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PROTON NMR SPECTRA OF β-CARBONYL PHOSPHONIUM YLIDS (1)

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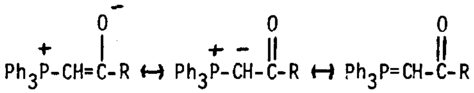
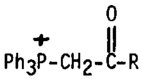
Although phosphonium ylids have been known for a long time, very little use has been made of proton NMR spectroscopy in the study of such ylids (3). In the few reports on the spectra of β-carbonyl phosphonium ylids (I) there has been a curious absence of geminal P-H coupling. For example, Ratts and Yao (4) noted that the methine proton of $Ph_3P=CH-CO-Ph$ gave a very broad singlet. Ito et al. (5) also reported that a similar β-sulfonyl phosphonium ylid showed a methine singlet. There seems no inherent reason why geminal P-H coupling should not be observable in such phosphonium ylids, especially when a coupling of about 13 cps is observable in the corresponding phosphonium salts (II) and a coupling of about 21 cps is observed in vinyl phosphonium salts (6).



$$Ph_3\overset{+}{P}-CH=\overset{\overset{O^-}{|}}{C}-R \leftrightarrow Ph_3\overset{+}{P}-\overset{-}{C}H-\overset{\overset{O}{\|}}{C}-R \leftrightarrow Ph_3P=CH-\overset{\overset{O}{\|}}{C}-R$$

Ia Ib Ic



$$Ph_3\overset{+}{P}-CH_2-\overset{\overset{O}{\|}}{C}-R$$

II

Recently, Bestmann and Snyder (7) reported the observation of geminal P-H coupling in several phosphonium ylids but only at low temperatures, the methine doublet collapsing at elevated temperatures. For example, for $Ph_3P=CH-CO-CH_3$ the methine doublet was centered at 6.32 τ (J_{PH}= 24.5 cps at -28°). These authors were unable to account for the apparent temperature-dependent geminal P-H coupling.

We have examined the proton NMR spectrum of highly purified triphenylphosphoniumphenacylide (I, R=Ph), mp 184-185°, focusing attention on the methine absorption as a function of temperature and additives (Table I). It is apparent that there is no significant temperature-dependence for the methine P-H coupling, contrary to the report by Bestmann and Snyder (7).

It does appear, however, that there is a temperature-dependent proton exchange effect caused by the presence of the conjugate acid (II, R=Ph) of the phenacylide. In other words, the normal methine doublet of the phenacylide is not collapsed by an increase in temperature but is collapsed by the presence of a proton source, the extent of the collapse being a function of the rate of exchange (i.e. the temperature).

TABLE I

Proton NMR Spectra of $Ph_3P=CH-CO-Ph$ Methine Proton

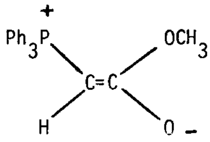
Solvent & Temperature	Additive	Peak Center	Half-width	Multiplicity	J_{PH}
CDCL$_3$					
25	none	5.57 τ	3 cps	sharp doublet	24.5 cps
50	none	5.57	4	doublet	24.5
25	1% of II (R=Ph)	5.57	9	broad doublet	22.0
50	1% of II (R-Ph)	5.57	28	broad singlet	--
DMSO-D$_6$					
37	none	5.46	1	sharp doublet	24.8
59	none	5.53	1	sharp doublet	24.8
67	none	5.53	1	sharp doublet	24.8
37	3% of II (R=Ph)	5.46	6	broad doublet	24.5
67	3% of II (R=Ph)	5.50	14	very broad doublet	--

Schmidbaur and Tronich (8) just recently have reported that the methylene doublet of $(CH_3)_3P=CH_2$ (III) was collapsed to a singlet by either heating the ylid solution to 100° or by adding a proton source. The collapse was attributed to proton exchange in both instances.

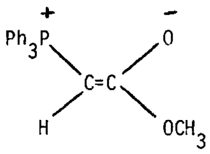
The magnitude of the methine P-H coupling (24.5 cps) in the phenacylide (I, R=Ph) is considerably larger than the 13 cps found for the conjugate acid (II, R=Ph). The latter is typical of geminal P-C-H couplings in phosphonium salts. The larger coupling in the ylids presumably reflects, in part, the change in hybridization of the α-carbon from sp^3 in the phosphonium salt (II) to sp^2 in the ylid (I). The magnitude of these couplings are comparable to those in vinyl phosphonium salts (6). The coupling reported by Bestmann and Snyder (7) for the methylene protons of $Ph_3P=CH_2$ (IV) was only 7.0 cps at -28°and that reported by Schmidbaur and Tronich (8) for the methylene protons of III was only 6.9 cps at 20°. These couplings seem very small for geminal P-H couplings but, since they are comparable to the 7.5 cps coupling reported for $Ph_3P=CHCN$ (7), they probably are not geminal H-C-H couplings. Since the mechanism of the couplings and the signs of the constants are as yet unknown, it is premature to draw further conclusions based on differences in magnitude of the geminal P-H coupling.

We have been unable to find evidence for restricted rotation about the C-C bond of the phenacylide (Ia, R=Ph), even down to as low as -60°. Bestmann et al. (9) reported such evidence for the ester ylid, $Ph_3P=C(CH_3)-COOCH_3$(V), and Ratts and Yao (4) suggested such a cause for methine broadening in dimethylsulfoniumphenacylides.

