One-pot synthesis of dimethyl 2-[acyl(1-naphthyl)amino]-3-(1,1,1-triphenyl-\(\lambda^5\)-phosphanylidene)succinates

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N'-\(1\)-naphthyl)acetamide and N'-\(1\)-naphthyl)benzamide react with the dimethyl acetylenedicarboxylate 4 in the presence of triphenylphosphine to give the corresponding substituted highly stabilized ylides 7. Isolated yields in the one-pot preparation of compounds 7 are fairly good. The structures of compounds 7a,b were deduced from an initial addition of triphenylphosphine to stabilized ylides 7. Isolated yields in the one-pot preparation of 7a (Scheme I) on the vinyltriphenylphosphonium cation to form highly stabilized ylide 7. Steric and dipole-dipole interactions between amide group of phosphorane 7 and indane-1,2,3-trione, may be the factors in the high reduction of reactivity of ylides (Scheme I).

The NMR spectra indicated that the solutions of compounds 7 (\(\text{CDCl}_3\) as solvent) contained ninhydrin and ylide 7. The NMR spectra of these compounds 7 (\(\text{CDCl}_3\) as solvent) only contained three rotamers with unequal population for each ylide 7. The relative percentages of rotamers in \(\text{CDCl}_3\) for each ylide 7 (Scheme II) were determined from their \(^1\)H NMR spectra.

In conclusion, we have developed a convenient, one-pot method for preparing highly stabilized ylides utilising \textit{in situ} generation of the phosphonium salts. The one-step nature of the present procedure makes it an interesting alternative to multistep approaches.

Experimental Section

Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer; IR spectra on a Shimadzu IR-460 spectrometer; \(^1\)H, \(^{13}\)C and \(^{31}\)P NMR spectra on a Bruker DRX-500 AVANCE spectrometer at 500, 125 and 202.44 MHz, respectively; and mass spectra on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

Dimethyl acetylenedicarboxylate, triphenylphosphine, acetic anhydride, benzoyl chloride were obtained from Fluka (Buchs, Switzerland) and were used without further purification. \(^1\)N-(1-naphthyl)acetamide 5a (m.p. 159-60°C) and \(^4\)N-(1-naphthyl)benzamide 5b (160-61°C) were prepared by known methods.

Dimethyl 2-[acyl(1-naphthyl)amino]-3-(1,1,1-triphenyl-\(\lambda^5\)-phosphanylidene)succinate 7a. General procedure. To a magnetically stirred solution of triphenylphosphine 3 (0.262 g, 1 mmole) and \(^1\)N-(1-naphthyl)acetamide 5a (0.186 g, 1 mmole) in \(\text{CH}_2\text{Cl}_2\) (10 mL) was added dropwise, a solution of dimethyl
Scheme I

\[
\begin{align*}
(C_6H_5)_3P + CH_3O_2CC\equivCCO_2CH_3 & \quad \xrightleftharpoons{\text{CH}_2Cl_2} \quad -10^\circ C \\
3 & \quad 4 \\
\left[ (C_6H_5)_3P \quad C=CHCO_2CH_3 \quad \text{N} \quad \text{O} \right] & \quad \rightarrow \quad (C_6H_5)_3P=CHCO_2CH_3 \\
6 & \quad 7 \\
7a: R = CH_3 & \quad 7b: R = C_6H_5
\end{align*}
\]

Scheme II

\[
\begin{align*}
(C_6H_5)_3P^+ \quad C=CHCO_2CH_3 & \quad \xrightleftharpoons{\text{N} \quad \text{O} \quad \text{R}} \quad (C_6H_5)_3P^+ \quad CHCO_2CH_3 \quad N \quad O \\
2 & \quad 4 \\
(C_6H_5)_3P^+ \quad C=CHCO_2CH_3 & \quad \xrightleftharpoons{\text{N} \quad \text{O} \quad \text{R}} \quad (C_6H_5)_3P^+ \quad CHCO_2OCH_3 \\
3 & \quad 1
\end{align*}
\]
acetylenedicarboxylate 4 (0.13 mL, 1 mmole) in CH₂Cl₂ (5 mL) at -10°C over 20 min. The mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure and the viscous residue was crystallized from hexane-dichloroethane (1:2). Light pink crystals of 7a (0.295 g, m.p. 198.7-99.1°C) were collected by filtration. UV (ethanol 95%) (λmax/nm, log ε): 204.0, 4.98; 220.6, 4.99; 274.6, 3.96; IR (KBr) (νmax, cm⁻¹): 3061 C-H, arom.; 1757 and 1657 (C=O, ester); 1H NMR (CDCl₃), rotamer 1, 43.6%; rotamer 2, 40.6% and rotamer 3, 15.8%; δH for rotamer 1: 1.59 (3H, s, CH₃), 3.18 and 3.91 (6H, s, 2xOCH₃); 5.54 (1 H, d, 3JPC =5.3 Hz, P=CH-CH), 5.83 (1 H, d, 3JPC =4.8 Hz, P=CH₂-CH), 6.9-8.5 (27 H, m, arom.); δH for rotamer 2: 1.57 (3H, s, CH₃), 3.65 and 3.85 (6H, s, 2xOCH₃); 5.33 (1 H, d, 3JPC =4.6 Hz, P=CH₂-CH), 6.8-9.2 (22 H, m, arom.); δH for rotamer 3: 1.67 (3H, s, CH₃), 2.33 and 3.75 (6H, s, 2xOCH₃); 5.33 (1 H, d, 3JPC =5.3 Hz, P=CH₂-CH), 6.9-8.5 (22 H, m, arom.).

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References
3 Zbiral E, Synthesis, 1974, 775.
5 Yavari I & Ramazani A, Phosphorus, Sulphur and Silicon, 130, 1997, 73.