Reactions of Phosphorus Compounds. Part XXIII.[1] Preparation and Reactions of Several α-Substituted Vinylphosphonium Salts

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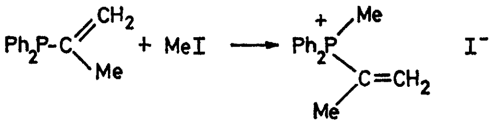
Isopropenylmethyldiphenylphosphonium iodide (1) and triphenyl-1-phenylvinylphosphonium bromide (5) have been prepared and characterized. Their reactivity with alcohols and amines has been compared with that of triphenylvinylphosphonium bromide. Evidence is presented for the formation of an allylically stabilized anion upon treatment of the salt (1) with base. Treatment of the salt (5) with piperidine results in a cleavage reaction.

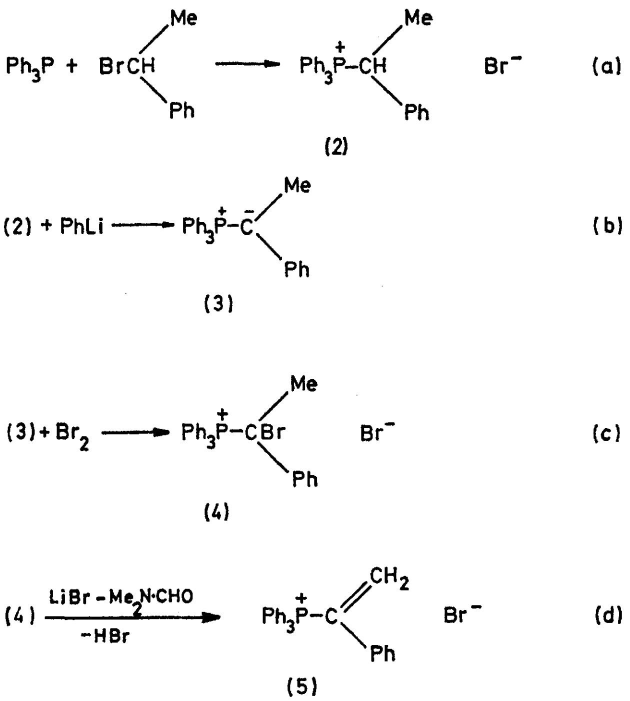
WE previously[1] have shown the usefulness of triphenylvinylphosphonium bromide in syntheses involving a conjugate, or Michael-type, addition followed by a Wittig reaction. Similar studies are being continued with the unsubstituted vinyl salt and in an attempt to broaden the scope of the reaction sequence, we have prepared two α-substituted vinylphosphonium salts and studied some of their reactions.

Deficiencies in reported preparations of isopropenyltriphenylphosphonium bromide,[2,3] have led us to examine the preparation of isopropenylmethyldiphenylphosphonium iodide (1). Quaternization of isopropenyldiphenylphosphine[4] with methyl iodide gave this compound in quantitative yield.

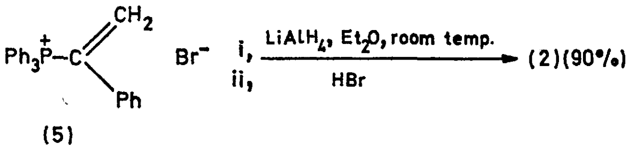


(1)

The hitherto unknown triphenyl-1-phenylvinylphosphonium bromide (5) was prepared in >90% purity and an overall yield of 25—30% by the four-step procedure shown (Scheme 1). Step (c) illustrates the known[5-7] bromination of ylides, but is novel in that it allows the isolation of the bromophosphonium salt (4), since transylidation[8] is impossible. Step (d) is an example of the novel and extraordinary properties of dimethylformamide–alkali metal halide combinations as dehydrohalogenation reagents.[9,10] However, in this preparation salt (5) was invariably contaminated with a small amount (*ca.* 10%) of salt (2). This salt could not have been carried over from step (a) since dehydrohalogenation [step (d)] was carried out with the pure salt (4). This apparent reduction is difficult to explain, but the ease with which it is accomplished is shown by the fact that all reactions of salt (5) investigated led to varying amounts of the salt (2) or products derived therefrom,[11] as well as by the ready conversion of salt (5) into salt (2) under mild conditions.



