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THE REACTION BETWEEN TRIETHYL PHOSPHITE AND DIPHENYLIODONIUM SALTS. FORMATION OF DIETHYL PHENYLPHOSPHONATE AND 1,4-DIIODOBENZENE.

A. G. Varvoglis
Laboratory of Organic Chemistry, University of Thessaloniki,
Thessaloniki, Greece.

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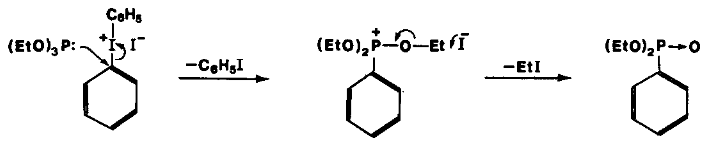
The Michaelis-Arbusov reaction is unusual in organophosphorus chemistry both for its long history and because it has been investigated in some detail[1]. Although most work has been concerned with alkyl halides there are instances where activated aromatic halides also react with trialkyl phosphites producing the corresponding phosphonates in low yields[2]; the latter may be obtained in much better yield from non-activated aryl halides and trialkyl phosphites either photolytically[3] or by use of copper bronze[4].

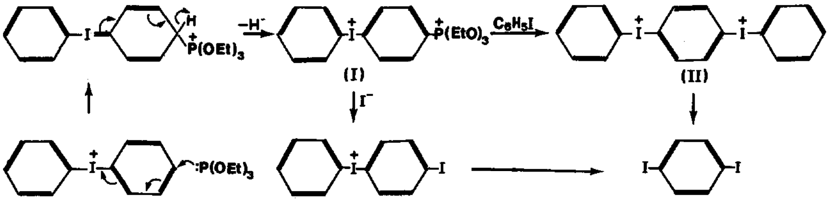
In this communication it is reported that diphenyliodonium (DPI) salts react with triethyl phosphite (TEP) and, besides the expected diethyl phenylphosphonate (DPP), substantial amounts of 1,4-diiodobenzene (DIB) are also formed. The following is an example of the procedure used at present: to an amount of DPI iodide (40.8g, 0.1mole) suspended in absolute ethanol (150ml) TEP (34.4ml, 0.2mole) and a small amount of cupric sulfate are added. The mixture is refluxed with stirring until a clear solution results and after a suitable work-up DPP (3.7g) and DIB (6g) are obtained. Their identity was established by elemental analysis and by comparison of their spectra with authentic samples. Among by-products significant quantities of ethyl iodide and iodobenzene have been detected.

The same products are obtained in varying yields by altering the solvent (toluene, pure TEP) and the catalyst (cuprous chloride; the non-catalyzed reaction proceeds easily at elevated temperature affording mainly DIB). Finally,both DPI bromide and chloride give the same products, the ratio of DPP:DIB increasing from iodide to chloride.

Apparently, two distinct reactions take place, ignoring thermolysis of DPI halides, which under these conditions is insignificant. In the first, nucleophilic attack by phosphorus at C-1 position of the aromatic ring leads to the formation of a quasiphosphonium salt, which is converted to DPP by reaction of the displaced anion on an ethyl group.



In the second reaction, nucleophilic attack by phosphorus is probably also involved but at C-4 of the aromatic ring. The addition product under hydride abstraction is transformed to the highly reactive dipositive species I, which may react in two ways: in the case of DPI iodide attack by iodide gives 4-iododiphenyliodonium ion which by further attack by iodide is transformed to DIB. Iodide may be also produced in the cases of DPI chloride and bromide by reduction of iodobenzene (formed during the first reaction) by hydride ion. Alternatively, I might be attacked by iodine of iodobenzene and bis-iodonium salt II formed, which would also finally decompose to DIB.



In accordance with the proposed mechanism DIB formation is favoured when DPI iodide is used. Also, 4-chloroiodobenzene has been detected in the reaction with DPI chloride. Finally, DIB along with diethyl-4-chlorophenylphosphonate is also formed from the reaction of TEP and 4,4 -dichlorodiphenyliodonium chloride. The reaction course is not affected when carried out in the presence of hydroquinone or dibenzoylperoxide.

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REFERENCES

1. A. J. Kirby and S. G. Warren, The Organic Chemistry of Phosphorus, Elsevier, 1967, Amsterdam, p. 37
2. a/ K. Sasse, Phosphor Verdindungen, Vol. 12/1, pp. 441 and 445, in Houben-Weyl Methoden der Organischen Chemie, Ed. E. Müller, G. Thieme Verlag, Stuttgart,1963
   b/ D. Redmore, J. Org. Chem. 35, 4114 (1970)
   c/ J. I. G. Cadogan, D. J. Sears and D. M. Smith, J. Chem. Soc. C 1314 (1969)
3. R. Obrycki and C. E. Griffin, J. Org. Chem. 33, 632 (1968)
4. P. Tavs and F. Korte, Tetrahedron 23, 4677 (1967)