CHEMISTRY LETTERS, pp. 1673-1674, 1983. © The Chemical Society of Japan 1983

PREPARATION OF DIPHENYLPHOSPHINE OXIDES BY DEOXYGENATION OF AN α-HYDROXYL GROUP WITH DIPHOSPHORUS TETRAIODIDE

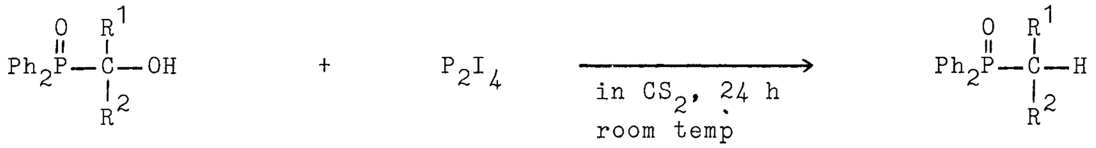
Mitsuji YAMASHITA,* Kenji TSUNEKAWA, Motoyuki SUGIURA,
Tatsuo OSHIKAWA, and Saburo INOKAWA†
Department of Chemistry, Faculty of Engineering,
Shizuoka University, Hamamatsu 432
† Department of Chemistry, Faculty of Science,
Okayama University, Okayama 700

Deoxygenation of (1-hydroxyethyl)diphenylphosphine oxide derivatives was first achieved by a reaction with diphosphorus tetraiodide to give ethyldiphenylphosphine oxide derivatives. The reaction was also successful to prepare cyclohexyldiphenylphosphine oxide.

Addition of phosphorus compounds having a P-H bond to carbonyl compounds have been known to give phosphorus compounds possessing a hydroxyl group on its α-carbon atom.[1,2] The conversion of the hydroxyl group directly into hydrogen has never been succeeded, however, that of the group into chlorine by thionyl chloride was successful only for aldehyde adducts, i.e., diethyl 1-hydroxyethylphosphonates.[3] This report describes the reaction of (1-hydroxyethyl)diphenylphosphine oxide and its homologs with diphosphorus tetraiodide, where deoxygenation took place due to promotion by the α-phosphinoyl group, to prepare directly the corresponding primary and secondary alkyl derivatives of diphenylphosphine oxides.

(1-Hydroxyethyl)diphenylphosphine oxides (**1a-d**) and 1-hydroxycyclohexyldiphenylphosphine oxide (**1e**) were treated with diphosphorus tetraiodide in carbon disulfide for 24 h at room temperature. Product analysis by HPLC on porous silica gel and spectroscopy revealed that the products were ethyldiphenylphosphine oxides (**2a-d**) and cyclohexyldiphenylphosphine oxide (**2e**), but not the corresponding iodides. This results indicates that diphosphorus tetraiodide acts as a deoxygenating reagent. The yields under the optimum condition for diphenylphosphine oxide derivatives were shown in Table 1.

Typical procedure for the preparation of (1-methylethyl)diphenylphosphine oxide (**2a**) is as follows: To a suspension of (1-hydroxy-1-methylethyl)diphenylphosphine oxide (**1a**, $R^1 = R^2 = Me$, 0.20 mmol) in carbon disulfide (2 ml) was added diphosphorus tetraiodide[4] (0.20 mmol) at room temperature, and then the mixture was stirred for 24 h. A small amount of potassium carbonate was added to the reaction mixture, and the product was taken up into chloroform (25 ml). The solution was washed with water (5 ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent *in vacuo* gave practically pure product (HPLC). Purification of the product by preparative TLC on silica gel afforded compound **2a** in 91% yield.



1a-e 2a-e

Table 1. Compounds 2a-e prepared from 1a-e.

Compound	R^1	R^2	Yield/%	MS (M^+)	^1H NMR ($CDCl_3$) δ	Mp/°C
2a	Me	Me	91	244	1.08 (dd, 2Me), 2.0-3.0 (m, CH), 7.1-8.0 (m, 2Ph)	144-145[5)]
2b	H	Me	87	230	1.13 (dt, Me), 2.20 (dq, CH_2), 7.1-7.9 (m, 2Ph)	123[6)]
2c	Me	Et	86	258	0.91 (t, Me), 1.13 (dd, Me) 1.1-2.5 (m, $C\underline{H}C\underline{H}_2$), 7.0-8.0 (m, 2Ph)	oil[7)]
2d	H	Et	73	244	0.96 (t, Me), 1.1-2.0 (m, $C\underline{H}_2C\underline{H}_2$), 7.2-8.1 (m, 2Ph)	100-101[8)]
2e	$-(CH_2)_5-$		100	284	1.0-2.5 (m, $c-C_6H_{11}$), 7.3-8.3 (m, 2Ph)	165[6)]

Although a little is known about the deoxygenation of alcohols with tervalent phosphorus compounds,[9,10)] the present results show that the deoxygenation of the hydroxyl group with diphosphorus tetraiodide was promoted by the α-phosphinoyl group, and that the present reaction provides an improved method for preparing tertiary phosphine oxides.

References

1) V. S. Abramov, Dokl. Akad. Nauk SSSR, 95, 991 (1954).
2) M. Yamashita, P. T. Long, M. Shibata, and S. Inokawa, Carbohydr. Res., 84, 35 (1980).
3) T. Gomyo, H. Yoshida, T. Ogata, H. Inokawa, and S. Inokawa, Nippon Kagaku Kaishi, 1974, 1093.
4) H. Suzuki and T. Fuchita, Nippon Kagaku Kaishi, 1977, 1679.
5) D. Howells and S. Warren, J. Chem. Soc., Perkin II, 1973, 1472.
6) L. Horner, P. Beck, and V. G. Toscano, Chem. Ber., 94, 1317 (1961).
7) A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, J. Chem. Soc., Perkin I, 1977, 550.
8) S. Trippett, J. Chem. Soc., 1961, 2813.
9) H. Suzuki, H. Tani, H. Kubota, N. Sato, J. Tsuji, and A. Osuka, Chem. Lett., 1983, 247.
10) A. G. Rowley, "Organophosphorus Reagents in Organic Synthesis," ed by J. I. G. Cadogan, Academic Press, London (1979), Chap. 7.

(Received July 14, 1983)