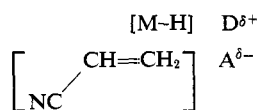


ample, the insertion of methyl acrylate or dimethyl fumarate is complete in 1 hr in toluene at room temperature whereas a higher temperature (80°) is required to effect the insertion with a more acidic olefin, *i.e.*, fumaronitrile or maleic anhydride, indicating lack of a simple correlation between the reaction rate and the π acidity of the olefin components. The insertion of acrylonitrile to Cp_2MoH_2 occurs unexpectedly slowly, leading exclusively to the α -metalated product $\text{Cp}_2\text{MoH}[\text{CHCH}_3\text{CN}]$,¹ in a direction opposite to that of the β -cyanoethylation of amines. Cis stereochemistry of Cp_2MoH_2 addition to disubstituted olefins, implying a multicentered transition state, has been established.¹⁵ Therefore, a similar transition state may be invoked to account for the observed metalation. The direction of the addition implies hydridic character of the hydride ligand of Cp_2MoH_2 . However, the partial positive character of $\text{D}^{\delta+}$ in the complex would tighten the metal-hydride bond, thus retarding the hydride transfer to the olefin. Kinetic aspects of insertion (eq 1), *inter alia*, the long induction period experienced



by olefins of high π -acidity,¹⁵ also argue against the EDA complex as an activated intermediate. The retarding effect seems to support involvement of essentially metal orbitals in the EDA interaction.

(15) A. Nakamura, Abstracts, 5th International Conference on Organometallic Chemistry, Moscow, 1971, p 555.

A. Nakamura, Sei Otsuka*

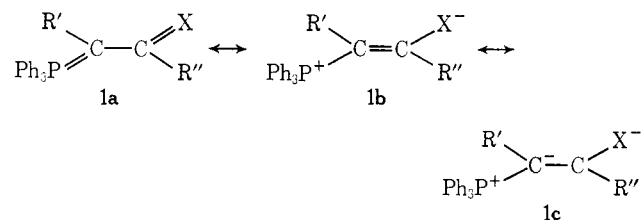
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Received February 27, 1973

¹³C Nuclear Magnetic Resonance of Organophosphorus Compounds. VII. Probing the Phosphorus-Carbon Ylide Bond

Sir:

Phosphorus ylides have provided challenging problems to both synthetic chemists and those attempting to explain their chemistry and molecular electronic structure.¹ It has been common to interpret their bonding in terms of valence-bond resonance hybrids of the type **1a-c** in explaining their stability,² isomerism,³ and



(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, **92**, 3929 (1970); D. B. Boyd and R. Hoffmann, *ibid.*, **93**, 1064 (1971).

(2) See, for example, R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, London, 1965.

(3) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, 866 (1968); H. J. Bestmann and J. P. Snyder, *J. Amer. Chem. Soc.*, **89**, 3936 (1967).

equilibria.⁴ The electronic differences within **1a-c** should give rise to fundamental differences in the ¹³C shieldings and ¹³C-³¹P nuclear spin couplings for atoms in the P-C-C-X group for any molecule described largely by one of the above resonance hybrids. Structure **1b** is essentially that of a phosphonium salt, shifts and couplings for which are available in other compounds. Structure **1c** represents a carbanion which could be, in principle, either trigonal or tetrahedral with formal sp² or sp³ hybridization schemes for the ylide carbon. The d π -p π "back-bonding" depicted by **1a** presents an electronic distribution for which few ¹³C data are available.⁵

We have determined ¹³C-³¹P couplings and ¹³C chemical shifts in a number of phosphorus ylides in an effort to better delineate the ylide carbon bonding description. The compounds in Table I were run as received (except for **3** and **6** which were recrystallized from CH_2Cl_2 -(C_2H_5)₂O and dried) from Aldrich Chemical Co. in saturated deuteriochloroform solution (usually 250-750 mg/ml) containing 1-5% tetramethylsilane as reference. Solutions were examined in 12-mm tubes using a Varian XL-100-15 nmr spectrometer in Fourier transform mode. Several hundred to several thousand transients were accumulated typically with acquisition times of 1.0-3.3 sec with 1.7 sec being normal for coupling measurements. Line positions were determined automatically by computer software using the Varian S-124XL Fourier transform accessory. ¹³C-¹H couplings were eliminated using broadband ¹H noise-modulated decoupling. Complete shift and coupling data will appear in a later publication.⁶

