Transylidation Promoted by Traces of Acid. Origin of Temperature-Dependent P–C–H Spin–Spin Coupling

Sir:

Recently we communicated[1a] that the spin–spin coupling between phosphorus and α hydrogen for a variety of triphenyl-substituted phosphorus ylides is temperature dependent. This observation was left unexplained, although ylide dimerization[1a] and reversible protonation at carbon[1b] were initially ruled out as mechanistic possibilities. It has now been determined that in fact the latter, rapid reversible carbon protonation by trace amounts of acid, is responsible for the nmr effect[2] in exactly the same fashion that alcohol protons are spin decoupled in circumstances of rapid hydroxyl proton exchange.

Phosphorus ylides are rapidly protonated by acids[3] to deliver the corresponding phosphonium salt. An acid–base equilibrium may then be established[4] which forms the basis for the well-known phosphorane synthesis, transylidation.[5] That this proton-exchange

$$L_3\overset{+}{P}\overset{-}{C}RR' + HX \longrightarrow [L_3\overset{+}{P}CHRR']X^-$$

$$L_3\overset{+}{P}\overset{-}{C}RR' + [L_3\overset{+}{P}CHRR']X^- \rightleftarrows [L_3\overset{+}{P}CHRR']X^- + L_3\overset{+}{P}\overset{-}{C}RR'$$

process is responsible for the above-mentioned temperature-dependent nmr effect can be demonstrated in four ways. At 23° in carefully purified dioxane the α protons of methylenetriphenylphosphorane (**1**) ($L = C_6H_5$; $R = R' = H$)[6] appear as a sharp doublet ($J_{PCH} = 7.0$ cps). The addition of a proton source such as water, methanol, or the insoluble triphenylmethylphosphonium iodide (**2**) ($L = C_6H_5$; $R = R' = H$) causes immediate collapse of the doublet to a broad singlet indicative of induced proton exchange *via* transylidation.[7] In no case, however, was the conjugate-acid phosphonium salt observable in the nmr.

Conversely, if the carbomethoxy derivative **1** ($L = C_6H_5$; $R = H$; $R' = CO_2CH_3$)[10] in commercial deuteriochloroform at 31° is treated with a few milligrams of solid lithium chloride, the original exchange-averaged α-proton singlet[1a] is immediately transformed to a slightly broadened doublet ($J_{PCH} = 21.6$ cps).[11]

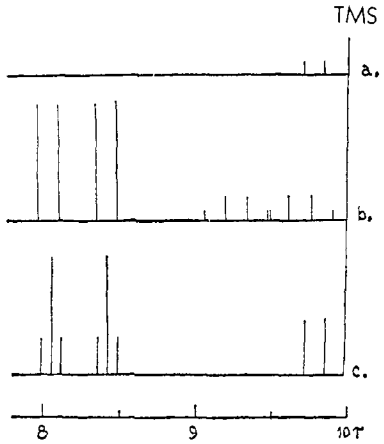

Figure 1. Schematic diagram of nmr spectra illustrating deuterium exchange between $(C_6H_5)_3P^+C^-D_2$ (**3**) and $(C_6H_5)_3P^+C^-HCH_3$ (**4**); (a) ylide **3** (isotopic purity approximately 80%); (b) ylide **4** (approximately the same molarity as in a); (c) solutions from a and b combined. Phenyl region omitted.

The transylidation described above and its dependence on very low concentrations of acid impurities are further established by the following isotope-exchange reaction. An approximate equimolar mixture of partially deuterated methylenetriphenylphosphorane **3**[14] and the protio methyl-substituted derivative **4**[6] were mixed at 23° in carefully purified dioxane. The accompanying schematic diagram of the nmr spectra of ylides **3** and **4** and their mixture (Figure 1) indicates the formal conversion of the latter pair to phosphoranes **5** and **6**.[15]

$$\underset{\mathbf{3}}{(C_6H_5)_3\overset{+}{P}\overset{-}{C}D_2} + \underset{\mathbf{4}}{(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_3} \longrightarrow \underset{\mathbf{5}}{(C_6H_5)_3\overset{+}{P}\overset{-}{C}HD} + \underset{\mathbf{6}}{(C_6H_5)_3\overset{+}{P}\overset{-}{C}DCH_3}$$

Traces of acid impurities apparently produce very small quantities of the phosphonium salts **7** and **8**, each of which can undergo transylidation with ylides **3** and **4**. Herein lies the explanation for the nmr observation of phosphoranes **5** and **6**.

