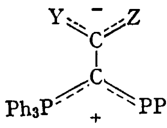
Mesomeric Phosphonium Inner Salts

By C. N. MATTHEWS, J. S. DRISCOLL, and G. H. BIRUM

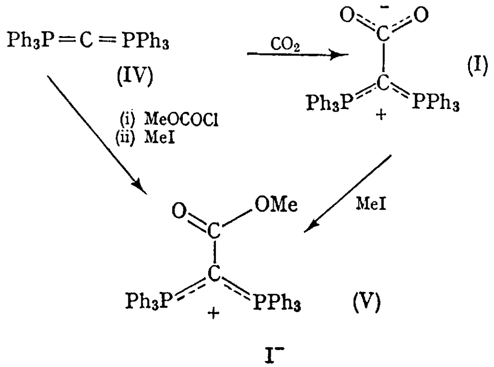
(*Central Research Department, Monsanto Company, St. Louis, Missouri* 63166; *and Monsanto Research Corporation, Everett Station, Boston, Massachusetts* 02149)

MESOMERIC phosphonium inner salts (I—III) are readily formed by the reaction of hexaphenylcarbodiphosphorane[1–3] (IV) with carbon dioxide, carbonyl sulphide, and carbon disulphide, respectively. In a typical reaction, gaseous carbon dioxide was dispersed in a stirred solution of (IV) (16·0 g., 0·03 mole) in dry Diglyme (50 ml.) under nitrogen at room temperature. A white solid was precipitated and the yellow colour of (IV) gradually disappeared. After 1½ hr. the temperature was raised to 65°, the gas addition was stopped, and the reaction mixture allowed to cool.



(I) Y = Z = O
(II) Y = O, Z = S
(III) Y = Z = S

Filtering under nitrogen, washing with Diglyme and with diethyl ether, and drying under nitrogen gave [(carboxy)(triphenylphosphoranylidene)methyl]triphenylphosphonium inner salt (I) (17·2 g., 96% yield) m.p. 140—141° (dec.).[4] Alkylation of the inner salt was readily accomplished. For example, addition of methyl iodide to a suspension of (I) in dimethylacetamide at room temperature rapidly gave a colourless solution. Precipitation with ether and recrystallization from ethanol yielded [(methoxycarbonyl)(triphenylphosphoranylidene)methyl]triphenylphosphonium iodide (V), a white solid, m.p. 219—220° (decomp.). The same product was obtained by the addition of methyl chloroformate to IV) followed by metathesis with methyl iodide.



Infrared spectra of (I) and (V) are consistent with the structures suggested, most relevant being a strong absorption band at 5·98 μ corresponding to the ester carbonyl group of (V), and a sharp doublet at 6·32 and 6·38 μ corresponding to the carboxylate group of (I). For (V), the ^{31}P n.m.r. spectrum has a single peak at −21·4 p.p.m. characteristic of mesomeric phosphonium cations,[3] while the proton n.m.r. spectrum has an aryl proton region centred at −7·64 and a methyl proton singlet at −3·08 p.p.m. with an area ratio of 10 : 1 as expected.[5] N.m.r. spectra could not be obtained for (I) because of its exceptionally low solubility in common aprotic solvents at room temperature. However, the correctness of structure (I) was further indicated by the fact that heating in solvents such as Diglyme gave only two decomposition products, triphenylphosphine oxide and a new cumulative organophosphorus compound, triphenylphosphoranylideneketen, $Ph_3P{=}C{=}C{=}O$.[6]

In protic solvents such as trifluoroacetic acid and fluoroboric acid, (I) appeared to dissolve readily, but a rapid effervescence observed indicated that decarboxylation had occurred instead to yield a soluble salt. The ^{31}P n.m.r. spectrum of the resulting solution had a peak at −18·8 p.p.m. characteristic of diphosphonium salts[3] as is a proton n.m.r. triplet (J_{HP} 16 c./sec.) found at −5·2 p.p.m. Evidently protonation of the carboxylate anion of (I) led to the elimination of carbon dioxide and the formation of a mesomeric phosphonium salt containing a [(triphenylphosphoranylidene)methyl]triphenylphosphonium cation[1-3] which, in the presence of an acid, was rapidly converted into a methylenebis(triphenylphosphonium) salt.[1,7]

Reactions of carbonyl sulphide and carbon disulphide with hexaphenylcarbodiphosphorane (IV) yielded the mesomeric inner salts (II) and (III), respectively, (II) being an off-white solid, m.p. 152—155° and (III) a bright yellow powder, m.p. 132—133°. As with (I) the marked insolubility of (II) and (III) precluded nuclear magnetic resonance and molecular-weight studies. While evidence obtained by chemical reactions supports the monomeric structures suggested, it is possible that the inner salts actually have pseudopolymeric character arising from intermolecular attractions.

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[2] C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *J. Amer. Chem. Soc.*, 1962, **84**, 4349.
[3] J. S. Driscoll, D. W. Grisley, Jr., J. E. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, 1964, **29**, 2427.
[4] Satisfactory elemental analyses were obtained for all new compounds.
[5] ^{31}P n.m.r. spectra are reported with respect to 85% phosphoric acid contained in a capillary. ^{1}H n.m.r. spectra are reported with respect to tetramethylsilane as internal standard.
[6] C. N. Matthews and G. H. Birum, to be published.
[7] D. W. Grisley, Jr., J. C. Alm, and C. N. Matthews, *Tetrahedron*, 1965, **21**, 5.