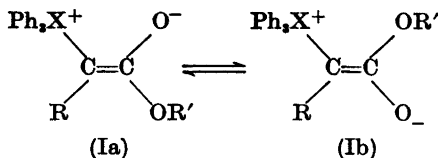


A Study of Internal Rotation in Ylides of Arsenic, Phosphorus and Sulphur

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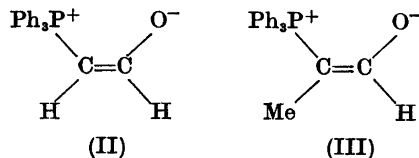
In a previous work¹ we have been concerned with the isomerization of carbomethoxymethylene triphenylarsenanes. The temperature dependence observed in the PMR spectra of these compounds has been assigned to restricted rotation about the enolate C—C bond, a mechanism well established for ester stabilized phosphoranes.²⁻⁴



In connection with our study on ester ylides,¹ we also looked for evidence of isomerization in a series of β -ketostabilized arsenic 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 carbonyl-stabilized phosphonium ylides to the nature of the various substituents both on phosphorus and on the carbanion portion of the ylides.^{5,7} 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 β -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, arsenic, and sulphur show temperature dependence which can be interpreted in terms of *cis/trans* equilibria no β -ketostabilized ylide so far examined shows any sign of internal rotation. Besides ester ylides, only formyl-

methylidene triphenylphosphorane (II) is reported to undergo restricted rotation about the enolate C—C bond.⁷

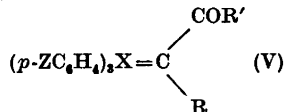


In the course of the present work we also prepared and studied the properties of ylide (II) and its methyl homologue (III). The PMR spectra of the two compounds were examined in the temperature range between -65 and 55°C . No sign of *cis/trans* isomerization could be detected in the ylide (III), whereas in (II), evidence of two rotamers was observed, in agreement with previous findings, in agreement with previous findings of Bestmann and Snyder.⁸ An extensive study of the formylmethylidene triphenylphosphorane (II) has later been published by the same authors.⁷

The negative result in the α -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 β -ketostabilized ylides as compared with the appropriate ester ylides. This agrees with the observation that ester stabilized ylides of phosphorus undergo alkylation on carbon^{9,10} 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 β -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 *cis* isomer (Ia) since there must be considerable attraction between oxygen and the positively charged heteroatom, (X=P, As, S). It seems reasonable that this interaction effectively counteracts internal rotation in the β -ketostabilized ylides.

That the temperature invariant PMR spectrum of ketophosphoranes is due to the presence of the *cis* isomer only, has been convincingly demonstrated.⁶ By analogy and from the above arguments, there are no reasons to doubt that the corre-

Table 1. Proton NMR and IR^a data of ylides (V). X=As.

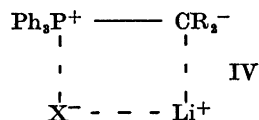
V	Z	R	R'	ν_{CO} (cm ⁻¹)	R, δ	R ₁ , δ
1	H	H	<i>p</i> -CH ₃ C ₆ H ₄	1500	4.68	
2	H	H	<i>p</i> -PhC ₆ H ₄	1506	4.78	
3	MeO	H	Ph	1506	4.08	
4	H	H	Ph	1514	4.71	
5	Me	H	Ph	1518	4.60	
6	H	H	Me	1525	3.98	2.10
7	H	H	<i>p</i> -NO ₂ C ₆ H ₄	1530	4.83	
8	H	H	NPh ₂	1542	3.11	
9	H	Ph	OMe	1585		3.65 (<i>cis</i>) 3.22 (<i>trans</i>)
10	H	H	OMe	1608	3.15	3.65 (<i>cis</i>) 3.30 (<i>trans</i>)
11	H	CN	OMe	1640		3.80 (<i>cis</i>) 3.43 (<i>trans</i>)
X=P						
12	H	H	Ph	1500	4.43 ^d	
13	H	H	NEt ₂	1538	2.75	
14	H	H	Me	1544	3.68 ^b	2.10 ^b
15	H	Me	H	1555	1.89	8.11
16	H	H	SEt	1582	3.66	
17	H	H	H	1565	4.19 (<i>cis</i>) 3.70 (<i>trans</i>)	8.28 (<i>cis</i>) ⁷ 8.92 (<i>trans</i>)
18	H	Me	OMe			3.62 (<i>cis</i>) ² 3.17 (<i>trans</i>)
19	H	H	OMe	1621	2.91 ^d	3.62 (<i>cis</i>) ² 3.36 (<i>trans</i>)
20	H	H	OPh	1635	3.17	

