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Three-Component Synthesis of Dialkyl 2-(Dicyanomethyl)-3-(triphenyl-λ^5)phosphoranylidene)succinates from Triphenylphosphine, Acetylenic Esters and Malononitrile in Solvent-Free Conditions

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Protonation of the highly reactive 1:1 intermediates, produced by the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by malononitrile under microwave irradiation in solvent-free conditions leads to vinyltriphenylphosphonium salts. These salts undergo Michael addition reaction with conjugate base to produce dialkyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates in fairly good yields. The structures of these compounds were confirmed by IR, ^{1}H, ^{31}P and ^{13}C NMR spectroscopy.

Key Words: Synthesis, Michael addition, Dialkyl 2-(dicyanomethyl)-3-(triphenyl-l5)-phosphoranylidene)-succinates.

INTRODUCTION

Development of simple synthetic routes for widely-used organic compounds from readily available reagents is one of the major tasks in organic chemistry[1]. In recent years there has been increasing interest in the synthesis of organophosphorus compounds, those bearing a carbon atom bond directly to a phosphorus atom. This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial and chemical synthetic uses. Phosphorus ylides are reactive systems, which take part in many valuable reactions in organic synthesis[2-4]. These ylides are usually prepared by treatment of a phosphonium salt with a base and phosphonium salts are usually obtained from the phosphine and an alkyl halide[2-10]. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophile to activated olefins among other methods[2-4]. In recent years we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[11-14]. In this paper, the preparation of phosphorus ylides from malononitrile in solvent-free conditions in fairly high yields has been reported (**Scheme-I**).

EXPERIMENTAL

Commercial oven Butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500, 125 and 202.44 MHz, respectively.

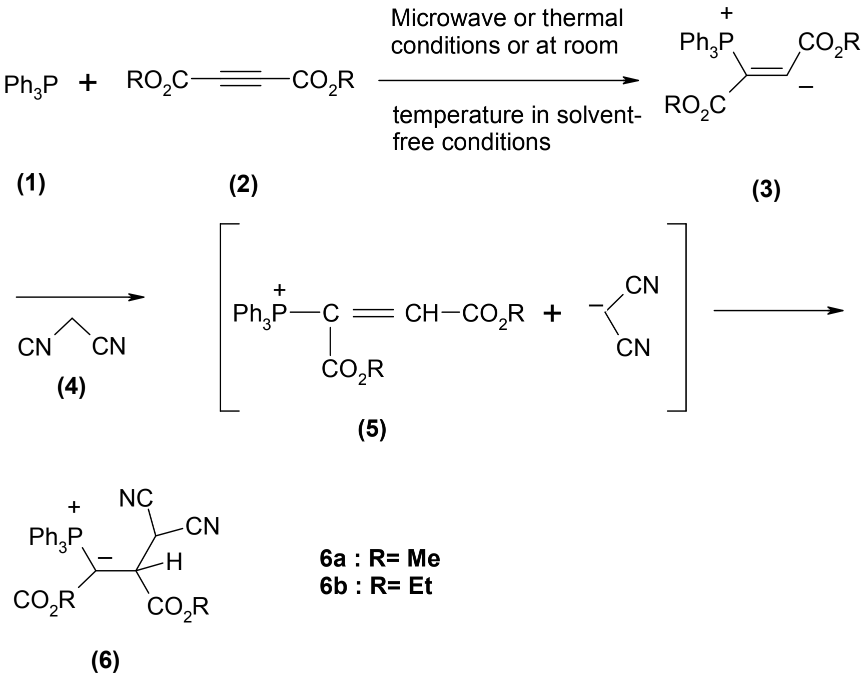
Preparation of dialkyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates (6a-b): A mixture of triphenylphosphine (1 mmol, 0.262 g), malononitrile (1 mmol, 0.066 g) and acetylenic ester (1 mmol) were ground at room temperature for 15 min (or under microwave irradiation, 0.5 KW, 2 min or under thermal conditions at 100°C, 4min). The viscous residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate). (**6a**, m.p. 168.0-169.2 ºC, **5b**, m.p. 166.0-168.5 ºC).

Spectral data for dimethyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinate (6a): IR (KBr, ν_{max}, cm^{-1}): 1738, 1620, 1481, 1435. ^{1}H NMR (CDCl$_3$), δ_H : 2.85-2.96 (1H, 1m, CHCO$_2$Me); 3.16, 3.57, 3.75 and 3.76 (6H, 4s, 4 OCH$_3$); 4.90 and 5.45 (1H, 2d, $^3J_{HH}$ = 10.5 Hz, CH(CN)$_2$); 7.26-7.73 (15H, m, arom). ^{13}C NMR (CDCl$_3$) δ_C : 24.92 (1d, $^3J_{PC}$ = 3.2 Hz) and 26.32 (1d, $^3J_{PC}$ = 4.5 Hz) (2 ^{13}CH(CN)$_2$); 39.62 (1d, $^1J_{PC}$ = 125.3 Hz) and 41.03 (1d, $^1J_{PC}$ = 127.5 Hz) (2 P=C); 46.23 (1d, $^2J_{PC}$ = 15.02 Hz) and 47.05 (1d, $^2J_{PC}$ = 16.12 Hz) (2P = C-^{13}C); 49.33, 50.50, 52.49 and 52.59 (4OCH$_3$) ; 113.55 and 113.95 (2CN); 124.3-134.0 (fairly complex, arom); 169.32 (1d, $^2J_{PC}$ = 13.66 Hz), 171.10 (1d, $^3J_{PC}$ = 4.69 Hz), 171.45 (1d, $^3J_{PC}$ = 4.39 Hz) and 171.60 (1d, $^2J_{PC}$ = 14.03 Hz) (4CO of esters). ^{31}P NMR (CDCl$_3$) δ_P : 22.89 and 23.58.

