

A Convenient One-Pot Synthesis of 1,5-Diaryl-1,2-epoxy-4-penten-3-ones

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The reaction between diethyl (2-oxopropyl)phosphonate (**1**), dry potassium carbonate, iodine, and various aromatic aldehydes in a liquid/solid two-phases system, gives 1,5-diaryl-1,2-epoxy-4-penten-3-ones **5** in good yields.

Wittig–Horner reactions can be carried out at room temperature using a liquid/solid two-phase system in the absence of a catalyst.^{1–4} We have studied the scope of the conditions for these reactions, and now report a new synthetic route to 1,5-diaryl-1,2-epoxy-4-penten-3-ones by the condensation of aromatic aldehydes with an ambident nucleophile **3**, generated *in situ* from diethyl (2-oxopropyl)phosphonate (**1**) and potassium carbonate in methanol, in the presence of iodine.⁵ In a

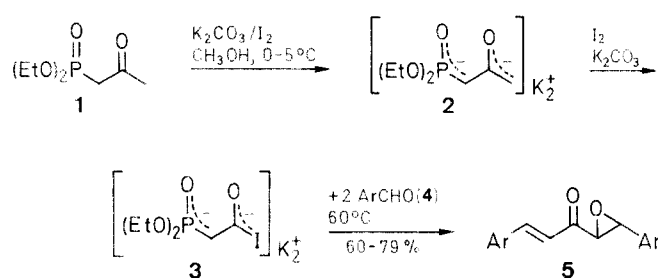
Table. 1,5-Diaryl-1,2-epoxy-4-penten-3-ones **5a-g** Prepared

Product	Yield (%)	mp (°C) ^a	Molecular Formula ^d or Lit. mp (°C)	IR (KBr) ^b ν _{C=O} (cm ⁻¹)	¹ H-NMR (CDCl ₃ /TMS) ^c δ, J (Hz)	MS (70eV) ^c m/z (%)
5a	65	85–86	83–84 ¹⁰	1680	3.75–4.10 (2d, 2H, <i>J</i> = 2, CH); 7.00–7.85 (2d, 2H, <i>J</i> = 16, =CH); 7.20–7.60 (m, 10H _{arom})	250 (M ⁺ , 21); 131 (100)
5b	60	87–88	C ₁₉ H ₁₈ O ₄ (310.3)	1675	3.77–3.80 (2s, 6H, OCH ₃); 3.75–4.05 (2d, 2H, <i>J</i> = 1.7, CH); 7.05–7.85 (2d, 2H, <i>J</i> = 16, =CH); 6.55–7.45 (m, 8H _{arom})	310 (M ⁺ , 10); 161 (100)
5c	69	89–90	C ₁₉ H ₁₈ O ₄ (310.3)	1670	3.82–3.90 (2s, 6H, OCH ₃); 3.70–4.40 (2d, 2H, <i>J</i> = 1.7, CH); 7.05–8.20 (2d, 2H, <i>J</i> = 16, =CH); 6.90–7.60 (m, 8H _{arom})	310 (M ⁺ , 8); 161 (100)
5d	70	215–216	215–216 ¹⁰	1665	3.75–4.22 (2d, 2H, <i>J</i> = 1.7, CH); 7.18–8.30 (2d, 2H, <i>J</i> = 16, =CH); 7.50–7.90 (m, 8H _{arom})	340 (M ⁺ , 10); 176 (100)
5e	71	157–158	C ₁₇ H ₁₂ N ₂ O ₆ (340.2)	1690	3.75–4.25 (2d, 2H, <i>J</i> = 1.8, CH); 7.10–7.90 (2d, 2H, <i>J</i> = 16, =CH); 7.50–7.95 (m, 8H _{arom})	340 (M ⁺ , 33); 176 (100)
5f	72	152–153	C ₁₇ H ₁₀ Cl ₄ O ₂ (388.0)	1655	3.53–4.37 (2d, 2H, <i>J</i> = 1.7, CH); 6.95–8.20 (2d, 2H, <i>J</i> = 16, =CH); 7.20–7.65 (m, 6H _{arom})	388 (M ⁺ , 8); 199 (100)
5g	79	145–155	C ₂₁ H ₂₂ O ₆ (370.3)	1660	3.77–3.85 (4s, 12H, OCH ₃); 3.65–4.40 (2d, 2H, <i>J</i> = 1.7, CH); 7.04–8.15 (2d, 2H, <i>J</i> = 16, =CH); 6.80–7.10 (m, 6H _{arom})	370 (M ⁺ , 16); 191 (100)

