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Reaction of Phosphorus Oxyacid Esters with *p*-Toluenesulfonic Acid

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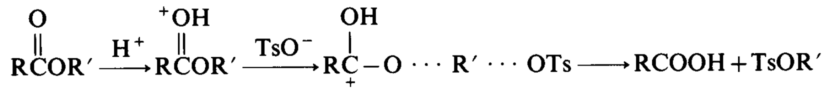
The reaction of primary alkyl esters of phosphorus oxyacids with *p*-toluenesulfonic acid (TsOH) in refluxing solvents gave the corresponding *p*-toluenesulfonates (TsOR). We found that the secondary alkyl esters reacted with TsOH at lower temperature (r.t.—40 °C) to afford TsOR^s in good yields. It is suggested that sulfonic acids may be useful for the selective dealkylation of mixed esters.

Keywords——*p*-toluenesulfonic acid; *p*-toluenesulfonate; trialkyl phosphate; trialkyl phosphite; dialkyl phenylphosphonate; transesterification; dealkylation; solvolysis

In a previous paper,[1] we reported the novel reaction of carboxylic acid esters with dehydrated *p*-toluenesulfonic acid (TsOH) to give the corresponding *p*-toluenesulfonates (TsOR) in moderate yields, and presented a possible mechanism for this reaction as follows:



$$\mathrm{R\overset{\overset{O}{\|}}{C}OR'} \xrightarrow{\mathrm{H^+}} \mathrm{R\overset{\overset{^+OH}{\|}}{C}OR'} \xrightarrow{\mathrm{TsO^-}} \mathrm{R\underset{+}{\overset{\overset{OH}{|}}{C}}-O\cdots R'\cdots OTs} \longrightarrow \mathrm{RCOOH+TsOR'}$$

In connection with our interest in the development of a more useful procedure for the preparation of TsOR, we extended our work to the reaction of inorganic acid esters with TsOH. During this investigation, it was found that some trialkyl phosphates, trialkyl phosphites, and dialkyl phenylphosphonates readily reacted with TsOH to afford TsOR in high yields, while tetraalkyl orthotitanates and orthosilicates reacted with TsOH to give TsOR in poor yields.[2] Although the reactions of phosphorus oxyacid esters with acids such as hydrogen halides,[3] sulfuric acid,[4] and carboxylic acids[5] are well known, to our knowledge, the reactions of phosphorus oxyacid esters with organic sulfonic acids have not previously been reported. Herein, we wish to report that primary and secondary alkyl esters of phosphorus oxyacids react with TsOH to give the corresponding TsOR in high yields, and the secondary alkyl esters are transesterified to give TsOR^s at room temperature.

First, we examined the reaction of the readily available trialkyl phosphates with dehydrated TsOH. These reactions were carried out in a manner similar to that used for the reaction of carboxylic acid esters with TsOH. The results are summarized in Table I. The reactions of tri-*n*-alkyl phosphates with 3 molar eq of TsOH in refluxing solvents resulted in the formation of TsOR^n in good yields. In the reaction of triethyl phosphate with TsOH in refluxing toluene, the formation of diethyl and monoethyl phosphates was checked by thin layer chromatography (TLC). After 72 h, TLC showed that these phosphates had disappeared completely. Phosphoric acid produced was converted into trimethyl phosphate by treatment of the mixture of phosphoric acid and TsOH with diazomethane. The structure of the product separated by column chromatography was identified by comparison of the proton nuclear magnetic resonance (^{1}H-NMR) spectrum with that of an authentic sample. Furthermore, we examined the reaction of TsOEt with phosphoric acid in order to confirm the irreversibility[1]: TsOEt was quantitatively recovered. Thus, it was found that all three alkyl groups in these esters could be efficiently utilized in the transesterification, as represented by the following equation:

$$3\,\mathrm{TsOH} + \mathrm{PO(OR)_3} \longrightarrow 3\,\mathrm{TsOR} + \mathrm{PO(OH)_3}$$

In contrast to the results observed in the reaction of ethyl esters of carboxylic acids with excess TsOH, in the present study, the use of a large excess of triethyl phosphate resulted in a marked increase in the yield of TsOEt: the reaction at a molar ratio of 1 : 1 of TsOH to triethyl phosphate [$\mathrm{TsOH} + \mathrm{PO(OR)_3} \rightarrow \mathrm{TsOR} + \mathrm{PO(OR)_2(OH)}$] led to the formation of the desired ester in high yield (89%) (run 8), as shown in comparison with runs 4, 6, and 7. In the reaction of other primary alkyl esters, a similar tendency was also observed. These results suggest that the rates of acidolysis of trialkyl phosphates are considerably faster than those of dialkyl phosphates and monoalkyl phosphates produced stepwise during the transesterification. It has been shown that dialkylphosphates are considerably less reactive than the triesters, owing to electrostatic repulsion between the nucleophile and ester.6) Further, it has