SCHEME 1



Both vinylphosphonium salts were characterized by n.m.r. spectra[12] and by hydrolysis by aqueous base which proceeds essentially in quantitative yield. The reactions of these two salts with nucleophilic reagents were investigated in order to compare the results with those reported for triphenylvinylphosphonium bromide (8).[13] Salt (8) reacts with alcohols and secondary amines to afford the corresponding 2-substituted ethyl

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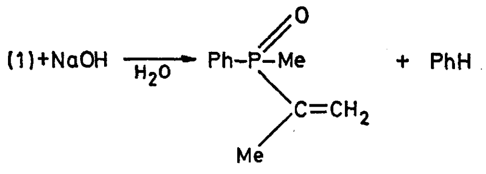


(6)

$$(5) + NaOH \xrightarrow[H_2O]{} Ph_3PO + PhCH{=}CH_2$$

(7)

phosphonium salts in high yield. Salts (1) and (5) did not react with alcohols alone, but gave addition products with simple alcohols when a catalytic amount of alkoxide was employed. The addition of piperidine to salt (1) produced the phosphonioethyl adduct (11) in 70% yield, whereas the addition of piperidine to salt (5) resulted in an interesting cleavage reaction. The formation of salt (12) and compound (13) (Scheme 2), may be explained as in Scheme 3. The reaction is apparently facilitated by the presence of an electrophilic substituent α- to the phosphorus atom, which would stabilize the ylide formed by cleavage. Thus salts (1) and (8) give none of the cleavage product.*

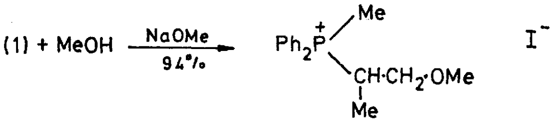
$$Ph_3\overset{+}{P}\cdot CH{=}CH_2Br^- + R^1XH \longrightarrow Ph_3\overset{+}{P}\cdot CH_2\cdot CH_2\cdot XR^1\ Br^-$$

(8)

$X = O$ or NR^2

$$(1) \text{ or } (5) + ROH \longrightarrow \text{no reaction}$$

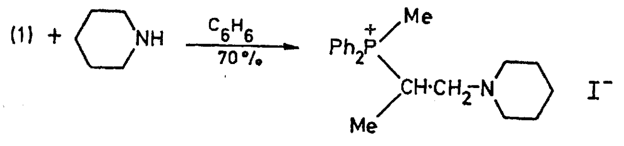
$R = Me, Et, CH_2Ph$, or Pr^i



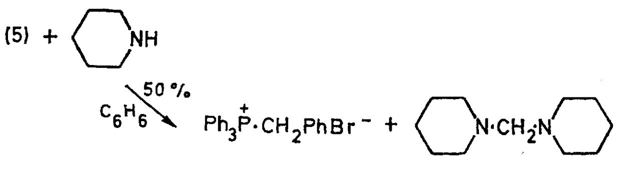
(9)

$$(5) + MeOH \xrightarrow{NaOMe} Ph_3\overset{+}{P}\cdot CHPh\cdot CH_2\cdot OMe\,Br^- + (2)(35\%)$$

(10)(65%)



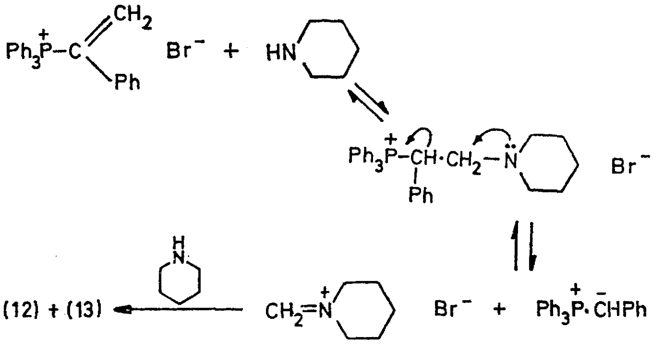
(11)



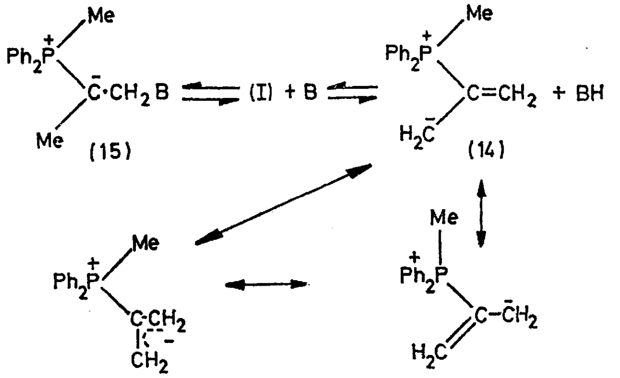
(12) (13)