^a Uncorrected and recorded with a Kofler apparatus.^b IR spectra were obtained on a Perkin Elmer spectrophotometer 297.^c ¹H-NMR spectra were recorded on a Bruker AM 300 WB spectrometer.^d Satisfactory microanalyses obtained: C ± 0.22, H ± 0.24, N ± 0.^e Obtained on a Nermag R10-10C instrument.

preceding work, we have found that the Wittig–Horner reaction of (ethoxycarbonyliodomethyl)triphenylphosphonium iodide⁶ and ethyl iodo(diethoxyphosphoryl)acetate⁷ with aromatic aldehydes under the same conditions gave acetylenic esters in good yields.

With the diethyl (2-oxopropyl)phosphonate (**1**), the deprotonation, which occurs on the surface of solid potassium carbonate, generates an intermediate dianion **2**. The α-CH group of **2** is less nucleophilic than the γ-CH₂ group, so that the latter attacks the substrate, here iodine, to give novel ambident nucleophile **3**, where the two CH groups have approximately equivalent reactivity. The aldehyde **4** reacts with the intermediate **3** in a simultaneous Wittig–Horner and Darzens condensation to yield the epoxy ketones **5** (Table).



4, 5	Ar	4, 5	Ar
a	C ₆ H ₅	e	3-NO ₂ C ₆ H ₄
b	4-CH ₃ OC ₆ H ₄	f	2,4-Cl ₂ C ₆ H ₃
c	2-CH ₃ OC ₆ H ₄	g	2,5-(CH ₃ O) ₂ C ₆ H ₃
d	4-NO ₂ C ₆ H ₄		

It is interesting to note the stereochemical outcome of the reaction, as determined by ¹H-NMR spectroscopy. The coupling constants for the hydrogens of the epoxy ring (*J* = ~2 Hz) and the double bond (*J* = ~17 Hz) revealed the *trans*- and *E*-configurations of the epoxy ring and the double bond, respectively.

This result is in accord with the stereospecificity of the Wittig–Horner reaction in the heterogenous media, and with the

transition state for the epoxy cyclization of the iodohydrin anion that requires the C=O⁻ and C–I groups in *anti* position to each other with the cinnamoyl and aryl groups having a minimum of interaction.⁸

The principal advantages of the procedure described here are the good yields, the short reaction time, the facile one-step procedure, the convenient work-up, and the easy availability of the starting material.⁹

1,5-Diaryl-1,2-epoxy-4-penten-3-ones **5**; General Procedure:

In a 500 mL round-bottomed flask, equipped with a thermometer and a stirrer are placed dry K₂CO₃ (8.28 g, 0.06 mol), CH₃OH (20 mL), and diethyl (2-oxopropyl)phosphonate (**1**; 3.88 g, 0.02 mol) under a nitrogen atmosphere. A solution of I₂ (5.08 g, 0.02 mol) in CH₃OH (40 mL) is added dropwise at 0–5°C during 1 h. After discoloration of the mixture, a solution of the aromatic aldehyde **4** (0.04 mol) in CH₃OH (10 mL) is added, and the mixture heated to 60°C for 2 h. The mixture is allowed to cool to room temperature, and CH₃OH is evaporated to dryness. The residue is partitioned between water (100 mL) and CH₂Cl₂ (100 mL). The layers are separated, and the organic layer is washed twice with aq. 10% HCl (2 × 20 mL), H₂O (2 × 20 mL), dried (MgSO₄) and evaporated under reduced pressure. The products **5b–g** are purified by recrystallization from CH₃OH and compound **5a** by chromatography on silica gel column using toluene as eluent (Table).

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