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Reaction of Carboxylic Acid Esters with *p*-Toluenesulfonic Acid

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The reaction of carboxylic acid esters with an excess of *p*-toluenesulfonic acid gave the corresponding *p*-toluenesulfonates. The mechanism of the transesterification is discussed.

Keywords——*p*-toluenesulfonic acid; carboxylic acid ester; transesterification; aromatic nucleus alkylation; ethyl *p*-toluenesulfonate; solvolysis

In a previous paper,[1] we reported the unexpected formation of ethyl *p*-toluenesulfonate (TsOEt) in the reaction of ethyl acetoacetate with an excess of *p*-toluenesulfonic acid (TsOH). This new finding appears to be the first example of the direct esterification of an arenesulfonic acid with a common carboxylic acid ester. There are few published methods for the direct esterification of sulfonic acids. Recently, Etienne *et al.* reported that when sulfonic acids were treated with chloroformates,[2] alkyl chlorosulfites,[3] orthoborates[4] or dialkyl sulfites,[5] the corresponding esters of the sulfonic acids were obtained. However, in terms of availability of reagents, their procedures do not represent a generally applicable synthetic method. Thus, we hoped to develop a convenient method for the direct esterification of sulfonic acids by using common carboxylic acid esters as the substrate. We now report in detail the influence of variation in the substrates and present a possible mechanism for this novel reaction.

As the initial substrate for this study, we selected the readily available ethyl esters of common carboxylic acids, and examined their reaction with TsOH in order to explore the reaction conditions and the influence of the structure of carboxylic acids. These reactions were carried out by the general procedure, *i.e.*, after refluxing of a solution of TsOH hydrate in dry solvents through a Dean–Stark trap for 3 h until no more water was collected, an acid ester was added to the solution and the mixture was refluxed for an appropriate time. The reaction mixture was treated with water and the organic portion was dried, then evaporated. The residue was distilled *in vacuo* to afford TsOEt which was identified by comparison (infrared (IR), nuclear magnetic resonance (NMR)) with an authentic sample. The results are summarized in Table I. *p*-Toluenesulfonic acid was readily recovered from the aqueous portion. The *p*-toluenesulfonate was obtained in yields varying from 30 to 64%. The yields were unsatisfactory, but were nearly quantitative based on the consumed acid esters.

By comparing runs 2, 3, 8—15 and 20—24 inTable I, it was found that when the sulfonic acid was used in large excess (usually 3-fold excess), as reported previously,[1] the corresponding esters were generally produced in good yields. It was also found that TsOEt was obtained in the best yield by using diethyl carbonate as the substrate. This result may be ascribed to the weaker acidity of carbonic acid, as discussed later. Yields were calculated based on the following equation:

$$2\ \mathrm{TsOH} + (\mathrm{EtO})_2\mathrm{CO} \longrightarrow 2\ \mathrm{TsOEt} + \mathrm{CO_2} + \mathrm{H_2O}$$

It is noteworthy that both alkyl groups in the esters could be utilized in the transesterification. However, since ethyl hydrogen carbonate, which seems to be formed as an

TABLE I. Reaction of Ethyl Esters of Carboxylic Acids with *p*-Toluenesulfonic Acid

Run	Carboxylic acid ester	Molar ratio (TsOH : ester)	Solvent	Reaction time (h)	TsOEt yield (%)
1	$CH_3COCH_2CO_2Et$	3 : 1	Benzene	24	37
2		3 : 1	Toluene	24	50
3		2 : 1	Toluene	24	35
4	$PhCOCH_2CO_2Et$	3 : 1	Toluene	24	60
5	$PhCO_2Et$	3 : 1	Benzene	24	30
6	$C_6H_{11}CO_2Et$	3 : 1	Toluene	24	51
7	$ClCO_2Et$	3 : 1	Toluene	24	37
8	$CO(OEt)_2$	3 : 1	Benzene	24	31
9		2 : 1	Benzene	24	19
10		1 : 1	Benzene	24	9
11		3 : 1	Toluene	8	50
12		3 : 1	Toluene	24	64
13		3 : 1	Toluene	48	58
14		2 : 1	Toluene	24	46
15		1 : 1	Toluene	24	40
16	$(CO_2Et)_2$	3 : 1	Toluene	24	31
17	$CH_2(CO_2Et)_2$	3 : 1	Toluene	24	38
18		3 : 1	Toluene	48	44
19		3 : 1	Toluene	72	39
20		6 : 1	Toluene	24	45
21	$EtO_2CCH=CHCO_2Et$	3 : 1	Toluene	48	44
22		6 : 1	Toluene	24	54
23	$EtO_2C(CH_2)_3CO_2Et$	3 : 1	Toluene	48	37
24		6 : 1	Toluene	24	44

