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FORMATION OF PHOSPHORUS YLIDE VIA 1,3-SILYL MIGRATION OF DIMETHYL TRIMETHYLSILYLMETHYLPHOSPHONATE. APPLICATION OF THE PHOSPHONATE TO A WITTIG REACTION

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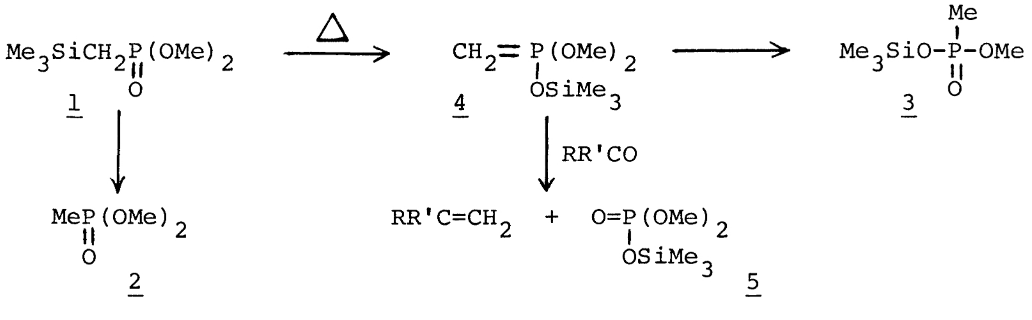
The reactions of carbonyl compounds with dimethyl trimethylsilylmethylphosphonate gave terminal olefins, dimethyl methylphosphonate, methyl trimethylsilyl methylphosphonate, and dimethyl trimethylsilyl phosphate. Terminal olefins may be formed by a Wittig type reaction of carbonyl compounds with a phosphorus ylide produced via 1,3-silyl migration of dimethyl trimethylsilylmethylphosphonate.

Several methods for the conversion of carbonyl compounds into olefins have been developed during the past years. One of the most useful synthesis of olefins from carbonyl compounds is the Wittig reaction by use of phosphorus ylides, which are usually prepared by the treatment of phosphonium salts with strong bases.1) We wish to report here the thermal isomerization of dimethyl trimethylsilylmethylphosphonate to a phosphorus ylide and the direct olefin formation by the reaction of the ylide with carbonyl compounds.

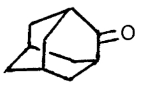
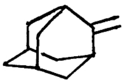
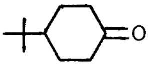
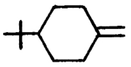
Dimethyl trimethylsilylmethylphosphonate 1 (3.40 mmol), prepared from chloromethyltrimethylsilane and dimethyl phosphite in the presence of sodium hydride,2) was heated in a sealed tube at 250°C for 30 min. Analysis of the reaction mixture by gas chromatography showed two products and no starting phosphonate 1. Separation by preparative gas chromatography afforded dimethyl methylphosphonate 2 (22%) and methyl trimethylsilyl methylphosphonate 3 (41%).3) No ethylene was detected.



The phosphonate 3 may be obtained from a phosphorus ylide 4, formed by 1,3-migration of a trimethylsilyl group, followed by presumably loss of methylene. Similar isomerization of a phosphorus ylide to a phosphonate has been reported.4,5) The phosphonate 2 may arise from the cleavage of the silicon-carbon bond of the phosphonate 1, followed by hydrogen abstraction. The thermal rearrangement of the phosphonate 1 seems to be similar to that of β-silyl sulfoxide to give a siloxysulfonium ylide intermediate, which then rearranges by the usual Pummerer pathway without undergoing intermolecular reaction.[6,7]

When a mixture of the phosphonate 1 (5.02 mmol) and benzophenone (1.04 mmol) was heated at 250°C for 30 min, 1,1-diphenylethylene (71%) and dimethyl trimethylsilyl phosphate 5 (50%)[8] were obtained together with the phosphonate 2, 3, and unreacted benzophenone. The phosphate 5 and 1,1-diphenylethylene might be formed by the reaction of the intermediate phosphorus ylide 4 with benzophenone through the Wittig type reaction. The reactions of the phosphonate 1 or dimethyl 1-trimethylsilylethylphosphonate 6 with carbonyl compounds are summarized in Table I. These results show that introduction of an α-methylene of the silylmethylphosphonate to carbonyl compounds leads to olefins.

Table I. Reactions of phosphonate 1 or 6 with carbonyl compounds[a]

Phosphonate	Ketone	Conversion of ketone(%)[b]	Product(%)[b]
$Me_3SiCH_2P(O)(OMe)_2$ 1	Ph_2CO	68	$Ph_2C=CH_2$ 71
"	$Me_3SiCOPh$	100	$Me_3Si(Ph)C=CH_2$ 41
"	$Et_3SiCOPh$	100	$Et_3Si(Ph)C=CH_2$ 21
"	PhCOMe		Ph(Me)$C=CH_2$ (33)
"		32	 50
"			 (24)
$Me_3SiCHMeP(O)(OMe)_2$ 6	PhCHO	100	PhCH=CHMe 52[c]
"	p-Cl-C_6H_4CHO	100	p-Cl-C_6H_4CH=CHMe 96[d](90)
"	Ph_2CO	68	$Ph_2C=CHMe$ 71

a; The reactions of ketones (1 mmol) and phosphonate (5 mmol) were carried out at 250°C for 30 min. b; Yields were determined by GLC based on the ketone consumed. Isolated yields are given in parentheses. c; A mixture of trans (29%) and cis (23%). d; A mixture of trans (64%) and cis (32%).

References and Notes

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3) Methyl trimethylsilyl methylphosphonate 3: NMR(CCl_4) δ 0.22(s,9H,SiMe), 1.32(d, J=18Hz,3H,P-Me), 3.57(d,J=11Hz,3H,POMe); IR(neat) 1260(P=O,SiMe) and 1040cm^{-1} (POMe).

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8) Dimethyl trimethylsilyl phosphate 5: NMR(CCl_4) δ 0.30(s,9H,SiMe) and 3.68(d,J=11Hz, 6H,POMe); IR(neat) 1290, 1260(P=O,SiMe) and 1040 cm^{-1}(POMe).

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