Scheme 2

Preliminary investigations of reactions of salt (1) with bases indicate ready formation of the resonance-stabilized anion (14) as well as ylide (15). The formation of both species is indicated by the fact that when salt (1) is heated with methan[^{2}H]ol–sodium methoxide, considerable deuteriation occurs at the *C*-methyl group. Certain observations[11] can only be explained on the basis of the formation of species (14).



Scheme 3



Investigations of the reactivity of these two vinylphosphonium salts directed toward their use in chain-extension and heterocyclic ring synthesis reactions are in progress.

EXPERIMENTAL

Elemental analyses were performed at MHW Laboratories, Garden City, Michigan. I.r. spectra were measured with a Perkin-Elmer model 137 instrument. N.m.r. spectra were recorded with a Varian A-60A instrument, with tetramethylsilane as internal standard.

The identity of known compounds with authentic samples was shown by the use of two or more of the following criteria: m.p., mixed m.p., i.r., and n.m.r. spectra, t.l.c. comparison, g.l.c. retention time and coinjection behaviour, and conversion into a known derivative.

Isopropenylmethyldiphenylphosphonium Iodide (1).—An excess of methyl iodide was added to a solution of isopropenylphosphine[4] (15·3 g, 0·0675 mol) in ether (750 ml). Salt (1) precipitated almost immediately. The mixture was then refluxed with stirring, under nitrogen, for 2 days.

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* An analogous cleavage reaction was observed when triphenyl-1-phenyl-2-carboxyvinyl phosphonium bromide was heated with a nitrogenous base (A. T. Wehman, unpublished results).

The resultant white solid (24 g, 97%) was filtered off and washed with ether; m.p. 157—158° (from CH_2Cl_2–EtOAc), $\nu_{max.}$ (KBr) 3020, 2920 (CH), 1485, 1430 (C–C), 1110 (P–Ph), and 1000 (P–Ph) cm^{-1}; δ($CDCl_3$) 2·23 (3H, ddd, *J* 14·5, 1·5, and 0·7 Hz, Me), 2·98 (3H, d, *J* 13·5 Hz, MeP), 5·97 (1H, dd, *J* 22·5 and 1·5 Hz, vinyl H *cis* to P), 6·60 (1H, dd, *J* 45·5 and 0·7 Hz, vinyl H *trans* to P), and 7·6—8·1 (10H, m, phenyl) p.p.m. (Found: C, 52·0; H, 5·05. $C_{10}H_{18}IP$ requires C, 52·2; H, 5·2%).

Triphenyl-1-*phenylethylphosphonium Bromide* (2).—A solution of 1-phenylethyl bromide (200 g, 1·08 mol) and triphenylphosphine (300 g, 1·14 mol) in ethyl acetate (2 l) was stirred under reflux for 3 days, cooled, and filtered. Salt (2) (375 g, 78%) was washed with ethyl acetate and ether, and recrystallized from CH_2Cl_2–EtOAc; m.p. 231—234°; $\nu_{max.}$ (KBr) 1480, 1430 (C–C), 1110 (P–Ph), and 1005 (P–Ph) cm^{-1}; δ($CDCl_3$) 1·85 (3H, dd, *J* 19 and 7 Hz, Me), 6·62 (1H, dq, *J* 14 Hz, CH), 7·2br (5H, phenyl), and 7·6—8·0 (15H, m, phenyl) p.p.m. (Found: C, 69·85; H, 5·45. $C_{26}H_{24}BrP$ requires C, 69·8; H, 5·4%).

Triphenyl-1-*bromo*-1-*phenylethylphosphonium Bromide* (4).—To a slurry of triphenyl-1-phenylethylphosphonium bromide (134 g, 0·3 mol) in dry benzene (250 ml) under nitrogen was added 1·91M-phenyl-lithium (165 ml, 0·315 mol) and the mixture was stirred and refluxed for 24 h, then cooled to room temperature. Meanwhile, a solution of bromine (64 g, 0·4 mol) in dry benzene (150 ml) was placed in a pressure-equalizing addition funnel, fitted in a three-necked receiver flask equipped with stirrer, reflux condenser, and Claisen adaptor. The flask containing the phosphonium salt–phenyl-lithium mixture [ylide (3)] was attached to the receiver flask by means of an adaptor equipped with a large-bore stopcock.