The yields in runs 16—24 are based on the following equation.

$$2TsOH + (R)_n(COOEt)_2 \longrightarrow 2TsOEt + (R)_n(COOH)_2$$

($R = CH_2$ and $CH=CH$, $n = 0$—3)

intermediate, is unstable and easily fragments into ethyl alcohol and carbon dioxide, the two ethyl groups of diethyl carbonate cannot be reacted completely. Since we confirmed the formation of ethanol qualitatively, the following process also appears to be involved, in which only one alkyl group is utilized in the transesterification:

$$TsOH + (EtO)_2CO \longrightarrow TsOEt + EtOH + CO_2$$

It is well known that sulfonic acids cannot be directly esterified by alcohols. Therefore, additional TsOEt is not produced from TsOH and ethanol. Etienne *et al.*[5] reported that when dialkyl sulfites were treated with sulfonic acids, only one alkyl group was utilized in the esterification as follows:

$$RSO_3H + (R'O)_2SO \longrightarrow RSO_3R' + R'OH + SO_2$$

Accordingly, dialkyl carbonates are an efficient and convenient substrate in the direct esterification of sulfonic acids.

Comparison of runs 12, 13, 18, and 19 in Table I reveals that the yield of ester decreases upon prolonged heating. This result was shown to be due to the fact that the ester produced in the reaction is consumed by solvolysis. We have ascertained that treatment of diethyl carbonate with an excess of TsOH for 48 h in refluxing toluene resulted in the formation of a mixture of ethylated toluenes derived from solvolysis in *ca.* 10% yield. It has been reported that alkyl *p*-toluenesulfonates (TsOR) on heating with aromatic hydrocarbons, toluene,

phenol or anisole, alkylate the aromatic nucleus.[6] However, our result appears to provide a one-pot alkylation of the aromatic nucleus by TsOR generated *in situ* in the reaction of carboxylic acid esters with an excess of TsOH. The one-pot alkylation of aromatic hydrocarbons by acid esters in the presence of an excess of TsOH is being further investigated. Attempts to prepare *p*-toluenesulfonates of ω-hydroxycarboxylic acids by using γ-lactones as a cyclic ester were unsuccessful.

Next, we examined the esterification of TsOH with various esters of carbonic acid. The results are listed in Table II. Treatment of diphenyl carbonate with TsOH afforded phenyl *p*-toluenesulfonate in poor yield. An attempted transesterification of ethylene carbonate as a cyclic carbonate by treatment with TsOH led to the formation of the β-hydroxyethyl ester of TsOH in low yield. This undesired result suggests that intermolecular reaction of two molecules of β-hydroxyethyl *p*-toluenesulfonate formed *in situ* afforded an ether compound. It

Table II. Reaction of Carbonates with *p*-Toluenesulfonic Acid in Refluxing Toluene for 24 h[a]

Run	Carbonate	Product	Yield (%)
1	Dimethyl carbonate	TsOMe	37[b]
2	Diethyl carbonate	TsOEt	64
3	Diphenyl carbonate	TsOPh	3
4	Ethylene carbonate	$TsOCH_2CH_2OH$	2

a) Reactions were run using a 3:1 molar ratio of TsOH to carbonates. *b*) The low yield seems to be due to the lower boiling point (91 °C) of dimethyl carbonate.

Table III. Esterification of Sulfonic Acids with Diethyl Carbonate[a]

$$RSO_3H \xrightarrow[\text{toluene, reflux, 8 h}]{CO(OEt)_2} RSO_3Et$$

Run	R	Yield (%)
1	*p*-Tolyl	50
2	Phenyl	58
3	*p*-Chlorophenyl	53
4	*p*-Nitrophenyl	14[b]
5	Methyl	40
6	Ethyl	39

a) Reactions were run using a 3:1 molar ratio of sulfonic acids to diethyl carbonate. *b*) Tar-like material was formed.

