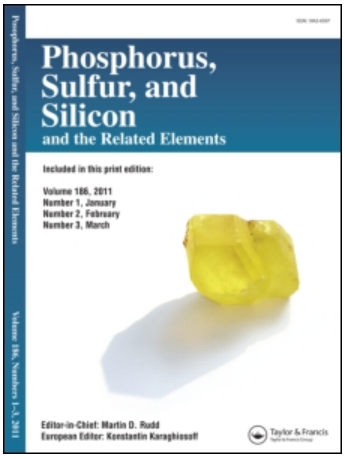

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ramazani, Ali , Kazemizadeh, Ali Reza and Ahmadi, Ebrahim(2005) 'Four-Component Synthesis of Dialkyl 2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates from Triphenylphosphine, Acetylenic Esters, 2,2,2-Trifluoroethanol, and Ninhydrin', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 8, 1781 — 1784
To link to this Article: DOI: 10.1080/104265090888405
URL: http://dx.doi.org/10.1080/104265090888405

Phosphorus, Sulfur, and Silicon, 180:1781–1784, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090888405

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Four-Component Synthesis of Dialkyl 2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates from Triphenylphosphine, Acetylenic Esters, 2,2,2-Trifluoroethanol, and Ninhydrin

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by 2,2,2-trifluoroethanol, leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce the corresponding fluorine-containing stabilized phosphorus ylides. Intermolecular Wittig reaction of the fluorine-containing stabilized phosphorus ylides with ninhydrin leads to the corresponding highly electron-poor fluorine-containing alkenes.

Keywords 2,2,2-trifluoroethanol; acetylenic ester; intermolecular Wittig reaction; ninhydrin; triphenylphosphine

INTRODUCTION

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.[1] Organophosphorus compounds have been extensively used in organic synthesis.[1–3] In the past we have established a convenient, one-pot method for preparing

Received August 10, 2004; accepted September 1, 2004.
This work was supported by the Zanjan Islamic Azad University Research Council via research project number ZIAURC82.13882. We also thank Dr Mehdi Rahnema (Rector of Zanjan Islamic Azad University Research Council) for helpful discussions and financial support.
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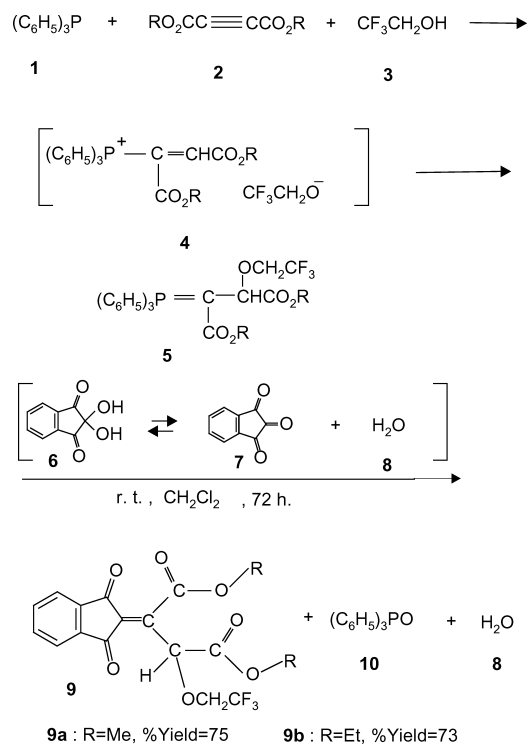

SCHEME 1

stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts.[1] In this article, we report on the one-pot synthesis of dialkyl 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates (**9**) from the reaction of 2,2,2-trifluoroethanol (**3**), dialkyl acetylenedicarboxylates (**2**), triphenylphosphine (**1**), and ninhydrin (**6**) in fairly high yields[3] (Scheme 1).

RESULTS AND DISCUSSION

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from a phosphorane and a carbonyl compound such as an aldehyde or ketone.[4–10] Thus, compounds **9** may be regarded as the product of an intermolecular Wittig reaction. Such addition-olefination products may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the anion of 2,2,2-trifluoroethanol on the

vinylphosphonium cation to form phosphorane **5**. Attack of the fluorine-containing stabilized phosphorus ylide **5** on the highly electron deficient carbonyl group of indane-1,2,3-trione **7** in a normal intermolecular Wittig reaction would lead to the dialkyl 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates **9** (Scheme 1). TLC indicated that the reaction was completed after 72 h in CH_2Cl_2 at room temperature. The reaction proceeds smoothly and cleanly under mild conditions and no side reactions are observed. We have also used fairly less reactive aldehydes (benzaldehyde and 4-nitrobenzaldehyde) and ketones (acetone and acetophenone) in this reaction, but no products were observed even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained ylide **5** and the starting aldehyde or ketone.

In summary, we have developed a convenient, one-pot method for the preparation of dialkyl 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates **9** utilizing *in situ* generation of the phosphorane **5** (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and were uncorrected. UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500, 125, and 470.6 MHz, respectively.

