(3) (a) G. J. Abruscato and T. T. Tidwell, *J. Am. Chem. Soc.*, **92,** 4125 (1970); (b) D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans 1*, 1793 (1974); (c) unpublished results in our laboratory.
(4) (a) J. E. McMurry, *Acc. Chem. Res.*, **7,** 281 (1974); (b) J. E. McMurry and M. P. Flemming, *J. Am. Chem. Soc.*, **96,** 4708 (1974); (c) J. E. McMurry and M. P. Flemming, *J. Org. Chem.*, **41,** 896 (1976); (d) E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *ibid.*, **41,** 260 (1976).
(5) (a) R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975); (b) D. S. Bombse and T. H. Morton, *ibid.*, 781 (1975).
(6) H. Wynberg, K. Lammertsma, and L. A. Hulshoff, *Tetrahedron Lett.*, 3749 (1975).
(7) (a) See also W. H. Richardson and K. W. Gunderson, *J. Org. Chem.*, **41,** 2054 (1976); (b) J. Ciabattoni, E. C. Nathan, A. E. Feiring, and P. J. Kocienski, *Org. Synth.*, **54,** 97 (1975).
(8) (a) Analysis by Galbrath Laboratories, Inc., Knoxville, Tenn. (b) Spectrum was taken in hexachloroacetone, shifts from capillary TMS.
(9) (a) D. T. Dix, G. Frankel, H. A. Karnes, and M. S. Newman, *Tetrahedron Lett.*, 517 (1966); (b) A. J. M. Reuvers, A. Sinnema, T. J. Nieumstad, F. V. Rantwijk, and H. V. Bekkum, *Tetrahedron*, **27,** 3713 (1971).
(10) S. Sternhell in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackmann and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, p 170.
(11) (a) G. Binch in "Topics in Stereochemistry", Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Wiley-Interscience, New York, N.Y., 1968, pp 180, 181. (b) Calculations were performed on a Univac 1108 computer equipped with a CALCOMP plotter. $\Delta G^{\ddagger}$ was calculated from the rate constants using the Eyring equation

$$\Delta G^{\ddagger} = 4.576\,TC\,(10.319 + \log TC/K)$$

In the equation the transmission coefficient (TC) was assumed to be unity. E_a was found to be 13.07 ± 0.5 kcal/mol from a linear Arrehenious plot. $\Delta H^{\ddagger}$ and $\Delta s^{\ddagger}$ were found to be 11.68 ± 0.5 kcal/mol and −20 ± 2.0 eu, respectively. (c) ^{13}C NMR: cumene, δ_{ipso} 149.40; neopentylbenzene, δ_{ipso} 140.30. (d) O. Ermer and S. Lifson, *Tetrahedron*, **30,** 2425 (1974).
(12) (a) N. Sheppard and D. M. Simpson, *Quart. rev. Chem. Soc.*, **6,** 1 (1962); (b) D. G. Rea, *Anal. Chem.*, **32,** 1638 (1960); (c) F. h. A. Rummens, *Recl. Trav. Chim., Pays-Bas*, **84,** 5 (1965).
(13) L. J. Bellamy. "Advances in Infrared Group Frequencies", Methuen and Co., London, 1968, pp 22-26, 30-32, 132-135.
(14) S. Bank, W. D. Closson, and L. T. Hodgins, *Tetrahedron*, **24,** 381 (1968).

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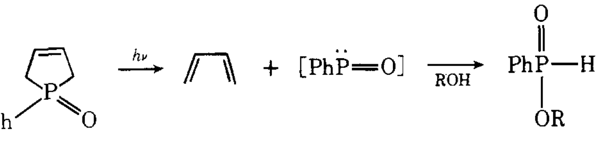
Stereochemistry and Kinetics of Photochemical Fragmentation of 1-Phenyl-3-Phospholene Oxides

Summary: The rate and stereospecificities of the novel photochemical extrusion of phosphinidene oxide from the excited singlet states of 3-phospholene oxides are shown to be sensitive to the configuration of an asymmetric leaving group, indicating that the steric influence on the transition state is substantial.

