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NOTE

Kaolinite Powder Catalyzed Stereoselective Conversion of Dialkyl-2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-3-(triphenylphosphoranylidene)succinates to Dialkyl-2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-2-butendioates in Solvent-free Conditions

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Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by saccharin leads to vinyltriphenyl-phosphonium salts, which undergo an addition reaction with counter anion in CH_2Cl_2 at room temperature to produce corresponding stabilized phosphorus ylides. Kaolinite powder was found to catalyze conversion of the stabilized phosphorus ylides to corresponding electron-poor N-vinylated isothiazoles in solvent-free conditions at 100ºC in 1 h in fairly good yields.

Key Words: Catalyst, Kaolinite, Saccharin, Phosphorus ylide, Solvent-free conditions.

Organophosphorus compounds have been extensively used in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts[1,2]. 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]. 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]. A convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts has already been reported[5]. In present communication, the catalytic role of kaolinite powder in the stereoselective conversion of dialkyl-2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-3-(triphenylphosphoranylidene)succinates (**5**) to

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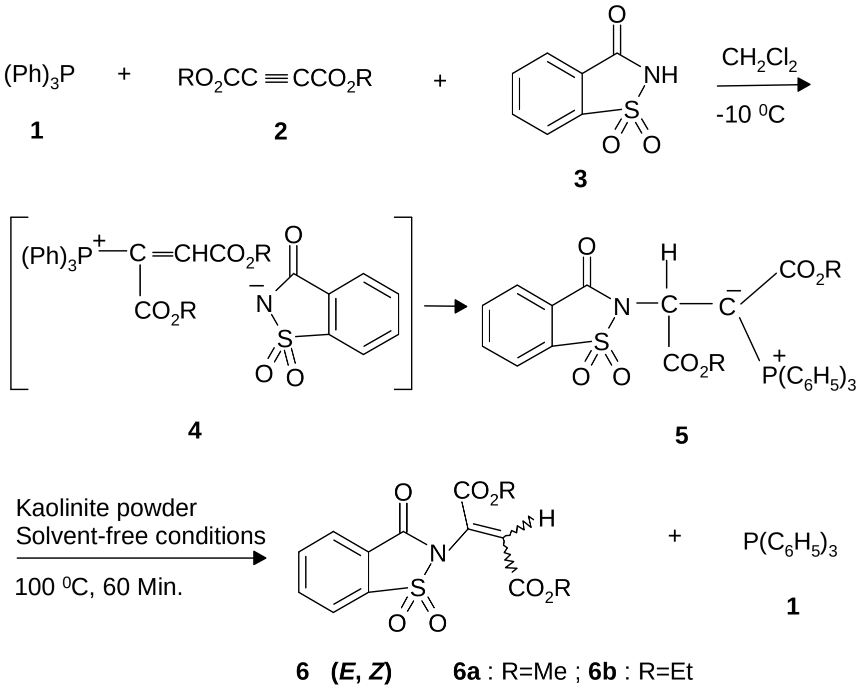
dialkyl-2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-2-butendioates (**6**) in solvent-free conditions at 100ºC in 1 h in fairly good yields is reported (**Scheme-1**).



Scheme-1

Commerical 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 and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively.

General procedure for the preparation of ylides 5 and compounds 6a-b: To a magnetically stirred solution of triphenylphosphine (**1**) (1 mmol) and saccharin (**3**) (1 mmol) in CH_2Cl_2 (6 mL) was added dropwise a solution of **2** (1 mmol) in CH_2Cl_2 (4 mL) at -10ºC over 15 min. The solution was allowed to warm up to room temperature. Kaolinite powder (2 g) was added and the solvent was evaporated. Dry silica gel and the residue were heated for 1 h at 100ºC and then placed over a column of silica gel (10 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent. The solvent was removed under reduced pressure and products **6a-b** were obtained (**6a**: White crystals, m.p. 130-137ºC; Yield: 43 %. Z-isomer: 83 %, E-isomer: 17 %; **6b**: Viscous colourless oil; Yield: 38 %. Z-isomer: 66 %, E-isomer: 34 %). The characterization data of the compounds **6a-b** are given in our previous reports[7].

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from phosphonium salts[5]. Thus, compounds **6a-b** may result from an initial addition of triphenylphosphine (**1**) to the acetylenic ester (**2**) and concomitant protonation of the 1:1 adduct by the saccharin (**3**) to form the corresponding triphenylphosphonium salts (**4**). Conjugate addition of the saccharin (**3**) anion to the vinyltriphenylphosphonium cation (**4**) leads to formation of the stabilized phosphorus ylide **5**. Kaolinite powder was found to catalyze stereoselective conversion of dialkyl-2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-3-(triphenylphosphoranylidene)succinates (**5**) to dialkyl 2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-2-butendioates (**6**) in solvent-free conditions at 100ºC in 1 h (**Scheme 1**). TLC indicated that the reaction was completed after 1 h at 100ºC. The following compound were also used *e.g.*, K_2HPO_4, KH_2PO_4, MgO, $MnSO_4$, $KHSO_4$, ZnO, Al_2O_3, $NaHCO_3$ and $MgSO_4$ in this reaction, but yields of corresponding products **6** in cases MgO, K_2HPO_4 and KH_2PO_4 were low and in other cases no product were observed. In the absence of the kaolinite powder the reactions were not completed at reflux temperature (toluene as solvent) after 24 h and decomposition of the starting materials and product were observed. The structures **6a-b** were confirmed from their IR, ^{1}H NMR and ^{13}C NMR spectra.

Conclusion

The kaolinite powder is able to catalyze stereoselective conversion of ylides **5** to compounds **6** in solvent-free conditions (**Scheme-1**). Other aspects of this process are under investigation.

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REFERENCES

1. J.I.G. Cadogan, Organophosphorus Reagents in Organic Synthesis, Academic Press, New York (1979).
2. I. Yavari and A. Ramazani, *Synth. Commun.*, **27**, 1449 (1997).
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. A. Ramazani, L. Yousefi, E. Ahmadi and A. Souldozi, *Phosphorus, Sulfur Silicon Rel. Elem.*, **179**, 1459 (2004) and references cited therein.
6. K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).
7. A. Ramazani, A. A-Motajadded and E. Ahmadi, *Phosphorus, Sulfur Silicon Rel. Elem.*, **181**, 233 (2006).

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