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Syntheses of Alkyl *p*-Toluenesulfinates by Use of *N,N'*-Dicyclohexylcarbodiimide[1]

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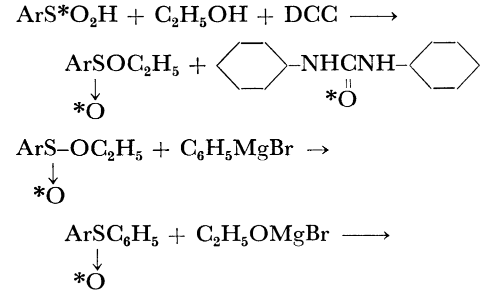
In contrast with the case of carboxylic acids, sulfinic acids cannot be converted to their esters by the reaction with alcohols in the presence of acid catalysts, since they readily undergo disproportionation to yield thiosulfonates and sulfonic acids under acid conditions. Ordinary procedures for synthesizing sulfinates utilize reactions between sulfinyl chlorides and anhydrous alcohols[2,3] or reactions between sodium sulfinates and chlorocarbonates in alcohols.[4] Investigations in our laboratories revealed that when an equimolar amount of dicyclohexylcarbodiimide (DCC) was present a sulfinic acid and an anhydrous alcohol were converted to a sulfinate in good yields. Results will be described in this paper.

Results and Discussion

The results are shown in Table 1. The procedure is very simple, and yet the yields are very good; 64—75% for ordinary sulfinates and 30% for unstable *t*-alkyl sulfinates. This method does not require sulfinyl chlorides which are thermally unstable and sensitive to moisture. This one-step synthesis of sulfinates at lower temperatures will be very effective for preparation of rather unstable sulfinates or isotope-labeled sulfinates.

When ^{18}O-labeled *p*-toluenesulfinic acid and ethanol were let to react, the ethyl ester formed contained a half of the oxygen-18 present in the acid as shown in Table 2. When this ethyl ester was made to react with phenylmagnesium bromide, the ^{18}O % of phenyl *p*-tolyl sulfoxide was the same as that of the original acid. Therefore, only one of the oxygen-18 of the sulfinic acid is contained in the sulfinate as the sulfinyl oxygen.



These findings suggest that the following mechanism is plausible for this reaction. Further investigation is necessary in order to determine whether the intermediate is I or II.

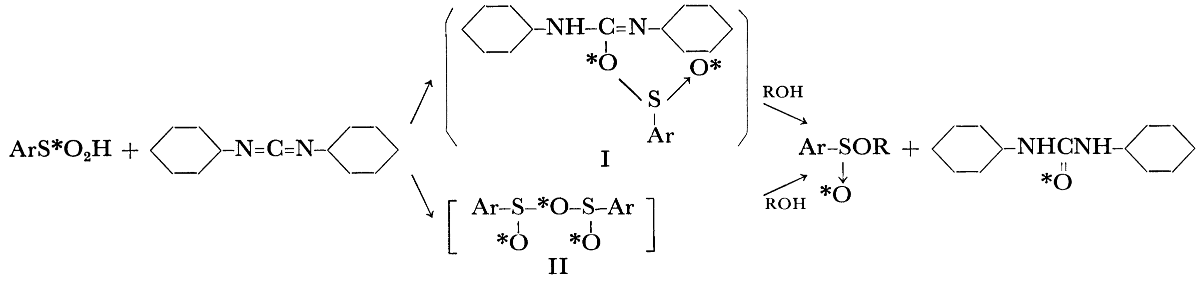


Table 1. Yields of alkyl *p*-toluenesulfinates by use of DCC

R	Method	Reagents used			Yields of products	
		$C_7H_7SO_2H$ g(mol)	ROH m*l*	DCC g(mol)	$C_7H_7SO_2R$ g(mol%)	C_6H_{11}-NHCONH-C_6H_{11} g(mol%)
Allyl	A	8.5(0.054)	50	11.4(0.055)	5.4(64.5)	8.5(73.3)
Et	A	7.5(0.048)	50	8.8(0.043)	5.7(76.0)	9 (93.8)
Et	no DCC	3.6(0.028)	18	—	0.6(14.1)	—
i-Pr	A	2.6(0.017)	25	3.1(0.015)	1.9(63.5)	2.7(80.0)
t-Bu	B	4.0(0.025)	3.8(0.050)	4.61(0.023)	1.3(30.0)	2.6(50.0)
l-Menthyl	B	20.5(0.132)	21.8(0.145)	25.3(0.124)	10.5(28.6)[a]	30.3(114)

a) Crystalline *l*-menthyl *p*-toluenesulfinate obtained from a mixture of diastereomeis.