TABLE I. Esterification of *p*-Toluenesulfonic Acid by Trialkyl Phosphates

$$3\ \mathrm{TsOH} + \mathrm{PO(OR)_3} \longrightarrow 3\ \mathrm{TsOR} + \mathrm{PO(OH)_3}$$

Run	R	Molar ratio (TsOH : ester)	Solvent	Reaction conditions		TsOR Yield (%)
				Temp.	Time (h)	
1	CH_3	3 : 1	Toluene	Reflux	24	71
2		1 : 1	Toluene	Reflux	48	87
3	C_2H_5	3 : 1	Toluene	Reflux	24	70
4		3 : 1	Toluene	Reflux	48	65
5		3 : 1	Methylcyclohexane	Reflux	48	64
6		5 : 1	Toluene	Reflux	24	73
7		2 : 1	Toluene	Reflux	48	75
8		1 : 1	Toluene	Reflux	48	89
9		1 : 1	Methylcyclohexane	Reflux	19	68
10		3 : 1	Toluene	20 °C	72	—
11	n-C_3H_7	3 : 1	Toluene	Reflux	9	39
12		3 : 1	Toluene	Reflux	24	—
13		3 : 1	Dichloroethane	Reflux	24	32
14	iso-C_3H_7	3 : 1	Toluene	Reflux	9	—
15		3 : 1	Dichloroethane	50 °C	24	56
16		3 : 1	Dichloroethane	r.t.	72	13
17		3 : 1	Dichloroethane	40 °C	72	35
18		9 : 1	Dichloroethane	40 °C	72	77
19	n-C_4H_9	3 : 1	Toluene	Reflux	9	46
20		3 : 1	Toluene	Reflux	24	—a)
21		3 : 1	Dichloroethane	Reflux	72	75
22		3 : 1	Methylcyclohexane	Reflux	24	50
23		2 : 1	Methylcyclohexane	Reflux	72	86
24		1 : 1	Toluene	Reflux	9	70
25	iso-C_4H_9	3 : 1	Toluene	Reflux	22	—
26	*sec*-C_4H_9	3 : 1	Benzene	50 °C	24	—
27		3 : 1	Benzene	30 °C	24	36
28		3 : 1	Dichloroethane	40 °C	72	66
29		3 : 1	Dichloroethane	r.t.	72	49
30		9 : 1	Dichloroethane	40 °C	72	79
31	n-C_8H_{17}	3 : 1	Toluene	Reflux	9	30b)

a) A mixture of 2- and 4-*sec*-butyltoluene was isolated in 73% yield, bp 73—75 °C (15 mmHg) [lit.7) bp 80 °C (19 mmHg)]. *b)* 4-*sec*-Octyltoluene was isolated in 60% yield, bp 106—109 °C (6 mmHg) [lit.8) bp 116 °C (7 mmHg)]. The identification of products described in *a)* and *b)* was based on their NMR spectra and MS.

been reported that the acidolysis of trialkyl phosphites by carboxylic acids occurs more readily than that of dialkyl phosphites.[5a)]

In the reaction of tri-*n*-propyl phosphate and tri-*n*-butyl phosphate with TsOH in refluxing toluene, when the reaction time was extended to 24 h, no desired products could be isolated (runs 12 and 20). In run 20, solvolysis products, a mixture of 2- and 4-*sec*-butyltoluene, were isolated in 73% yield. However, the use of an aliphatic solvent such as dichloroethane or methylcyclohexane in place of toluene gave good results due to the avoidance of solvolysis, giving the alkylated toluenes.[1)] Thus, the reaction of tri-*n*-propyl phosphate in dichloroethane led to the isolation of TsOPr^n in 32% yield, even after 24 h, and the reaction at a molar ratio of 2 : 1 of TsOH to tri-*n*-butyl phosphate led to the isolation of TsOBu^n in 89% yield when run in a higher boiling solvent, methylcyclohexane. Accordingly, it is usually advisable to conduct these reactions in aliphatic solvents to avoid the undesired solvolysis.

