# Products Analysis in the Reaction of Substituted 1-Phenylethyl Alcohols with *p*-Toluenesulfonyl Chloride

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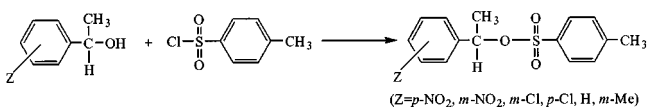
Previously, many researcher[1-8] have been reported on the mechanism of benzylation with tertiary amines, in which benzyl substrates are the primary alkyl carbon exhibiting different behaviors from secondary and tertiary alkyl carbons. Therefore, detailed information on the reaction mechanism of secondary benzyl systems, 1-phenylethyl tosylates, with tertiary amines is needed. In the preparation of substituted 1-phenylethyl tosylates, a remarkable effect occurred. In this study we present unexpected results concerning the reaction of substituted 1-phenylethyl alcohols and *p*-toluenesulfonyl chloride.

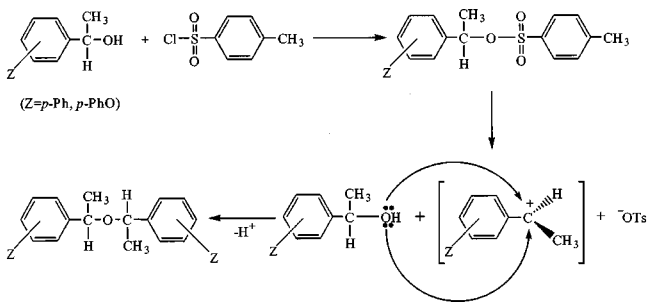
The methods of preparation of tosylate esters of phenols and aliphatic alcohols have been authoritatively studied by Tipson,[9] Drahowal and Klamann,[10] and Gilman and Beaber[11] and reviewed by Suter.[12] Most of these procedures represent variations of the Schotten-Baumann reaction utilizing the parent hydroxylic component and *p*-toluenesulfonyl chloride in the presence of a base. Kochi and Hammond[13,14] considered it desirable to prepare it in an entirely anhydrous condition. The method consists of the tosylation of a suspension of the appropriate sodium benzylate, prepared by refluxing an ethereal solution of alcohol and sodium hydride, with tosyl chloride at temperatures which vary with the reactivity of the alkoxide.

Substituted 1-phenylethyl tosylates were prepared by a new method modifying the literature (Scheme 1).[9-14]

A property which is characteristic of the activated 1-phenylethyl tosylates studied is the spontaneous transmutation of the white crystalline solids into colored, amorphous materials. The colors of the degradation products vary widely with the nature of the substituent and fade with time. 1-phenylethyl tosylate on decomposing first turns brown and then gradually becomes colorless. The rate of this decomposition varies greatly with the nature of the aromatic substituent and the purity of the tosylate. For example, 1-(*m*-methylphenyl)-ethyl tosylate decomposes rapidly even at room temperature, so it takes custody of ether at -20 °C (see the experimental part). The yields are much lower than others. Dimer may be prepared from the route of Scheme 2. 1-(*p*-nitrophenyl)ethyl tosylate can be kept for prolonged periods without apparent decomposition. The order of stability of these tosylates appears to be roughly consistent with the expected nucleophilic reactivity of the derived 1-phenylethyl carbonium




**Scheme 1**




**Scheme 2**

ions, $ArC(CH_3)H^+$. Thus, more electron-donating substituents (*p*-methyl, *p*-phenyl, *p*-phenoxy, *p*-methoxy etc) are so reactive they could not be successfully isolated in pure form at room temperature.

Surprisingly the reaction of 1-(*p*-phenoxyphenyl)ethyl alcohol with *p*-toluenesulfonyl chloride gives a dimer, di-1-(*p*-phenoxyphenyl)ethyl ether, contrary to expectation. On the other hand, activated benzyltosylates are polymerized slowly at -60 °C and very rapidly at room temperature.[10,15-17]

The authors proposed the reaction mechanism for the preparing racemate as follows (Scheme 2).

