

SYNTHESIS AND REACTION OF DIALKYL 1-(TRIMETHYLSILOXY)ALKYLPHOSPHONATES

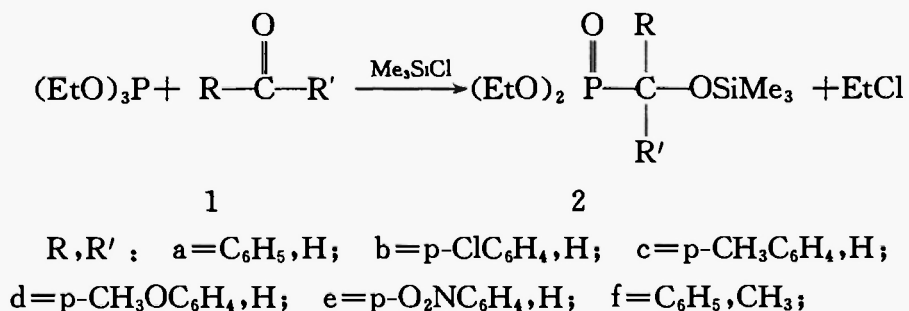
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Dialkyl 1-(trimethylsilyloxy)alkylphosphonates $(RO)_2P(O)CR'R''OSiMe_3$ ($R = Me, Et$; R' and $R'' = H, alkyl, aryl$ and substituted aryl groups) were synthesized by the reaction of trialkylphosphite, trimethylchlorosilane, and aldehydes or ketones. Their structures were characterized by IR, 1H and ^{31}P NMR, and mass spectrometry. The reaction conditions were investigated.

Introduction

Dialkyl 1-(trimethylsilyloxy)alkylphosphonates, organic compounds containing both phosphorus and silicon atoms, have some special properties and manifold uses. They are used as flame-proofing agents¹, plasticizers², lubricants and gasoline additives³. Many of them have physiological activities and medical functions. Their pesticidal and pharmaceutical properties⁴ are improved by the presence of organosilyl groups and thus possess longer periods of effectiveness and lower poisonousness than the corresponding alkyl phosphonates. The present paper deals with the synthesis of diethyl 1-(trimethylsilyloxy)alkylphosphonates (2) by the reaction of triethyl phosphite, trimethylchlorosilane, and a variety of carbonyl compounds (1). The process, conducted under very mild conditions, is easy to operate. Nine title compounds (2a—2i) were obtained by this method and their structures were verified by IR, 1H and ^{31}P NMR, and MS respectively.





Discussion

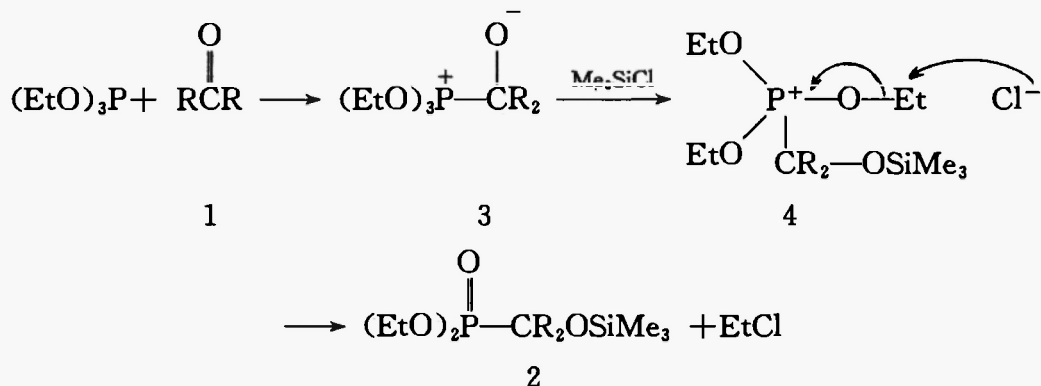
Dialkyl 1-(trimethylsilyloxy) alkylphosphonates are generally synthesized in good yield by the reaction of silylphosphites with carbonyl compounds⁵⁻⁷. Numerous examples of this reaction have been reported. Much of the original work was done by Russian chemists. But this method needs first the synthesis of a very unstable silylphosphite and the reaction must be conducted under an inert dry atmosphere⁸.

The reaction of trialkyl phosphite, trimethylchlorosilane, and carbonyl compounds to synthesize dialkyl 1-(trimethylsilyloxy) alkylphosphonates is readily conducted in the absence of solvent or catalyst, and the reaction may be carried out smoothly even in the atmosphere environment. Formation of the desired product is accompanied by the formation of an alkyl halide as by-product, which is easily removed and the pure product is easily obtained by vacuum distillation.

