

Table 1. Formation of Deoxybenzoins and β -keto Sulfides (5)^a

| Run | R ¹ | R ² | Isolated yields, % ^a | Mp. or bp. °C/torr | |
|-----|----------------|-----------------------------------|---------------------------------|--------------------|--------------------------|
| | | | | Found | Lit. |
| 1 | Ph | Ph | 92 | 54-55 | 55-56.5 ² |
| 2 | Ph | 4-MeC ₆ H ₄ | 83 | 108-110 | 108.5-110 ² |
| 3 | Ph | 2-MeC ₆ H ₄ | 32 | 153-156/0.5 | 150-155/0.5 ⁷ |
| 4 | Ph | 4-ClC ₆ H ₄ | 85 | 106-107 | 105-107 ² |
| 5 | PhS | Ph | 50 | 53-54 | 53-54 ⁸ |
| 6 | PhS | 4-MeC ₆ H ₄ | 60 | 58-60 | 59-60 ⁸ |
| 7 | PhS | Ph | 90 | 103-108/2 | 100-104/2 ⁹ |
| 8 | MeS | 4-MeC ₆ H ₄ | 85 | 122-125/2 | 120-125/2 ⁹ |
| 9 | Me | Ph | — | — | — |

^aThe hydrolysis was normally completed within 2 h at room temperature. ^bThe numbers indicate purified yield after crystallization or distillation (Kugelrohr) and all products had identical spectral properties with reported data.

As shown in Scheme 1, phosphonate **1** is deprotonated by *n*-butyllithium to form an α -lithio anion of phosphonate within 1 h at -78°C , which reacts with aromatic nitrile to form a ketimine intermediate **2**. The direct treatment of a ketimine intermediate **2** with 5 N-NaOH solution gives the deoxybenzoin or β -keto sulfide **5** in good yield within 2 h. The present reaction is assumed to proceed through the enamine intermediate **4** which is formed by attack of hydroxide anion on the phosphoryl P-atom of **3**.

There is also other possibility of the mechanism involving attack of the hydroxide ion on the imino carbon atom of the ketimine intermediate, the hydrated intermediate then undergoing an intramolecular Horner-Emmons type reaction.

As shown in Table 1, the reaction works well with aromatic nitriles. In the case of nitriles bearing an α -hydrogen dimerized products (α -cyano ketones) were obtained as a major product, as previously reported by Sumrell³.

α -Lithio anion of phosphonates derived from benzyl-, thiophenyl-, and thiomethyl phosphonates react with aromatic nitriles to give ketones, generally, in good yield. However, under identical conditions, α -lithio anion derived from ethyl phosphonate is able to bring about little conversion of nitrile to ketone (Run 9). Instead corresponding β -keto phosphonate is obtained. Thus it appears to be of fundamental importance that the only anion of phosphonate stabilized at the α -position reacts with nitrile to give ketone, which is in accord with the fact that efficient Wittig elimination can only be brought about if the intermediate is activated at the α -position to the phosphorus atom by an electron-withdrawing group⁴. On the other hand, the hydrolysis is carried out with 5 N-NaOH solution within 2 h. The hydrolysis using H₂SO₄ solution also can be carried out, but requires longer reaction time for completion (12 h with 5 N-H₂SO₄).

Deoxybenzoins⁵ and β -keto sulfides⁶ are well recognized in organic synthesis as a versatile precursors of a large number of interesting organic compounds.

In conclusion, the present method, which uses phosphonates, is mechanistically interesting and practical in terms of increased reactivity, easy separation of products, and readily available starting materials.

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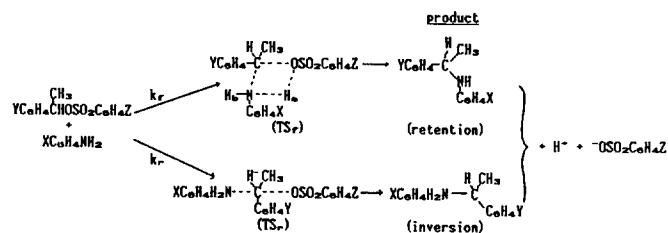
Stereochemistry of Substitution in the Reaction of 1-Phenylethyl Benzenesulfonates with Anilines

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In our studies on the nucleophilic substitution reactions of 1-phenylethyl benzenesulfonates (1-PEB) with anilines,¹ we proposed involvement of a four-center transition state (TS), TS_f in Scheme 1, based on the unusually large cross interaction between substituents X in the nucleophile and Z in the leaving group (LG) with a large magnitude of ρ_{XZ} ,¹



Scheme 1.

defined in equation (1).³

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (1)$$

In the four-center TS (TS_f) substituents X and Z can interact *via* two routes, an extra interaction route being provided by hydrogen bonding of an amine hydrogen (H_a) toward the oxygen atom in the LG. We report here the results of our stereochemical studies providing direct evidence for the in-