Sir: During a study of the photochemical reactions of phosphorus heterocycles,[1] we have found, upon UV irradiation, that 1-phenyl-3-phospholene oxides efficiently cleave to dienes and phenylphosphinidene oxide. In contrast to the other closely related five-membered cheletropic cycloregressions,[2,3] this formally cheletropic reaction[4] has an asymmetric leaving group and would be expected to reveal how the direction of ring opening and the rate of the reaction depend on the stereochemical disposition of the leaving group.

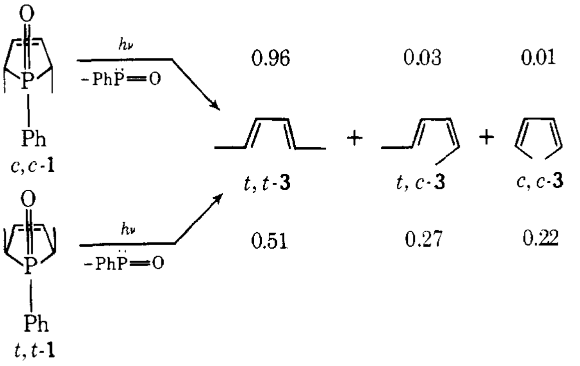


It was found that the stereochemical disposition of the leaving group exerted a substantial effect on the rate of the fragmentation. This can be explained by considering the steric influence in the transition state during bond reorganization. The all-trans isomers furnished a mixture of dienes, whereas the all-cis isomers gave predominantly the all-trans olefins. This is the first five-membered cheletropic cycloregression observed to proceed through the singlet excited state.

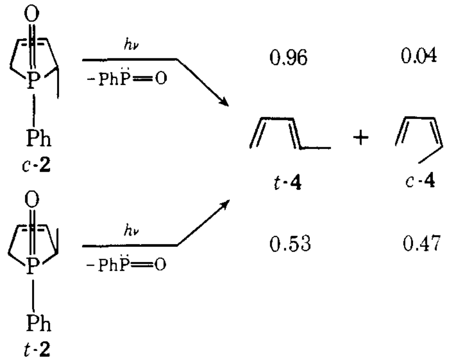
The stereoisomeric pairs of 3-phospholene oxides (**1** and **2**) were prepared according to Quin[5] and the isomers[6] were separated by silica gel chromatography followed by short-path distillation at 10^{-3} mm.

Direct irradiation of **1** and **2** with 254-nm light from a monochromator was performed in methanol containing methylcyclohexane as the internal standard. This resulted in quantitative formation of 1,3-dienes (**3** and **4**) and methyl phenylphosphinate. No photochemical cis–trans isomerization of **1** and **2** was observed even after prolonged irradiation. These phospholene oxides were thermally stable and gave no trace of dienes in refluxing diethyl phthalate (300 °C). Prolonged refluxing caused rearrangement to the 2-phospholene oxide isomer.

Irradiations were interrupted at low conversion (<2%) and yields of 1,3-diene were extrapolated to zero conversion[7] as an appropriate correction for possible sensitized diene isomerization by phospholene oxide (vide infra). The results are shown in eq 1 and 2.[8]



(1)



(2)

Quenching of the reactions 1 and 2 occurred with 1,3-dienes (e.g., 2,5-dimethyl-2,4-hexadiene) to yield linear Stern–Volmer plots. The 1,3-diene photoproduct compositions were the same as those obtained by extrapolation. Triplet sensitization[9] (benzophenone) of **1** and **2,** however, gave no detectable amount of **3** and **4.** Fluorescence quenching of **1** and **2** by 1,3-diene also occurred. The quenching gave good linear Stern–Volmer plots whose slopes are in agreement within experimental errors with those obtained in the quenching of the photochemical reactions (Table I). Unlike other closely related systems,[3] photofragmentation of the phospholene oxides proceeds via the lowest excited singlet state.

