A Study of Internal Rotation in Ylides of Arsenic, Phosphorus and Sulphur

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In a previous work \(^1\) we have been concerned with the isomerization of carbomethoxy-methylene triphenylarsenanes. The temperature dependence observed in the PMR spectra of these compounds has been assigned to restricted rotation about the enolate C—C bond, a mechanism well established for ester stabilized phosphoranes.\(^4\)

\[
\begin{align*}
\text{Ph}_2P^+ & \quad \text{O}^- \quad \text{Ph}_2P^+ \\
\text{C} & \quad \equiv \quad \text{C} & \quad \text{OR} \quad \equiv \quad \text{OR}'
\end{align*}
\]

\(\text{(Ia)}\) \(\text{(Ib)}\)

In connection with our study on ester ylides,\(^1\) we also looked for evidence of isomerization in a series of \(\beta\)-ketostabilized arsencyl ylides, and when this appeared negative, analogous phosphorus and sulphur ylides were also examined. However, no sign of temperature dependence which could be attributed to rotation about the enolate C—C bond was observed.

Recently considerable interest has been focused on the sensitivity of the configurational stability of carboxylstabilized phosphonium ylides to the nature of the various substituents both on phosphorus and on the carbanion portion of the ylides.\(^5,6\) In view of the recent publication of the work of Bestmann and co-workers\(^7,8\) in this field, we wish to report the detailed results from our experiments on \(\beta\)-keto-stabilized ylides. The essential data from this study are summarized in Table 1. Some ester ylides have been included in the table for the sake of comparison with the keto ylides. It is a striking fact that whereas PMR spectra of ester ylides both of phosphorus, arsencyl, and sulphur show temperature dependence which can be interpreted in terms of \(\text{cis}/\text{trans}\) equilibria no \(\beta\)-ketostabilized ylide so far examined shows any sign of internal rotation. Besides ester ylides, only formyl-dimethylidene triphenylphosphorane (II) is reported to undergo restricted rotation about the enolate C—C bond.\(^7\)

\[
\begin{align*}
\text{Ph}_2P^+ & \quad \text{O}^- \quad \text{Ph}_2P^+ \\
\text{C} & \quad \equiv \quad \text{C} & \quad \text{Me} & \quad \equiv \quad \text{H} \\
\text{H} & \quad \equiv \quad \text{H} & \quad \equiv \quad \text{H} & \quad \equiv \quad \text{H}
\end{align*}
\]

\(\text{(II)}\) \(\text{(III)}\)

In the course of the present work we also prepared and studied the properties of ylide (II) and its methyl homologue (III). The PMR spectra of the two compounds were examined in the temperature range between −65 and 55°C. No sign of \(\text{cis}/\text{trans}\) isomerization could be detected in the ylide (III), whereas in (II), evidence of two rotamers was observed, in agreement with previous findings of Bestmann and Snyder.\(^9\) An extensive study of the formyl-dimethylidene triphenylphosphorane (II) has later been published by the same authors.\(^9\)

The negative result in the \(\alpha\)-methyl substituted ylide (III) is rather interesting in view of the close similarity of the two compounds.

As can be seen from Table 1, the carbonyl stretching frequencies suggest a significant higher contribution from the enolate structure (Ia, b) in the \(\beta\)-ketostabilized ylides as compared with the appropriate ester ylides. This agrees with the observation that ester stabilized ylides of phosphorus undergo alkylation on carbon \(^5,10\) whereas keto ylides are alkylated on oxygen.\(^11\) On the basis of infrared data, the present authors are of the opinion that the greater polarity of the carbonyl bond in \(\beta\)-keto ylides leads to stronger stabilizing interaction between phosphorus and oxygen as compared to corresponding ester ylides. Especially, in relatively non-polar media, the higher contribution from the enolate structure is expected to favour the \(\text{cis}\) isomer (Ia) since there must be considerable attraction between oxygen and the positively charged heteroatom, \((X=P, \text{As, S})\). It seems reasonable that this interaction effectively counteracts internal rotation in the \(\beta\)-ketostabilized ylides.

That the temperature invariant PMR spectrum of ketophosphoranes is due to the presence of the \(\text{cis}\) isomer only, has been convincingly demonstrated.\(^*\) By analogy and from the above arguments, there are no reasons to doubt that the corre-
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Table 1. Proton NMR and IR \(^a\) data of ylides (V). X = As.