The whole assembly was flushed with nitrogen, and benzene (300 ml) was placed in the receiver flask, which was cooled in ice. The bromine solution and the ylide mixture were slowly added to the vigorously stirred benzene at such a rate that refluxing did not occur. The resultant orange suspension was then stirred for an additional 0·5 h. The solvent was decanted and the gummy residue was dissolved in dichloromethane. The solution was treated with cyclohexene until its colour was pale yellow. Celite was added, and the mixture was filtered. The filtrate was concentrated and ethyl acetate was added to produce the phosphonium salt (4), m.p. 168—169° (from CH_2Cl_2–EtOAc); $\nu_{max.}$ (KBr) 1480 (C–C), 1100 (P–Ph), and 1000 (P–Ph) cm^{-1}; δ($CF_3{\cdot}CO_2H$) 2·82 (3H, d, *J* 15 Hz, Me), 7·3br (5H, s, phenyl), and 7·6—8·1 (15H, m, phenyl) (Found: C, 59·45; H, 4·1. $C_{26}H_{23}Br_2P$ requires C, 59·35; H, 4·4%).

Triphenyl-1-*phenylvinylphosphonium Bromide* (5).—To a mixture of triphenyl-1-bromo-1-phenylethylphosphonium bromide (52·6 g, 0·10 mol) and lithium bromide (15·0 g, 0·143 mol) was added dry dimethylformamide (250 ml), and the mixture was heated at 100° for 3 h, cooled, added to water (500 ml), and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and concentrated while ethyl acetate was added, to give crystals (26·5 g), m.p. 213—214°, homogeneous on t.l.c., but showing the presence of 10% of salt (2) by n.m.r. The two components could not be separated; $\nu_{max.}$ 1600 (C=C), 1490, 1440 (C–C), 1120 (P–Ph), and 1005 (P–Ph) cm^{-1}; δ($CDCl_3$) 6·45 (1H, dd, *J* 21 and 0·7 Hz, vinyl H *cis* to P), 7·18 (1H, dd, *J* 46 Hz, vinyl H *trans* to P), 7·2—7·4 (5H, m, phenyl), and 7·5—8·0 (15H, m, phenyl) p.p.m. (Found: C, 70·5; H, 5·2. Calc. for $C_{26}H_{22}BrP$: C, 70·1; H, 5·0%).

Reduction of Triphenyl-1-*phenylvinylphosphonium Bromide* (5) *with Lithium Aluminum Hydride*.—To a suspension of salt (5) (8·9 g, 0·02 mol) in dry ether (125 ml) was added lithium aluminium hydride (0·38 g, 0·01 mol) and the resultant slurry was stirred at room temperature for 2 days. Hydrogen bromide gas was bubbled in until the mixture was colourless, and then water was added. The phases were separated and the water layer was extracted with dichloromethane. The dried ($MgSO_4$) extract was poured into ether to yield triphenyl-1-phenylethylphosphonium bromide (8·1 g, 91%).

Aqueous Basic Hydrolysis of Isopropenylmethyldiphenylphosphonium Iodide (1).—Salt (1) (7·35 g, 0·02 mol) was warmed to *ca.* 40° with stirring in aqueous 10% NaOH (100 ml) for 0·5 h. The cooled mixture was diluted with water and extracted with dichloromethane. The dried ($MgSO_4$) extract was evaporated to yield the phosphine oxide (6) (3·6 g, 98%), m.p. 27—28° (ether–hexane); $\nu_{max.}$ (Nujol) 1185 (P–O), 1110 (P–Ph), and 960 (terminal CH_2) cm^{-1}; δ($CDCl_3$) 1·81 (3H, d, *J* 12·5 Hz, MeP), 1·83 (3H, ddd, *J* 11·5, 1·2, and 0·9 Hz, Me), 5·78 (1H, dq, *J* 39 and 0·9 Hz, vinyl H *trans* to P), 5·93 (1H, dq, *J* 19 and 1·2 Hz, vinyl H *cis* to P), and 7·3—8·0 (5H, m, phenyl) p.p.m. (Found: C, 66·5; H, 7·35. $C_{10}H_{13}OP$ requires C, 66·65; H, 7·25%).

