Asian Journal of Chemistry Vol. 18, No. 1 (2006), 701–703

NOTE

Silica Gel Powder Catalyzed Intermolecular Wittig Reaction of Fluorine-containing Stabilized Phosphorus Ylides with Ninhydrin in Solvent-free Conditions

ALI RAMAZANI*, ALI REZA KAZEMIZADEH, EBRAHIM AHMADI† and MASSOUMEH RAHNEMA‡

Chemistry Department, Zanjan Islamic Azad University, P.O. Box 49195-467, Zanjan, Iran
E-mail: iramazani@yahoo.com

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. Silica gel powder was found to catalyze intermolecular Wittig reaction of the fluorine-containing stabilized phosphorus ylides with ninhydrin in solvent-free conditions at 92°C in 30 min in high conversions.

Key Words: Silica gel, Fluorine-containing stabilized phosphorus ylides, Intermolecular Wittig reaction, Ninhydrin.

Organophosphorus compounds have been extensively used in organic synthesis[1, 2]. Silica gel as an additive promotes the Wittig reactions of phosphorus ylides with aldehydes, including sterically hindered aldehydes to increase the rate and yields of alkenes[3, 4]. In the past, a convenient one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[1] has been established. In this article, we report on catalytic role of silica gel powder in the intermolecular Wittig reaction of the fluorine-containing stabilized phosphorus ylides (**5**) with ninhydrin (**6**) in solvent-free conditions **(Scheme-1).**

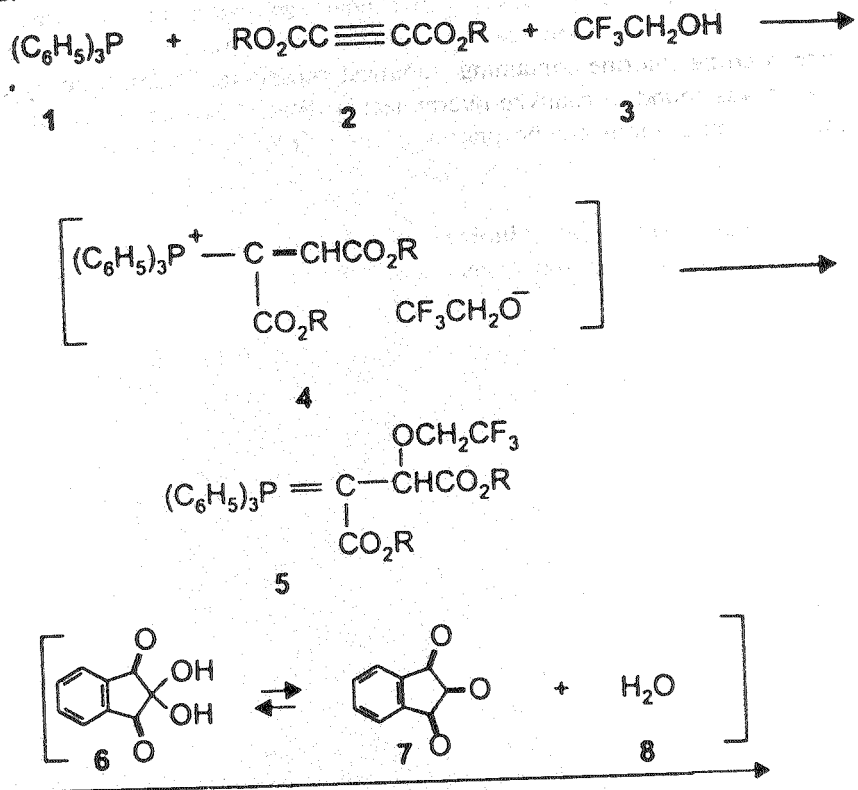
Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500, 125 and 470.6 MHz, respectively.

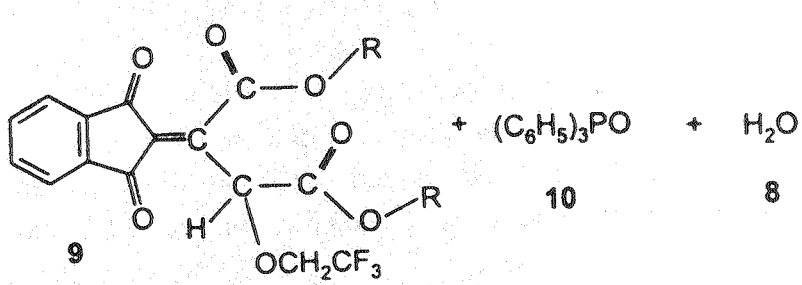
General procedure for the preparation of dialkyl 2-(1,3-dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(2,2,2-trifluoroethoxy)succinates (9a–b): To a magnetically stirred solution of triphenylphosphine (**1**) (0.524 g, 2 mmol) and 2,2,2-trifluoroethanol (**3**) (0.15 mL, 2 mmol) in CH_2Cl_2 (7 mL) was added dropwise a mixture of (**2**) (0.26 mL, 2 mmol) in CH_2Cl_2 (7 mL) at –10°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 the solvent was removed under reduced pressure. The dry residue was heated for 30 min at 92°C and then placed

†Chemistry Department, Zanjan University, P.O. Box 45195-313, Zanjan, Iran.
‡The Education of Tehran, Tehran, Iran.

over a column of silica gel (12 g). The column chromatography was washed using ethyl acetate-light petroleum ether as eluent. 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). The characterization data of the compounds (**2a–d**) are previously reported[6].

Silica gel powder was found to catalyze the intermolecular Wittig reaction of the fluorine-containing stabilized phosphorus ylides (**5**) with ninhydrin (**6**) in solvent-free conditions[5] (**Scheme-1**) at 92°C with high conversions. TLC indicated that the reaction was completed after 30 min. The reaction proceeds smoothly and cleanly under solvent-free conditions[5] at 92°C (in all cases the reaction works efficiently with high conversions) and no side reactions were observed.





9a : R=Me

9b : R=Et

Scheme-1

In summary, the silica gel powder is able to catalyze the intermolecular Wittig reaction of the fluorine-containing stabilized phosphorus ylides (**5**) with ninhydrin (**6**) in solvent-free conditions[5]. Other aspects of this process are under investigation.

ACKNOWLEDGEMENTS

This work was supported by the Zanjan Islamic Azad University Research Council *via* research project number ZIAURC82.13882. Thanks are also due to Dr Mehdi Rahnema (Rector of Zanjan Islamic Azad University Research Council) for helpful discussions and financial supports.

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: J.I.G. Cadogen (Ed.), Organophosphorus Reagents in Organic Synthesis, Academic Press, New York (1979).
3. V.J. Patil and U. Mavers, *Tetrahedron Lett.*, **37**, 1281 (1996).
4. C. Xu, G. Chen, C. Fu and X. Huang, *Synth. Commun.*, **25**, 2229 (1995).
5. K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).
6. A. Ramazani, A.R. Kazemizadeh and E. Ahmadi, *Phosphorus, Sulfur and Silicon*, **180**, 1781 (2005).

(*Received*: 14 January 2005; *Accepted*: 5 September 2005) AJC-4462