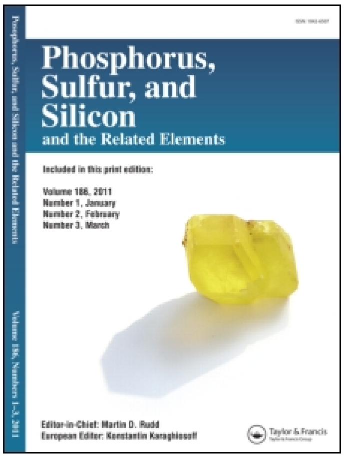

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Synthesis of Dialkyl 2-(2-Oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates from Triphenylphosphine, Acetylenic Ester and 4,4,4-Trifluoro-1-phenyl-1,3-butanedione in the Presence of Basic Alumina Powder

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Synthesis of Dialkyl 2-(2-Oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates from Triphenylphosphine, Acetylenic Ester and 4,4,4-Trifluoro-1-phenyl-1,3-butanedione in the Presence of Basic Alumina Powder

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 4,4,4-trifluoro-1-phenyl-1,3-butanedione leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce corresponding phosphorus ylides. Basic alumina powder was found to catalyze conversion of the phosphorus ylides to dialkyl 2-(2-oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates in solvent-free conditions under microwave (0.9 KW, 3 min) and thermal (25°C, 120 min) conditions.

Keywords 4,4,4-trifluoro-1-phenyl-1,3-butanedione; acetylenic esters; basic alumina; michael addition; microwave irradiation; solvent-free conditions; vinyltriphenylphosphonium salt

INTRODUCTION

Phosphorus ylides are important reagents in synthetic organic chemistry,[1–16] especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity.[6] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[18–30] Phosphorus ylides are a class of special type of zwitterions, which bear strongly nucleophilic electron rich carbanions. The electron distribution around the P^+–C^- bond and its consequent chemical implications had been probed

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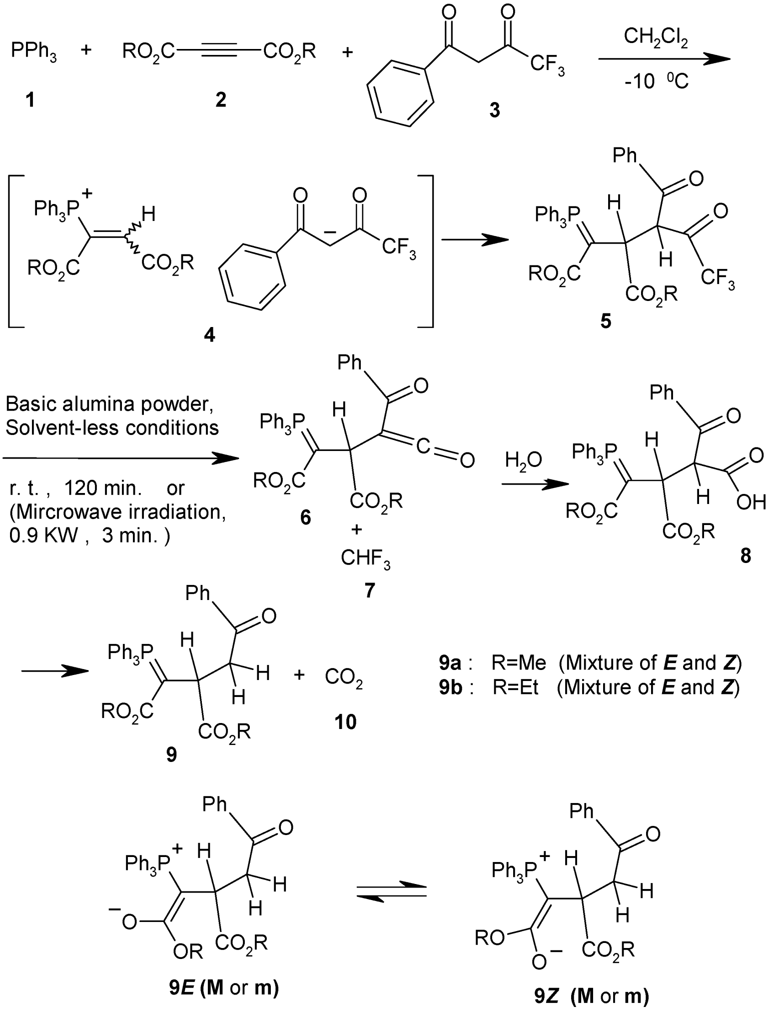
and assessed through theoretical, spectroscopic and crystallographic investigations.[30] Proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[17,30] The nucleophilicity at the ylidic carbon is a factor of essential mechanistic importance in the use of these ylides as Wittig reagents.