Hydrolysis of Triphenyl-1-*phenylvinylphosphonium Bromide* (5).—By the same procedure as for the hydrolysis of salt (1), hydrolysis of salt (5) furnished a quantitative yield of triphenylphosphine oxide (7). G.l.c. of the organic extract indicated the presence of styrene containing a small amount of benzene.

Base-catalysed Addition of Methanol to Isopropenylmethyldiphenylphosphonium Iodide (1).—The salt (1) was refluxed for 24 h in methanol to which had been added a tiny piece of sodium. The mixture was poured into ether to produce a quantitative yield of (1-methoxymethylethyl)methyldiphenylphosphonium iodide (9); m.p. 186—187° (from acetone), $\nu_{max.}$ (Nujol) 1100 (P–Ph) and 1000 (P–Ph) cm^{-1}; δ($CF_3{\cdot}CO_2H$) 1·52 (3H, dd, *J* 18 and 6·5 Hz, Me), 2·60 (3H, d, *J* 13·5 Hz, Me–P), 3·4 (3H, s, Me), 3·5—4·0 (3H, m, $CH{\cdot}CH_2$), and 7·6—8·0 (10H, m, phenyl) p.p.m. (Found: C, 50·9; H, 5·45; I, 31·8. $C_{17}H_{22}IOP$ requires C, 5·0; H, 5·55; I, 31·7%). Repetition of the reaction in methan[^{2}H]ol gave the adduct (9), m.p. 185—187°, which contained deuterium in both the methylene and *C*-methyl groups, as shown by n.m.r.

Treatment of Triphenyl-1-*phenylvinylphosphonium Bromide* (5) *with Sodium Methoxide in Methanol*.—To a solution of methanol containing a tiny piece of sodium was added the salt (5) (4·45 g, 0·01 mol) and the mixture was refluxed for 24 h, cooled, and poured into ether to produce a white solid (4·3 g). T.l.c. displayed one spot, but n.m.r. analysis showed the presence of a mixture of salt (10) (65%) and salt (2) (35%). This could not be separated by fractional crystallization. The n.m.r. spectrum of salt (10) showed δ($CDCl_3$) 3·22 (3H, s, OMe), 4·0—4·5 (2H, d, CH_2), 6·6—6·9 (1H, m, CH), and 7·1—8·0 (20H, m, phenyl) p.p.m.

Addition of Piperidine to Isopropenylmethyldiphenylphosphonium Bromide (1).—A mixture of the salt (1) (3·68 g, 0·010 mol) and piperidine (0·8 g, 0·010 mol) in benzene (125 ml) was refluxed for 2 days. Filtration gave a white solid (4·2 g), containing the salt (11) (70%) and salt (1) as shown by n.m.r. A pure sample of the salt (11) was obtained by refluxing a sample of (1) in piperidine (35 ml) for 1 day, followed by filtration and recrystallization (from $CHCl_2$–

EtOAc). The pure salt (11) had m.p. 211—213°; $\nu_{max.}$ (Nujol) 1440 ($CH_2{\cdot}N$), 1120 (P–Ph), and 1000 (P–Ph) cm^{-1}; $\delta(CDCl_3)$ 0·8—1·4 (6H, m, piperidine ring), 1·22 (3H, dd, *J* 19 and 5·7 Hz, MeC), 1·8—2·9 (6H, m, piperidine ring and CH_2), 2·87 (3H, d, *J* 14 Hz, MeP), 4·2—4·8 (1H, m, CH), and 7·5—8·3 (10H, m, phenyl) p.p.m. (Found: C, 55·85; H, 6·5. $C_{21}H_{29}INP$ requires C, 55·65; H, 6·45%).

Reaction of Triphenyl-1-*phenylvinylphosphonium Bromide* (5) *with Piperidine*. The salt (5) (4·45 g, 0·01 mol) was slurried in benzene (125 ml) and piperidine (0·86 g, 0·010 mol) was added. The mixture was refluxed for 2 days and then filtered. Dipiperidinomethane (13) was obtained from the filtrate (0·78 g, 42·8%), b.p. 89—90° at 3·5 mmHg (lit.,[14] 88° at 4·6 mmHg). Fractional crystallization of the filtration residue afforded benzyltriphenylphosphonium bromide (12) (47·2%) and triphenylvinyl-1-phenylphosphonium bromide (5) (49·4%).

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