Keto-Enol Tautomers in a Carbonyl Phosphonium Salt

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Since January 1994, our third-year organometallic course has incorporated an excellent experiment involving carbonylstabilized ylides published in this *Journal* (1). More than 70 students have completed this procedure with a high rate of success. The chemistry of ylides is still a current topic, as indicated by the number of citations of the original synthesis (more than 50 in the last five years) (2). We wish to bring to the attention of the readership an additional observation of this synthesis, which we have not found noted in the related literature.

$$Ph_{3}P + CICH_{2}CCH_{3} \longrightarrow$$

$$Ph_{3}P + CICH_{2}CCH_{3} \longrightarrow Ph_{3}P = CHCCH_{3}$$

$$Ph_{3}PCH_{2}CCH_{3}CI \longrightarrow Ph_{3}P = CHCCH_{3}$$

On the last two occasions that this experiment has been offered, our undergraduates have had access to a 250-MHz Fourier transform NMR spectrometer for recording their data (rather than the 60-MHz continuous-wave instrument of earlier times). The proton spectra for the first step of the synthesis quite clearly and consistently show another species as well as the dominant one attributed by the original authors as being [Ph₃PCH₂C(O)CH₃]Cl (1). The key features of this new species include a doublet at 4.44 ppm resulting from J(PH) 20 Hz and an OH peak at 12.6 (but this may be shifted by up to 0.5 ppm in various samples). The ¹³C and 135-DEPT

spectra indicate that there is a *C*H at 70.68 ppm coupled to the ³¹P nucleus with J(PC) 99 Hz. An HMQCB (heteronuclear multiple-quantum coherence with bilinear rotation decoupling) experiment confirmed that the *C*H correlates with the proton resonance at 4.44 ppm and that there are two coincident methyl resonances.

The ³¹P NMR spectrum indeed exhibits two resonances (in approximately 30:70 ratio) at 15.37 ppm for the "new" species and 21.87 ppm for [Ph₃PCH₂C(O)CH₃]Cl—the ³¹P chemical shift assignment is based on the relative integration of the proton spectrum. The microanalytical figures for a crystalline sample of the mixture do not indicate variation from that expected of an authentic sample of [Ph₃PCH₂C(O)CH₃]Cl, so we propose that the enol form of this phosphonium salt is the minor component. The keto-enol tautomers of the phosphonium ion are shown in the structures below. Vicente et al. gave resonance forms for the carbonyl-stabilized ylides (2) that included an enolate-type structure (1). The NMR evidence appears to confirm that this form is a possibility even in the protonated precursor to the ylide. Related work with the phosphonium salt generated by reacting triphenylphosphine with dichloroacetone appears to have given a similar result for [Ph₃PCH₂COCH₂Cl]Cl (3).

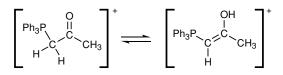


Table	1. 9	pectrosco	pic Data
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		Species			
Group	NMR °	[Ph ₃ PCH ₂ C(O)CH ₃]Cl 1	[Ph ₃ PCH=C(OH)CH ₃]Cl	Ph ₃ P=CHC(O)CH ₃ 2	
CH ₂	¹ H	d 5.91, <i>J</i> (PH) 12	_	_	
	¹³ C	d 40.62, J 59	-	_	
CH	¹ H	_	d 4.44 <i>J</i> (PH) 20	d 3.66, J (PH) 27	
	¹³ C	—	d 70.68, J(PC) 99	d 51.56 J (PC) 108	
C=O/C-O	H ¹ H	_	12.6	_	
¹³ C		181.5 or 201.5		d 190.78 J(PC) 2	
CH ₃ ¹ H		2.32		2.06, J 2	
	¹³ C	32.11 <i>J</i> (PC) 7 8	23.63, J (PC) 13 ^b	d 28.54, J (PC) 15	
³¹ P shift/pp	m ^c	21.87	15.37	14.52	

^aAll spectra were recorded in CDCl₃.¹

^bBoth ¹³C signals correlate with the ¹H resonance at 2.32 ppm, suggesting overlap of the two types of methyl resonances in the proton spectrum.

Recorded in CD₂Cl₂. The assignment is based on the relative integration from the ¹H spectrum. Shifts are in ppm relative to external H_3PO_4 .

The spectroscopic information presented here will allow students to discuss these resonance structures with a little more authority.

The addition of D_2O to the NMR sample did remove the signal attributed to the OH, but it also broadened and reduced the signals for the CH_2/CH resonances. The treatment of the mixture of tautomers with aqueous NaOH gave a clean sample of the ylide, $Ph_3P=CHC(O)CH_3$. The reverse reaction, the addition of acid to the ylide, is reported to regenerate the phosphonium salt (2). By the published method, we regenerated the same tautomeric mixture of phosphonium ions.

Spectroscopic data are summarized in Table 1, but they do not contradict data previously described (1).

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Note

1. Chicote, M. T.; Vicente, J. Personal communication (9 May, 2001). The NMR spectrum of the tautomeric mixture of **1** has been confirmed at 200 MHz. At 300 MHz, the methyl resonances separated into two singlets at 2.539 and 2.547 ppm. The latter resonance appeared as the larger of the two, but separate integration was not possible. The *CH* resonance was found at 4.60 ppm as a doublet of doublets (²*J*(PH) = 19 Hz, ⁴*J*(HH) = 2 Hz). The *CH*₂ resonance was found at 6.14 ppm (d, ²*J*(PH) = 11.4 Hz) and the *OH* at 12.93 ppm (d, *J* = 2 Hz). The relative integration between the resonance at 6.14 and 4.60 ppm was 9:2. No such tautomeric mixture has been found for [Ph₃PCH₂COR]Cl where R = OMe, OEt, Ph.

Literature Cited

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