Table IV. Reaction of Higher Alkyl Esters of Carboxylic Acids with *p*-Toluenesulfonic Acid[a]

Run	Carboxylate	Solvent	Reaction time (h)	TsOR[b] yield (%)
1	*n*-Butyl acetate	Benzene	24	19
2	*n*-Butyl isobutyrate	Toluene	9	14
3		Toluene	24	—
4	*n*-Hexyl acetate	Benzene	24	20
5	*n*-Octyl acetate	Benzene	24	9
6	*n*-Octyl butyrate	Toluene	9	9

a) Reactions were run using a 3:1 molar ratio of TsOH to carboxylates. *b*) R=*n*-alkyl group.

is known that the reaction of TsOR with alcohol even in the absence of base results in the formation of an alkylated alcohol.[7]

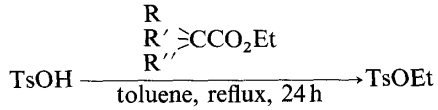
Furthermore, the esterification of aromatic and aliphatic sulfonic acids by diethyl carbonate were examined in order to elucidate the character of the transesterification. The results are presented in Table III. The reactions were carried out under reflux for 8 h at all runs in order to compare the yields of sulfonic acid esters produced. It appears that substituents on the benzene ring do not influence the reactivity. Yields of aliphatic sulfonic acid esters were lower than those of aromatic sulfonic acid esters.

In connection with the mechanism of our reaction, the reactions of various alkyl esters of carboxylic acids with TsOH were examined. As shown in Table IV, we found that TsOR may be formed by bimolecular nucleophilic substitution, since isomerization of the alkyl groups did not occur. If the reaction involves a unimolecular reaction, such as the migration of the normal alkyl carbonium ion to the more stable secondary alkyl carbonium ion, the products would be the secondary alkyl esters of TsOH. However, only the normal alkyl esters of TsOH were obtained, although the yields were low. Accordingly, the formation of *p*-toluenesulfonates may take place *via* a nucleophilic attack of the *p*-toluenesulfonate ion on the alkyl group.

The low yields listed in Table IV were shown to be due to the fact that the esters produced in the reaction are consumed by solvolysis, as described above. The susceptibility of relatively higher alkyl groups of *p*-toluenesulfonates to solvolysis by aromatic hydrocarbons such as benzene and toluene was particularly apparent in runs using toluene. Treatment of higher *n*-alkyl esters of carboxylic acids with TsOH in refluxing toluene for 9 h resulted in a mixture of solvolysis products and TsOR. *p*-Toluenesulfonates were isolated in poor yields, but isomerized esters were not detected. On the other hand, refluxing in toluene for 24 h (run 3) caused nearly complete solvolysis to give a mixture of *sec*-butylated toluenes which showed two multiplets (δ 2.56 and δ 2.88) due to the CH proton and other characreristic signals of the *sec*-butyl group, but no signal at higher field due to the CH_3 protons of the *n*-butyl group in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum.

Furthermore, we examined the reaction of ethyl esters of substituted acetic acids having an electron-donating group or electron-withdrawing group with TsOH. The results are summarized in Table V. It was found that the transesterifying ability of acid esters decreased with increasing electron-withdrawing activity of the R, R′ and R″ groups in the acyloxy moiety, and among carboxylic acid esters, the maximum decrease in the yield of TsOEt was

TABLE V. Reaction of Ethyl Esters of Substituted Acetic Acids with *p*-Toluenesulfonic Acid[a]



Run	R	R′	R″	Yield (%)	pK_a of parent acid[8] (25 °C, H_2O)
1	CH_3	CH_3	CH_3	51	5.05
2	CH_3	CH_3	H	41	4.86
3	CH_3CH_2	H	H	35	4.82
4	Cl	H	H	29	2.86
5	Cl	Cl	H	25	1.29
6	Cl	Cl	Cl	16	0.63

a) Reactions were run using a 3 : 1 molar ratio of TsOH to carboxylates.

observed with the ester of the strongest acid, that is, ethyl trichloroacetate. Moreover, treatment of TsOH with ethyl pivalate, in which the acidity of the parent acid is lowest, resulted in the formation of TsOEt in the highest yield.

