Included in Table I are four further lines of evidence which point toward the involvement of sensitizer singlets: (1) adding 0.1 M piperylene, an effective quencher of triphenylene triplets but not singlets, does not alter the quantum yield of decomposition of **1**; (2) decreasing the concentration of **1** from 0.02 M to 0.00475 M causes the quantum yield to fall by over 50%, which is consistent with energy transfer from a short-lived excited state; (3) producing triphenylene triplets by benzophenone sensitization results in virtually no azo decomposition; and (4) using 9,10-diphenylanthracene whose fluorescence quantum yield[9] is 1.0 leads to quite efficient decomposition. The high efficiency of hydrocarbon sensitizers is best explained either by singlet energy transfer or by a mechanism wherein azo compound complexes with excited singlet sensitizer and the complex breaks up by partitioning enough energy into the azo moiety to cause decomposition.

Aromatic ketones which undergo extremely rapid intersystem crossing[10] are inefficient sensitizers for decomposition of **1**. We have found that **1** is capable of quenching the benzophenone–benzhydrol photoreduction[11] with a Stern–Volmer slope of 760. Furthermore azomethane is efficiently photoisomerized[12] by benzophenone. These observations prompt us to suggest that triplets of acyclic azo compounds undergo geometric changes rather than decomposition in solution, at least up to the highest energy sensitizer which we have tried.

In light of the ideas that hydrocarbon singlets can be important in sensitized decompositions and that the triplet of **1** does not decompose under our conditions, the data in Table I become understandable. The efficiency of sensitizers, such as anthracene, whose triplet energy lies considerably below estimates of the azo compound triplet[13] can be rationalized by involvement of the singlet instead of nonvertical triplet energy transfer. The lack of a spin correlation effect in azomethane and other cases[1,2,4] can be explained by saying that triplet-sensitized decomposition did not occur.

Our results have led us to reexamine the sensitized decomposition of 2,3-diazabicyclo[2.2.1]heptene-2 (**2**). Indeed this compound was found to be an efficient quencher of the fluorescence of triphenylene and phenanthrene[14] but not of anthracene and pyrene. Addition of 0.1 M piperylene to the triphenylene-sensitized decomposition did not alter the quantum yield. Thus sensitizer singlets apparently can be involved here also, and triphenylene and phenanthrene should not be included in the list of triplet sensitizers. Further investigation with other sensitizers continued to reveal a cutoff in quantum yield as reported,[13] though about 3 kcal lower. Singlet energy transfer is probably absent with the ketonic sensitizers used since 0.1 M piperylene reduces the quantum yield of the benzophenone-sensitized reaction of **2** by a factor of 10. Thus the behavior of **2** constrasts with that of **1** in that its triplet is exceedingly unstable toward decomposition. This may be a consequence of its ring strain and the fact that geometric changes are virtually excluded by its rigid structure. The interpretation here presented explains why a spin correlation effect was not seen in solution photolysis of acyclic azo compounds,[1,2] whereas it was readily observed in the cases of a ketenimine[1] and of rigid cyclic azo compounds.[3,5,6]

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[9] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press Inc., New York, N. Y., 1965.

[10] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[11] *Cf.* P. J. Wagner, *ibid.*, **89**, 2820 (1967), and references cited therein.

[12] R. F. Hutton and C. Steel, *ibid.*, **86**, 745 (1964).

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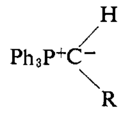
[14] The published[13] value for phenanthrene is incorrect on account of an impurity in our sample and should actually be 0.90. Zone-refined phenanthrene which was used in subsequent work does not absorb significantly at 366 mμ.

An Observation of Facile Transylidation by Nuclear Magnetic Resonance Spectroscopy

Sir:

An unusual and unexplained temperature and solvent dependency of P–C–H coupling in the nmr spectrum of an ylide has recently been reported.[1] Since temperature variation of a P–C–H coupling has no precedent or theoretical basis,[2] this problem has been reexamined, and evidence is presented which defines the source of the apparent effect and provides a rational mechanism for the process.