Subsequently, we examined the reaction of tri-*sec*-alkyl phosphates with TsOH in order to obtain TsOR^s as products, which decompose[9)] on heating in a solvent at temperatures in the neighborhood of 100 °C to give olefins in good yields. Interestingly, it was found that the reaction proceeded at lower temperature (r.t.—40 °C) than that required in the case of tri-*n*-alkyl phosphates. Thus, the reaction of triisopropyl phosphate in dichloroethane at 50 °C led to the formation of TsOPr^i in 56% yield (run 15), while the reaction at room temperature gave the product in 13% yield. In the case of sterically more hindered tri-*sec*-butyl phosphate, the reaction proceeded more readily than with triisopropyl phosphate to give TsOBu^s at room temperature in 49% yield (run 29), while the reaction in benzene resulted in no formation of TsOBu^s even at 50 °C because of solvolysis of TsOBu^s to give *sec*-butylbenzene; however, at 30 °C TsOBu^s was isolated in 36% yield. Among the results obtained under a variety of reaction conditions, the best yields were obtained by the use of a large excess of TsOH as shown at runs 18 (77%) and 30 (79%).

In general, TsOR are obtained by reacting TsCl with alcohols in the presence of pyridine at low temperature. Secondary alcohols react less readily, and few TsOR^t can be prepared by using these conditions.[10)] Alternatively, TsOR^s can be prepared by the reaction of diazoalkanes with TsOH,[11)] but the diazoalkanes are less readily available as starting materials. The esterification of sulfonic acids by treating the silver sulfonates with alkyl halides in acetonitrile solution under mild conditions is also a less useful method, since the dehydrohalogenation of secondary halides takes place under these conditions.[12)]

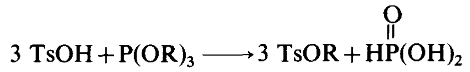
In order to determine whether the reactions of mixed trialkyl phosphates involving secondary and primary alkyl groups with TsOH at 40 °C result in the formation of TsOR^s alone, we examined the reactions of diethyl *sec*-butyl and diethyl isopropyl phosphates with TsOH. Only secondary alkyl groups were selectively transesterified to give TsOBu^s and TsOPr^i in 53 and 49% yields, respectively, and no formation of TsOEt was apparent from the ^{1}H-NMR spectrum or TLC behavior. When triethyl phosphate was treated in a similar manner (48 h), the unreacted phosphate was quantitatively recovered. From these results, it is suggested that selective transesterification in mixed esters might be useful as a partial dealkylation method applicable to the synthesis of nucleotides and other organophosphorus compounds possessing biological activities.

In addition, we attempted to isolate the solvolysis products of TsOR generated *in situ* in refluxing aromatic solvents. As a typical example, a solution of tri-*sec*-butyl phosphate and TsOH in *m*-xylene, which is more reactive than toluene, was stirred at room temperature for 20 h, and then heated at 80 °C for 4 h. After the usual work-up, we obtained 1-*sec*-butyl-2,4-dimethylbenzene in high yield (82%). The *p*-toluenesulfonate group is a particularly useful leaving group in the initiation of carbonium ion reactions. It has been reported that, by heating aromatic hydrocarbons with TsOR^s, secondary alkyl groups can be introduced smoothly into the aromatic nucleus.[13] Thus, our novel procedure is valuable as a one-pot alkylation of aromatic hydrocarbons.

Next, we examined the effectiveness of using trialkyl phosphites. As shown in Table II, it was found that trialkyl phosphites reacted more smoothly with TsOH than did trialkyl phosphates. Although there are no reports comparing the reactivity of trialkyl phosphites in nucleophilic reactions with that of trialkyl phosphates, it seems likely that, in contrast to trialkyl phosphates, trialkyl phosphites (tervalent phosphorus compounds having a lone pair on the phosphorus atom) are readily protonated to give quasi-phosphonium salts which subsequently react with *p*-toluenesulfonate ion to form preferentially the pentacovalent phosphorus compounds by P = O bond formation. Such a process may play an important role in the reactions of tervalent phosphorus compounds.[14]

The reaction of trimethyl and triethyl phosphites in refluxing toluene for 24 h led to the formation of the corresponding esters of TsOH in 81 and 75% yields, respectively. Treatment of higher tri-*n*-alkyl phosphites with TsOH in refluxing methylcyclohexane or dichloroethane also gave good yields of the corresponding TsOR. The lower yields obtained in runs 6 and 17 using dichloroethane as a solvent may be attributable to the lower reaction temperature: a significant increase in the yield could be obtained by prolonged heating (run 18). The use of excess tri-*n*-butyl phosphite did significantly increase the yield of TsOBu^n. These observations are reminiscent of the findings in the reaction of trialkyl phosphates with TsOH. The reaction at a molar ratio of 1:1 of TsOH to triethyl phosphite [$P(OEt)_3 + TsOH \rightarrow HP(O)(OEt)_2 + TsOEt$] at room temperature led to the quantitative formation of diethyl phosphonate and TsOEt; diethyl phosphonate did not react with TsOH even at 40 °C. The reaction at a molar ratio of 3:1 at room temperature resulted in the formation of TsOEt