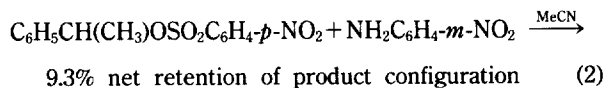
Table 1. Net Stereochemistry of Substitution in the Reaction of 1-Phenylethyl *p*-NO₂-Benzenesulfonate (1-PEB-*p*-NO₂) with *m*-NO₂-Aniline in Acetonitrile at 25.0°C^a

| Compound | α_D^{25} | $[\alpha]_D^{25}$ |
|----------------------------------|-----------------|-----------------------------------|
| 1-PEA ^{b,c} | +42.14 | 41.81 (neat) |
| 1-PEB- <i>p</i> -NO ₂ | +0.81 | 26.80 (3.02g) |
| Product Amine ^d | +0.030 | 1.62 (1.86g) |
| | | [9.3% net retention] ^e |
| Product Amine ^f | +0.229 | 17.48 (1.31g) |

^a5 determinations at 589.6 nm, 1 dm, MeCN solvent (Perkin-Elmer 241-MC). Error in the reproducibility was less than $\pm 5\%$.

^bR absolute configuration from (+)-1-phenylethyl amine. ^cOptical purity, 98% ref.; R. C. Weast, ed., 'Handbook of Data on Organic Compounds', CRC Press, Boca Raton, Florida, 1985. ^dIsolated reaction product. ^eNet stereochemistry referred to authentic product. ^fAuthentic product; ref. 8.

involvement of a front-side attack with retained product stereochemistry. In addition to the unusually large magnitude of ρ_{XZ} (-0.56 for $Y=H$ at 25.0°C),¹ we observed a significant value of primary kinetic isotope effect (KIE) ($k_H/k_D=2.35$ with $X=m\text{-NO}_2$ and $Z=p\text{-NO}_2$) using the deuterated aniline nucleophiles.^{1b} In the TS_f (Scheme 1) the N-H_α stretching mode should give a primary KIE due to the partial bond cleavage in hydrogen bond formation, as we have indeed observed. Replacement of the two hydrogen atoms on N in aniline by CH₃ groups gave the ρ_{XZ} value of the magnitude less than half that for the reactions with aniline⁴ (N,N-dimethyl aniline gave $\rho_{XZ}=-0.23$ at the same reaction condition due mainly to the impossibility of forming the four-center TS).⁴ However, one might argue that these can only be indirect evidence for the involvement of TS_f.



We have carried out optical rotation measurements and found that *ca.* 55% of the original reactant (1-PEB) stereochemistry was retained in the product, equation (2). This means that the k_f and k_r pathways are approximately 55 (54.7) and 45% (45.3) respectively. Accordingly, we estimated the ρ_{XZ} value for TS_f to be *ca.* -0.8 assuming ρ_{XZ} for TS_f of $-0.2 \sim -0.3$.⁵ Likewise the k_H/k_D value corresponding to TS_f rises to *ca.* 3.45, which is approximately half of the maximum primary KIE for complete N-H (or C-H) bond cleavage or symmetrical linear three center TS.⁶ The optical rate constant for reaction 2 at 30.0°C was found to be $3.22 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$, which compares well with the total rate constant obtained by conductivity measurements ($3.53 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$).¹ These stereochemical results also support strongly bound TS_f structures for TS_f and TS_r, since ion-pair formation were involved complete racemization would have resulted in the product.^{2,7} Experimental details are shown in Table 1.

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- $|\rho_{XZ}|$ for the dissociative (benzyl benzenesulfonates) and associative (phenacyl- and ethylbenzenesulfonates) S_N2 reactions under similar reaction conditions are 0.10⁹ and 0.32–0.33⁹ respectively. 1-Phenyl-2-propyl benzenesulfonates gave $|\rho_{XZ}|=0.16$.¹⁰ These $|\rho_{XZ}|$ for normal back-side attack S_N2 reactions lead us to an estimated $|\rho_{XZ}|$ of 0.2–0.3 for TS_f of 1-PEB.
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An Alternative Route for the Synthesis of Monoalkyltin Trichloride, CH₃OOCCH₂CH(COOCH₃)CH₂SnCl₃

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Hutton and Oakes reported a novel synthetic route to "estertin" compounds,¹ which have attracted considerable interest because of the bonding mode of the ester group and also because of their applicability as a PVC stabilizer with low mammalian toxicities.^{2–8} According to the route, monoalkyltin trihalide is prepared by the reaction(1) of α , β -unsaturated carbonyl compound with stannous chloride in the presence of hydrogen chloride, and dialkyltin dihalide is prepared by the reaction(2) with metallic tin in place of stannous