On the other hand, the relative steric hindrance of methyl, ethyl and *n*-propyl groups are not significantly different and this was reflected in the product yields. A significant increase in the steric bulk around the carbon adjacent to the ethoxycarbonyl function in ethyl isobutyrate resulted in a significant increase in the yield and the extremely hindered ethyl pivalate provided TsOEt in the yield of 51%. From the relation between the bulkiness and the reactivity, it is also evident that this reaction process involves a nucleophilic attack of the *p*-toluenesulfonate ion on the alkyl group but not on the carbonyl group, although alkyl–oxygen fission is not common.

It can be further concluded from these observations that the protonation of acid esters under strongly acidic reaction conditions may be involved in the transition state, since the protonation of acid esters is facilitated with decreasing acidity of the parent acid due to the formation of a reasonably stable carbonium ion[9] and, in turn, this mechanism suggests that the presence of excess TsOH in the reaction mixture can accelerate the protonation of the carboxylic ester, facilitating the formation of TsOEt.

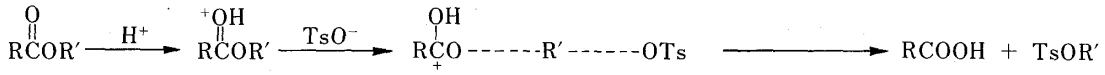


Chart 1

Based on the above considerations, the most plausible mechanism for this reaction is considered to be that shown in Chart 1. Although the sulfonate ion is a much weaker nucleophile, in this reaction the sulfonic acid may serve as both an acidic catalyst and a source of nucleophile which attacks the alkyl groups of the protonated carboxylic acid esters, leading to the formation of alkyl esters of the sulfonic acid by alkyl–oxygen fission. A large excess of the sulfonic acid induced a higher concentration of protonated acid esters, favoring the nucleophilic displacement.

The mechanism is also supported by the fact that the reverse reaction of TsOEt with trichloroacetic acid gave no ethyl trichloroacetate: the reverse reaction would be energetically unfavorable since an unstable intermediate involving the protonated sulfonate would have to be formed from the stable intermediate shown in Chart 1.

Experimental

Melting points were determined on a Yanaco melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded in chloroform-*d* solution on a JEOL JNH-MH-100 spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained on a JASCO IR-2 spectrophotometer. Mass spectral (MS) measurements were run on a JEOL JMS-D100 instrument. Gas chromatography (GC) was carried out on a Shimadzu GC-8A apparatus. Column chromatography was carried out on silica gel (Kieselgel 60, 70—230 mesh, E. Merck) or on alumina (Aluminiumoxid 90, 70—230 mesh, E. Merck).

General Procedure for the Reaction of Carboxylic Acid Esters with *p*-Toluenesulfonic Acid——A solution of commercial *p*-toluenesulfonic acid monohydrate (19.0 g, 100 mmol) in a dry solvent (30 ml) such as benzene or toluene was heated under reflux with azeotropic removal of water in a Dean–Stark trap for 3 h to give anhydrous TsOH. After the solution had cooled, the appropriate aliphatic or aromatic carboxylic acid ester (34 mmol) was added, and then the mixture was refluxed for the time indicated in the tables. Ice-water was added to the reaction mixture after cooling. The whole was extracted with benzene. The benzene layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting oil could be purified by column chromatography (alumina, benzene). Conditions and yields are given in the tables.

An example of the recovery of unchanged carboxylic acid esters and excess TsOH is as follows. A solution of anhydrous TsOH [obtained from TsOH hydrate (9.5 g, 50 mmol) by the general procedure] and ethyl cyclohexanecar-

boxylate (2.6 g, 17 mmol) in toluene (15 ml) was refluxed for 24 h. Ice-water was added to the reaction mixture after cooling. The whole was extracted with benzene. The solvent layer was washed with 2 N NaOH, dried over anhydrous sodium sulfate and concentrated under reduced pressure. Distillation of the resulting oil under reduced pressure gave 0.96 g (37%) of ethyl cyclohexanecarboxylate, bp 70—71 °C (21 mmHg) and then yielded 1.70 g (51%) of TsOEt, bp 118—121 °C (2 mmHg). Cyclohexanecarboxylic acid (1.26 g, 58%) was obtained from the aqueous NaOH solution by routine work-up. The aqueous layer which remained after benzene extraction of the reaction mixture was concentrated to dryness *in vacuo*; the resulting oil solidified on standing. The solid was dried under reduced pressure to recover 7.0 g of TsOH. TsOH was also recovered as TsONa by using the salting-out procedure.

