined at 75 eV on a JEOL 01SG mass spectrometer.

When **1** (2 mmol) was allowed to react with *tert*-butyl alcohol (2 mmol) or phenol (2 mmol), *p*-tolyl *p*-toluenethiolsulfonate was obtained. The product was recrystallized from EtOH. Yields were 82% and 24%, respectively. mp 77—78°. *Anal.* Calcd for $C_{14}H_{14}S_2O_2$: C, 60.40; H, 5.70. Found: C, 60.49; H, 5.19. IR ν_{max}^{KBr} cm^{-1}: 1300, 1130 (SO_2). NMR ($CDCl_3$): 2.33 (*s*, 3H, CH_3), 2.38 (*s*, 3H, CH_3), 7.10 (*s*, 4H, arom.), 7.23 (q, 4H, arom.).

Method B: Using *γ*-Saccharine Chloride (**9**): Powdered **9** (1.2 mmol) was added in small portions with stirring to a solution of **1** (1 mmol), **4** (1 mmol) or **5** (1 mmol), and triethylamine (2.4 mmol) in dichloromethane (20 ml) at room temperature under nitrogen stream. Stirring was continued for 3—6 hr and chloroform (50 ml) was added to the solution. The mixture was washed with 0.1 N HCl (40 ml), 1% aqueous $NaHCO_3$ (40 ml) and H_2O (40 ml) twice each and then dried over anhyd. Na_2SO_4. After removal of the solvent by evaporation, the residue was purified by recrystallization from MeOH or by column chromatography on silica gel in the case of **6**, and by distillation or silica gel column chromatography in the case of **7**.

The reaction of **1** with phenol, picric acid and 2-hydroxypyridine afforded *p*-tolyl *p*-toluenethiolsulfonate in 19%, 90% and 85% yields, respectively. The structure was confirmed by comparison of its IR spectrum with that of *p*-tolyl *p*-toluenethiolsulfonate obtained by Method A.

Method C: Using DEAD (**12**) and Triphenylphosphine (**13**): A solution of **1** (10 mmol) in dry benzene (10 ml) was added to a solution of **12** (10 mmol) and **13** (10 mmol) in dry benzene (20 ml) at room temperature. The mixture was stirred for 30 min, then **5** (10 mmol) was added. Stirring was continued for 10—12 hr at room temperature. The resulting precipitates were filtered off and the filtrate was washed with 1 N HCl (20 ml), 1% aqueous $NaHCO_3$ (15 ml) and twice with H_2O (15 ml), then dried over anhyd. Na_2SO_4, and evaporated to dryness. The residue was extracted twice with *n*-hexane (20 ml). After removal of the solvent, the residue was passed through a silica gel column, eluting with a mixture of *n*-hexane and $CHCl_3$ (1:1). In this procedure, the reaction of **1** with *tert*-butyl alcohol afforded *p*-tolyl *p*-toluenethiolsulfonate in 31% yield. The structure was comfirmed by comparison of its IR spectrum with that of *p*-tolyl *p*-toluenethiosulfonate obtained by Method A.

Method D: Using DCC (**19**): A solution of **19** (5.5 mmol) in anhyd. dioxane (5 ml) was added dropwise with stirring to a solution of **1** (5 mmol) and **4** (5 mmol) in anhyd. dioxane under cooling with ice. Stirring was continued at room temperature for 12 hr. The precipitated dicyclohexylurea was filtered off and the filtrate was evaporated to dryness under reduced pressure below 50°. The residue was dissolved in AcOEt to remove dicyclohexylurea. After removal of the solvent, the residue was recrystallized from MeOH or purified by column chromatography on silica gel.

Method E: Ammonolysis of Sulfinates (**7**)—With NaH: A solution of amine (0.55 mmol) in anhyd. dioxane (10 ml) or THF (10 ml) was added to a suspension of NaH (0.5 mmol) in anhyd. dioxane (10 ml) under a nitrogen atmosphere, and the mixture was stirred for 15 min. A solution of **7** (0.55 mmol) in anhyd. dioxane (10 ml) or THF (10 ml) was then added to the stirred mixture and the whole was heated for 4—5 hr under reflux. After removal of the solvent by distillation, the residue was extracted with ether or $CHCl_3$. The extract was washed with 1 N HCl, 1% aqueous $NaHCO_3$ and H_2O, dried over anhyd. Na_2SO_4, and evaporated to dryness. The residue was recrystallized from MeOH to give **6**.

With Bifunctional Catalyst: A solution of **7** (0.2 mmol), amine (0.2 mmol) and a catalyst (0.2 mmol) in a solvent (10 ml) was heated for 7—48 hr under reflux. After removal of the solvent by distrillation, the residue was extracted with $CHCl_3$ and the extract was washed with 0.5 N HCl, 1% aqueous $NaHCO_3$ and H_2O, dried over anhyd. Na_2SO_4, and concentrated. The residue was purified by recrystallization or by column chromatography on silica gel to give **6**. These results are summarized in Table III.

Method F: Alcoholysis of Sulfinamides (**6**): A solution of **6** (0.5 mmol), alcohol (0.5 mmol) and conc. H_2SO_4 (0.5 mmol) in benzene (10 ml) was heated for 3 hr under reflux. After cooling, benzene (10 ml) was added and the solution was washed with 1 N HCl (10 ml), 1% aqueous $NaHCO_3$ (5 ml) and finally with H_2O (10 ml), then dried over anhyd. Na_2SO_4, and concentrated by distillation. The residue was purified by distillation under reduced pressure or by recrystallization to give **7**. The yields are listed in Table II.