Table I. Quantum Yield, Quenching Constant, Fluorescence, and Relative Rate Data for the Photofragmentation of 1-Phenyl-3-phospholene Oxides

Compd	Φ_r[a]	$k_q\tau_r$ ($k_q\tau_f$),[b] M^{-1}	$k_f \times 10^{-6}$,[c] sec^{-1}	$\Phi_{f(rel)}$[d]	$k_{r(rel)}$[e]
3,4-Dimethyl	0.88		1.3	0.11	467
c,c-**1**	0.35	28 (25)	1.8	0.23	123
3-Methyl	0.18		1.4	0.30	37
c-**2**	0.14	23 (26)	1.5	0.26	35
t-**2**	0.031	35 (39)	1.3	0.35	5.0
t,t-**1**	0.020	36 (35)	1.7	0.91	1.7
Parent[f]	0.016		1.4	1.00	1.0

[a] The quantum yields were measured at 254 nm in methanol for the total diene production. [b] Slopes of Stern–Volmer plots for 2,5-dimethyl-2,4-hexadiene quenching of the fragmentation (r) and fluorescence (f), respectively. [c] Rate constants for fluorescence calculated from the absorption spectrum. [d] The relative intensities at the maximum (288 nm) in the fluorescence spectrum. [e] Relative rates of the fragmentation calculated from the equation $k_r/k_{r0} = \Phi_r\Phi_{f0}k_f/\Phi_{r0}\Phi_f k_{f0}$. See ref 10. [f] Unsubstituted 1-phenyl-3-phospholene oxide.

Quantum yields of the fragmentation at 254 nm were determined and are listed in Table I. Since quantum yields are not always an indication of relative rates, the relative rates[10] of the fragmentation were calculated using absorption and fluorescence data (Table I).

The lack of stereospecificity in the present reaction is reminiscent of other closely related photoextrusion reactions,[3] whereas thermal processes have been found to be stereospecific in related systems.[2] The apparent photochemical nonstereospecificity has been interpreted as a consequence of dual linear and nonlinear concerted pathways for photodecarbonylation[3a] of cyclopentenone and concerted loss of SO_2 followed by SO_2-catalyzed isomerization of the resulting dienes in the photolysis[3b] of sulfolene. The present stereochemical and kinetic results, indicating increased stereospecificity and reactivity of the cis isomers relative to the trans isomers, can be attributed to steric forces operative during the concerted bond reorganization necessary for phosphinidene oxide extrusion. As disrotatory[11] bond rotation in *c,c*-**1** would commence to give *c,c*-**3**, two methyl groups are effectively brought into close proximity to the phenyl group. The conrotatory counterpart to give *t,c*-**3** also suffers from 1,2-phenyl–hydrogen and nonbonded methyl–hydrogen interactions occurring in the rotation. Such repulsive forces, which are absent when disrotation to *t,t*-**3** is effected, are apparently sufficient to raise the energy of activation associated with rotation to *t,c*- and *c,c*-**3** to extent which permits exclusive formation of *t,t*-**3**. Similar repulsive forces also determined the mode of fragmentation of *c*-**2**, in spite of the fact that such steric demand seems to be less severe. *trans*-1,3-Pentadiene probably is formed via the disrotatory process since the alternative conrotatory pathway suffers from a concomitantly high degree of steric interaction.

The much lower degree of product specificity (*t,t*-**3**/*c,c*-**3** $\approx$ 2) from *t,t*-**1** might be explained as a steric effect superimposed on the concerted motion. Disrotatory opening to *t,t*-**3** from *t,t*-**1** suffers from substantial repulsive phenyl–hydrogen interaction, while competing disrotation to *c,c*-**3** has severe nonbonded methyl–methyl repulsion in the transition state. Consequently, conrotatory motion appears to occur as a minor process.[12]