TABLE II. Esterification of *p*-Toluenesulfonic Acid by Trialkyl Phosphites



$$3\,TsOH + P(OR)_3 \longrightarrow 3\,TsOR + H\overset{\overset{\displaystyle O}{\|}}{P}(OH)_2$$

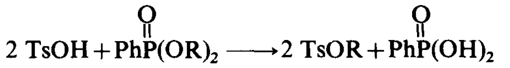
Run	R	Molar ratio (TsOH : ester)	Solvent	Reaction conditions		TsOR Yield (%)[a]
				Temp.	Time (h)	
1	CH_3	3:1	Toluene	Reflux	24	81
2	C_2H_5	3:1	Toluene	Reflux	24	75
3		3:1	Dichloroethane	r.t.	24	33
4		1:1	Dichloroethane	r.t.	24	100[b]
5	*n*-C_3H_7	3:1	Toluene	Reflux	10	41
6		3:1	Dichloroethane	Reflux	24	52
7	iso-C_3H_7	3:1	Dichloroethane	r.t.	48	69
8		3:1	Dichloroethane	r.t.	72	71
9	*n*-C_4H_9	3:1	Methylcyclohexane	Reflux	24	60
10		2:1	Methylcyclohexane	Reflux	24	72
11		1:1	Dichloroethane	r.t.	24	100[c]
12	*sec*-C_4H_9	3:1	Dichloroethane	r.t.	48	71
13	*n*-C_6H_{13}	3:1	Toluene	Reflux	8	41
14		3:1	Methylcyclohexane	Reflux	24	65
15	*n*-C_8H_{17}	3:1	Toluene	Reflux	8	41
16		3:1	Methylcyclohexane	Reflux	24	62
17	*n*-$C_{10}H_{21}$	3:1	Dichloroethane	Reflux	24	46
18		3:1	Dichloroethane	Reflux	48	66

a) The yields in runs 4 and 11 are based on the following equation.

$$TsOH + P(OR)_3 \longrightarrow TsOR + HP(O)(OR)_2\,.$$

b) Diethyl phosphonate was obtained in 98% yield. *c*) Di-*n*-butyl phosphonate was obtained in 98% yield.

TABLE III. Esterification of *p*-Toluenesulfonic Acid by Dialkyl Phenylphosphonates



$$2\ \mathrm{TsOH} + \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}(\mathrm{OR})_2 \longrightarrow 2\ \mathrm{TsOR} + \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}(\mathrm{OH})_2$$

Run	R	Molar ratio (TsOH : ester)	Solvent	Reaction conditions		TsOR Yield (%)
				Temp.	Time (h)	
1	C_2H_5	2 : 1	Toluene	Reflux	24	37
2		2 : 1	Toluene	Reflux	48	60
3		6 : 1	Toluene	Reflux	24	90
4		6 : 1	Dichloroethane	Reflux	85	71
5	*n*-C_4H_9	2 : 1	Dichloroethane	Reflux	48	43
6		6 : 1	Dichloroethane	Reflux	72	70
7	iso-C_3H_7	6 : 1	Dichloroethane	40 °C	48	82
8	*sec*-C_4H_9	2 : 1	Dichloroethane	40 °C	48	16
9		6 : 1	Dichloroethane	r.t.	72	70
10		6 : 1	Dichloroethane	40 °C	48	85
11	*cyclo*-C_6H_{11}	6 : 1	Dichloroethane	r.t.	96	74

TABLE IV. Esterification of *p*-Toluenesulfonic Acid by Secondary Butyl Esters of Carboxylic Acids[a)]

$$\mathrm{TsOH} + \mathrm{RCOOBu^s} \longrightarrow \mathrm{TsOBu^s} + \mathrm{RCOOH}$$

Run	R	Molar ratio (TsOH : ester)	Reaction conditions	$TsOBu^s$ Yield (%)
1	CH_3	1 : 1	40 °C, 72 h	14
2		3 : 1	40 °C, 72 h	46
3	*cyclo*-C_6H_{11}	1 : 1	Reflux, 20 h	Trace[b)]
4		3 : 1	40 °C, 72 h	38[c)]

a) Dichloroethane was used as the solvent. *b*) Cyclohexanecarboxylic acid was isolated in 86% yield. The recovery of the unreacted ester was 13%. *c*) Yield was based on the consumed ester.

in 33% yield. These results are consistent with the fact that the reactions of trialkyl phosphites with hydrogen halides[3)] or carboxylic acids[5c)] are much faster than those of dialkyl phosphonates, and further with our finding that trialkyl phosphites react more smoothly with TsOH than do trialkyl phosphates.

