Tetrahedron Letters,Vol.26,No.1,pp 105-106,1985
Printed in Great Britain

0040-4039/85 $3.00+ .00

REACTION OF GEM-DIBROMOCYCLOPROPANES WITH DIPHENYLPHOSPHIDE ION

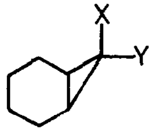
Gordon F. Meijs

Department of Organic Chemistry, University of Adelaide,
Adelaide, S.A. 5001, Australia.

Abstract: Diphenylphosphide ion undergoes a photostimulated reaction with 7,7-dibromobicyclo[4.1.0]heptane and 1,1-dibromo-2,2,3,3-tetramethylcyclopropane involving both ionic and radical steps to afford cyclopropyldiphenylphosphines resulting from substitution and reduction.

I have recently reported that the photostimulated reactions of several nucleophiles (e.g. PhS^-, $CH_3COCH_2^-$) with 7,7-dibromobicyclo[4.1.0]heptane afford products in which both halogen atoms are replaced by the nucleophile.[1] Such processes appear to involve radical intermediates and can be visualised as occurring *via* an elaborated $S_{RN}1$ pathway similar to that known in aromatic substitution.[2]

It is now reported that the reaction of *gem*-dibromocyclopropanes with diphenylphosphide ion, a known $S_{RN}1$ nucleophile,[2,3] affords cyclopropyldiphenylphosphines (e.g. 1) in a reaction involving both reduction and substitution steps. These products are conveniently isolated as the phosphine oxides (e.g. 2) after oxidative work-up.



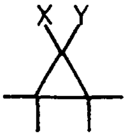
1 X = H Y = PPh_2

2 X = H Y = $\overset{\overset{O}{\|}}{P}Ph_2$

3 X = Y = Br

4 X = H Y = Br

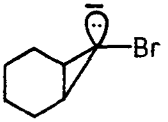
5 X = Br Y = H



6 X = Y = Br

7 X = H Y = $\overset{\overset{O}{\|}}{P}Ph_2$

8 X = H Y = Br

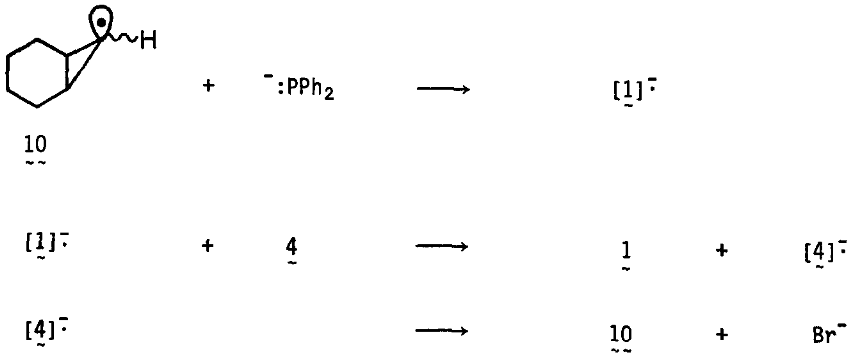


9

Irradiation of 3 (1 mmol) for 4 h with diphenylphosphide ion (6 mmol) in liquid ammonia (40 ml) gave, after treatment with hydrogen peroxide, 2 (38%) accompanied by 4 (24%). The reaction is conveniently carried out under nitrogen in a Rayonet photochemical reactor equipped with "350 nm" lamps. In dimethylsulfoxide solvent (10 ml) at ambient temperature the yield of 2 was raised to 49%. Only a trace of 2 was detected when the reaction was repeated in the dark; the product was the monobromide 4 (87%) uncontaminated by 5. The formation of this product was complete after only 10 min, even in the dark. Although di-*tert*-butyl nitroxide (1 mmol) was shown not to affect the conversion of 3 to 4, the rate of formation of the phosphine 1, however, was reduced when the amount of nitroxide was only 0.2 mmol.

It is noteworthy that irradiation of a mixture of 4 and 5 (1:3.8) in liquid ammonia also gave 1. Again, the reaction returned only starting materials when protected from light. Similar treatment of 6 in dimethylsulfoxide gave 7 (44%) accompanied by the monobromide 8 (29%).

The above experiments indicate a pathway to 4 which involves non-radical intermediates. It is likely that diphenylphosphide ion initially undergoes a nucleophilic attack *on* bromine[4] affording the anion 9. Reaction of 9 probably with *tert*-butyl alcohol (a by-product from the preparation of the nucleophile from potassium *tert*-butoxide and diphenylphosphine) affords 4. The reaction giving 1, which is clearly derived from 4, however, appears to involve a radical chain and possible propagation steps within the $S_{RN}1$ framework are sketched in Scheme 1.



Scheme 1

The reactions described herein present a simple route to cyclopropyldiphenylphosphine oxides from the readily available *gem*-dibromocyclopropanes. Such phosphine oxides are envisaged to be of use in modified Wittig olefin syntheses.[5]

Acknowledgement: The support of the Australian Research Grants Committee is gratefully acknowledged.

References and Notes

1. G.F. Meijs, J.Org.Chem., 1984, 49, in press.
2. J.F. Bunnett, Acc.Chem.Res., 1978, 11, 413.
3. (a) J.E. Swartz and J.F. Bunnett, J.Org.Chem., 1979, 44, 340;
   (b) R.A. Rossi, S.M. Palacios, and A.N. Santiago, J.Org.Chem., 1982, 47, 4654.
4. See for example: R.R. Bard, J.F. Bunnett, and R.P. Traber, J.Org.Chem., 1979, 44, 4918; and references therein.
5. See: B. Lythgoe, T.A. Moran, M.E.N. Nambudiry, S. Ruston, J. Tideswell, and P.W. Wright, Tetrahedron Letters, 1975, 3863; L. Fitjer, Angew.Chem.,Int.Ed.Engl., 1976, 15, 762.

(Received in UK 1 October 1984)