

Phosphorus-31 Chemical Shifts of Some Air-sensitive Phosphinemethylenes

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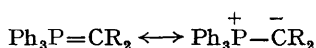
ALTHOUGH Wittig reagents have been used extensively in organic syntheses, little physical data have been gathered on these important compounds, especially the air-sensitive ones.¹

We report here the phosphorus-31 chemical shifts of some air-sensitive phosphinemethylenes in dimethyl sulphoxide solution. The quaternary triphenylphosphonium salt (1—1.5 g), precursor of the phosphinemethylene, was placed in a 15 × 125 mm. test tube which was flushed with nitrogen and capped with a serum stopper. About 5 ml. of a freshly prepared solution of

1M-dimethylsulphinyl carbanion² in dimethyl sulphoxide was injected into the tube. The methyltriphenylphosphonium bromide produced a greenish-yellow solution; the n-alkyltriphenylphosphonium salts produced orange-red solutions; and the s-alkyltriphenylphosphonium salts gave opaque red solutions. The ³¹P spectra were measured with a Varian Associates DP60 instrument at 24.3 MHz. and standardized with a small reference tube of (85%) H₃PO₄ which was inserted through the serum stopper.

The results are given in the Table. Several

points are of interest. First, the chemical shifts of the phosphinemethylenes are in the order expected from inductive effects, *i.e.*, the phosphinemethylenes from the secondary phosphonium salts are at higher field (corresponding to higher shielding) than those from the normal alkyl salts. In the phosphonium salts, the reverse trend is observed,³ *viz.*, salts with secondary alkyl groups are at lower field. It has been suggested³ that hyperconjugation is a cause of the reverse trend in the phosphonium salts. Removal of the positive charge from the phosphonium salt in the formation of the ylid,



places a negative charge on the methylene carbon which makes hyperconjugative participation by the alkylidene group unlikely. As a result, the chemical shifts are in the approximate expected inductive order.

Secondly, the last column in the Table illustrates the similarity between several groups of compounds, *i.e.*, methyl, whose ³¹P shift goes upfield only slightly on ylid formation; normal alkyls, upfield about 12 p.p.m. on ylid formation and secondary alkyls, upfield about 20 p.p.m. The slightly exceptional behaviour of the cyclopentyl compound is not understood at present.

TABLE

³¹P Chemical shifts of [Ph₃PR]Br and their corresponding ylids

R	δ _{salt} (p.p.m.)	δ _{ylid} (p.p.m.)	δ _{ylid} — δ _{salt}
methyl ..	-22.7	-20.3	+2.4
ethyl ..	-26.2	-14.6	+11.6
n-propyl ..	-24.1	-12.2	+11.9
n-butyl ..	-24.0	-12.6	+11.4
n-hexyl ..	-24.4	-12.2	+12.2
2-propyl ..	-30.9	-11.3	+19.6
2-butyl ..	-30.2	-10.5	+19.7
3-pentyl ..	-30.1	-10.9	+19.2
3-hexyl ..	-30.3	-10.7	+19.6
cyclopentyl	-30.7	-4.8	+25.9
cyclohexyl ..	-26.6	-6.4	+20.2

These results are to be contrasted with the air-stable ylids, whose ³¹P chemical shifts are only slightly different from those of their respective phosphonium salts.¹ Therefore, as one expects, the air-sensitive ylids shield phosphorus better than those ylids which have the negative charge somewhat delocalized.

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¹ A. W. Johnson, "Ylid Chemistry", Academic Press, 1966, pp. 76-79.

² E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 866.

³ S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, 1966, **70**, 581.