^a NMR measurements were performed in CDCl₃, IR measurements in KBr.

sponding isomers detectable in the PMR spectrum of ketoarsenanes resp. sulphuranes also are *cis* isomers. From Table 1 it is also seen that the chemical shift of the methyl signal in acetonilidene triphenylarsenane (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 ³¹P NMR data for β -carbonyl triphenylphosphoranes and formylmethylidene triphenylphosphorane imply that there is little interaction between phosphorus and oxygen in these compounds.⁷ The significance of the ³¹P NMR data for the assignment of

ylide structure may be doubtful, however. The situation reminds on that reported by Schlosser and Christmann¹² for the adducts between unstabilized phosphorus ylides and lithium salts. (IV).

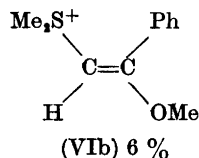
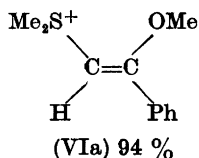


³¹P NMR spectra of these compounds are not different from spectra of the corresponding salt free ylides. However, the reactivity of the ylides in the presence of alkali salts, especially lithium salts, is

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 phenoxy group with the phenyl groups at phosphorus. The divergent behaviour of the two formyl ylides 15 and 17, the keto-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 ($X=P$, $P_1=NEt_3$) 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 -60° . The methine proton doublet (due to coupling with phosphorus), showed no sign of broadening at this temperature.

The NMR spectrum of phenacylidene dimethylsulphurane was observed in the temperature range down to -60° , but the spectrum remained essentially unchanged. The PMR spectrum of this compound has previously been reported to be temperature invariant between -30 and 100° .¹³ Alkylation of the ylide with trimethyloxonium tetrafluoroborate gave high yield of the O-alkylated product (VI a, b).



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 -60° 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 $CDCl_3$ 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

1. Dale, A. J. and Frøyen, P. *Acta Chem. Scand.* *In press.*
2. Zeliger, H. I., Snyder, J. P. and Bestmann, H. J. *Tetrahedron Letters* **1969** 2199.
3. Bestmann, H. J., Joachim, G., Lengyel, I., Oth, J. F. M., Merényi, R. and Weitkamp, H. *Tetrahedron Letters* **1966** 3355.
4. Randall, F. J. and Johnson, A. W. *Tetrahedron Letters* **1968** 2841.
5. Crouse, D. M., Wehman, A. T. and Schweizer, E. E. *Chem. Commun.* **1968** 866.
6. Zeliger, H. I., Snyder, J. P. and Bestmann, H. J. *Tetrahedron Letters* **1970** 3313.
7. Snyder, J. P. and Bestmann, H. J. *Tetrahedron Letters* **1970** 3317.
8. Bestmann, H. J. and Snyder, J. P. *J. Am. Chem. Soc.* **89** (1967) 3936.
9. Bestmann, H. J. and Schultz, H. *Tetrahedron Letters* **1960** 5.
10. Bestmann, H. J. and Schultz, H. *Chem. Ber.* **95** (1962) 2921.
11. Ramirez, R. and Dershowitz, S. *J. Org. Chem.* **22** (1957) 41.
12. Schlosser, M. and Christmann, K. F. *Annalen* **708** (1967) 1.
13. Smallcombe, S. H., Holland, R. J., Fish, R. H. and Caserio, M. C. *Tetrahedron Letters* **1968** 5987.
14. Frøyen, P. *Acta Chem. Scand.* *In press.*

Received November 16, 1970.