Journal of Organometallic Chemistry, 93 (1975) C20—C22

Preliminary communication

ELECTRONIC STRUCTURE AND REACTIVITY OF YLIDIC SYSTEMS

V*. YLID STRUCTURE INFORMATION FROM NMR DATA

K.A. OSTOJA STARZEWSKI** and M. FEIGEL

Fachbereich Chemie der Universität Frankfurt, Laboratorium Niederrad, Theodor-Stern-Kai 7, (6) Frankfurt/Main (Germany)

(Received May 9th, 1975)

Summary

Bond systems in triphenylphosphorus ylids, methylenetrimethylphosphorane and their tricarbonylnickel salts are discussed by interpretation of ^{13}C NMR results.

^{13}C—^{1}H coupling constants depend on various factors e.g. *s*-orbital contribution of the CH-bonds, effective nuclear charge, and excitation energies for ground-to-excited state transitions [2]. For hydrocarbons there exists an empirical linear correlation with *s*-character [3]:

$$^{1}J(\mathrm{CH}) = 500\ \mathrm{Hz} \cdot \%s(\mathrm{CH}) \qquad (1)$$

Recently ^{13}C NMR data have been frequently used for investigating the structure and bond system of ylids and related compounds. Using empirical relation 1, the one bond ^{13}C—$^{1}H_2$ coupling constant of 149 Hz in methylenetrimethylphosphorane $(CH_3)_3PCH_2$ suggested approximate sp^2-hybridisation [4]. This conclusion concerning the highly negative charged phosphonium-substituted carbon atom [5], agrees well with the X-ray structures of planar carbanion centers in several triphenylphosphorus ylids [6]. The approximation also applies for the protonated ylid (= corresponding phosphonium salt) $(CH_3)_3P^+CH_3\ X^-$ with $J(CH_3) = 133$ Hz [7], as well as for the nickel complex $(CH_3)_3PCH_2Ni(CO)_3$ with $J(CH_2) = 123$ Hz [8], again in agreement with X-ray results for the related $(C_6H_{11})_3PCHCH_3Ni(CO)_3$, which indicates a distorted tetrahedral arrangement about the complexed ylid carbon.

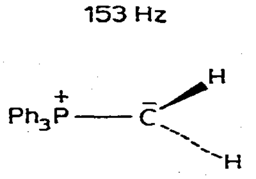
In a very recent paper by Albright, Freeman and Schweizer marked discrepancies were reported for methylenetriphenylphosphorane

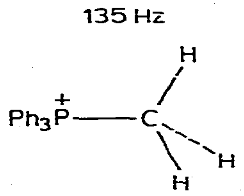
---

[*] For part IV see ref. 1.

[**] Author to whom correspondence should be addressed.

$(C_6H_5)_3PCH_2$ ($J(CH_2) = 133$ Hz!) [9]. Their results conflict with ours, which are fully consistent with the known structural properties of ylid [6a] and salt [10], and indeed *s*-contribution appears to be the decisive factor for the ylid carbon ^{13}C—^1H coupling constants.





Their NMR data cannot be assigned to salt-free [11] Ph_3PCH_2, but exhibit characteristic features of sp^3-carbons connected to phosphorus*. Consequently their interpretations, based on changes in effective nuclear charge, led to rather confusing conclusions, involving variations in the "ylid double bond contribution":

$$R_3\overset{+}{P}\text{—}\overset{-}{C}H_2 \longleftrightarrow R_3P{=}CH_2$$

From our values of the methyl/phenyl *P*-substituted phosphinemethylenes $Ph_{3-n}Me_nPCH_2$ ($n = 0, 1, 2, 3$) no "dramatic change" in the bond system can be discerned (Table 1). The slight increase in $^1J(^{13}C$—$^1H)$ from IV to I is paralleled by a more pronounced increase in $^1J(^{31}P$—$^{13}C)$. The value of the carbon atom coupling in the ylid I was reported to be 52 Hz, but is in fact, 100 Hz which compares with 90 Hz [4] in IV.

TABLE 1

METHYL AND METHYLENE COUPLING CONSTANTS $^1J(^{13}C$—$^1H)$ (Hz) FOR YLIDS

No	Compound	CH_3	CH_2	Reference
I	Ph_3PCH_2		153	own work
II	$(CH_3)Ph_2PCH_2$	129	151	own work
III	$(CH_3)_2PhPCH_2$	129	149	own work
IV	$(CH_3)_3PCH_2$	127	149	4

We will publish later a more detailed account of our ^{13}C NMR of substituent effects in ylidic systems, which reveal strong influences on the ylid carbon ^{31}P—^{13}C couplings and chemical shifts [12].

Experimental

Salt-free pure ylids were prepared as described by Köster [11] by use of $NaNH_2$ in boiling THF, with rigorous exclusion of air and moisture. PFT-NMR spectra were recorded on a Bruker HX-90/4-15, equipped with a Nicolet computer series 290/1080. Sealed tube samples of ylids in benzene-d_6 or THF-d_8 (no ΔJ values were observed) were used, while the triphenylmethylphosphonium salt was dissolved in $CDCl_3$.

---

*Depending on the procedure used in isolating the ylid, we find that the CH-coupling is reduced by interactions with lithium halides.

Acknowledgement

This work was supported by Prof. H. tom Dieck, Prof. H. Kessler and the Deutsche Forschungsgemeinschaft.

References

1 K.A. Ostoja Starzewski, W. Richter and H. Schmidbauer, Chem. Ber., (1975) in press.
2 G.E. Maciel, J.W. McIver, Jr., N.S. Ostlund and J.A. Pople, J. Amer. Chem. Soc., 92 (1970) 1 and references therein.
3 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, N.Y., 1972 and ref. therein.
4 H. Schmidbaur, W. Buchner and D. Scheutzow, Chem. Ber., 106 (1973) 1251.
5 K.A. Ostoja Starzewski, H. tom Dieck and H. Bock, J. Organometal. Chem., 65 (1974) 311.
6 a J.C.J. Bart, J. Chem. Soc., B, (1969) 350.
6 b A.J. Speziale and K.W. Ratts, J. Amer. Chem. Soc., 87 (1965) 5603.
6 c F.S. Stephens, J. Chem. Soc., (1965) 5640 and 5658.
6 d P.J. Wheatley, J. Chem. Soc., (1965) 5758.
7 V.H. Elser and H. Dreeskamp, Ber. Bunsenges. Phys. Chem., 73 (1969) 619.
8 F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E.G. Hoffmann, G. Schroth, K. Seevogel and W. Stempfle, Isr. J. Chem., 10 (1972) 293.
9 T.A. Albright, W.J. Freeman and E.E. Schweizer, J. Amer. Chem. Soc., 97 (1975) 940.
10 C.J. Fritchie, Acta Cryst., 20 (1966) 107.
11 R. Köster, D. Simic and M.A. Grassberger, Liebigs Ann. Chem., 739 (1970) 211.
12 K.A. Ostoja Starzewski and H. tom Dieck, Chem. Ber., (1975) in press.