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A New Synthesis of β-Keto Phosphonate from Aryl Epoxysulfones and Dialkyl Hydrogen Phosphite

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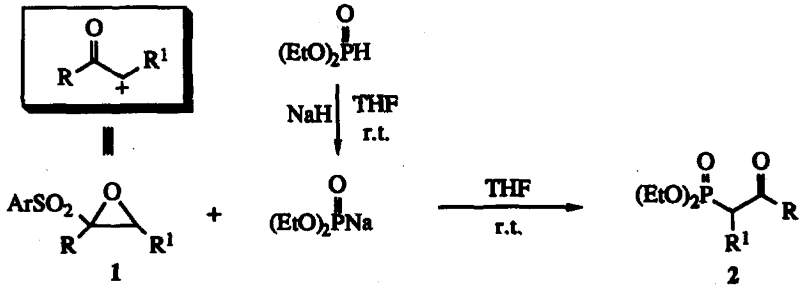
Abstract ; Reaction of α-substituted arylsulfonyl epoxide with diethyl phosphite sodium salt gave β-keto phosphonate in good yield.

In recent years, β-keto phosphonates have become valuable intermediates in organic synthesis, especially for the preparation of α,β-unsaturated carbonyl compounds by the Wadsworth-Horner-Emmons condensation.[1] However, synthetic routes to β-keto phosphonates are rather limited in contrast with the significant progress that has expanded the original scope of the Wittig-Horner reaction. Among a variety of synthetic methods of β-keto phosphonate, the use of dialkyl phosphite as nucleophile has not been nearly reported because reaction of dialkyl phosphites under Michaelis-Becker reaction condition with α-halocarbonyls generally proceeds to give "Perkow-type" products, enol phosphate, rather than direct displacement of halide.[2] In continuation of our studies on synthesis of β-keto phosphonate,[3] we designed the reaction of dialkyl phosphite anion with α-substituted epoxy sulfones which function as ketone equivalents with α-cation reactivity. (Scheme 1)



Scheme 1

Epoxy sulfones were prepared by three methods: i) epoxidation of α,β-unsaturated sulfone[4], ii) Darzen type condensation of α-haloalkyl sulfone with carbonyl compounds,[5] and iii) α-alkylation of phenyl epoxysulfone at -105 °C.[6] To a THF(5 ml) solution of diethyl phosphite (21mg, 1.5 mmol) was added 80 % mineral oil dispersion of sodium hydride (45mg, 1.5 mmol) at r. t. under nitrogen. After 10 min, **2a** (198mg, 1.0 mmol) in THF (5ml) was added and stirred for 30 min at room temperature. After quenching with aq.

Table I. Synthesis of β-Keto Phosphonate from Aryl Epoxysulfone

epoxy sulfone	Ar	R	R^1	time(h)	yield of 2^a(%)
1a	Ph	Me	H	0.5	70
1b	p-Tol	n-C_3H_7	H	0.5	90
1c	p-Tol	n-C_5H_{11}	H	0.5	87
1d[b]	Ph	CH_3=CH-CH_2	H	0.5	82
1e	Ph	Me	Me	6	60
1f	Ph	Me	Ph	12	75
1g	p-Tol	Et	Ph	12	78
1h	Ph	Me_3Si	H	0.5	-[c]
1i	Ph	H	Ph	12	-[d]

[a] Isolated yield based on Aryl epoxy sulfone. [b] As reaction runs for 2 hr, double bond isomerization occurs to give more stable enone, γ,δ-unsaturated β-keto phosphonate. [c] Phenylsulfonyl oxirane was obtained quantitatively. [d] *trans*-$(EtO)_2P(O)CH$=CHPh was obtained.

NH_4Cl and purification by column chromatography, 135 mg(70%) of **2a** was obtained. It could be assumed that diethyl phosphite anion attacked on the carbon β to sulfone group regiospecifically followed by epoxide ring opening and elimination of phenyl sulfinate sodium salt. The results were summarized in Table I.

When 2-phenylsulfonyl-2-trimethylsilyl oxirane **1h** was reacted, desilylated phenylsulfonyl oxirane was produced with diethyl trimethylsilyl phosphite which is supposed to be formed by the attack of phosphite anion on trimethylsilyl group. In the case of α,β-substituted arylsulfonyl oxirane, we could obtain a broad range of α-alkyl-β-keto phosponates **2e-g** . Especially, α-phenyl-β-ketophosphonate is difficult to prepare by conventional methods(Arbuzov reaction, Acylation of benzylphosphonate anion). Unexpectedly, when 2-phenyl-1-(phenylsulfonyl)-1,2-epoxyethane **1i** was reacted, *trans*-styryl phosphonate was produced in 40% yield instead of expected α-phenyl-β-formyl phosphonate. Yield was optimized by the use of 3 eq. diethyl phosphite as 87 %. It is supposed that initially formed α-phenyl-β-formyl phosphonate reacts with additional sodium diethyl phosphite. A further study on this result is under way.

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