In the case of the reaction of triisopropyl phosphite with TsOH in dichloroethane, the isopropyl group was cleaved at room temperature to give $TsOPr^i$ in good yield. A similar result was obtained in the reaction of tri-*sec*-butyl phosphite. In addition, the reaction of di-*sec*-butyl phosphonate with 2 molar eq of TsOH at 40 °C for 48 h also gave $TsOBu^s$ in 40% yield.

Furthermore, the reactions of dialkyl phenylphosphonates with TsOH were examined. The results are presented in Table III. In every case examined, these esters afforded good yields of TsOR. These esters were more or less reactive than trialkyl phosphates.[15)] The secondary alkyl esters were smoothly transesterified to produce $TsOR^s$ by using a large excess of TsOH.

The mechanism of the reaction of tri-*n*-alkyl phosphites with TsOH may be as depicted in Chart 1. Quasi-phosphonium salts similar to intermediates thought to occur in the Arbuzov reaction are formed by protonation at the phosphorus atom[16)] in the trialkyl phosphites and subsequently undergo bimolecular nucleophilic attack on the primary alkyl groups by *p*-toluenesulfonate ion, giving rapidly the preferred pentacovalent dialkyl phosphonates and

$TsOR^n$. In fact, isomerization of the alkyl groups did not occur, while solvolysis of $TsOR^n$ by toluene gave *sec*-alkyltoluene, as described already. Subsequently, the oxygen atom[16] of the phosphoryl group in the dialkyl phosphonates is protonated to give monoalkyl phosphonates and $TsOR^n$ by similar nucleophilic attack, and finally phosphonic acid and a third molecule of $TsOR^n$ are produced. The reactions of trialkyl phosphates and dialkyl phenylphosphonates with TsOH may be also interpretable in terms of an analogous mechanism.

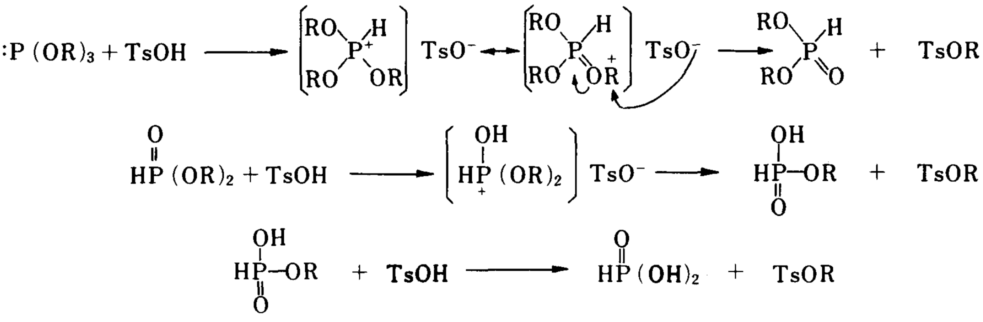


Chart 1

In contrast to the primary alkyl esters of phosphorus oxyacids, the secondary alkyl esters reacted smoothly with TsOH at lower temperature (r.t.—40 °C). It seems likely that this result reflects the difference in mechanism of reaction between primary and secondary alkyl esters in the formation of TsOR.[17] Therefore, in order to clarify whether a unimolecular nucleophilic displacement is involved in these reactions, the reaction of an optically active ester with TsOH was attempted. When (−)-(*R*)-di-2-octyl phenylphosphonate was allowed to react with TsOH at 40 °C in dichloroethane solution, racemic $TsOC_8H_{17}^s$ was obtained in 22% yield. The yield of $TsOC_8H_{17}^s$ is poor compared with that (85%) of $TsOBu^s$ in run 10 (Table III). It is suggested that the poor yield of $TsOC_8H_{17}^s$ may arise from preferential conversion of the 2-octyl cation into olefins in contrast to that of the *sec*-butyl cation. In fact, we found that the relatively large-scale reaction of di-2-octyl phenylphosphonate with TsOH gave a mixture of 1-octene and *trans*- and *cis*-2-octene (isolated by distillation) in 59% yield along with $TsOC_8H_{17}^s$ (21%). The optically active *p*-toluenesulfonate [(−)-(*R*)-$TsOC_8H_{17}^s$] was found to show complete racemization under the same reaction conditions: thus, it is not clear whether the racemization is a direct consequence of the reaction, or a secondary reaction. Thus, the stereochemical results provide no direct support for a unimolecular mechanism. However, the formation of octenes suggests that the reaction involves a unimolecular mechanism, as shown in Chart 2. The reactions of tri-*sec*-alkyl phosphates and phosphites with TsOH may also involve a similar mechanism. It seems likely that carbon–oxygen bond cleavage in protonated trialkyl phosphates, trialkyl phosphites, and dialkyl phenylphosphonate is facilitated by the ability of the alkyl groups to leave as carbonium ions.[18d]