$$\underset{\mathbf{7}}{[(C_6H_5)_3\overset{+}{P}CHD_2]I^-} + (C_6H_5)_3\overset{+}{P}\overset{-}{C}D_2 \rightleftarrows (C_6H_5)_3\overset{+}{P}\overset{-}{C}HD + [(C_6H_5)_3\overset{+}{P}CD_3]I^-$$

$$\mathbf{7} + (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_3 \rightleftarrows (C_6H_5)_3\overset{+}{P}\overset{-}{C}HD + [(C_6H_5)_3\overset{+}{P}CHDCH_3]I^-$$

$$\underset{\mathbf{8}}{[(C_6H_5)_3\overset{+}{P}CHDCH_3]I^-} + (C_6H_5)_3\overset{+}{P}\overset{-}{C}D_2 \rightleftarrows (C_6H_5)_3\overset{+}{P}\overset{-}{C}DCH_3 + [(C_6H_5)_3\overset{+}{P}CHD_2]I^-$$

$$\mathbf{8} + (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_3 \rightleftarrows (C_6H_5)_3\overset{+}{P}\overset{-}{C}DCH_3 + [(C_6H_5)_3\overset{+}{P}CH_2CH_3]I^-$$

The reversible proton or deuteron transfer must be very rapid at room temperature as the exchange was

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[1] (a) H. J. Bestmann and J. P. Snyder, *J. Am. Chem. Soc.*, **89**, 3936 (1967); (b) suggested by referee III in footnote 14 of ref 1a.

[2] Two other groups have come to this conclusion independently: (a) methylenetrialkylphosphoranes: H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 604 (1968); (b) carbethoxymethylenetriphenylphosphorane: P. Crews, *J. Am. Chem. Soc.*, **90**, 2961 (1968). Dr. Crews kindly made his results known to us prior to publication.

[3] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).

[4] H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962)

[5] H. J. Bestmann, *Angew. Chem.*, 77, 609, 651, 851 (1965).

[6] (a) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954). (b) The isolation and characterization of this and other "unstable" phosphorus ylides will be reported shortly: H. G. Liberda, Dissertation, Erlangen, Germany, 1968.

[7] Trimethylsilylmethylenetrimethylphosphorane (**1**, $L = CH_3$; $R = H$; $R' = Si(CH_3)_3$) possesses methine doublet character in the nmr even at 130°.[8] This is in accord with the proton-exchange mechanism since the silyl ylide is converted to nonacidic products in the presence of acid.[8,9]

[8] H. Schmidbauer and W. Tronich, *Angew. Chem.*, 79, 412 (1967).

[9] N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965).

[10] Mp 171–173°; C. Ruchardt, P. Panse, and S. Eichler, *Chem. Ber.*, **100**, 1144 (1967), report mp 168°.

[11] The methine doublet character indicates that lithium chloride complexation[12] precludes proton transfer but not hindered internal rotation. This is confirmed by the display of the rotation-averaged methoxyl group as a sharp singlet.[1a,13]

[12] (a) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 186–187; (b) M. Schlosser and K. F. Christmann, *Ann. Chem.*, 708, 1 (1967).

[13] H. J. Bestmann, G. Joachim, I. Lengyel, S. F. M. Oth, J. Mereny, and J. Weitkamp, *Tetrahedron Letters*, 3335 (1966).

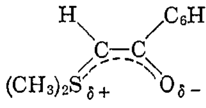
[14] Phosphorane **3** was prepared in approximately 80% isotopic purity by phenyllithium abstraction of deuterium from triphenyl(trideuterio)methylphosphonium iodide.

[15] Figure 1c represents the superposition of nmr spectra of ylides **4, 5** and **6**. The methine hydrogen octet of compound **4** is too weak to observe.

essentially complete within 30 min.[16] However the exchange rate is not so high that phosphorus coupling with α hydrogens of phosphorane **5** is suppressed.[17] The limit of proton donor concentration for transylidation is thus even below that necessary to prohibit P–C–H coupling. This realization explains the variable results reported earlier concerning coupling as a function of solvent. Solvent source is a serious determinant as regards the extent of observed phosphorus–hydrogen coupling.

Removal of acid altogether eliminates the P–C–H temperature effect. Carbomethoxyphosphorane **1** (L = C_6H_5; R = H; R′ = CO_2CH_3)[10] at 23° in carbon tetrachloride (distilled from aluminum oxide) displays the static spectrum expected for a pair of rotamers free from proton exchange.[1a] Acid exclusion thus not only prevents reversible proton transfer by eliminating traces of phosphonium salt but also raises the barrier to hindered internal rotation for carbalkoxyphosphoranes.[1a,13]

As a practical matter, the chemical shifts and coupling constants of protons α and β to hetero atoms in ylide systems can be reliably determined by the successive addition of milligram portions of basic aluminum oxide to the nmr tube at room temperature. The effect of lowering the temperature, *i.e.*, suppressing the rate of proton exchange, is simulated until clean sharp peaks are obtained.[18] This technique has been utilized to demonstrate the nature of the broadened methine proton for dimethylsulforanes[19] **9** and **10** as identical with that described above for phosphorus ylides.[20]



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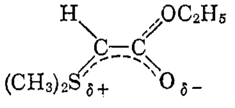

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Acknowledgment. We are grateful to the Deutsche Forschungs-Gemeinschaft, Farbwerke Hoechst, and the American Philosophical Society for financial assistance.