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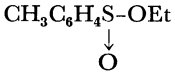
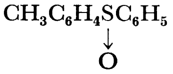
1) Organic Sulfur Compounds. XXIII.

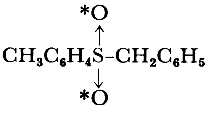
2) H. Phillips, *J. Chem. Soc.*, **1925**, 2552.

3) J. W. Wilt, R. G. Stein, and W. J. Wagner, *J. Org. Chem.*, **32**, 2097 (1967).

4) A. Yamamoto and M. Kobayashi, This Bulletin, **39**, 1292 (1966).

TABLE 2. OXYGEN-18 DISTRIBUTION

Sample	Excess atom% ^{18}O	
	Found	Calcd
$CH_3C_6H_4SO_2H$[a]	0.895	—
 $CH_3C_6H_4\underset{\underset{O}{\downarrow}}{S}\text{-}OEt$	0.462	0.448
 $CH_3C_6H_4\underset{\underset{O}{\downarrow}}{S}C_6H_5$	0.901	0.896


a) as $CH_3C_6H_4\overset{\overset{*O}{\uparrow}}{\underset{\underset{*O}{\downarrow}}{S}}\text{-}CH_2C_6H_5$

Experimental

Alkyl p-*toluenesulfinates. Method A*: *p*-Toluenesulfinic acid was dissolved in large excess of an anhydrous alcohol, and 0.9—0.95 mol of DCC per mol of the sulfinic acid was slowly stirred into the solution cooled with ice. The solution immediately became turbid, and in some cases some heat was evolved. Stirring was continued for several hours or overnight. White precipitates formed were filtered off, water was added to the filtrate, and oil-soluble products were extracted with *n*-hexane. The hexane extracts were washed with a sodium carbonate solution and water, dried and then distilled. A pure alkyl sulfinate was obtained by distillation under reduced pressure or recrystallization.

Method B: To a dichloromethane solution of *p*-toluenesulfinic acid an equimolar or a little excess amount of an alcohol was added. A dichloromethane solution of DCC was slowly stirred into the sulfinic acid solution cooled with ice, and the stirring was continued for several hours or overnight. White precipitates formed were filtered off, the solvent was removed by evaporation, and the residue was dissolved in hexane. When white precipitates were formed they were removed by filtration. The rest of the procedure was the same as described in method A.

The reason why the amount of DCC used as less than equimolar is that the unreacted DCC cannot be easily separated from sulfinates by distillation. The DCC reacted can be easily removed as dicyclohexylurea. Method B is suitable for these alcohols which are solid or do not dissolve sulfinic acids readily. In this case DCC or dicyclohexylurea dissolves in dichloromethane to some extent, and these compounds must be removed by reprecipitation by addition of *n*-hexane to the residue of distillation.

Oxygen-18 Labeled Compounds. p-*Toluenesulfinic Acid*-^{18}O: Eleven grams of *p*-toluenesulfinic acid was dissolved in a mixture of 20 m*l* of $D_2{}^{18}O$ (^{18}O: 1.5 atom%) and 8.5 m*l* of dioxane. The solution was kept at 84°C for 1 hr, during which the exchange of ^{18}O is expected to be complete. After neutralization with a sodium carbonate solution and evaporation of solvent, the residue was dissolved in water. Acidification of the solution by addition of sulfuric acid yielded 8.7 g of *p*-toluenesulfinic acid-^{18}O.

Benzyl p-*Tolyl Sulfone*-^{18}O: The *p*-toluenesulfinic acid-^{18}O prepared as described above was neutralized by an aqueous sodium carbonate solution, and evaporation of the solvent yielded sodium *p*-toluenesulfinate-^{18}O. A mixture of 1 g of this sulfinate and 2 m*l* of benzyl bromide was heated at 118°C for 5 hr in a sealed tube. Benzyl *p*-tolyl sulfone produced was extracted with ether, washed with a sodium carbonate solution and water, and then dried. The ether was evaporated, and the residue was recrystallized from *n*-hexane.

The ^{18}O analyses were carried out according to the method of Rittenberg and Ponticorvo.[5]

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5) D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Rad. Isotopes*, **1**, 208 (1956).