Ig, R = CO_2CH_3

$[Ph_3P^+CH_2R]X^-$
IIa, R = CO_2Et; $X^- = Br$
b, R = H; X = Br
c, R = Ph; X = Cl
d, R = CO_2Et; X = OH

Low-temperature nmr spectra of ylide Ig[3] (Figure 1) were taken at both 60 and 100 Mc and at each frequency $\Delta\nu = 21$ cps for the methine proton; therefore, this must be a coupling constant (the double doublet observed is the net result of hindered rotation and P–C–H coupling).[1,4] Adding D_2O to a solution of the ylide Ig in $CDCl_3$ and shaking for 5 sec result in almost complete exchange of the α proton for deuterium (Figure 1). Addition of 0.5 equiv of IIa (δ 5.42 ppm, $J_{PH} = 13$ cps) to Ig in $CDCl_3$ results in the appearance of a single extremely broad peak (25°) for the α protons of Ig and IIa (δ 4.00 ppm). Cooling this solution to $-76°$ gives for Ig a double doublet (δ 3.00 ppm, $J = 21$ cps) and a broad peak for IIa (δ 5.45 ppm, $W_{1/2} = 30$ cps). Upon heating, the broad peaks for the two types of protons merge into a single broad peak, but decomposition takes place at 110° before complete coalescence occurs ($\Delta G^{\ddagger}$ for transylidation > 17.5 kcal).

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[1] H. J. Bestmann and J. P. Snyder, *J. Am. Chem. Soc.*, **89**, 3936 (1967).

[2] J. A. Pople, W. G. Schneider, and H. J. Berstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

[3] A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 3878 (1963).

[4] H. J. Bestman, G. Joackim, T. Lengyel, J. F. M. Oth, R. Merenyi, and H. Weitkamp, *Tetrahedron Letters*, 3355 (1966).

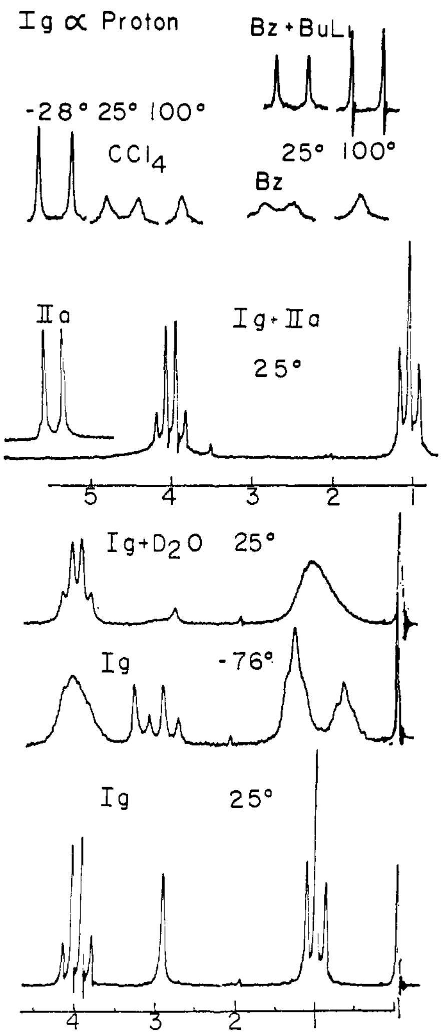

Figure 1. Nmr spectrum with $CDCl_3$ as solvent at 60 Mc; the phenyl region is not shown; insert in 1d is the methylene proton doublet for salt IIa.

Addition of either phosphonium salts IIb or IIc[5] to Ig in $CDCl_3$ gives no broadening for the α protons.