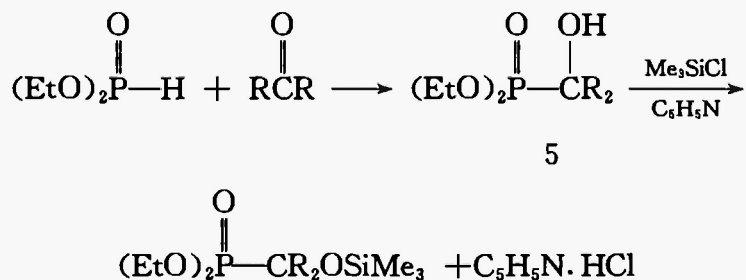
This reaction takes place advantageously by mixing the three reactants in equimolecular proportions at room temperature. In a continuous process, gradual contact of the reactants is usually recommended in order to obtain smooth reaction. The optimum conditions comprise gradual addition of an aldehyde or ketone to the mixture of phosphite and trimethylchlorosilane with application of external cooling and stirring. When all the carbonyl compound has been added, moderate heating of the obtained mixture assures the completion of the reaction. When the carbonyl compound is a ketone, the reaction is generally not so rapid as with an aldehyde. In practice, only methyl ketones and cycloketones appear to undergo the reaction smoothly.

A control experiment demonstrated that this reaction does not involve prior formation of a P—O—Si bond phosphite. Upon heating an equimolar mixture of triethyl phosphite and trimethylchlorosilane at 100°C for 5 hours, there was no evidence (by ¹HNMR) for the formation of diethyl trimethylsilyl phosphite or any other product⁹. Since the control experiment was carried out under similar conditions as the real reaction, an alternative possibility for the reaction of triethyl phosphite, trimethylchlorosilane and carbonyl compound involves nucleophilic attack by phosphorus on the carbonyl carbon of the aldehyde or ketone (1) to yield a zwitterionic intermediate (3), in which the negatively charged alkoxide anion attacks

the silicon of trimethylchlorosilane to give a triethoxy 1-(trimethylsilyloxy) alkylphosphonium and chloride ion pair (4); then the chloride ion attacks one ethyl group attached at phosphorus in an Arbuzov reaction to give ethyl chloride and the desired product (2).



An alternative method for the preparation of the desired product (2) is a reaction of dialkyl 1-hydroxyphosphonates(5), which is obtained by the reaction of a dialkyl phosphonate and a carbonyl compound¹⁰, with trimethylchlorosilane in the presence of a base like pyridine to remove the hydrogen chloride by-product, e. g.



Experimental

All reactants or reagents were freshly distilled. IR spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer; NMR spectra were recorded on a Varian Associates XL-200 spectrometer, chemical shifts were reported in ppm relative to a TMS internal standard for ¹H or 85% phosphoric acid external standard for ³¹P (s=singlet, d=doublet, t=triplet, q=quartet, m=mutiplet); Mass spectra were obtained with a HP5988A GC-MS spectrometer. The thermometer and manometer were not corrected.

Diethyl 1-(trimethylsilyloxy) benzylphosphonate (2a); 5.3g (50mmol) benzaldehyde was added by dropwise to a mixture of 8.4g (50mmol) triethyl phosphite¹¹ and

5. 4g (50mmol) trimethylchlorosilane with stirring in an ice-bath. After addition of the benzaldehyde, the resulting mixture was stirred at room temperature for 10 min, and then warmed to 50°C for 5 hours. Low boiling by-products were distilled off and the residual material was distilled at reduced pressure to give 12g colorless liquid of 2a, (76%), bp. 135 – 138°C/2mm. (Lit.⁶ 105°C/0.3mm, 66%), IR: 1252 (P=O), 1045, 1028 (P–O–C, Si–O); ¹HNMR: 0.1 (s, 9H, 3SiCH₃), 1.2 (t, 6H, 2CH₃), 4.1 (m, 4H, 2OCH₂), 4.9 (d, 1H, CHP), 7.2–7.6 (m, 5H, C₆H₅); ³¹PNMR: 19.8; MS: 316 (M⁺).

Compounds 2b – 2i were synthesized similarly and only their results and characteristic data were given.

Diethyl 1-(trimethylsilyloxy)-4-Chlorobenzyl phosphonate (2b): bp. 154 – 156°C/2mm, 78% yield. IR: 1250 (P=O), 1028 (Si–O–C); ¹HNMR: 0.2 (s, 9H, 3SiCH₃), 1.2 (t, 6H, 2CH₃), 4.1 (m, 4H, 2OCH), 5.0 (d, 1H, CHP), 7.2–7.8 (m, 4H, C₆H₄); ³¹PNMR: 19.3.

