The Reaction of Allylidene Triphenylphosphoranes with α-Halocarbonyl Compounds: a Convenient Synthesis of Cyclopentadienes

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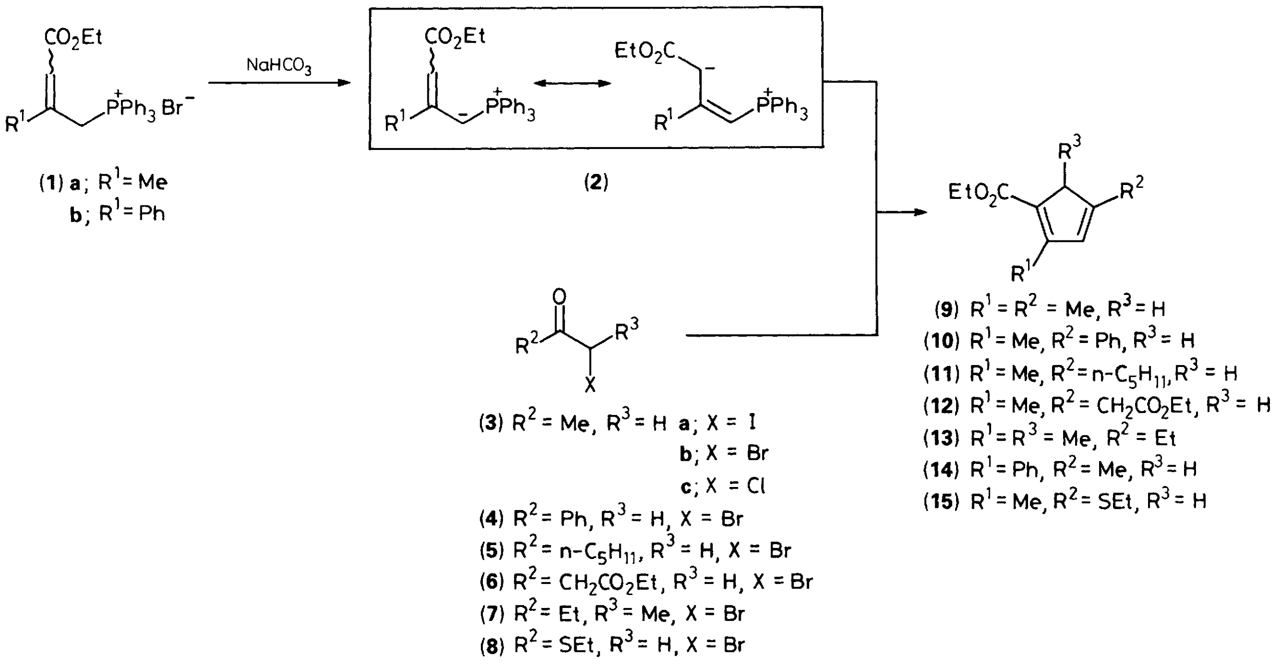
A convenient method has been developed for the synthesis of substituted cyclopentadienes, starting from allylidene triphenylphosphoranes and α-halocarbonyl compounds, *via* a [3 + 2] annulation process.

It is well known that allylidene triphenylphosphoranes take part in an interesting annulation reaction with α,β-unsaturated carbonyl compounds leading to the formation of cyclohexadienes.[1] However, the synthetic utility of these phosphoranes in annulation reactions has been little explored. Previously, we reported that the reaction of the cephalosporin 3′-triphenylphosphonium ylide with glyoxals occurs *via* initial Aldol condensation at the γ-position (C-2) of the ylide, followed by an intramolecular Wittig reaction to give the tricyclic cephalosporin which is bridged by a hydroxycyclopentene ring between C-2 and C-3.[2] This led us to investigate the reaction of allylidene triphenylphosphoranes with ketones having a proper leaving group at the α-position. This communication describes that the reaction of stabilized allylidene phosphoranes (**2**) with α-haloketones provides regioselective formation of substituted cyclopentadienes *via* a [3 + 2] annulation.[3]

The reactions proceed smoothly under very mild conditions on mixing equimolar amounts of the triphenylphosphonium bromide (**1a**)[4] and α-haloketones in a heterogeneous medium of dichloromethane and saturated aqueous $NaHCO_3$, at room temperature under nitrogen for 12 h, to give good yields of cyclopentadienes. Although this reaction could be carried out under anhydrous conditions using Pr^i_2NEt and K_2CO_3 as the base in solvents such as CH_2Cl_2, MeCN, and dimethylformamide (DMF), the best results were obtained under the heterogeneous conditions mentioned above. Representative results are summarized in Table 1. Among iodo-, bromo-, and chloro-acetones (Table 1, entries 1—3), bromoacetone gave the highest yield of (**9**) (96%); the lower yield with iodoacetone seems to be due to the instability of the iodide under the reaction conditions. Primary bromides (**4**)—(**6**) gave excellent yields of the corresponding cyclopentadienes. It is noteworthy that because no strong base is required, reaction with the secondary halide took place (entry 7) to give the polysubstituted cyclopentadiene (**13**) without competitive elimination. Phosphonium bromide (**1b**) also reacted with bromoacetone to give the corresponding cyclopentadiene (**14**). Furthermore, reaction of α-bromothioester (**8**) with (**1a**) gave the 4-ethylthiocyclopentadiene (**15**), which could be readily converted by treatment with titanium tetrachloride[5] into cyclopentenone (**17**) (73%).

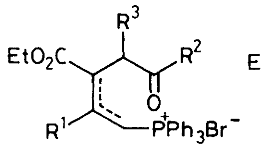


Scheme 1

Table 1. Synthesis of cyclopentadienes from allylidene triphenylphosphonium bromides and α-halocarbonyl compounds.[a]

Entry	Allylidene triphenyl-phosphonium bromide	α-Halo-carbonyl compound	Cyclo-pentadiene[b]	Isolated yield/%
1	**(1a)**	**(3a)**	**(9)**	62
2	**(1a)**	**(3b)**		96
3	**(1a)**	**(3c)**		72
4	**(1a)**	**(4)**	**(10)**	78
5	**(1a)**	**(5)**	**(11)**	71
6	**(1a)**	**(6)**	**(12)**	50
7	**(1a)**	**(7)**	**(13)**	72
8	**(1b)**	**(3b)**	**(14)**	48
9	**(1a)**	**(8)**	**(15)**	51

[a] For reaction conditions see text. [b] All compounds produced satisfactory ^1H NMR, IR, UV, and mass spectra.



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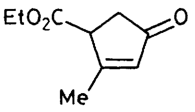

(17)

It is most likely that the annulation proceeds stepwise. The first step may be nucleophilic substitution of the halide by the carbanion of the 1,4-dipolar resonance form **(2)** to yield **(16)** which, after the regeneration of the phosphorane, undergoes an intramolecular Wittig reaction to give cyclopentadiene.

The present work provides a one-pot [3 + 2] annulation reaction leading to the regioselective formation of cyclopentadienes with a variety of substituents. This method is useful because of the simple procedure, mildness of the reaction conditions (no strong bases or acids), and ready availability of the starting materials.

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3 The synthesis of five-membered carbocycles has attracted much attention. For excellent reviews, see: L. A. Paquette, *Top. Curr. Chem.*, 1984, **119**, 1; M. Ramaiah, *Synthesis*, 1984, 529; B. M. Trost, *Chem. Soc. Rev.*, 1982, **11**, 141; T. Kauffmann, *Top. Curr. Chem.*, 1980, **92**, 109.

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