The most striking aspect of the data is the high shielding exhibited by the ylide carbons, comparable with that of the aliphatic analog **11**, a conjugate acid. Compound **10** has a carbon which is definitely of **1b** type and shows the expected deshielding of the olefinic phosphorus-bound carbon. This deshielding is reasonable in light of the analogous methine carbon shift in the enol form of acetylacetone of 99 ppm⁷ and the expected ~16 ppm shielding in replacing its COCH₃ group with a proton and ~10 ppm shielding in replacing a proton on an sp² carbon with a Ph₃P⁺ group. Other examples of pure sp² carbon bound to phosphorus are those in the triphenylphosphonium group. Their shifts range from 126 to 128 ppm and their directly bonded ¹³C-³¹P couplings from 89 to 92 Hz, values far from those of the ylide carbons. *It is clear that 1b does not provide a reasonable bonding description for phosphorus ylides* although it is commonly written as an explanation of the existence of cis-trans isomerism. Structure **1c** places a large negative charge density on the ylide carbon. This is consistent with the high shieldings experienced by the ylide carbon and is reminiscent of the high shieldings observed in alkyl-

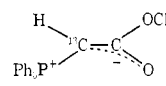
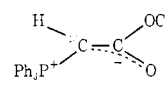
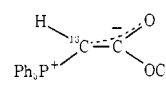
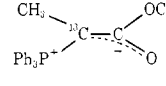
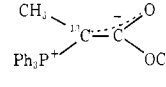
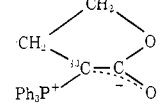
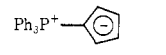
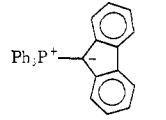
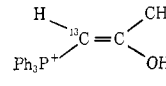
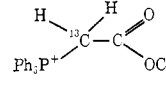
(4) F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968).

(5) Phosphorus ylides have been examined using ¹H and ³¹P nmr; (a) ¹H nmr data appear in ref 3 and 4 as well as in H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 604 (1968); W. Malisch, D. Rankin, and H. Schmidbaur, *ibid.*, **104**, 145 (1971); R. K. Harris, J. R. Woplin, K. Issleib, and R. Lindner, *J. Magn. Resonance*, **7**, 291 (1972); (b) ³¹P nmr studies on the series Ph₃P=CR₂, R = alkyl: S. O. Grim, W. McFarlane and T. J. Marks, *Chem. Commun.*, 1191 (1967); (c) ³¹P nmr data on air-stable ylides are discussed in A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 76-79.

(6) G. A. Gray, submitted for publication.

(7) J. H. Billman, S. A. Sojka, and P. R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2034 (1972).

Table I. One-Bond ^{13}C - ^{31}P Nuclear Spin Couplings and ^{13}C Chemical Shifts for Ylide and Related Carbons

No.		$^1J_{\text{CP}}^a$	$\delta_{^{13}\text{C}}^b$
2		126.7	29.78
3 ^c		130 ± 3	29.6
4 ^c		117 ± 3	29.8
5		127.7	32.96
6		120.7	31.68
7		135.1	30.83
8		113.1	78.26
9		128.7	53.28
10 ^d		99.2	70.92
11		55.5	32.89

^a In Hz, accurate to ± 0.2 Hz, except where noted. ^b In ppm with respect to internal TMS- ^{13}C , accurate to ± 0.01 ppm, except for **3** and **4** where shifts are accurate to ± 0.2 ppm. ^c Isomers are resolved at *ca.* -30° . However, lines were ~ 10 Hz wide. ^d One enol form of $\text{Ph}_3\text{PCH}_2\text{COCH}_3^+\text{Cl}^-$. Only one set of enol resonances observed, either through rapidly interconverting *cis* and *trans* isomers or preferential equilibrium.

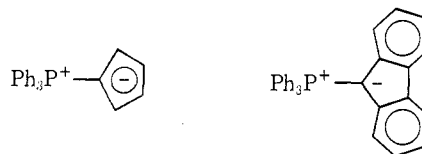
lithiums.⁸ It has been suggested⁸ that sp^2 hybridized carbanions (as organolithiums) are heavily *deshielded* with respect to their protonated versions (43 ppm in the case of $\text{C}_6\text{H}_5\text{Li}$, 30 ppm for $(\text{C}_6\text{H}_5)_3\text{CLi}$, and 43 ppm for $(\text{C}_6\text{H}_5)_2\text{CHLi}$)⁸ whereas the supposedly sp^3 hybridized carbanions in methyl lithium and benzyl lithium are *shielded* (or slightly *deshielded* in some solvents in the case of the latter) with respect to their protonated analogs. In comparing **4** and **11** we see only a 3 ppm *deshielding* in going from the conjugate acid to the ylide. Although these large ylide carbon shieldings might then be interpreted as indicating sp^3 hybridized ylide carbons, their ^{13}C - ^{31}P couplings point toward greater *s* character in the ylide bonding orbital. Their values are even 20–40% greater than the 88–100 Hz range observed for typical sp^2 carbons bound to phosphorus(IV). Compound **11** shows the smaller

(8) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Amer. Chem. Soc.*, **88**, 1272 (1966); L. C. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *ibid.*, **91**, 1057 (1969); R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, 117 (1969).

coupling expected for sp^3 -hybridized carbon bound to the same type of phosphorus(IV). X-Ray studies of various ylides⁹ have shown that the ylide carbon is basically trigonal and thus, to a first approximation, sp^2 hybridized. The explanation for the high shielding is therefore not simply derived from hybridization arguments and awaits future clarification.