In attempting to establish the nature of this variable P–C–H coupling, Bestmann and Snyder ruled out a rapid exchange of ylide protons with a trace of conjugate acid salt.[1,6,7] Such an exchange process would be analogous to that observed for alcohols in the presence of a trace of acid. Discounting rapid exchange between Ig and its conjugate acid in $CDCl_3$ is not consistent with the above-described data. Rapid H–D exchange (half-life $\sim$<5 sec) and the nmr spectrum of a mixture of Ig and IIa in $CDCl_3$ establish that formal transylidation (1) is a rapid process at 25° (in $CDCl_3$ solvent). As expected, rapid transylidation does not occur between Ig and a phosphonium salt of relatively

$$Ph_3P^+C^-HCO_2Et \rightleftharpoons [Ph_3P^+CH_2CO_2Et]Br^- \qquad (1)$$

weak acidity (*i.e.*, IIb or IIc).[8,9]

Contrary to the results of Bestmann and Snyder, the spectra of Ig are identical in benzene, benzene-d_6, and CCl_4 (Figure 1). At 25° the methine proton appears as a broad doublet, $\Delta\nu = 21$ cps, at both 60 and 100 Mc ($J_{PH} = 21$ cps). Cooling each of these solutions below 10° allows considerable sharpening of the doublet, and heating to greater than 100° results in collapse of the doublet to a single peak. On the other hand, Ig dissolved in nitrobenzene or $CDCl_3$ shows a sharp singlet for the methine proton at room temperature, and cooling in $CDCl_3$ below $-37°$ results in the appearance of a broad doublet ($J_{PH} = 21$ cps). Thus, the spectral differences of the α proton in various solvents appear to be associated with the variation in the exchange rate as a function of the solvent dielectric constant.[12]

The presence of trace amounts of Ig conjugate acid in the ylide solutions[13] can be established by the nmr behavior upon the addition of a suitable base to Ig solutions. When *ca.* one drop of *n*-butyllithium solution (1.69 *M* in hexane) is added to Ig in either benzene, benzene-d_6, or nitrobenzene the α proton appears as a well-defined doublet in each solvent. The appearance of this doublet is also temperature independent, for heating each solution to >100° causes no change in the appearance of the doublet.

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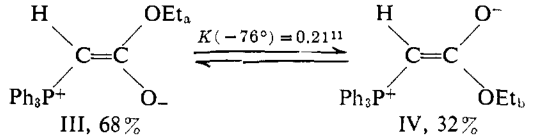
(5) O. Isler, H. Gutman, M. Montavan, R. Puezy, G. Reyser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1212 (1957) (preparation for salt IIa; salts IIb and IIc were purchased from Aldrich Chemical Co.).

(6) H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).

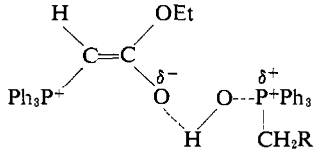
(7) H. Schmidbaur and W. Tronich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 448 (1967), have reported rapid exchange for the α protons of methylenetrimethylphosphorane in the presence of a trace of methanol.

(8) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 65–69.

(9) From a variable-temperature study it is possible to measure the coalescence temperature and calculate $\Delta G^{\ddagger}$ for *cis–trans* isomerization.[10] For Ig in $CDCl_3$ and Ig–IIa in $CDCl_3$ $\Delta G^{\ddagger}$ is 10.3 kcal/mole ($T_c = -42.5 \mp 1°$); however, when Ig in $CDCl_3$ is shaken with D_2O, $\Delta G^{\ddagger}$ becomes 13.3 kcal/mole ($T_c = 24°$). Mixing the ylide Ig in $CDCl_3$



with D_2O may cause the formation of a significant amount of phosphonium hydroxide IId, and the energy barrier to rotation may be increased as a result of hydrogen bonding.



(10) J. W. Emseley, J. Feeney, and L. H. Sutcliffe, "High resolution Nuclear Magnetic Spectroscopy," 1st ed, Pergamon Press, Inc., New York, N. Y., 1966, pp 550–560. The energies were calculated assuming equal populations; therefore, they can be taken only as approximations.

(11) Integration obtained with the aid of a Du Pont 310 curve resolver.

(12) The solvent dependency of the proton-exchange rate could be a function of the solubility of the conjugate acid contaminant. Saturation of CCl_4, C_6H_6, and C_6D_6 solutions with IIa causes no significant change for the Ig α proton and no resonance can be found for IIa alone in any of these solvents. Furthermore, the solutions of Ig were in all cases homogeneous.

(13) Ylide Ig purified according to ref 3.

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