Waste prevention and environmental protection are major requirements in an overcrowded world of increasing demands. Synthetic chemistry continues to develop various techniques for obtaining better products with less environmental impact. One of the more promising approaches is solvent-free organic synthesis.[31] In this regard, solvent-free catalytic organic reaction has received tremendous attention in recent times.[32] We have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts, in the past.[18–28] In this article, we report on the catalytic role of Basic alumina powder in the conversion of phosphorus ylides (**5**) to dialkyl 2-(2-oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates (**9**) in solvent-free conditions[33] under microwave (0.9 KW, 3 min) and thermal (25°C, 120 min.) conditions (Scheme 1).

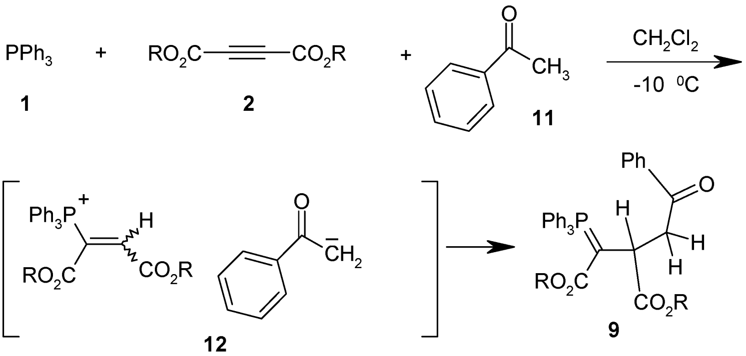
RESULTS AND DISCUSSION

The phosphorus ylide (**5**) may result from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct by 4,4,4-trifluoro-1-phenyl-1,3-butanedione **3** leads to vinyltriphenylphosphonium salts **4,** which undergo Michael addition reaction with conjugate base to produce phosphorus ylide (**5**). TLC indicated formation of ylides **5** in CH_2Cl_2. Basic alumina powder was found to catalyze conversion of the phosphorus ylide (**5**) to dialkyl 2-(2-oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates (**9**) in solvent-free conditions[33] under microwave (0.9 KW, 3 min) and thermal (25°C, 120 min.) conditions (Scheme 1). We have also used silica gel powder in this reaction instead of basic alumina powder, but the yield of product was very low and several products were observed. The reaction also was not occurred in dichloromethane solutions after two days and several others products were observed. We have also used acetophenone **11** in this reaction instead of 4,4,4-trifluoro-1-phenyl-1,3-butanedione **3**, but the yield of products **9** were very low (Scheme 2).[28,34] The weak acidity of acetophenone **11** relative to 4,4,4-trifluoro-1-phenyl-1,3-butanedione **3** may be the factor in the reduction of yields (Scheme 2).[28,34] The mechanism of the reaction has not been established experimentally. However, a possible explanation is proposed in Scheme

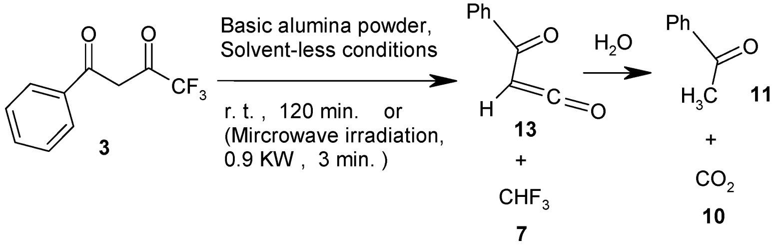


SCHEME 1 **M** = major rotamer; and **m** = minor rotamer.

1. We have also examined roll of basic alumina powder in the conversion of 4,4,4-trifluoro-1-phenyl-1,3-butanedione **3**, to acetophenone **11** (Scheme 3).[28,34] Basic alumina powder is able to convert 4,4,4-trifluoro-1-phenyl-1,3-butanedione **3** to acetophenone **11** in the reaction conditions (Scheme 3).[28,34] The structures of the products **9** were deduced from their IR, ^{1}H NMR, ^{13}C NMR, and ^{13}P NMR spectra (See Experimental section). The NMR spectra indicated that solutions of compound **9** ($CDCl_3$ as solvent) contain two rotamers (**9*E*** and **9*Z***). The relative



