The Reaction of Cyclopropyl-lithium with Tetraphenylphosphonium Bromide. Cyclopropylidenetriphenylphosphorane

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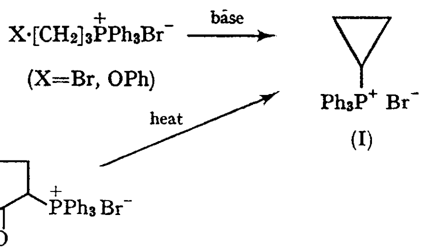
CYCLOPROPYLTRIPHENYLPHOSPHONIUM BROMIDE (I) has recently been prepared by several groups of investigators.[1] The reported syntheses have involved as immediate precursors structures which lack the cyclopropane part [equation (A)]. Attempts to generate (I) from cyclopropane derivatives have generally been unrewarding.[1e,2] We report the successful conversion of cyclopropyl bromide into (I) using a reaction of potentially wide application.

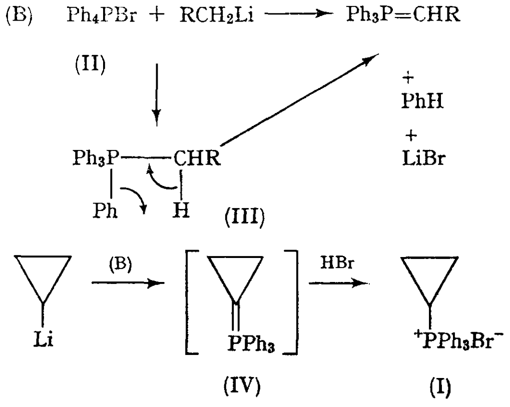
(A)



For a general route to methylenecyclopropanes *via* the Wittig olefin synthesis, we were attracted to the illuminating studies of Seyferth and his coworkers. Seyferth has shown[3] that the major reaction occurring between alkyl-lithium species and tetraphenylphosphonium bromide is that summarized by equation (B). A mechanism consistent with experimental observations is one in which a quinquecovalent phosphorus intermediate (III), formed by attack of alkyl-lithium on phosphorus, suffers concerted loss of benzene to give the observed products. These results suggested the analogous conversion of cyclopropyl halides, readily available, into the corresponding cyclopropylidenetriphenylphosphoranes—a transformation which is not achieved *via* the reaction of the cyclopropyl halide with triphenylphosphine.[1e,2a].

We find that the reaction of cyclopropyl-lithium and tetraphenylphosphonium bromide affords cyclopropylidenetriphenylphosphorane (IV) in useful yields, isolated as the hydrogen bromide salt (I). In a typical experiment, a suspension of (II) in ether is treated at room temperature with a molar equivalent of ethereal cyclopropyl-lithium.[4] The phosphonium salt (II) largely dissolves and a red-orange solution is formed. After 30 min. at the reflux temperature the solution is cooled, anhydrous hydrogen bromide is introduced until the colour is discharged, and then dilute hydrobromic acid is added to dissolve all solids. The chloroform extracts of the aqueous layer yield product (I) (35%), contaminated with some (II). Purification, if necessary, is accomplished by column chromatography. The generation of ylid (IV) from (I) and its use in the synthesis of alkylidenecyclopropanes have been described.[1c–e]

The reaction reported here is more complex than that summarized by equation (B). Only about 40% of the starting materials can be accounted for as characterizable products. The best yield of benzene (determined by gas chromatography) has been 50%, based on unrecovered (II). As a competing mode of decomposition for the presumed intermediate (III), collapse to triphenylphosphine and cyclopropylbenzene[5] would account for the low yield of benzene. We have no evidence, however, that this occurs to a significant extent.



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[2] (a) R. R. Doyle, *Diss. Abs.*, 1965, **26**, 2468; (b) N. Sherman, *ibid.*, 1966, **27**, *B*, 117.

[3] D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, 1965, **87**, 3467.

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