Ethyl *p*-toluenesulfonate obtained was identified by comparison of its IR and NMR spectra with those of an authentic sample prepared as described in the previous paper.[1)]

n-Butyl *p*-toluenesulfonate was obtained as a colorless liquid: bp 138—140 °C (2 mmHg) [lit.[10)] bp 170—172 °C (10 mmHg)]. IR ν_{max}^{neat} cm^{-1}: 1360 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 0.89 (3H, t, J=7 Hz, CH_3), 1.1—1.8 (4H, m, $CH_2CH_2CH_3$), 2.46 (3H, s, Ar-CH_3), 4.10 (2H, t, J=7 Hz, O–CH_2), 7.46 (2H, d, J=9 Hz, aromatic H), 7.94 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 228 (M^+). In the reaction of *n*-butyl isobutyrate with TsOH, additional lower-boiling material was obtained as a colorless liquid, bp 60—75 °C (9 mmHg). The product was shown to be a mixture of *sec*-butylated toluenes through NMR comparison with a sample of *sec*-butylbenzene. The product showed characteristic signals of the *sec*-butyl group and no signal at higher field due to the CH_3 protons of an *n*-butyl group.

n-Hexyl *p*-toluenesulfonate was obtained as a colorless liquid: bp 151—153 °C (2 mmHg) [lit.[11)] bp 145 °C (0.5 mmHg)]. IR ν_{max}^{neat} cm^{-1}: 1355 (SO_3), 1174 (SO_3). NMR ($CDCl_3$) δ: 0.89 (3H, t, J=7 Hz, CH_3), 1.0—1.9 (8H, m, $(CH_2)_4CH_3$), 2.48 (3H, s, Ar-CH_3), 4.10 (2H, t, J=7 Hz, O–CH_2), 7.48 (2H, d, J=9 Hz, aromatic H), 7.95 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 256 (M^+).

n-Octyl *p*-toluenesulfonate was obtained as a colorless liquid: bp 129—137 °C (1 mmHg). This fraction was purified by column chromatography (silica gel, benzene). IR ν_{max}^{neat} cm^{-1}: 1360 (SO_3), 1175 (SO_3). NMR ($CDCl_3$) δ: 0.90 (3H, t, J=7 Hz, CH_3), 1.0—1.9 (12H, m, $(CH_2)_6CH_3$), 2.47 (3H, s, Ar-CH_3), 4.10 (2H, t, J=7 Hz, O–CH_2), 7.42 (2H, d, J=9 Hz, aromatic H), 7.93 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 284 (M^+).

Reaction of Carbonic Acid Esters with *p*-Toluenesulfonic Acid——The reaction was carried out by the general procedure. Generation of CO_2 and EtOH in the reaction of diethyl carbonate with TsOH was confirmed by using aqueous barium hydroxide and hexanitrocerate reagent, respectively.

Methyl *p*-toluenesulfonate was obtained as a colorless liquid: bp 115—117 °C (2 mmHg) [lit.[12)] bp 144.6—145.2 °C (5 mmHg)]. IR ν_{max}^{neat} cm^{-1}: 1360 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 2.42 (3H, s, Ar-CH_3), 3.78 (3H, s, O–CH_3), 7.40 (2H, d, J=9 Hz, aromatic H), 7.82 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 186 (M^+).

Phenyl *p*-toluenesulfonate was obtained as white needles: mp 93—94 °C (from hexane–benzene) [lit.[13)] mp 94—95 °C]. IR ν_{max}^{KBr} cm^{-1}: 1360 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 2.44 (3H, s, Ar-CH_3), 7.00 (2H, m, aromatic H), 7.31 (5H, m, aromatic H), 7.77 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 248 (M^+).