1-(*p*-phenoxyphenyl)ethyl tosylate is separated to yield an intermediate secondary carbocation. Since the trivalent carbon is $sp^2$-hybridized, the cation has no stereocenters, has a plane of symmetry, and is achiral. As a result, it can be attacked by a lone-pair electron of the other 1-(*p*-phenoxyphenyl)ethyl alcohol equally well from either the top or the

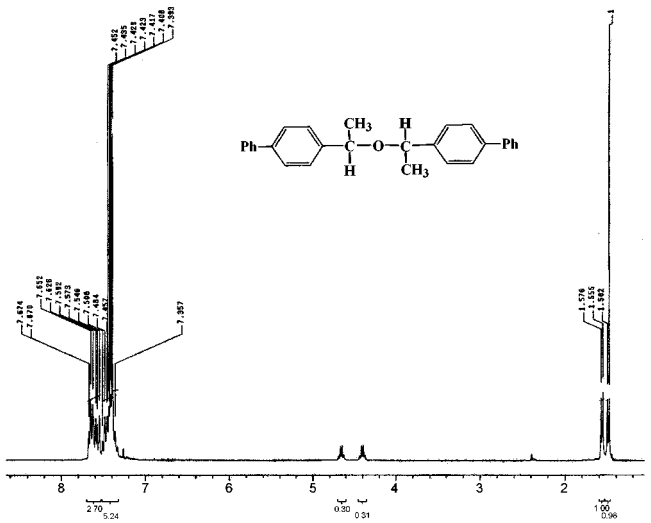


**Figure 1**. $^1H$ NMR spectrum of (±) di-1-(*p*-phenylphenyl)ethyl ether ($CDCl_3$).

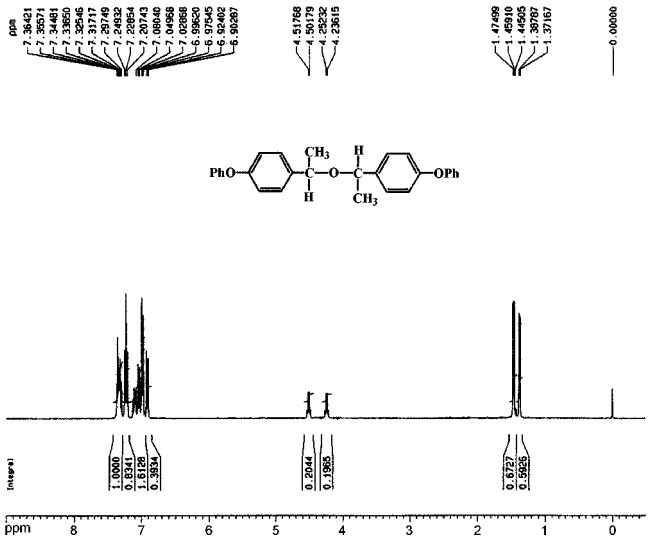


**Figure 2**. $^1$H NMR Spectrum of (±) di-1-(*p*-phenoxyphenyl)ethyl ether ($CDCl_3$).

bottom, and then it is deprotonated. Attack from the top and bottom leads to (±) di-1-(*p*-phenoxyphenyl)ethyl ether. Since both pathways occur with probability, a racemic product mixture results.

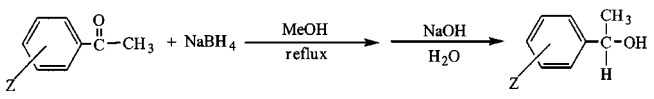
The $^1$H NMR data for the phenyl and phenoxy racemates support the proposed structure.

As shown in Figure 1, the two H seem to be equivalent at first glance, but chemical shifts are different from each other; the two H are split into two quartets by adjacent methyl hydrogens at 4.40 and 4.65 ppm, respectively. We can also explain the splitting of the two doublets at 1.49 and 1.56 ppm of the $CH_3$ groups. From the results, we can immediately deduce that the racemate of dimer is prepared from equal amounts of (+) and (–) enantiomeric molecules.

The kinetics and mechanism for the reaction of substituted 1-phenylethyl tosylates with nucleophiles will be reported in due course.