(16) Time lapse between admixture and taking of spectrum.

(17) At high temperature the methyl quartet of pure methyl ylide **4** collapses to a doublet; the PCCH coupling retained even under conditions of very rapid transylidation.[6b]

(18) Neutral aluminum oxide and powdered KOH suffice as well. Dr. Crews[2b] has utilized *n*-butyllithium.

(19) (a) Dimethylsulforane **9**, mp 48–52° (lit.[19b] 50–55°); dimethylsulforane **10**, oil (lit.[19b] oil),nmr as reported; (b) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

(20) Ratts and Yao[19b] were unable to locate the methine proton of sulforane **10** in the nmr due to serious band broadening. Treatment of betaine **10** with basic alumina results in a sharp singlet for the appropriate hydrogen at τ 7.10 ($CDCl_3$). Likewise the broadened proton α to sulfur in betaine **9** appears at τ 5.70 as a sharp spike ($CDCl_3$). The presence of a fine suspension of Al_2O_3 does not prevent sharp bands with excellent ringing.

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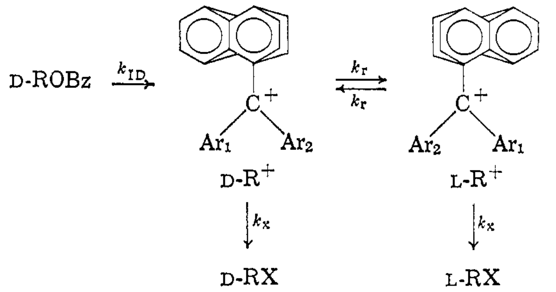
Stereochemistry of Trityl Compounds. III. Ionization–Dissociation of Phenylbiphenyl-α-naphthylmethyl Benzoate and Cation Conformational Changes[1]

Sir:

The three mechanisms proposed earlier[2] to account for stereoselective solvolysis of phenylbiphenyl-α-naphthylmethyl benzoate (ROBz) have now been distinguished in a study of the racemization of D-ROBz.

Mechanism 1 entails formation of one cation (D-R⁺) by ionization–dissociation. The substituting agent attacks only one face of D-R⁺ at a rate comparable to formation of L-R⁺ (k_r[D-R⁺]) by rotation of the naphthyl group.



(1)

Alternatively, ionization–dissociation might produce only D-R⁺, but the reagent could attack *both* faces of D-R⁺ (mechanism 2) much faster than naphthyl group rotation.

$$\begin{tikzcd}
 & & \text{D-RX} \\
\text{D-ROBz} \arrow[r, "k_{\text{ID}}"] & \text{D-R}^+ \arrow[ur, "k_x^{\text{D}}"] \arrow[dr, "k_x^{\text{L}}"'] & \\
 & & \text{L-RX}
\end{tikzcd} \tag{2}$$

Finally, both cations might be produced with subsequent attack by reagent on only one face of each enantiomeric cation (mechanism 3).

$$\begin{tikzcd}
 & \text{D-R}^+ \arrow[r, "k_x"] & \text{D-RX} \\
\text{D-ROBz} \arrow[ur, "k_1^{\text{D}}"] \arrow[dr, "k_1^{\text{L}}"'] & & \\
 & \text{L-R}^+ \arrow[r, "k_x"] & \text{L-RX}
\end{tikzcd} \tag{3}$$

Mechanism 1 can be distinguished from the other two by comparing the racemization rate (k_{rac}) of D-ROBz in the presence of *n*-Bu_4NOBz to the ionization–dissociation rate[3] (k_{ID}). In racemization, the entering and leaving groups are identical, and mechanisms 2 and 3 are indistinguishable as a result of microscopic reversibility and the requirement of equal energies of enantiomeric ion pairs. Thus, if benzoate ion attacks both faces of D-R⁺, ionization–dissociation must produce both D-R⁺ and L-R⁺.

Qualitatively, if solvolysis proceeds by mechanism 1, the rates of solvent capture of D-R⁺ (k_x) and naphthyl group rotation (k_r) must be about equal ($k_x/k_r = 0.98$) to satisfy the observed optical yield at 54° (Table I). Mass-law data require that at 1.67×10^{-2} *M* *n*-Bu_4NOBz the dissociated cation must be formed an average of 30 times before solvent capture and, therefore, before

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(1) This work was supported by National Science Foundation Grants GP 3537 and GP 6406.

(2) B. L. Murr and C. Santiago, *J. Am. Chem. Soc.*, **88**, 1826 (1966).

(3) This rate was taken as the solvolysis rate in the absence of benzoate ion corrected for salt effects.[4] The correction was 5%. In mechanisms 3 and 4, $k_{\text{ID}} = k_1^{\text{D}} + k_1^{\text{L}}$.

(4) S. Winstein and B. R. Appel, *J. Am. Chem. Soc.*, **86**, 2720 (1964).