The electronic difference between **1a** and **1c** is vague at this point. Stabilization *via* $d\pi$ - $p\pi$ interaction can still occur while retaining substantial anionic charge on the ylide carbon because of the size and directionality of the more diffuse *d* orbital on the phosphorus atom. The ylide carbon shift does, however, indicate a significant polarity to this π bond. The large increase in coupling is more difficult to explain.¹⁰ The high negative charge should actually *decrease* the ^{13}C - ^{31}P coupling in comparing **10** with **2–7**, for example, if effective nuclear charge arguments hold.¹¹ The ylide **8** seems to fall part-way between the phosphonium salt model and the ylides **2–7**. Note that its coupling is smaller than the corresponding value in **9**, an apparently close analog. Its shift is very similar to that of odd-numbered carbons in delocalized aliphatic carbanions reported recently¹² (65–99 ppm). Cyclopentadienide anion itself has a shift of 102 ppm.¹³ The observed 78 ppm shift is significantly more shielded than might be predicted from a simple substituent effect aspect. The situation becomes even more perplexing in going to the related ylide **9**. β substitution usually leads to a *deshielding* so that the ylide carbon shielding in **9** should be smaller than that in **8**, but instead it is larger by 25 ppm.

The ylide carbon ^{13}C shifts then definitely mirror important electronic differences between **8** and **9** which possibly imply a greater localization of the anionic charge on the ylide carbon in **9** than **8**. Thus, they may be better depicted as



The ylide carbon ^{13}C - ^{31}P couplings are stereospecific with respect to *cis*-*trans* isomerism, in **3–6**, greater in the *trans* isomer than in the *cis* isomer. This stereospecificity may reflect different degrees of importance of **1a–c** within the isomers.

These initial data on the ^{13}C resonance parameters pertaining to the ylide bond show great promise in providing a direct, sensitive, and informative probe

(9) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **87**, 5603 (1965); J. C. J. Bart, *J. Chem. Soc. B*, 350 (1969).

(10) Although signs of $^1J_{\text{CP}}$ were not determined it is highly likely based on previous data that they are positive. The sign of $^1J_{\text{CP}}$ is essentially controlled by the oxidation state of the phosphorus atom, positive for P(IV) and P(V), negative for P(III): see W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968); G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3470 (1972); T. Bundgaard and H. J. Jakobsen, *Acta Chem. Scand.*, **26**, 2548 (1972). The striking similarity of shifts and couplings of the various phenyl carbons in the ylides and conjugate acids⁶ indicate that the phosphorus is electronically P(IV), in a Ph_3P^+ bonding situation, and therefore has positive directly bound couplings to ^{13}C .

(11) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965); W. M. Litchman and D. M. Grant, *ibid.*, **89**, 6775 (1967).

(12) R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *ibid.*, **95**, 926 (1973).

(13) H. Spiesscke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

for examination of the ground-state electronic nature of phosphorus ylides, divorced from the complicating dynamical problems encountered when kinetic and reaction data are used to accomplish the same end. The large shieldings and spin couplings, outside the range of more typical compounds, give a quick and unambiguous test for ylide existence and provide a challenging theoretical problem in their explanation.

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Received May 5, 1973

Superfast Singlet Excited State Di- π -methane Rearrangement and Decay Rates: Picosecond Range Measurements by Single Photon Counting and Use of Magic Multipliers. Mechanistic Organic Photochemistry. LXXXI¹

Sir:

Previously we have noted the generality of the di- π -methane rearrangement.² Hitherto, in assessing structural control of reactivity, we were limited to indirect methods of rate measurement of these exceedingly fast reactions.³

Presently we report: (1) a method of direct measurement of excited singlet decay rates appreciably faster than the flash lamp, routinely affording lifetimes of the order of 100 psec, (2) an amplified approach allowing measurement of decay rates of excited singlets with lifetimes two orders of magnitude still shorter, (3) evidence that the earlier indirect method³ is reliable in giving relative rates of reaction but capricious for absolute rates, (4) application of the new method to the acyclic di- π -methane systems previously studied, (5) evidence that vinyl-vinyl bridging is rate limiting, and (6) with two exceptions, an almost perfect parallel between the rates of the di- π -methane rearrangement and rates of decay.

