

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

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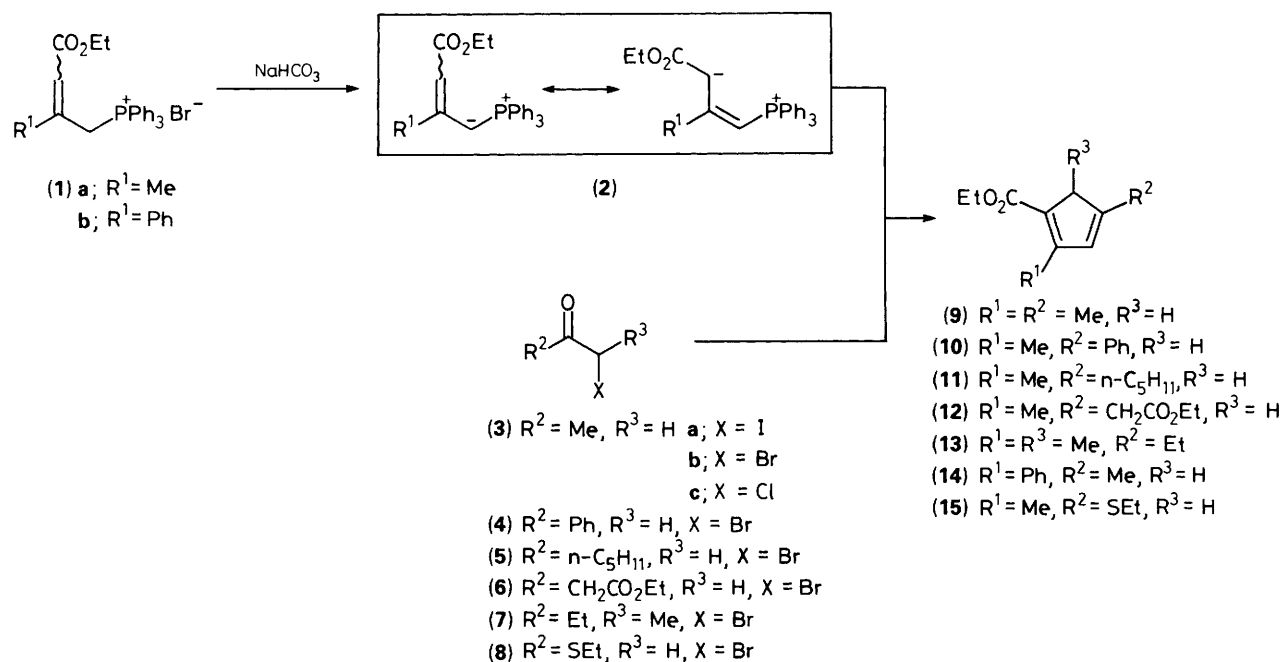
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A convenient method has been developed for the synthesis of substituted cyclopentadienes, starting from allylidene triphenylphosphoranes and α -halocarbonyl compounds, *via* a [3 + 2] annulation process.

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 NaHCO₃, 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 Pr₂NEt and K₂CO₃ as the base in solvents such as CH₂Cl₂, 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 poly-substituted 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 tetrachloride⁵ into cyclopentenone (**17**) (73%).

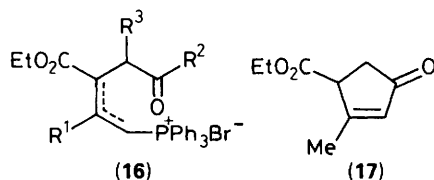


Scheme 1

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

Entry	Allylidene triphenylphosphonium bromide	α -Halo-carbonyl compound	Cyclopentadiene ^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.



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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References

- G. Bücki and H. Wüest, *Helv. Chim. Acta*, 1971, **54**, 1767; F. Bohlmann and C. Zdero, *Chem. Ber.*, 1973, **106**, 3779; W. G. Dauben and J. Ipaktschi, *J. Am. Chem. Soc.*, 1973, **95**, 5088; W. G. Dauben, D. J. Hart, J. Ipaktschi, and A. P. Kozikowski, *Tetrahedron Lett.*, 1973, 4425; A. Padwa and L. Brodsky, *J. Org. Chem.*, 1974, **39**, 1318; E. Vedejs and J. P. Bershas, *Tetrahedron Lett.*, 1975, 1359; S. F. Martin and S. R. Desai, *J. Org. Chem.*, 1977, **42**, 1664; M. Hatanaka, Y. Yamamoto, and T. Ishimaru, *J. Chem. Soc., Chem. Commun.*, 1985, 1705.
- M. Hatanaka, Y. Yamamoto, T. Ishimaru, and T. Takai, *Chem. Lett.*, 1985, 183.
- 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.
- Triphenylphosphonium bromide (1a) was used in the form of a ca. 1:1 mixture of the (*E*)- and (*Z*)-isomers: E. J. Corey and B. W. Erickson, *J. Org. Chem.*, 1974, **39**, 821. The compound (1b) was prepared under the standard conditions from ethyl (*Z*)-3-bromomethylcinnamate.
- T. Mukaiyama, S. Kamio, S. Kobayashi, and H. Takei, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3723.