Alternatively, one cannot exclude two-step mechanisms since such considerations can equally be applied to mechanisms involving phosphorus centered biradicals or zwitterions which retain their configuration on the time scale of the reaction.[13] The approximate 100-fold acceleration in decomposition of cis isomer of **1** relative to the trans isomer, along with the slower rate of *t,t*-**1** compared to *t*-**2**, indicates that a steric strain in the transition state for the concerted rotation is substantial. A similar configurational effect of an α-methyl group on the rate of decomposition has been observed in the concerted SO_2 extrusion from sulfolene.[2e] The larger rate enhancement by β-methylation compared to cis α-methylation in the present reaction is rather unusual since alkylation in the β position markedly reduced the rate of the thermal SO_2 extrusion[2e] by stabilizing the starting sulfolene. The rate of α cleavage to give biradicals is enhanced only by α-methylation in the photolysis[14] of cycloalkanone derivatives. It would appear that product (diene) stabilities have some influence on the transition state since emission and absorption data seem to exclude the possible destabilization of reacting excited state by β-methylation.

The present evidence is not yet conclusive as to which mechanisms are operative and further work is required to distinguish between the possibilities.

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References and Notes

(1) H. Tomioka and Y. Izawa, *Tetrahedron Lett.*, 5059 (1973); H. Tomioka, Y. Hirano, and Y. Izawa, *ibid.*, 1865 (1974).

(2) For stereochemical studies of thermal five-membered ring cheletropic reactions, see (a) S. D. McGregor and D. M. Lemal, *J. Am. Chem. Soc.*, **88,** 2858 (1966), and references cited therein; (b) W. L. Mock, *ibid.*, **88,** 2857 (1966); (c) D. M. Lemal and S. D. McGregor, *ibid.*, **88,** 1335 (1966); (d) J. E. Baldwin, *Can. J. Chem.*, **44,** 2051 (1966). (e) W. L. Mock, *J. Am. Chem. Soc.*, **97,** 3666, 3673 (1975), and references therein.

(3) For photochemical five-membered-ring cheletropic reactions, see (a) J. Saltiel and L. Metts, *J. Am. Chem. Soc.*, **89,** 2232 (1967); (b) T. R. Darling, J. Pouliquen, and N. J. Turro, *ibid.*, **96,** 1247 (1974).

(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.

(5) L. D. Quin and T. P. Barket, *J. Am. Chem. Soc.*, **92,** 4303 (1970).

(6) Configurational assignments for the isomeric 3-phospholene oxides are based on the NMR spectra.

(7) Aliquots were removed at 1-min intervals and analyzed by GLC on a 3-m column packed with 10% β,β'-oxydipropionitrile on Diasolid L at 32 °C.

(8) The symbols *c* and *t* in **1** and **2** refer to the cis and trans orientation of phenyl with respect to the methyl(s).

(9) That energy transfer occurred was indicated by the observation of quenching of photoreduction of benzophenone in isopropyl alcohol by **1** and **2.**

(10) S. S. Hixon, *J. Am. Chem. Soc.*, **94,** 2507 (1972).

(11) We could not use the label "linear" or "nonlinear" in this reaction since we do not know the exact nature of the reacting excited state at present.

(12) Other explanation for the difference in the stereochemical results between trans and cis isomers might involve a consideration of conformational ef-

fects. With the all-cis compound, the ground state is already distorted with all carbon substituents in pseudoequatorial position, owing to the Me–Ph nonbonded repulsion along a pathway which could lead to *t,t*-diene. The trans isomer, on the other hand, should exist as two rapidly equilibrating envelope conformers leading to *t,t*- and *c,c*-dienes since there is no such steric demand. We thank referee for drawing our attention on this point.

(13) The fact that even a rather long-lived intermediate can possess sufficient stereochemical integrity has been shown in the SO–diene cycloaddition; see P. Chao and D. M. Lemal, *J. Am. Chem. Soc.*, **95,** 920, 922 (1973).

(14) (a) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Am. Chem. Soc.*, **93,** 7213 (1971); (b) P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *ibid.*, **96,** 924 (1974).

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