The general method of single photon counting⁴ was used. A PDP-8/I computer was used on-line both as a multichannel analyzer and as a data processor. By a reiterative convolution technique⁵⁻⁷ we could obtain decay rates much faster than the ~ 2 -nsec lamp flash. From the observed fluorescence decay and the experimental lamp flash, one derives the true excited state decay. Direct measurement of 100-psec lifetimes and thus decay rates of 10^{10} sec⁻¹ proved accessible.

However, most of our di- π -methane singlets, excepting 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (1),

(1) For the previous paper of this series, see H. E. Zimmerman, D. R. Amick, and H. Hemetsberger, *J. Amer. Chem. Soc.*, **95**, 4606 (1973).

(2) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(3) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

(4) (a) J. B. Birks, *Progr. React. Kinet.*, **4**, 239 (1967); (b) W. R. Ware, Office of Naval Research Technical Report No. 3, March 1969; (c) L. M. Bellinger and G. E. Thomas, *Rev. Sci. Instrum.*, **32**, 1044 (1961).

(5) Full experimental details, mathematical treatment, and elaboration of the method will be reported in our full paper.

(6) This convolution method proved reliable in contrast with deconvolution which often is unstable; see ref 7.

(7) A. E. W. Knight and B. K. Selinger, *Spectrochim. Acta, Part A*, **27**, 1223 (1971).

rearrange and decay too rapidly for even these techniques. The observation of rates of decay at 77°K slow enough to measure directly suggested a trick to obtain the desired room temperature rates. Thus from the definitions of low and room temperature fluorescence quantum yields (eq a and b) one can obtain, by divi-

$$\phi_i^{77} = k_i/k_{dt}^{77} \quad (a)$$

$$\phi_i^{RT} = k_i/k_{dt}^{RT} \quad (b)$$

sion, the ratio, M , of the room temperature to the low-temperature decay rate (eq c). Here k_{dt} is the total of

$$M = \phi_i^{77}/\phi_i^{RT} = k_{dt}^{RT}/k_{dt}^{77} \quad (c)$$

excited singlet decay (*i.e.*, $k_r + k_d + k_f$). The assumption that k_i is temperature independent is expected theoretically (in view of constancy of the Stokes shift with temperature), has been observed in the literature,⁸ and was checked for two test cases.

We term the ratio M our "magic multiplier," since one merely has to multiply a measured low-temperature rate by M to obtain a superfast rate constant not ordinarily measurable. This is tantamount to amplification of the direct method. The required ratio of fluorescence quantum yields is the ratio of emission intensities at the two temperatures.

With k_{dt} 's available for the compounds of interest, one can obtain the rates (the k_r 's of singlet excited state rearrangement) since $k_r = \phi_i k_{dt}$ and the reaction quantum yields are known. Table I summarizes the

Table I. Direct Measurement of Singlet Lifetimes and Decay Rates

Compound	Lifetime, ^a nsec	Decay rate, ^a sec. ⁻¹	Temp, °K	No. of runs	Standard devia- tion, %
Naphthalene	107 ^b	9.35×10^6	295	4	10
	284 ^c	3.25×10^6	77	4	3
Tetraphenyl- ethylene	1.13 ^d	8.9×10^8	295	3	5
	4.36	2.4×10^9	77	3	1
Triphenyldiene 1	0.025	4×10^{10}	295	2	$\sim 50^e$
	2.91	3.4×10^8	77	9	6
Diphenyldiene 2	3.11	3.2×10^6	77	6	2
1,1,3,3-Tetra- phenyldiene 3	1.90	5.3×10^8	77	7	14
1,1,5,5-Tetra- phenyldiene 4	0.124	8.1×10^9	77	11	50
1,1,5,5-Tetra- phenylbisor- diene 5	0.701	1.4×10^9	77	5	8

^a In methylcyclohexane-isopentane (4:1). ^b Lit.^{8a} 110 nsec (*n*-hexane), 120 nsec (cyclohexane). ^c Lit.^{8a} 260-270 nsec at 100°K. ^d Lit. 1.1 nsec: I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965. ^e Estimated.

direct measurement of singlet lifetimes. Equations 1-5 in Chart I delineate the room temperature results using the amplified direct method, that is, employing

(8) (a) N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, **9**, 367 (1967); (b) W. R. Dawson and J. L. Kropp, *J. Phys. Chem.*, **73**, 693 (1969); (c) J. L. Kropp, W. R. Dawson, and M. W. Windsor, *J. Phys. Chem.*, **73**, 1747 (1969).