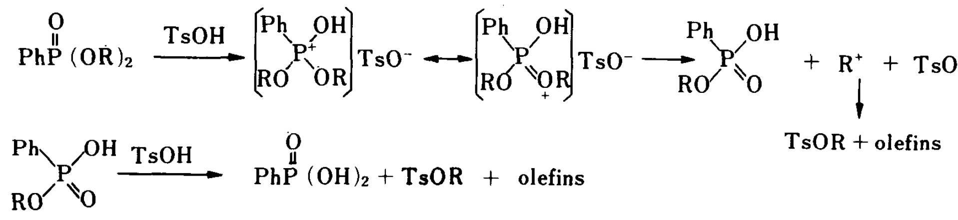


Chart 2

Finally, we examined the reaction of secondary butyl esters of carboxylic acids with TsOH in order to test whether the reaction also gives $TsOBu^s$ near room temperature. As shown in Table IV, TsOBu^s was obtained in moderate yields by using excess TsOH at 40 °C. The result in run 3 indicated that secondary alkyl esters of carboxylic acids can be dealkylated satisfactorily with TsOH in refluxing dichloroethane solution.

In conclusion, we have shown that our transesterification method under anhydrous and mild conditions is useful as a selective dealkylation procedure for mixed esters of phosphorus oxyacids bearing primary and secondary alkyl groups as well as a convenient procedure for the preparation of TsOR, particularly of TsOR^s.

The applications of ready dealkylation of the secondary alkyl esters of organophosphorus compounds are being further investigated. Preliminarily, we have examined the reaction of a mixed phosphate bearing primary and secondary alkyl groups with a polymer-supported arenesulfonic acid (Amberlite 200C), instead of TsOH. We readily isolated the desired product, which was quantitatively produced by the selective dealkylation of the secondary alkyl group alone without affecting the primary group. Details of these findings will be the subject of a forthcoming report.

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 using tetramethylsilane as an internal standard. Infrared (IR) spectra were obtained on a JASCO IR-2 spectrophotometer. Mass spectra (MS) were measured with a JEOL JMS-D100 instrument. Column chromatography was carried out on silica gel (Kieselgel 60, 70—230 mesh, E. Merck). Optical rotations were measured with a JASCO DIP-4 spectrometer.

General Procedure for the Preparation of Diethyl Alkyl Phosphates——To a solution of secondary alkanol (0.10 mol) in pyridine (10 ml) was added dropwise a solution of diethyl phosphorochloridate (0.12 mol) in benzene (20 ml) under ice-cooling, and the mixture was heated under reflux for 2 h. The reaction mixture was filtered to remove pyridinium chloride. The filtrate was diluted with benzene, and then shaken with H_2O. The aqueous layer was separated and the benzene layer was successively washed with sat. $NaHCO_3$ and H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was distilled under reduced pressure.

Diethyl isopropyl phosphate was obtained as a colorless oil, bp 104—106 °C (18 mmHg). NMR ($CDCl_3$) δ: 1.35 (6H, t, $J=7$ Hz, $2\times CH_2C\underline{H}_3$), 1.35 (6H, d, $J=6$ Hz, $CH(C\underline{H}_3)_2$), 4.11 (4H, dq, $J=8$, 7 Hz, $2\times C\underline{H}_2CH_3$), 4.68 (1H, m, $C\underline{H}$).

Diethyl *sec*-butyl phosphate was obtained as a colorless oil, bp 118—120 °C (24 mmHg). NMR ($CDCl_3$) δ: 0.95 (3H, t, $J=7.5$ Hz, $CHCH_2C\underline{H}_3$), 1.34 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.35 (6H, t, $J=7.5$ Hz, $2\times CH_2C\underline{H}_3$), 1.64 (2H, m, $C\underline{H}_2CH_3$), 4.08 (4H, dq, $J=8$, 7 Hz, $2\times C\underline{H}_2CH_3$), 4.42 (1H, m, $C\underline{H}$).

General Procedure for the Reaction of Phosphorus Oxyacid Esters with *p*-Toluenesulfonic Acid——A solution of commercial $TsOH\cdot H_2O$ (100 mmol) in a dry solvent (30 ml) such as benzene or toluene was heated under reflux with azeotropic removal of H_2O using a Dean-Stark trap for about 3 h to give dehydrated TsOH. The solution was cooled, the appropriate phosphorus oxyacid ester (11—100 mmol) was added, and the mixture was stirred under the conditions (time and temperature) 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 H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting oil was purified either by distillation under reduced pressure, or by column chromatography (silica gel, benzene). Dehydrated TsOH obtained by heating at 120 °C (4 mmHg) for 2—3 h could also be used. In the case of reactions in aliphatic solvents, TsOH dried under reduced pressure was used.