We also have examined the proton NMR spectrum of highly purified (by crystallization and sublimation) carbomethoxymethylenetriphenylphosphorane (I, $R=OCH_3$), mp 168-169°. Spectra were recorded in $CDCl_3$ solution at -60°, -31, +37, +43, and +48 and the methyl and methine regions of the pure ylid are shown in Figure I. At -60° the methyl absorption was an unequal sharp doublet at 6.28τ and 6.57τ in the ratio of 2:1 respectively. The doublet collapsed to a singlet as the temperature was increased. This observation is attributed to the temperature -dependent equilibrium between the geometric isomers VI and VII (i.e. the result of restricted rotation). The coalescence temperature was about 43°, compared to 55° reported for the α-methyl ylid (V) (9). The dominant isomer would be expected to be VII on electrostatic grounds and it also should have the least shielded methyl group. From the spectrum it is clear that the dominant isomer, in fact, does have the least shielded methyl group. The pattern of the methine absorptions also indicates that VII is the dominant isomer.



VI



VII

The methine absorption of the pure ester ylid appeared as a pair of overlapping doublets of unequal intensity at -60°. Raising the temperature to +48° also led to the gradual collapse of this quartet but only to a doublet centered at 7.09τ with J_{PH}= 21.5 cps. This collapse is attributed to the same temperature-dependent equilibrium between VI and VII. The methine absorption of the pure ylid could not be collapsed further from a doublet to a singlet by temperature variations as recently claimed (7). Therefore, the geminal P-H coupling does not appear to be temperature dependent.

We propose that an additional process, specifically the proton exchange process

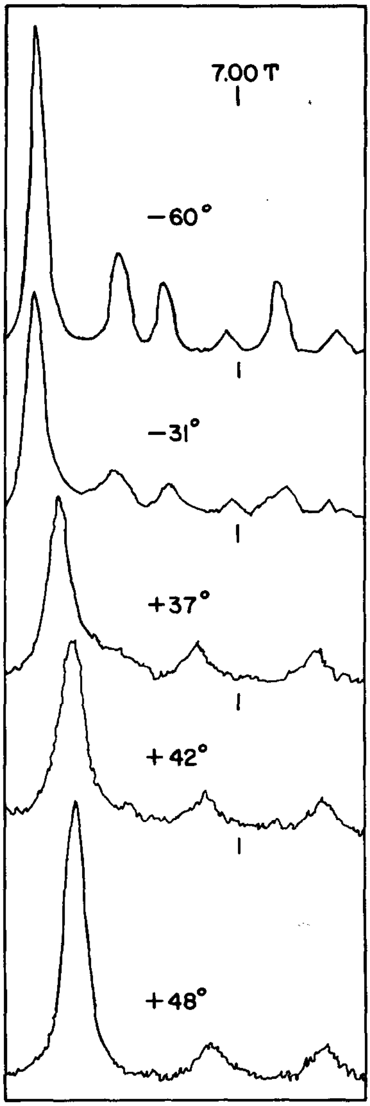


FIGURE I

Methyl and Methine absorption of $Ph_3P{=}CHCOOCH_3$ in $CDCl_3$

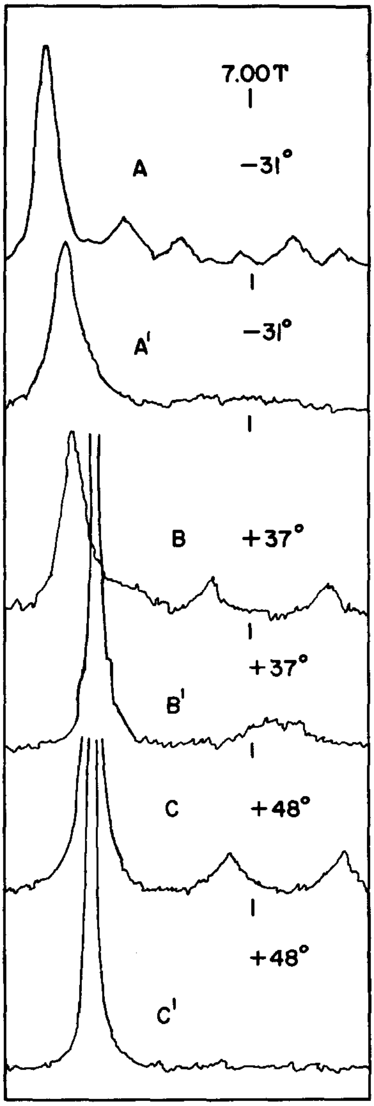


FIGURE II

Methyl and Methine absorption of $Ph_3P{=}CHCOOCH_3$. A, B, C: pure ylid. A', B', C': conjugate acid added to solution described above for the phenacylide, was responsible for the collapse of the methine absorption to a singlet and for the absence of an observable P-H coupling in the high temperature spectra reported by Bestmann and Snyder (7). Verification of the proposed exchange process was obtained by the observation that at -31, +37 and +48° we were able to achieve collapse of the methine doublet by the addition of small amounts (1%) of the ylid conjugate acid (II, R=OCH_3) (Figure II). There was more complete collapse at the higher temperature, presumably reflecting a faster proton exchange process between the ylid and its conjugate acid. The use of proton sources of increasing pKa led to an increase in the exchange rates at a given temperature. For example, addition of water or benzyltriphenylphosphonium bromide did not collapse the doublet whereas the two conjugate acids (II, R=Ph and R=OCH_3) led to substantial collapse.

Accordingly, in β-carbonyl phosphonium ylids there exists the possibility of two separate temperature-dependent phenomena affecting the multiplicity of the absorption of the methine proton. The two phenomena may have different coalescence temperatures. One effect results from the equilibrium between the geometric isomers of the enolate form (VI and VII) of the ylid. The other effect results from a proton exchange process on the ylid carbanion. If special care is used to ensure the absence of traces of proton sources only the one phenomenon, that resulting from restricted rotation, is observable. The methine-broadening phenomena reported by several groups (4,5,7,8) can be explained by one or both of these phenomena.

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