## Experimental Section

**Preparation of substituted 1-phenylethyl alcohols**: Substituted 1-phenylethyl alcohols were prepared by the reduction of corresponding acetophenones with sodium tetrahydroborate ($NaBH_4$) as described below.[18] Acetophenone was reacted with sodium tetrahydroborate (0.05 mole) in dry-methanol (200 mL) with stirring for 4 hour at 50 °C. Dry-methanol was removed under reduced pressure and reacted with 5% aqueous sodium hydroxide (200 mL) solution with stirring for 30 minute; crude alcohol was extracted with ether and water. The upper organic layer was dried over sodium sulfate and activated charcoal, and distilled under reduced pressure, giving 90% degree of pure substituted 1-phenylethyl alcohol. Identification of substituted 1-phenylethyl alcohol was reported Lim.[19]



**Scheme 3**

**Preparation of substituted 1-phenylethyl tosylates**: Substituted 1-phenylethyl tosylates were reacted with substituted 1-phenylethyl alcohols (0.015 mole) and *p*-toluenesulfonyl chloride (0.015 mole) in dioxane (20 mL) with stirring at ice-bath temperature. After stirring for 30 minute, a 33% aqueous sodium hydroxide solution (15 mL) was added to the reaction mixture, and the whole mixture was well stirred. This mixture was poured into ice-water, and crystal was obtained. The resulting substituted 1-phenylethyl tosylates were dried on anhydrous calcium chloride. Crude solid tosylates were purified by recrystallization from ether.

**1-(*m*-Methylphenyl)ethyl tosylate**: 48% yield; mp. decomposition at room temp.; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.53-1.55 (d, 3H, $CH_3$), 2.39 (s, 3H, $CH_3$), 2.41 (s, 3H, $CH_3$), 5.55-5.58 (q, 1H), 7.11-7.36 (m, 4H, Ph), 7.66-7.76 (d, 2H, Ph), 7.73-7.76 (d, 2H, Ph).

**1-Phenylethyl tosylate**: 65% yield; mp. 29-30 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.60-1.62 (d, 3H, $CH_3$), 2.39 (s, 3H, $CH_3$), 5.54-5.60 (q, 1H), 7.11-7.26 (m, 7H, Ph), 7.62-7.65 (d, 2H, Ph).

**1-(*p*-Chlorophenyl)ethyl tosylate**: 74% yield; mp. 38-40 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.57-1.59 (d, 3H, $CH_3$), 2.40 (s, 3H, $CH_3$), 5.50-5.57 (q, 1H), 7.09-7.13 (d, 2H, Ph), 7.18-7.26 (m, 4H, Ph), 7.61-7.64 (d, 2H, Ph).

**1-(*m*-Chlorophenyl)ethyl tosylate**: 77% yield; mp. 46-48 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.57-1.59 (d, 3H, $CH_3$), 2.39 (s, 3H, $CH_3$), 5.47-5.54 (q, 1H), 7.04-7.22 (m, 6H, Ph), 7.61-7.64 (d, 2H, Ph).

**1-(*m*-Nitrophenyl)ethyl tosylate**: 92% yield; mp. 91-92 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.63-1.65 (d, 3H, $CH_3$), 2.38 (s, 3H, $CH_3$), 5.60-5.67 (q, 1H), 7.21-7.23 (d, 2H, Ph), 7.44-7.49 (t, 1H, Ph), 7.58-7.67 (m, 3H, Ph), 7.95 (s, 1H, Ph), 8.09-8.12 (d, 1H, Ph).

**1-(*p*-Nitrophenyl)ethyl tosylate**: 89% yield; mp. 84-85 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.60-1.6 2(d, 3H, $CH_3$), 2.40 (s, 3H, $CH_3$), 5.61-5.67 (q, 1H), 7.23-7.26 (d, 2H, Ph), 7.36-7.40 (d, 2H, Ph), 7.66-7.69 (d, 2H, Ph), 8.09-8.13 (d, 2H, Ph).

**(±) di-1-(*p*-Phenylphenyl)ethyl ether**: 59% yield; mp. 96-98 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.48-1.50 (d, 3H, $CH_3$), 1.55-1.57 (d, 3H, $CH_3$), 4.37-4.44 (q, 1H), 4.62-4.69 (q, 1H), 7.36-7.67 (m, 18H, Ph); MS *m/z* 378 ($M^+$).

**(±) di-1-(*p*-Phenoxyphenyl)ethyl ether**: 65% yield; mp. 88-90 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.37-1.39 (d, 3H, $CH_3$), 1.46-1.48 (d, 3H, $CH_3$), 4.22-4.27 (q, 1H), 4.48-4.54 (q, 1H), 6.90-6.92 (d, 2H, Ph), 6.98-7.08 (d, 8H, Ph), 7.21-7.25 (t, 4H, Ph), 7.30-7.36 (m, 4H, Ph); MS *m/z* 410 ($M^+$).

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