Methyl, ethyl, *n*-butyl, *n*-hexyl, and *n*-octyl *p*-toluenesulfonates obtained were identified by comparison of their IR and NMR spectra with those of authentic samples prepared in the previous study.$^{1)}$

n-Propyl *p*-toluenesulfonate was obtained as a colorless oil, bp 140—143 °C (2 mmHg) [lit.$^{19)}$ 154—156 °C (3 mmHg)]. IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1360 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=7$ Hz, $C\underline{H}_3$), 1.4—1.9 (2H, m, $C\underline{H}_2CH_3$), 2.42 (3H, s, Ar-$C\underline{H}_3$), 3.98 (2H, t, $J=7$ Hz, $C\underline{H}_2CH_2CH_3$), 7.34 (2H, d, $J=9$ Hz, aromatic protons), 7.80 (2H, d, $J=9$ Hz, aromatic protons). MS *m/e*: 214 (M^+).

Isopropyl *p*-toluenesulfonate was obtained as a colorless oil. IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1356 (SO_3), 1178 (SO_3). NMR ($CDCl_3$) δ: 1.24 (6H, d, $J=6$ Hz, $C\underline{H}_3CHC\underline{H}_3$), 2.48 (3H, s, Ar-$C\underline{H}_3$), 4.4—4.9 (1H, m, $C\underline{H}$), 7.20 (2H, d, $J=9$ Hz, aromatic protons), 7.62 (2H, d, $J=9$ Hz, aromatic protons). MS *m/e*: 214 (M^+).

sec-Butyl *p*-toluenesulfonate was obtained as a colorless oil. IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1360 (SO_3), 1182 (SO_3). NMR ($CDCl_3$) δ: 0.84 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 1.26 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.4—1.8 (2H, m, $C\underline{H}_2CH_3$), 2.46 (3H, s, Ar-$C\underline{H}_3$), 4.4—4.8 (1H, m, $C\underline{H}$), 7.36 (2H, d, $J=9$ Hz, aromatic protons), 7.84 (2H, d, $J=9$ Hz, aromatic protons). MS *m/e*: 228 (M^+).

n-Decyl *p*-toluenesulfonate was obtained as a colorless powder, mp 42.5—44 °C (petroleum ether) [lit.[20] mp 43—44 °C]. IR ν_{max}^{KBr} cm^{-1}: 1362 (SO_3), 1180 (SO_3). NMR ($CDCl_3$) δ: 0.6—1.0 (9H, m, $(C\underline{H}_2)_3C\underline{H}_3$), 1.0—2.0 (10H, m, $(C\underline{H}_2)_5$), 2.48 (3H, s, Ar-$C\underline{H}_3$), 3.9—4.3 (2H, m, $OC\underline{H}_2$), 7.40 (2H, d, J=9 Hz, aromatic protons), 7.80 (2H, d, J=9 Hz, aromatic protons).

Preparation of Optically Active (−)-(*R*)-Di-2-octyl Phenylphosphonate——To a solution of phenylphosphonic dichloride (4.0 g, 20.5 mmol) in benzene (10 ml) was added dropwise a solution of (−)-(*R*)-2-octanol (5.0 g, 38.4 mmol) in pyridine (4 ml) under ice-cooling. After standing overnight at room temperature, the mixture was filtered. The filtrate was diluted with benzene. The whole was successively washed with 10% HCl, H_2O, sat. $NaHCO_3$, and H_2O, dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a pale yellow oil (10 g). The crude product was purified by column chromatography (silica gel, $CHCl_3$) to afford the pure phosphonate (4.88 g, 65%) as a colorless oil, $[\alpha]_D^{25}$ −16.9° (c=1.0, $CHCl_3$). NMR ($CDCl_3$) δ: 0.7—1.0 (6H, m, $2\times CH_2C\underline{H}_3$), 1.0—2.0 (26H, m, $2\times C\underline{H}_3CH(C\underline{H}_2)_5$), 4.3—4.7 (2H, m, 2×CH), 7.3—7.5 (3H, m, aromatic protons), 7.6—7.9 (2H, m, aromatic protons). IR ν_{max}^{neat} cm^{-1}: 1438 (P–Ph), 1250 (P=O), 980 (P–O–C).