SCHEME 2



SCHEME 3

percentages of rotamers in $CDCl_3$ for each ylide **9** were determined from the ^{1}H NMR spectra. The IR spectrum of **9a** showed strong adsorptions at 1734 (C=O, ester), 1695 (C=O, ester), 1634 (C=O, ketone) and 1109 (C—O, ester) cm^{-1} indicating the presence of two the ester carbonyls and the ketone carbonyl functionalities respectively. The ^{1}H NMR spectrum of **9a** (major rotamer (M)) compound exhibited four signals readily recognized as arising from two OMe groups (δ = 3.09 and 3.66 ppm), CH_2 and CH (δ = 3.00–4.00 ppm,m) and aromatic moieties (δ = 7 .26–7.97 ppm, m). The ^{1}H decoupled ^{13}C NMR spectrum of **9a** (major rotamer (M)) showed 16 distinct resonances in agreement with the **9a** (major rotamer (M)) structure. Partial assignment of these resonances is given in the spectral analysis section (See experimental section). The^{31}P NMR spectrum of **9a** (major rotamer (M)) exhibited one signal readily recognized as arising from phosphorus atom of P=C group (δ = 2 3.37 ppm). The ^{1}H, ^{31}P, and ^{13}C NMR signals of compound **9a** (minor rotamer (m)) are similar to those of **9a** (major rotamer (M)), except for the signal intensities which related to the relative populations of two rotamers of**9a** in $CDCl_3$ solution (see spectral analysis section). The ^{1}H, ^{31}P, and ^{13}C NMR spectra of compound **9b** are similar to those of **9a**, except for the ester groups (^{1}H and ^{13}C NMR), which exhibit characteristic signals with appropriate chemical shifts (see spectral analysis section).[28,34]

CONCLUSION

In summary, we have found a new and efficient method for the preparation of dialkyl 2-(2-oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates (**9**) from triphenylphosphine (**1**), acetylenic ester (**2**) and 4,4,4-trifluoro-1-phenyl-1,3-butanedione (**3**) in the presence of basic alumina powder (Scheme 1). We believe the reported method offers a simple and efficient route for the preparation of the stabilized phosphorus ylides 9 (Scheme 1). Its ease of work up and good yields make it a useful addition to modern synthetic methodologies.[28,34] Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Commercial oven Butane M245 was used for microwave irradiation. IR spectra were recorded on a FT-IR Mattson 1000 spectrometer. ^{1}H, ^{31}P, and ^{13}C NMR spectra were measured with a BRUKER DRX-250 AVANCE spectrometer at 250.00, 101.25, and 62.50 MHz, respectively.

General Procedure for the Preparation of Ylides 5 and Compounds 9a-b

To a magnetically stirred solution of triphenylphosphine 1 (0.262 g, 1 mmol) and 4,4,4-trifluoro-1-phenyl-1,3-butanedione 3 (0.216 g, 1 mmol) in CH_2Cl_2 (5 ml) was added dropwise a mixture of 2 (0.13 ml, 1 mmol) in CH_2Cl_2 (2 ml) at -10°C over 15 min. Then 1 g of basic alumina powder (Merck) was poured into the reaction mixture quickly, and the mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure, and the residue was allowed to stand for 2 h at room temperature (or under microwave; 0.9 KW, 3 min) in the solvent-free conditions. The reaction mixture was placed in a short glassy column. The column was washed using MeOH as eluent. The solvent was removed under reduced pressure and products were obtained as white crystals (9a–b) (Scheme 1). The products were recrystallized from ethanol. The characterization data of the compounds (9a–b) are given below.

Methyl 2-(2-oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (9a)

White crystal; m.p.: 196–197°C; Yield: 56.2% IR (KBr) (ν_{max}, cm^{-1}): 1734 and 1695 (2 C=O, Ester); 1634 (C=O); 1441 (C=C, Aromatic); 1109 (C—O); 3061 (C—H, Aromatic); 2860 and 2915 (C—H, Aliphatic). ^{1}H NMR (CDCl$_3$) (major rotamer (M) 67% and minor rotamer (m) 33%).

^{1}H NMR (CDCl$_3$) (major rotamer (M)) δ: 3.09 and 3.66 (6 H, 2 s, 2 OMe); 3.00–4.00 (3 H, m, CH$_2$ and CH); 7.26–7.97 (20 H, Aromatic).

^{13}C NMR (CDCl$_3$) (major rotamer (M)) δ: 41.34 (d, $^1J_{PC}$ = 122.7 Hz); 40.12 (d, $^2J_{PC}$ = 12.80 Hz); 40.30 (s); 48.63 and 51.76 (2 OMe); 127.52 (d, $^1J_{PC}$ = 91.3 Hz, C$_{ipso}$); 128.40 (d, $^2J_{PC}$ = 11.8 Hz, C$_{ortho}$); 131.72 (d, $^4J_{PC}$ = 2.5 Hz, C$_{para}$); 131.83 (d, $^3J_{PC}$ = 10.0 Hz C$_{meta}$); 128.59 (s, C4); 128.41 (s, C3 and C5); 132.58 (s, C2 and C6); 137.75 (s, C1); 169.47 (d, $^2J_{PC}$ = 14.0 Hz, CO of ester); 176.23 (d, $^3J_{PC}$ = 5.6 Hz, CO of ester); 200.29 (s, CO of ketone).