\[
\begin{array}{cccccccc}
\text{V} & \text{Z} & \text{R} & \text{R'} & \nu_{CO} (\text{cm}^{-1}) & \text{R}, \delta & \text{R}_1, \delta \\
1 & H & H & \text{p-CH}_2\text{C}_6\text{H}_4 & 1500 & 4.68 & \\
2 & H & H & \text{p-PhC}_6\text{H}_4 & 1506 & 4.78 & \\
3 & \text{MeO} & H & \text{Ph} & 1506 & 4.08 & \\
4 & H & H & \text{Ph} & 1514 & 4.71 & \\
5 & \text{Me} & H & \text{Ph} & 1518 & 4.60 & \\
6 & H & H & \text{Me} & 1525 & 3.98 & 2.10 \\
7 & H & H & \text{p-NO}_2\text{C}_6\text{H}_4 & 1530 & 4.83 & 3.11 \\
8 & H & H & \text{NPh} & 1542 & & \\
9 & H & \text{Ph} & \text{OMe} & 1585 & 3.65 (cis) & 3.22 (trans) \\
10 & H & H & \text{OMe} & 1608 & 3.15 & 3.65 (cis) \\
11 & H & \text{CN} & \text{OMe} & 1640 & 3.80 (cis) & 3.43 (trans) \\
\text{X = P} & \\
12 & H & H & \text{Ph} & 1500 & 4.43 \(^4\) & \\
13 & H & H & \text{NEt}_3 & 1538 & 2.75 & \\
14 & H & \text{Me} & \text{H} & 1544 & 3.68 \(^8\) & 2.10 \(^8\) \\
15 & H & \text{Me} & \text{H} & 1555 & 1.89 & 8.11 \\
16 & H & \text{H} & \text{SEt} & 1582 & 3.66 & \\
17 & H & \text{H} & \text{H} & 1565 & 4.19 (cis) & 8.28 (cis) \(^7\) \\
18 & H & \text{Me} & \text{OMe} & & 3.70 (trans) & 8.92 (trans) \\
19 & H & \text{H} & \text{OMe} & 1621 & 2.91 \(^4\) & 3.62 (cis) \(^8\) \\
20 & H & H & \text{OPh} & 1635 & 3.17 & 3.36 (trans) \\
\end{array}
\]

\(^a\) NMR measurements were performed in CDCl\(_3\), IR measurements in KBr.

Corresponding isomers detectable in the PMR spectrum of ketoarsenanes resp. sulphur-
anes also are cis isomers. From Table 1 it is also seen that the chemical shift of the
methyl signal in acetylenedene triphenyl-
arsenane (6) equals that of the methyl signal in the analogous phosphorus ylide
(14). This result strongly indicates that the two compounds have the same
configuration.

It has been argued that the \(^{31}\)P NMR
data for \(\beta\)-carbonyl triphenylphosphoranes and formylmethylidene triphenylphos-
phorane imply that there is little interaction between phosphorus and oxygen in
these compounds.\(^7\) The significance of the \(^{31}\)P NMR data for the assignment of
ylide structure may be doubtful, however.

The situation reminds on that reported by Schlosser and Christmann\(^13\) for the
adducts between unstabilized phosphorus ylides and lithium salts. (IV).

\[
\text{Ph}_3\text{P}^+ \quad \begin{array}{c}
\text{CR}_4^- \\
1^\text{+} \\
1^\text{+} \\
\text{IV} \\
\text{X}^- \quad \text{Li}^+ \\
1^\text{+} \\
1^\text{+} \\
1^\text{+} \\
1^\text{+}
\end{array}
\]

\(^{31}\)P NMR spectra of these compounds are not different from spectra of the corre-
sponding salt free ylides. However, the reactivity of the ylides in the presence of
alkali salts, especially lithium salts, is

seriously affected. The contribution from steric hindrance is shown by the fact that the ester stabilized ylide (20) gives a temperature invariant spectrum. As can be seen from molecular models, rotation about the enolate C—C bond in this case leads to serious interactions of the phenoxo group with the phenyl groups at phosphorus. The divergent behaviour of the two formyl ylides 15 and 17, the ketoyl ylide 14, and the ester ylide 16, also indicates that small steric effects may in certain cases be determining for the geometry of the ylide. The carbonyl stretching frequency seems, however, to be of considerable predictive value as to the possibility of internal rotation in carbonyl stabilized ylides.

In the spectrum of the ylide 13 (X=P, P₁=NEt₃) temperature dependence due to restricted rotation about the amide C—N bond was observed. The high field part of the spectrum due to the ethyl groups coalesced at approximately —60⁰. The methine proton doublet (due to coupling with phosphorus) showed no sign of broadening at this temperature.

The NMR spectrum of phenacyclidene dimethylsulphurane was observed in the temperature range down to —60⁰, but the spectrum remained essentially unchanged. The PMR spectrum of this compound has previously been reported to be temperature invariant between —30 and 100⁰. Alkylation of the ylide with trimethylxonium tetrafluoroborate gave high yield of the O-alkylated product (VI a, b).

\[
\begin{align*}
\text{Me}_2\text{S}^+ & \quad \begin{array}{c}
\text{OMe} \\
\text{C} \\
\text{H} \\
\text{Ph}
\end{array} \\
\text{Me}_2\text{S}^+ & \quad \begin{array}{c}
\text{Ph} \\
\text{C} \\
\text{H} \\
\text{OMe}
\end{array}
\end{align*}
\]

(VIa) 94 %  (VIIb) 6 %

The authors concluded that the ylide was either rapidly rotating between cis and trans forms, or that the PMR method was insensitive to the rate process in question.

The fact that the spectrum remains temperature invariant down to —60⁰ is arguing against the theory of rapid rotation. There is, of course, the possibility that the PMR method is insensitive to the process, but it seems equally possible that the temperature invariant spectrum is due to the dominance of the cis isomer. It may be very difficult to detect the trans rotamer if the cis rotamer is favoured by as much as 20:1 over the trans.

**Experimental.** The PMR spectra were recorded at 60 MHz with a JEOL JNM-C-60H spectrometer in CDCl₃ in the presence of basic aluminium oxide to prevent intermolecular exchange reactions. New compounds were characterized by spectra and microanalysis. The syntheses of new compounds will be reported elsewhere.¹⁴


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