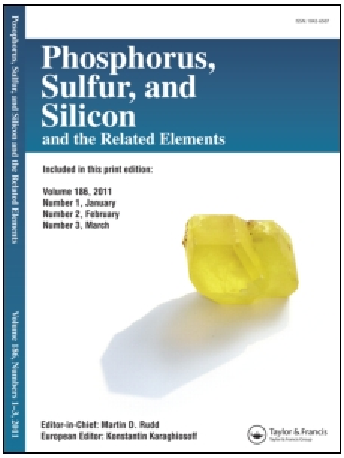

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Fortion and Reactions of Phosphonium Inner Salt, $\equiv P\ C_6H_4O^-p$

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FORMATION AND REACTIONS OF PHOSPHONIUM INNER SALT, $\equiv\overset{+}{P}C_6H_4O^{-}$-p

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Abstract Thermolysis and reactions of methyltris(p-methoxyphenyl)phosphonium iodide with triphenylphosphine are reported. NMR and mass spectral evidence for the formation of phosphonium inner salts, $\geqslant\overset{+}{P}C_6H_4O^{-}$-p, is presented.

Earlier workers[1,2] have reported the formation of phosphonium inner salts from their corresponding hydroxyphenylphosphonium salts in the presence of a base. We recently reported a novel reaction between tris(p-methoxyphenyl)phosphine and neopentyl iodide which gave a mixture of eight phosphonium salts, $(p\text{-}ROC_6H_4)_3P^+R\ I^-$, where R groups are all possible combinations of methyl and neopentyl.[3] Their formation was interpreted in terms of the intermediacy of inner phosphonium salts:

The actual presence of the inner salts was not observed as they reacted straightway with the neopentyl iodide to give the final products. We have now demonstrated the formation of the above postulated inner salts from the reactions of methyltris(p-methoxyphenyl)phosphonium iodide with triphenylphosphine. Their NMR and mass spectral data are reported.

Methyltris(p-methoxyphenyl)phosphonium iodide (1) was prepared as follows: To 17.60 g (0.05 mol) of tris(p-methoxyphenyl)phosphine was added dropwise during stirring 50 ml CH_3I at a rate as to ensure gentle refluxing. The mixture was then cooled to room temperature and 50 ml of ethyl acetate was added to complete precipitation of the phosphonium salt which was then collected by filtration, dried in a vacuum oven at 60°C; yield 23.0 g (93%).

An analytically pure sample was prepared by crystallization from chloroform-ethyl acetate; mp 219-20°C (dec). Anal. Calcd. for $C_{22}H_{22}IO_3P$: C, 53.44; H, 4.86. Found: C, 53.19; H, 4.61. Its NMR data (DMSO-d_6): δCH_3 2.99 ppm; $^2J_{PH}$ 14.4 Hz; δOCH_3 3.89 ppm; $\delta {}^{31}P$ 21.34 ppm.

The above salt was reacted with (a) equimolar (0.005 mol) and (b) termolar equivalents (0.015 mol) of triphenylphosphine at 210°C under N_2 with stirring during six hours. The reaction mixtures on cooling gave yellow solids which were analyzed by proton and ^{31}P NMR (in anhydrous DMSO-d_6) and mass spectrometry. Their proton spectra showed four doublets which, from their chemical shifts and $^2J_{PH}$ given in Table I were assigned to phosphonium cations 1 and 2 and the phosphonium inner salts 3 and 4 shown in scheme 1. Their ^{31}P spectra also showed four absorptions corresponding to these species. However, no evidence for the formation of 5 was detected even in the reaction (b) when

