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

Run	R^1	R^2	Isolated yields, %^{a}	Mp. or bp. ℃/torr Found	Mp. or bp. ℃/torr 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	–	–	

[a] The hydrolysis was normally completed within 2 h at room temperature. [b] The 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℃, 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 Sumrell[3].

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 group[4]. On the other hand, the hydrolysis is carried out with 5 N-NaOH solution within 2 h. The hydrolysis using H$_2$SO$_4$ solution also can be carried out, but requires longer reaction time for completion (12 h with 5 N-H$_2$SO$_4$).

Deoxybenzoins[5] and β-keto sulfides[6] 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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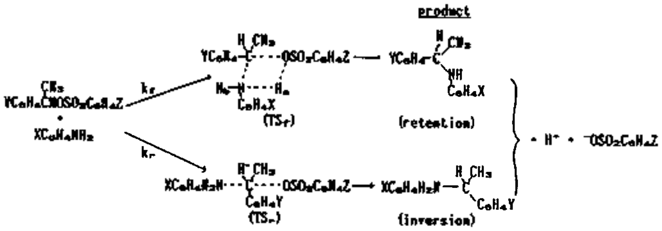
In our studies on the nucleophilic substitution reactions of 1-phenylethyl benzenesulfonates (1-PEB) with anilines,[1] we proposed involvement of a four-center transition state (TS), TS$_f$ in Scheme 1, based on the unusually large cross interaction between substituents X in the nucleophile and Z in the leaving group (LG) with a large magnitude of ρ_{XZ},[1] defined in equation (1).[3]



Scheme 1.

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

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-NO_2-Benzenesulfonate (1-PEB-p-NO_2) with m-NO_2-Aniline in Acetonitrile at 25.0℃[a]

Compound	α_D^{25}	$[\alpha]_D^{25}$
1-PEA[b,c]	+42.14	41.81 (neat)
1-PEB-p-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)

[a] 5 determinations at 589.6 nm, 1 dm, MeCN solvent (Perkin-Elmer 241-MC). Error in the reproducibility was less than ±5%. [b] R absolute configuration from (+)-1-phenylethyl amine. [c] Optical purity, 98% ref.; R. C. Weast, ed., 'Handbook of Data on Organic Compounds', CRC Press, Boca Raton, Florida, 1985. [d] Isolated reaction product. [e] Net stereochemistry referred to authentic product. [f] Authentic product; ref. 8.

volvement 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℃),[1] we observed a significant value of primary kinetic isotope effect (KIE) ($k_H/k_D=2.35$ with X=m-NO_2 and Z=p-NO_2) using the deuterated aniline nucleophiles.[1b] In the TS_f (Scheme 1) the N-H_a streching 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 CH_3 groups gave the ρ_{XZ} value of the magnitude less than half that for the reactions with aniline[4] (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.

$$C_6H_5CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}NO_2+NH_2C_6H_4\text{-}m\text{-}NO_2 \xrightarrow{MeCN} \text{9.3\% net retention of product configuration} \quad (2)$$

We have carried out optical rotation measurements and found that *ca.* 55% of the original reactant (1-PEB) stereochmistry 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.* $\underline{-0.8}$ assumming 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℃ was found to be $3.22\times10^{-4}\ M^{-1}s^{-1}$, which compares well with the total rate constant obtained by conductivity measurements ($3.53\times10^{-4}\ M^{-1}s^{-1}$).[1] These stereochemical results also support strongly bound TS[7] structures for TS_f and TS_f, 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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An Alternative Route for the Synthesis of Monoalkyltin Trichloride, $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$

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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