^{31}P NMR (CDCl$_3$) (major rotamer (M)) δ: 23.37.

^{1}H NMR (CDCl$_3$) (minor rotamer (m)) δ: 3.58 and 3.66 (6 H, 2 s, 2 OMe); 3.00–4.00 (3 H, m, CH$_2$ and CH); 7.26–7.97 (20 H, Aromatic).

^{13}C NMR (CDCl$_3$) (minor rotamer (m)) δ: 42.16 (d, $^1J_{PC}$ = 132.9 Hz); 39.29 (d, $^2J_{PC}$ = 12.80 Hz); 41.79 (d, $^2J_{PC}$ = 1.8 Hz); 50.01 and 51.67 (2 OMe); 126.84 (d, $^1J_{PC}$ = 91.3 Hz, C$_{ipso}$); 137.67 (s, C1); 170.74 (d, $^2J_{PC}$ = 15.6 Hz, CO of ester); 176.32 (d, $^3J_{PC}$ = 5.8 Hz, CO of ester); 199.79 (s, CO of ketone).

^{31}P NMR (CDCl$_3$) (minor rotamer (m)) δ: 23.15.

Ethyl 2-(2-oxo-2-phenylethyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (9b)

White crystal; m.p.: 150–151°C; Yield: 49.0% IR (KBr) (ν_{max}, cm^{-1}): 1734 and 1695 (2 C=O, Ester); 1626 (C=O); 1441 (C=C, Aromatic); 1109 (C—O); 3061 (C—H, Aromatic); 2984 and 2907 (C—H, Aliphatic). ^{1}H NMR (CDCl$_3$) (major rotamer (M) 77% and minor rotamer (m) 23%).

^{1}H NMR (CDCl$_3$) (major rotamer (M)) δ: 0.36 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH$_3$); 1.53 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH$_3$); 3.00–4.30 (7 H, m, CH$_2$, 2 OCH$_2$ and CH); 7.26–7.99 (20 H, Aromatic).

^{13}C NMR (CDCl$_3$) (major rotamer (M)) δ: 13.91 and 14.25 (2 Me); 41.02 (d, $^1J_{PC}$ = 126.3 Hz); 40.23 (d, $^2J_{PC}$ = 13.1 Hz); 40.22 (d, $^3J_{PC}$ = 4.4 Hz); 57.23 and 60.53 (2 OCH$_2$); 127.53 (d, $^1J_{PC}$ = 88.1 Hz, C$_{ipso}$); 128.33 (d, $^2J_{PC}$ = 11.9 Hz, C$_{ortho}$); 133.91 (d, $^3J_{PC}$ = 9.4 Hz, C$_{meta}$); 131.72 (d, $^4J_{PC}$ = 2.5 Hz C$_{para}$); 128.56 (s, C4); 128.42 (s, C3 and C5); 132.60 (s, C2 and C6); 137.76 (s, C1); 169.21 (d, $^2J_{PC} = 13.1$ Hz, CO of ester); 175.79 (d, $^3J_{PC} = 5.6$ Hz, CO of ester); 200.62 (s, CO of ketone).

^{31}P NMR ($CDCl_3$) (major rotamer (M)) δ: 23.20.

^{1}H NMR ($CDCl_3$) (minor rotamer (m)) δ: 0.36 (3 H, t, $^3J_{HH} = 7.1$ Hz, CH_3); 1.53 (3 H, t, $^3J_{HH} = 7.1$ Hz, CH_3); 3.00–4.30 (7 H, m, CH_2, 2 OCH_2 and CH); 7.26–7.99 (20 H, Aromatic).

^{13}C NMR ($CDCl_3$) (minor rotamer (m)) δ: 18.40 and 15.22 (2 Me); 42.28 (d, $^1J_{PC} = 133.8$ Hz); 39.52 (d, $^2J_{PC} = 12.9$ Hz); 41.74 (d, $^3J_{PC} = 3.7$ Hz); 57.96 and 58.20 (2 OCH_2); 126.84 (d, $^1J_{PC} = 91.3$ Hz, C_{ipso}); 128.44 (d, $^2J_{PC} = 10.6$ Hz, C_{ortho}); 133.84 (d, $^3J_{PC} = 9.4$ Hz, C_{meta}); 137.68 (s, C1); 170.37 (d, $^2J_{PC} = 18.3$ Hz, CO of ester); 175.92 (d, $^3J_{PC} = 6.9$ Hz, CO of ester); 200.06 (s, CO of ketone).

^{31}P NMR ($CDCl_3$) (minor rotamer (m)) δ: 23.14.

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