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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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. LXXXI[1]

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 method[3] 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 counting[4] 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 technique[5–7] 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**), 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 division, the ratio, *M*, of the room temperature to the low-temperature decay rate (eq c). Here k_{dt} is the total of

$$\phi_f^{77} = k_f/k_{dt}^{77} \tag{a}$$

$$\phi_f^{RT} = k_f/k_{dt}^{RT} \tag{b}$$

$$M = \phi_f^{77}/\phi_f^{RT} = k_{dt}^{RT}/k_{dt}^{77} \tag{c}$$

excited singlet decay (*i.e.*, $k_r + k_d + k_f$). The assumption that k_f 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 $k_r = \phi_r k_{dt}$ and the reaction quantum yields are known. Table I summarizes the direct measurement of singlet lifetimes. Equations 1–5 in Chart I delineate the room temperature results using the amplified direct method, that is, employing

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 deviation, %
Naphthalene	107[b]	9.35×10^6	295	4	10
	284[c]	3.25×10^6	77	4	3
Tetraphenylethylene	1.13[d]	8.9×10^8	295	3	5
	4.36	2.4×10^8	77	3	1
Triphenyldiene **1**	0.025	4×10^{10}	295	2	~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-Tetraphenyldiene **3**	1.90	5.3×10^8	77	7	14
1,1,5,5-Tetraphenyldiene **4**	0.124	8.1×10^9	77	11	50
1,1,5,5-Tetraphenylbisnordiene **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.

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[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).

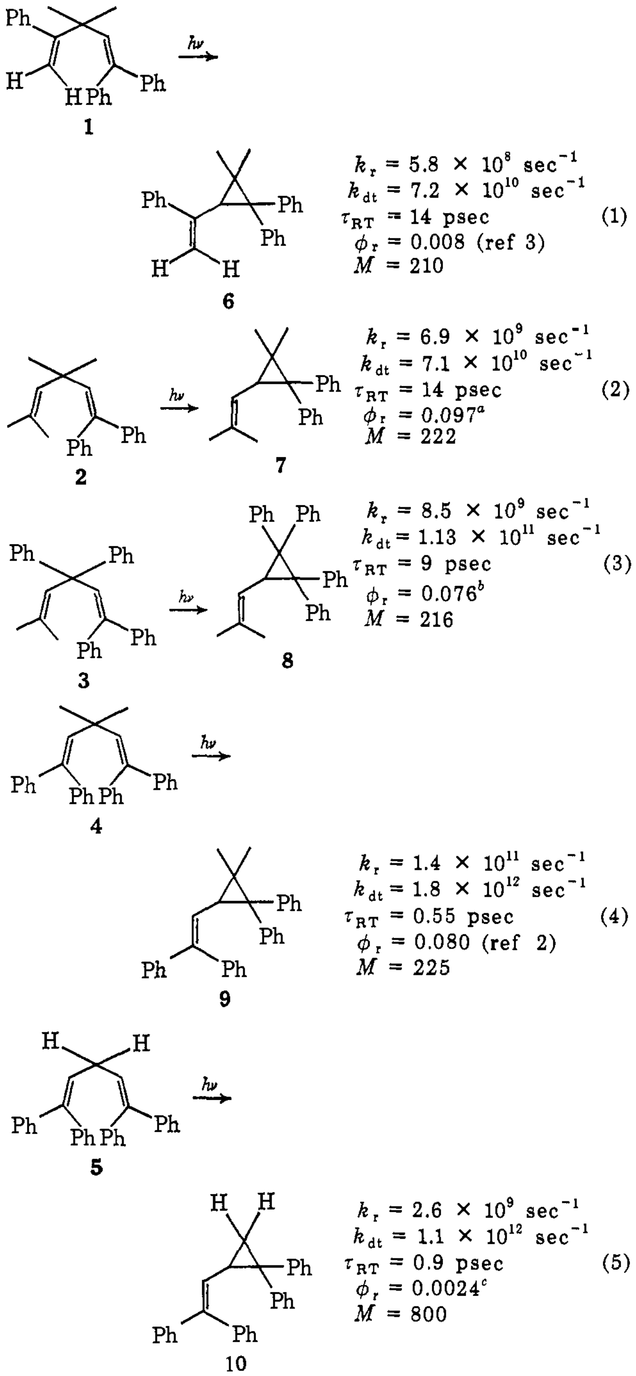
[5] Full experimental details, mathematical treatment, and elaboration of the method will be reported in our full paper.

[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).

[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).

