[3 + 2] Annulation of Allylidene(triphenyl)phosphorane with 1,2-Diacylethylenes: Synthesis of Substituted Cyclopentadienes

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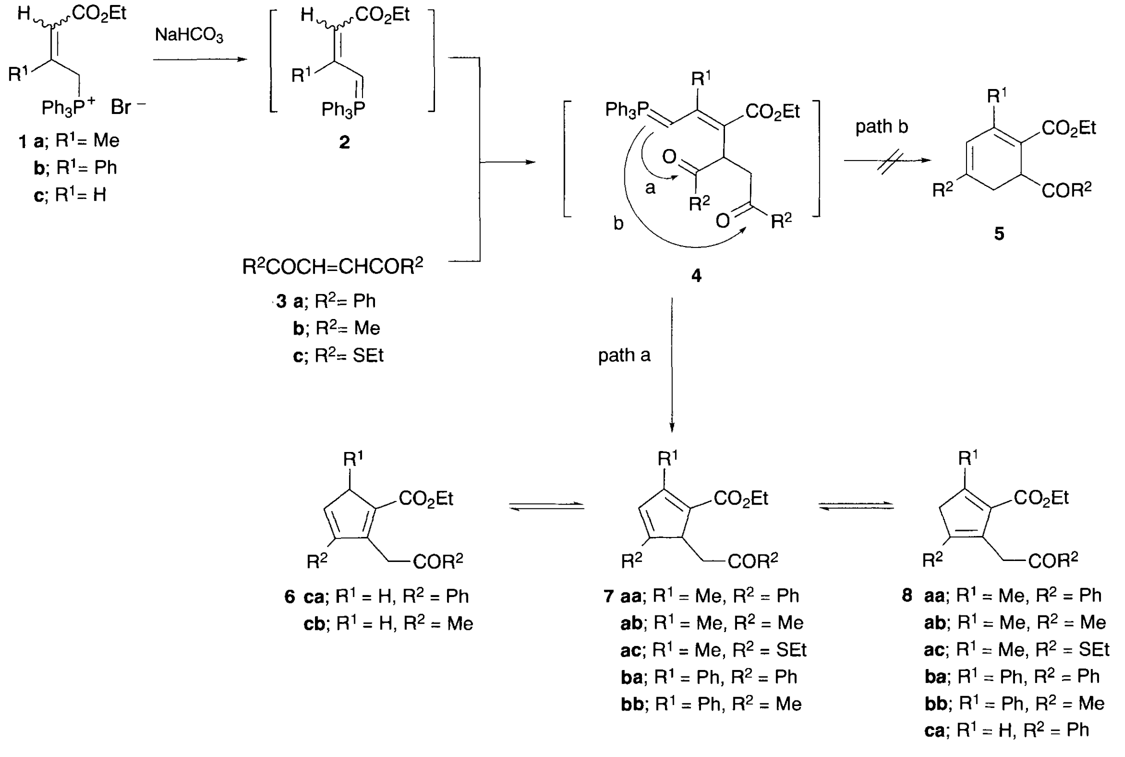
Allylidene(triphenyl)phosphorane reacts with 1,2-diacylethylenes at room temperature to give cyclopentadienes having various substituents.

Recently, we demonstrated that allylidene(triphenyl)phosphorane undergoes a [3 + 2] annulation with α-haloketones to give cyclopentadienes.[1] In this annulation, allylidenephosphorane acts as a bifunctional reagent, first nucleophilic substitution at the γ-position of the phosphorane followed by an intramolecular Wittig reaction.[2] The [3 + 2] annulation proceeds nicely to give cyclopentadienes in better yields than those of cyclohexadienes in the known [3 + 3] annulation of allylidenephosphorane with α,β-unsaturated aldehydes and ketones.[3,4] This prompted us to investigate the reaction of allylidenephosphorane with 1,2-diacylethylenes **3**, in which there are two possible pathways for annulation, leading to formation of either cyclopentadienes or cyclohexadienes. Here, we report that allylidene(triphenyl)phosphorane reacts with 1,2-diacylethylenes to undergo a [3 + 2] annulation to give cyclopentadienes exclusively.

When the allylphosphonium bromide **1a** was treated with dibenzoylethylene **3a** in a heterogeneous medium of dichloromethane and saturated aqueous $NaHCO_3$ at room temp., the [3 + 2] annulation gave the cyclopentadiene as a 1 : 1 mixture of the double bond isomers in 80% yield without formation of cyclohexadiene **5**. One isomer was isolated from the mixture in a pure crystalline form, which was assigned to the structure **7aa**† on the basis of the observation of the C-5 methine proton (δ 4.70) and the C-3 vinyl proton (δ 6.65) in the ^1H NMR spectra. Another observed isomer should correspond to the 1,4-diene **8aa**, as indicated by an absorption (δ 3.50) due to the C-3 methylene protons. The isomer **7aa** was stable at room temp. against 1,5-sigmatropic migration, which was observed to a small extent upon heating in refluxing benzene. When **7aa** was stirred in a heterogeneous medium of dichloromethane and saturated aqueous $NaHCO_3$ in the presence of **1a**, migration of the double bond occurred smoothly to give a 1 : 1 equilibrium mixture of **7aa** and **8aa**.