General Procedure for the Preparation of Dialkyl 2-(1,3-Dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates (9a–b)

To a magnetically stirred solution of triphenylphosphine **1** (0.524 g, 2 mmol) and 2,2,2-trifluoroethanol **3** (0.15 mL, 2 mmol) in CH_2Cl_2 (7 mL) was added dropwise to a mixture of **2** (0.26 mL, 2 mmol) in CH_2Cl_2(7 mL) at $-10^{\circ}C$ over 15 min. The mixture was allowed to warm up to room temperature, powdered ninhydrin **6** (0.36 g, 2 mmol) was added and stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate). The solvent was removed under reduced pressure and the products were obtained as white solids (**9a**, m.p. 113.4–115.9°C; **9b**, m.p. 79.5–80.9°C).

Spectral Data for Dimethyl 2-(1,3-Dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinate (9a)

UV(ethanol, 95%), λ_{max}/nm (logε): 260.0 (3.72), 272.0 (3.71) and 283.0 (3.74). IR(KBr) (ν_{max}, cm^{-1}): 3031, 2962, 1759, 1728, 1597, 1443, 1280, 1165, 1072, and 1026. ^{1}H NMR($CDCl_3$) δ_H: 3.79 and 3.88 (6 H, 2 s, 2 OCH_3), 4.06 and 4.32 (2 H, 2 qd, $^2J_{HH} = -17.2$ Hz and $^3J_{HF} = 8.5$ Hz, $OCH_AH_BCF_3$), 6.00 (1 H, s, OCH), 7.67 (1 H, t, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 7.81(1H, t, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 7.88(1 H, d, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 8.31 (1 H, d, $^3J_{HH} = 7.8$ Hz, CH(arom.)). ^{13}C NMR($CDCl_3$) δC: 52.46, 52.99, 62.31 (q, $^2J_{CF} = 35.7$ Hz), 90.00, 112.54, 123.29 (q, $^1J_{CF} = 277.4$ Hz), 123.41, 125.61, 128.47, 132.68, 136.51, 138.21, 139.73, 148.21, 161.84, 167.70, and 188.92.^{19}F NMR($CDCl_3$) δF: 74.81.

Spectral Data for Diethyl 2-(1,3-Dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinate (9b)

UV(ethanol, 95%), λ_{max}/nm (logε): 249.0 (3.16), 263.0 (3.11) and 278.0 (3.16). IR(KBr) (ν_{max}, cm^{-1}): 2985, 2931, 1751, 1712, 1596, 1457, 1380, 1349, 1288, 1164, and 1064. ^{1}H NMR($CDCl_3$) δ_H: 1.29 and 1.36 (6 H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et), 4.06 (1 H, qd, $^2J_{HH} = -17.1$ Hz, and $^3J_{HF} = 8.4$ Hz, $OCH_AH_BCF_3$), 4.15–4.40 (5 H, m, 2 OCH_2 of 2 Et and $OCH_AH_BCF_3$), 5.98 (1 H, s, OCH), 7.66 (1 H, t, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 7.81(1H, t, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 7.87(1 H, d, $^3J_{HH} = 7.6$ Hz , CH(arom.)), 8.33 (1 H, d, $^3J_{HH} = 7.8$ Hz, CH(arom.)). ^{13}C NMR($CDCl_3$) δg: 13.97, 14.15, 61.71, 62.17, 62.28 (q, $^2J_{CF} = 35.6$ Hz), 90.26, 112.58, 123.28 (q, $^1J_{CF} = 277.5$ Hz), 123.95, 125.56, 128.56, 132.55, 136.42, 138.32, 139.68, 147.95, 161.43, 167.32, and 189.05.^{19}F NMR($CDCl_3$) δ_F: 74.72.

REFERENCES

[1] A. Ramazani, L. Yousefi, E. Ahmadi, and A. Souldozi, *Phosphorus, Sulfur, and Silicon,* **179,** 1459 (2004) and references cited therein.

[2] J. I. G. Cadogan, in *Organophosphorus Reagents in Organic Synthesis,* J. I. G. Cadogon, (Ed.), New York: Academic Press, 1979).

[3] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).

[4] S. W. McCombie and C. A. Luchaco, *Tetrahedron Lett*., **38,** 5775 (1997).

[5] A. Barco, S. Benetti, C. D. Risi, P. Marchetti, G. P. Pollini, and V. Zanirato, *Tetrahedron Lett*., **39,** 7591 (1998).

[6] G. S. Bhatia, R. F. Lowe, and R. J. Stoodley, *Tetrahedron Lett*., **39,** 9245 (1998).

[7] X. Wei and R. J. K. Taylor, *Tetrahedron Lett*., **39,** 3815 (1998).

[8] A. Barco, S. Benetti, C. D. Risi, P. Marchetti, G. P. Pollini, and V. Zanirato, *Tetrahedron Lett.*, **39,** 1973 (1998).

[9] V. J. Patil and U. Mavers, *Tetrahedron Lett*., **37,** 1281 (1996).

[10] C. Xu, G. Chen, C. Fu, and X. Huang, *Synth. Commun.,* **25,** 2229 (1995).