Chart I



$$k_r = 5.8 \times 10^8 \text{ sec}^{-1} \quad k_{dt} = 7.2 \times 10^{10} \text{ sec}^{-1} \quad \tau_{RT} = 14 \text{ psec} \quad \phi_r = 0.008 \text{ (ref 3)} \quad M = 210 \qquad (1)$$

$$k_r = 6.9 \times 10^9 \text{ sec}^{-1} \quad k_{dt} = 7.1 \times 10^{10} \text{ sec}^{-1} \quad \tau_{RT} = 14 \text{ psec} \quad \phi_r = 0.097^a \quad M = 222 \qquad (2)$$

$$k_r = 8.5 \times 10^9 \text{ sec}^{-1} \quad k_{dt} = 1.13 \times 10^{11} \text{ sec}^{-1} \quad \tau_{RT} = 9 \text{ psec} \quad \phi_r = 0.076^b \quad M = 216 \qquad (3)$$

$$k_r = 1.4 \times 10^{11} \text{ sec}^{-1} \quad k_{dt} = 1.8 \times 10^{12} \text{ sec}^{-1} \quad \tau_{RT} = 0.55 \text{ psec} \quad \phi_r = 0.080 \text{ (ref 2)} \quad M = 225 \qquad (4)$$

$$k_r = 2.6 \times 10^9 \text{ sec}^{-1} \quad k_{dt} = 1.1 \times 10^{12} \text{ sec}^{-1} \quad \tau_{RT} = 0.9 \text{ psec} \quad \phi_r = 0.0024^c \quad M = 800 \qquad (5)$$

[a] H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970). [b] H. E Zimmerman, R J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973). [c] H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **95**, 2957 (1973).

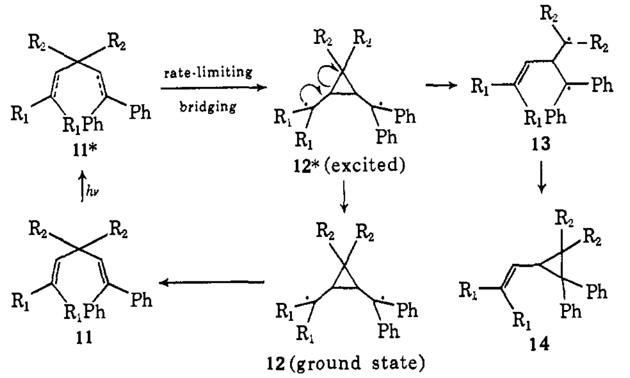
the magic multiplier.[9-11] Room temperature lifetimes of naphthalene (129 nsec *vs.* lit.[8a] 120 nsec) and tetraphenylethylene (1.07 nsec *vs.* lit.[8a] 1.1 nsec), derived using M, were used to check the method. It is seen that lifetimes of the order of 100 psec are readily measured directly and that use of the magic multiplier extends the range to *ca.* 1 psec!

Comparison of this method with the earlier indirect approach[3] reveals that the indirect method rate constants are too large by a nearly constant factor (within experimental error). This will be discussed in our full paper. Nevertheless, the previous indirect method[3,12] is convenient and excellent for relative rate constants but subject to difficulties in obtaining absolute values.

The sequence of reactivity revealed in the comparison of the singlet rates for the five reactions allows insight into the molecular details of the di-π-methane rearrangement. Thus the reactivity of the excited states of **1**, **2**, **3**, and **4** increases in this order as stabilizing terminal substitution is increased. This suggests that vinyl–vinyl bridging is rate limiting. The very similar quantum yields of tetraphenyldiene **4** and diphenyldiene **2** previously were surprising in view of the change in substitution. This quantum yield agreement is not reflected in the present rates and the tetraphenyldiene **4** is more reactive. The triphenyldiene **1** is the least reactive in terms of singlet reaction rates, and this indeed has the least terminal substitution. In the case of tetraphenyldiene **5**, lacking central substitution, the low rate constant for **5** relative to **4** accords with formation of **10** by a route less facile than the unavailable[13] di-π-methane mechanism.

Another exciting result is the nearly perfect ratio between rate of singlet decay and the rate of di-π-methane rearrangement, the exception being triphenyldiene **1**. Hence bridging is required for decay as well as reaction. Note Scheme I. We conclude that the excited state biradical undergoes the di-π-methane rearrangement competitively with decay but that the ground state counterpart merely reverts to di-π-methane reactant.

Scheme I. Qualitative Valence Bond Mechanism for the Di-π-methane Rearrangement



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(9) The estimated nonsystematic errors in M are 10% for naphthalene and tetraphenylethylene, 20% for **1–3**, 40% for **4**, and 30% for **5**. Temperature effects owing to changes in optical density[10] and refractive index proved minor (<20%) as evidenced by independent measurement of M for naphthalene and tetraphenylethylene *via* lifetimes. Polarization effects[11] were also found to be neglectable.[5]

(10) W. W. Mantulin and J. R. Huber, *Photochem. Photobiol.*, **17**, 139 (1973).

(11) M. Shinitzky, *J. Chem. Phys.*, **56**, 5979 (1972).

(12) J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971).

(13) H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **95**, 2957 (1973).

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