Diethyl 1-(trimethylsilyloxy)-4-methylbenzyl phosphonate (2c): bp. 148 – 150°C/2mm, 65% yield. IR: 1245 (P=O), 1030 (Si–O–C); ¹HNMR: 0.2 (s, 9H, 3SiCH₃), 1.2 (t, 6H, 2CH₃), 2.5 (s, 3H, CH₃), 4.1 (m, 4H, 2OCH₂), 4.9 (d, 1H, CHP), 7.1–7.5 (m, 4H, C₆H₄); ³¹PNMR: 22.1.

Diethyl 1-(trimethylsilyloxy)-4-methoxybenzyl phosphonate (2d): bp. 160 – 163°C/1mm, 62% yield. IR: 1250 (P=O), 1035, 1050 (Si–O–C); ¹HNMR: 0.1 (s, 9H, 3SiCH₃), 1.25 (t, 6H, 2CH₃), 3.7 (s, 3H, OCH₃), 4.2 (m, 4H, 2OCH₂), 4.9 (d, 1H, CHP), 6.7–7.4 (m, 4H, C₆H₄); ³¹PNMR: 21.3; MS: 346 (M⁺).

Diethyl 1-(trimethylsilyloxy)-4-nitrobenzyl phosphonate (2e): 62% yield (by TLC), IR: 1248 (P=O), 1028 (Si–O–C); ¹HNMR: 0.1 (s, 9H, 3SiCH₃), 1.3 (t, 6H, 2CH₃), 4.2 (m, 4H, 2OCH₂), 5.1 (d, 1H, CHP), 7.2–7.6 (m, 4H, C₆H₄); ³¹PNMR: 18.7.

Diethyl 1-(trimethylsilyloxy)-1-phenylethylphosphonate (2f): bp. 152 – 154°C/3mm, 26% yield. IR: 1250 (P=O), 1048 (Si–O–C), 976 (P–O–C); ¹HNMR: 0.1 (s, 9H, 3SiCH₃), 1.1–1.4 (m, 9H, 3CH₃), 4.1 (m, 4H, 2OCH₂), 7.2–7.5 (m, 5H, C₆H₅); ³¹PNMR: 23.6.

Diethyl 1-(trimethylsilyloxy)-1-methyl-2-methylpropylphosphonate (2g): bp. 114 – 117°C/3mm, 42% yield. IR: 1252 (P=O), 1045 (Si–O–C), 974 (P–O–C); ¹HNMR: 0.1 (s, 9H, 3SiCH₃), 0.9 (d, 6H, (CH₃)₂), 1.1–1.5 (m, 10H, CH₃COCH, 2CH₃), 4.2 (m, 4H, 2OCH₂); ³¹PNMR: 25.5; MS: 296 (M⁺).

Diethyl 1-(trimethylsilyloxy)-1-methyl-3-butanonylphosphonate (2h): bp. 140

–143°C/3mm, 54% yield. IR: 1250 (P=O), 1030 (Si–O–C), ¹HNMR: 0.2 (s, 9H, 3SiCH₃), 1.2 (t, 6H, 2CH₃), 1.8–2.2 (s, 6H, 2COCH₃), 2.6 (s, 2H, CH₂), 4.1 (m, 4H, 2OCH₂); ³¹PNMR: 23.2.

Diethyl 1-(trimethylsilyloxy) cyclohexylphosphonate (2i); bp. 134 – 136°C/3mm, 63% yield. IR: 1255 (P=O), 1025 (Si–O–C), 965 (P–O–C); HNMR: 0.1 (s, 9H, 3SiCH₃), 1.2 (t, 6H, 2CH₃), 1.2–1.5 (m, 10H, 5CH₂), 4.2 (m, 4H, 2OCH₂); ³¹PNMR: 27.3; MS: 309 (M⁺).

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References

1. Teijin Ltd. Jpn Tokkyo Koho 8030026 (1980). C. A., 94:66697(1981).
2. James W. Hyland, Fr. 1582921 (1969). C. A., 73:36094(1970).
3. G. H. Birum, G. A. Richardson, US 3113139 (1963). C. A., 60:5551(1964).
4. John E. Franz, US 4471131 (1984). C. A., 102:7086(1985).
5. G. A. Kulyrev, R. A. Cherkasov, Russ. Chem. Rev. 53, 971(1984).
6. L. V. Nesterov, N. E. Krepyshova, R. A. Sabirova, Zh. Obsh. Khim. 41, 1449 (1971).
7. Z. S. Novikova, S. N. Mashoshina, I. F. Lutsenko, *ibid.* 41, 2622(1971).
8. Z. H. Li, C. F. Zhu, Y. Z. Zhao, Phosphorus, Sulfur, and Silicon, 86, 229 (1994).
9. D. A. Evans, K. M. Hurst, J. M. Takacs, J. Am. Chem. Soc. 100, 3467(1978).
10. T. Texier-Boullet, A. Foucaud, Synthesis, 165, 916(1982).
11. A. H. Ford-Moore, B. J. Perry, Organic Synthesis, 31, 111(1951).

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