β-Hydroxyethyl *p*-toluenesulfonate was obtained as a pale yellow liquid.[14)] This liquid was purified by column chromatography (alumina, benzene). IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1355 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 2.44 (3H, s, CH_3), 2.94 (1H, s, OH), 3.80 (2H, t, J=5 Hz, CH_2OH), 4.14 (2H, t, J=5 Hz, CH_2OTs), 7.36 (2H, d, J=9 Hz, aromatic H), 7.82 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 216 (M^+).

Esterification of Aromatic and Aliphatic Sulfonic Acids with Diethyl Carbonate——Esterification was carried out by the general procedure and the following esters were prepared.

Ethyl benzenesulfonate was obtained as a colorless liquid: bp 117 °C (2 mmHg) [lit.[15)] bp 96—98 °C (0.3 mmHg)]. IR ν_{max}^{neat} cm^{-1}: 1360 (SO_3), 1190 (SO_3). NMR ($CDCl_3$) δ: 1.30 (3H, t, J=7 Hz, CH_2CH_3), 4.10 (2H, q, J=7 Hz, CH_2CH_3), 7.52 (3H, m, aromatic H), 7.82 (2H, dd, J=1.5, 9 Hz, aromatic H). MS *m/e*: 186 (M^+).

Ethyl *p*-chlorobenzenesulfonate was obtained as a colorless liquid: bp 125 °C (2 mmHg). IR ν_{max}^{neat} cm^{-1}: 1355 (SO_3), 1182 (SO_3). NMR ($CDCl_3$) δ: 1.30 (3H, t, J=7 Hz, CH_2CH_3), 4.12 (2H, q, J=7 Hz, CH_2CH_3), 7.42 (2H, d, J=9 Hz, aromatic H), 7.76 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 220 (M^+).

Ethyl *p*-nitrobenzenesulfonate was obtained as colorless needles: mp 91—92 °C (from hexane–benzene, 2:1) [lit.[15)] mp 92—92.5 °C]. IR ν_{max}^{KBr} cm^{-1}: 1592 (NO_2), 1300 (NO_2), 1315 (SO_3), 1150 (SO_3), 810 (C–N). NMR ($CDCl_3$) δ: 1.37 (3H, t, J=7 Hz, CH_2CH_3), 4.25 (2H, q, J=7 Hz, CH_2CH_3), 8.10 (2H, d, J=9 Hz, aromatic H), 8.42 (2H, d, J=9 Hz, aromatic H). MS *m/e*: 231 (M^+).

Ethyl methanesulfonate was obtained as a colorless liquid: bp 88 °C (15 mmHg) [lit.[16)] bp 90 °C (10 mmHg)]. IR ν_{max}^{neat} cm^{-1}: 1340 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 1.42 (3H, t, J=7 Hz, CH_2CH_3), 3.00 (3H, s, CH_3), 4.32 (2H, q, J=7 Hz, CH_2CH_3). MS *m/e*: 124 (M^+).

Ethyl ethanesulfonate was obtained as a colorless liquid: bp 96 °C (15 mmHg) [lit.[17)] bp 210 °C (760 mmHg)]. IR ν_{max}^{neat} cm^{-1}: 1350 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 1.42 (6H, t, J=7 Hz, CH_3), 3.15 (2H, q, J=7 Hz, S–CH_2CH_3), 4.32 (2H, q, J=7 Hz, O–CH_2CH_3). MS *m/e*: 138 (M^+).

Attempted Reaction of Trichloroacetic Acid with Ethyl *p*-Toluenesulfonate——A solution of $TsOH \cdot H_2O$ (2.0 g) and trichloroacetic acid (8.1 g, 50 mmol) in dry toluene (30 ml) was heated under reflux with azeotropic removal of water in a Dean–Stark trap for 3 h. After the solution had cooled, TsOEt (10.0 g, 50 mmol) was added, and then the mixture was refluxed for 24 h. After cooling, no ethyl trichloroacetate was detectable in the reaction mixture by GC.

Ice-water was added to the mixture. The whole was extracted with benzene. The benzene layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting oil was purified by column chromatography (silica gel, benzene) to give TsOEt (9.8 g).

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