Scheme 1

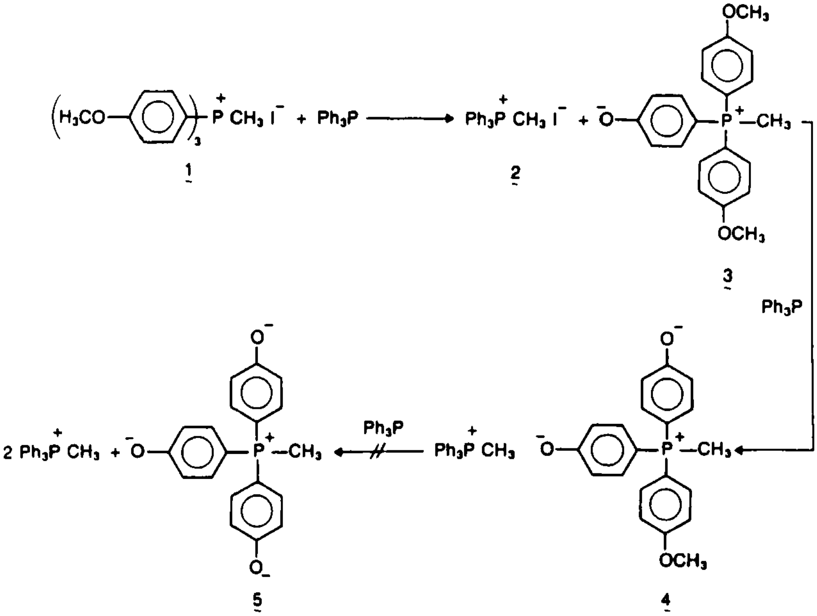

TABLE I. PROTON AND ^{31}P NMR DATA

ction		2	1	3	4	(Rel. Molar Ratios)
Ph_3P	δCH_3, ppm[a]	3.17	2.98	2.68	2.51	(10:2.2:6.5:c)
	$^2J_{PH}$, Hz	14.6	14.3	13.8	c	
	$\delta 31_P$, ppm[b]	23.94	21.33	18.33	17.04	(10:2.2:6.7:3.6)
3 Ph_3P	δCH_3, ppm[a]	3.21	d	2.67	2.42	(10:~0:2.9:3.9)
	$^2J_{PH}$, Hz	14.7	d	13.8	13.5	
	$\delta 31_P$, ppm[b]	23.93	21.32	17.97	16.17	(10:~0:3.0:3.6)

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rom TMS as internal reference.

rimethylphosphite (141.64 ppm) was used as an external reference.

nterfered by a DMSO peak.

ractically all consumed.

excess triphenylphosphine was used. Presumably, the excess negative charge on 4 deactivates its remaining methoxy group and consequently no further nucleophilic attack by triphenlyphosphine occurs to give 5.

Fast Atom Bombardment mass spectral analysis in glycerol-thioglycerol-methylene chloride showed masses corresponding to the phosphonium cations 1 (367.5) and 2 (277.12). The inner salts 3 and 4, associated with appropriate number of protons, appeared at masses 353.12 and 339.12, respectively. Interestingly, phosphonium salt 1 showed no fragment of mass 339.12, suggesting that formation of 4 is indeed occurring from 3 thus supporting the formation of these phosphonium inner salts in the above reactions. Again, no evidence for 5 was discovered from the mass spectra.

The molar ratios listed in Table I, which were calculated both from ^{1}H and ^{31}P NMR spectra, indicate that more of the inner salts 3 and 4 were formed than would be estimated from 2, especially when equimolar amounts of the reactants were used; suggesting that they might also be forming directly via thermolysis of 1. We checked by carrying out its thermolysis at 240°C, where the reaction mixture stayed liquid, for 6 hrs. Both NMR and mass spectra showed the presence of 3 and 4 in the reaction mixture. Obviously the iodide causes a nucleophilic attack on the *p*-methoxy groups eliminating CH_3I. The starting phosphonium cation acts as a counter ion especially for 4.

REFERENCES

1. L. Horner, H. Hoffmann, H. G. Wippel, and G. Hassel, *Chem. Ber.*, **91**, 52 (1958).
2. N. A. Nesmeyanor and O. A. Reutov, *Doklady Chem. (USSR) (English transl.)*, **171**, 1042 (1966).
3. G. Singh, *J. Org. Chem.*, 52, 1647 (1987).