Reaction of (−)-(*R*)-Di-2-octyl Phenylphosphonate with *p*-Toluenesulfonic Acid——To a solution of the phosphonate (0.64 g, 1.7 mmol) in dichloroethane (5 ml) was added dehydrated TsOH obtained from commercial TsOH·H_2O (1.90 g, 10 mmol). The mixture was stirred at 40 °C for 48 h, and then concentrated under reduced pressure. The residual oil was purified by column chromatography (silica gel, benzene) to give racemic $TsOC_8H_{17}^s$ (0.21 g, 22%) as a colorless oil: $[\alpha]_D^{25}$ 0° (c=1.0, $CHCl_3$).

Preparation of (−)-(*R*)-2-Octyl *p*-Toluenesulfonate——To a solution of (−)-(*R*)-2-octanol (1.0 g, 7.7 mmol) in pyridine (5 ml) was added dropwise a solution of TsCl (1.6 g, 8.4 mmol) in pyridine (5 ml) at 5—10 °C. After standing overnight in a refrigerator, the reaction mixture was diluted with benzene. The mixture was washed successively with 10% HCl, H_2O, sat. $NaHCO_3$, and H_2O. After drying of the organic layer and evaporation of solvent, the resulting oil was purified by column chromatography (silica gel, benzene) to give (−)-(*R*)-$TsOC_8H_{17}^s$ (1.5 g, 68%) as a colorless oil: $[\alpha]_D^{25}$ −3.94° (c=1.0, $CHCl_3$) [lit.[21] $[\alpha]_D^{25}$ −4.0° (c=5, acetone)].

Stability of Optically Active *p*-Toluenesulfonate to Above Reaction Conditions——To a solution of (−)-(*R*)-$TsOC_8H_{17}^s$ (0.3 g, 10 mmol) and phenylphosphonic acid (0.3 g, 19 mmol) in dichloroethane (5 ml) was added dehydrated TsOH obtained from commercial TsOH·H_2O (1.9 g, 10 mmol). The mixture was stirred at 40 °C for 48 h and then concentrated under reduced pressure. The residual oil was purified by column chromatography (silica gel, benzene) to give racemic $TsOC_8H_{17}^s$ (0.17 g, 57%): $[\alpha]_D^{25}$ 0° (c=1.0, $CHCl_3$).

Reaction of Di-2-octyl Phenylphosphonate with *p*-Toluenesulfonic Acid: the Isolation of Olefins——A solution of di-2-octyl phenylphosphonate (2.6 g, 6.8 mmol) and dehydrated TsOH (6.9 g, 40 mmol) in dichloromethane (20 ml) was kept at 40 °C for 48 h. The reaction mixture was washed with H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to a half of its original volume under reduced pressure. The residual liquid was distilled under reduced pressure to give octenes (0.9 g, 59%), bp 59—61 °C (100 mmHg). The octenes were shown by the NMR spectrum to be a mixture of 1-octene and *trans*- and *cis*-2-octene. The above residue was purified by column chromatography (silica gel, $CHCl_3$) to give $TsOC_8H_{17}^s$ (0.78 g, 21%).

Solvolysis of Alkyl *p*-Toluenesulfonates Generated *in Situ*——Synthesis of 1-*sec*-Butyl-2,4-dimethylbenzene: A solution of tri-*sec*-butyl phosphate (4.5 g, 20 mmol) and dehydrated TsOH obtained from commercial TsOH·H_2O (9.5 g, 50 mmol) in *m*-xylene (30 ml) was stirred at room temperature for 20 h and then heated at 80 °C for 4 h. The mixture was cooled, then ice-water was added. The whole was extracted with benzene. The benzene layer was washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting oil was distilled under reduced pressure to give 1-*sec*-butyl-2,4-dimethylbenzene as a colorless oil, bp 92—94 °C (17 mmHg) [lit.[13] bp 96 °C (16 mmHg)], in 82% yield. *Anal.* Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.53; H, 11.31.

The reaction of tri-*n*-butyl phosphate with TsOH in refluxing *m*-xylene for 5 h similarly produced 1-*sec*-butyl-2,4-dimethylbenzene in 70% yield.

General Procedure for the Reaction of Secondary Butyl Esters of Carboxylic Acids with *p*-Toluenesulfonic Acid——Dehydrated TsOH obtained from commercial TsOH·H_2O (10 mmol) was added to a solution of the appropriate carboxylic acid ester (3.4—10 mmol) in dichloroethane (5 ml). The mixture was stirred under the conditions (time and temperature) indicated in Table IV. After usual work-up the resulting oil could be purified by column chromatography (silica gel, $CHCl_3$) to give pure $TsOBu^s$. Conditions and yields are given in Table IV.

References and Notes

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