Tetrahedron Letters No. 7, pp. 435-437, 1963. Pergamon Press Ltd.
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# DEBROMINATION OF BROMOMETHYLTRIPHENYLPHOSPHONIUM BROMIDE WITH TRIPHENYLPHOSPHINE IN ALCOHOLS

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During an attempt to prepare methylenebis(triphenylphosphonium bromide) by the reaction of triphenylphosphine with bromomethyltriphenylphosphonium bromide in refluxing ethanol, an unexpected debromination occurred in high yield[1,2]:

$$\emptyset_3P + \emptyset_3\overset{\oplus}{P}\text{-}CH_2Br\ Br^{\ominus} \xrightarrow{EtOH} \emptyset_3\overset{\oplus}{P}\text{-}CH_3\ Br^{\ominus} + \emptyset_3P{\rightarrow}O$$

83% [3] 87% [4]

In the absence of triphenylphosphine, no reaction occurred.

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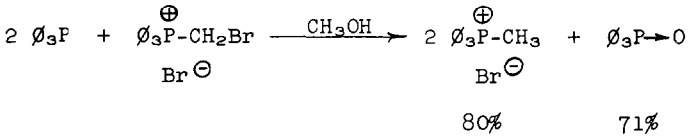
1 During the course of this investigation, a general statement concerning this type of reaction was reported; H. Hoffmann and H. J. Diehr, Tetrahedron Letters No. 13, p. 583 (1962), "Enthalogenierung durch gleichzeitige Einwirkung von t-Phosphinen und Protonen finden statt bei: o- und p-Halogenarylaminen und -phenolen, α-Halogenphosphoniumsalzen und α-Halogenphosphinoxyden."

2 The debromination of secondary and tertiary α-bromoketones with triphenylphosphine in refluxing methanol-benzene has been reported; I. J. Borowitz and L. I. Grossman, Tetrahedron Letters, No. 11, p. 471 (1962).

3 Yield represents recrystallized material from hot isopropanol-ethyl acetate. Identified by m.p. and m.m.p. and by comparison of the infrared spectrum with that of an authentic sample.

4 Yield represents material isolated directly from the reaction mixture. Identified by m.p. and infrared spectrum.

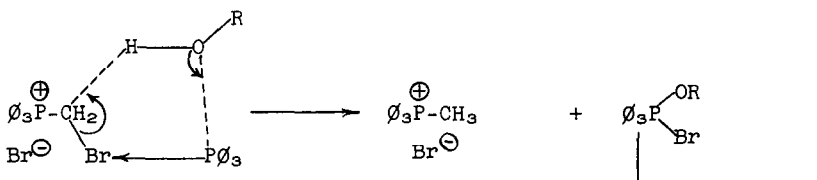
That the α-bromine was incorporated into the alkylbromide derived from the alcohol was demonstrated by trapping the alkylbromide with excess triphenylphosphine, i.e.,



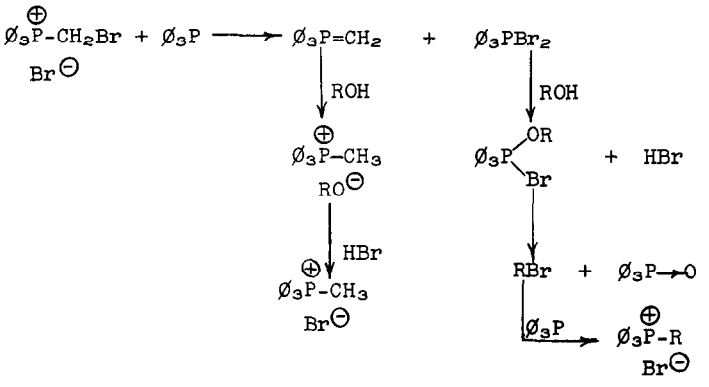
80% 71%

The foregoing observations can be accommodated by either of the follcwing reaction paths.

(1)



(2)



An "ylide" mechanism similar to (2) has been postulated for the reaction of triphenylphosphine with dibromomethyltriphenylphosphonium bromide in moist methylenechloride[5]. Further work is implicated to determine the mechanism of the debromination reaction.

Acknowledgments

Gratitude is expressed to C. N. Matthews and J. E. Harris with whom many stimulating discussions were held.

[5] F. Ramirez, N. B. Desai, and N. McKelvie, J.Am.Chem.Soc. 84, 1745 (1962).