These results can be rationalized as follows. A Michael addition of the allylidenephosphorane **2** to dibenzoylethylene **3a** produces the intermediate **4**. Subsequent intramolecular Wittig reaction occurs exclusively *via* path a to provide cyclopentadiene **7aa**, which is readily equilibrated with **8aa** under the reaction conditions.

The annulation is applicable to the preparation of various cyclopentadienes, as illustrated in Table 1. The phosphonium bromide **1a** reacted with diacetylethylene **3b** in the heterogeneous medium to give a 1 : 2 mixture of **7ab** and **8ab**. Diethyl thiofumarate **3c** afforded a mixture of **7ac** and **8ac** in 53% yield when the reaction was carried out in THF using sodium hexamethyldisilazide (NaHMDS) as a base; lower yield in the heterogeneous medium is due to the accompanying hydrolysis of **3c**. The 2-phenylphosphonium bromide **1b** also reacted with **3a** and **3b** to give the corresponding cyclopentadienes as mixtures of the 1,3-diene **7** and the 1,4-diene **8** (entries 4 and 5). On the other hand, the phosphonium bromide **1c** having no substituent at C-2 reacted with **3a** to give a 4 : 1 mixture of the 1,3-dienes **6ca** and **8ca**. Reaction of **1c** with **3b**



Scheme 1

Table 1 Synthesis of cyclopentadienes from allyl(triphenyl)phosphonium bromides and diacylethylenes

Entry	Phos-phonium bromide	Diacyl-ethylene	Cyclopentadiene[a]	Total yield[b] (%)
1	**1a**	**3a**	**7aa** + **8aa** (1 : 1)	80
2	**1a**	**3b**	**7ab** + **8ab** (1 : 2)	53
3	**1a**	**3c**	**7ac** + **8ac** (1 : 1)	32 (53[c])
4	**1b**	**3a**	**7ba** + **8ba** (1 : 3)	90
5	**1b**	**3b**	**7bb** + **8bb** (1 : 8)	51
6	**1c**	**3a**	**6ca** + **8ca** (4 : 1)	49
7	**1c**	**3b**	**6cb**	29

[a] The ratio of isomers was estimated on the basis of their NMR spectra. [b] Isolated yield. [c] The yield obtained under anhydrous conditions in THF in the presence of 1 equiv. of NaHMDS.

produced the 1,3-diene **6cb**‡ as a single isomer. The location of the double bonds in the 1,3-dienes was determined by a combination of COSY and NOESY spectra.

Although attempted annulation with non- and semi-stabilized phosphoranes, prop-2-enylidene- and 3-phenylprop-2-enylidene(triphenyl)phosphorane, failed to give cyclopentadienes, the stabilized allylidenephosphoranes as described above underwent cyclization. The resulting cyclopentadienes§ contained the double bond isomers, except for **6cb**, arising through an equilibrium process from the initially formed **7** under the weakly basic reaction conditions. The product distribution in each case may depend on the thermodynamic stability of their isomers. Thus, the [3 + 2] annulation between allylidenephosphoranes and 1,2-diacylethylenes provides an efficient method for the preparation of cyclopentadienes having various substituents.

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Footnotes

† Saturated aq. $NaHCO_3$ solution (10 cm^3) was layered on a solution of (3-ethoxycarbonyl-2-methylprop-2-enyl)triphenylphosphonium bromide **1a** (470 mg, 1.0 mmol) in dichloromethane (10 cm^3). To this well-stirred mixture was added **3a** (236 mg, 1.0 mmol) and the mixture was stirred at 25 °C for 12 h under N_2. The aqueous layer was separated and extracted with dichloromethane. Evaporation of the solvent and flash chromatography on SiO_2 of the residue gave a 1 : 1 mixture of **7aa** and **8aa** (276 mg, 80%). Crystallisation from ethyl acetate–hexane afforded **7aa** as colourless crystals.

Selected data for **7aa**: ν_{max} (Nujol)/cm^{-1} 1688, 1615 and 1489; δ_H (300 MHz; $CDCl_3$) 1.08 (3H, t, *J* 7.1 Hz), 2.41 (3H, d, *J* 1.4), 3.12 (1H, dd, *J* 3.5, 17.0), 3.46 (1H, dd, *J* 6.1, 17.0), 3.97–4.10 (2H, m), 4.70 (1H, m), 6.65 (1H, bs), 7.53–7.23 (8H, m), 7.86 (2H, dd, *J* 1.0, 8.0); λ_{max} (MeOH)/nm 330 (ε/dm^3 mol^{-1} cm^{-1} 14800) and 235 (16500); mp 115.5–117 °C (from ethyl acetate).

‡ *Selected data* for **6cb**: ν_{max} (neat)/cm^{-1} 1698, 1628 and 1557; δ_H (300 MHz; $CDCl_3$) 1.31 (3H, t, *J* 7.1), 1.92 (3H, m), 2.23 (3H, s), 3.27 (2H, bs), 4.00 (2H, s), 4.21 (2H, q, *J* 7.1) 6.28 (1H, bs); λ_{max} (MeOH)/nm 285 (ε/dm^3 mol^{-1} cm^{-1} 22600).

§ The cyclopentadienes prepared above were stable for at least a week at room temp., except for **6cb** that easily dimerized especially in a condensed state.

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