Selected data for diethyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinate (6b): IR (KBr, ν_{max}, cm^{-1}): 1735, 1638, 1435. ^{1}H NMR (CDCl$_3$), δ_H : 0.45, 1.15, 1.18 and 1.31 (6H, 4t, $^3J_{HH}$ = 7.25 Hz, 4 CH$_3$); 2.83-2.96 (1H, 1m, CHCO$_2$Et); 3.67-3.75, 3.94-4.03 and 4.14-4.30 (4H, 3m, 4OCH$_2$); 4.91 and 5.44 (1H, d, $^3J_{HH}$ = 10.25 Hz) (CH(CN)$_2$) 7.26-7.78 (15H, m, arom). ^{13}C NMR (CDCl$_3$) δ_C : 13.79, 14.04, 14.11 and 14.91 (4CH$_3$); 24.85 (1d, $^3J_{PC}$ = 4.5 Hz) and 26.42 (1d, $^3J_{PC}$ = 3.4 Hz) (2 ^{13}CH(CN)$_2$); 39.72 (1d, $^1J_{PC}$ = 124.3 Hz) and 40.96 (1d, $^1J_{PC}$ = 128.3 Hz) (2 P=C); 46.49 (1d, $^2J_{PC}$ = 16.24 Hz) and 46.21 (1d, $^2J_{PC}$ = 17.22 Hz) (2P=C-^{13}C); 58.01, 58.63, 61.33 and 61.87 (4OCH$_2$) ; 113.87 and 114.02 (2CN); 124.5-134.0 (fairly complex, arom); 168.92 (1d, $^2J_{PC}$ = 12.97 Hz), 170.73 (1d, $^3J_{PC}$ = 5.01 Hz), 171.32 (1d, $^3J_{PC}$ = 4.97 Hz) and 169.43 (1d, $^2J_{PC}$ = 13.12 Hz) (4CO of esters). ^{31}P NMR (CDCl$_3$) δ_P : 22.79 and 23.59.

RESULTS AND DISCUSSION

The stabilized phosphorus ylides (**6a-b**) are produced from the reaction of triphenylphosphine (**1**), dialkyl acetylenedicarboxylates (**2**) and malononitrile in solvent-free conditions in fairly high yields. A plausible mechanism for the formation of products (**6a-b**) is shown in **Scheme-I**. The reaction starts from addition of Ph_3P to electron-deficient acetylenic ester (**2**) to form the zwitter ionic intermediate (**3**), which is subsequently protonated by the CH-acid (**4**) to give vinyltriphenylphosphonium cation (**5**). Then the addition of conjugate base of the CH-acid (**4**) to (**5**) produces dialkyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates (**6a-b**). TLC indicated that the reaction was completed under solvent-free conditions at room temperature after 15 min. The reaction was completed in solvent-free conditions under microwave irradiation (0.5 KW) after 2 min. Moreover, the reaction was also completed in solvent-free conditions under thermal conditions at 100°C after 4 min. The reaction proceeds smoothly and cleanly under the reaction conditions. The structures of (**6a-b**) were deduced from their ^1H, ^{13}C and ^{31}P NMR spectra. In summary, we have developed a new and efficient, one-step method for preparing of compounds (**6a-b**) in solvent-free conditions. Other aspects of this process are under investigation.



Scheme-I

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REFERENCES

1. P. Laszlo, Organic Reactions: Simplicity and Logic, Wiley, New York (1995).
2. J.I.G. Cadogan, Organophosphorus Reagents in Organic Synthesis, Academic Press, New York (1979).
3. R. Engel, Synthesis of Carbon-Phosphorus Bonds, CRC Press, Boca Raton, FL (1988).
4. L.D. Quin, A Guide to Organophosphorus Chemistry, Wiley, Interscience, New York (2000).
5. D.E.C. Corbridge, Phosphorus, An Outline of Chemistry, Biochemistry and Technology, Elsevier, Amsterdam, edn. 5 (1995).
6. A.W. Johnson, Ylide Chemistry, Academic Press, New York (1966).
7. H.R. Hudson, in ed.: F.R. Hartley, In The Chemistry of Organophosphorus Compounds, Primary, Secondary and Tertiary Phosphines and Heterocyclic Organophosphorus(III) Compounds, Wiley, New York, Vol. 1, pp. 382-472 (1990).
8. R.A. Cherkasov and M.A. Pudovik, *Russ. Chem. Rev.*, **63**, 1019 (1994).
9. O.I. Kolodiazhnyi, *Russ. Chem. Rev.*, **66**, 225 (1997).
10. Y. Shen, *Acc. Chem. Res.*, **31**, 384 (1998).
11. A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41**, 567 (2000).
12. A. Ramazani, A.R. Kazemizadeh and E. Ahmadi, *Phosphorus, Sulfur, Silicon Rel. Elem.*, **180**, 1781 (2005) and references cited therein.
13. A. Ramazani, A.R. Kazemizadeh and F. Marandi, *Phosphorus, Sulfur, Silicon Rel. Elem.*, **180**, 1537 (2005) and references cited therein.
14. A. Ramazani, A.R. Kazemizadeh, E. Ahmadi, K. Slepokura and T. Lis, *Z. Naturforsch.*, **61b**, 1128 (2006) and references cited therein.

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