

Substitution of all chlorine atoms by dimethylamino groups is essentially quantitative, and assuming that this substitution at each phosphorus atom proceeds by the same mechanism, the configurations of the derived dimethylamides will be the same as those of the chloro compounds, regardless of whether the amination takes place with or without inversion.

It can be seen that each dimethylamino group in the derivatives of isomers I, III, and IV is in a single magnetic environment, although the environment is different for each of the three isomers. Consequently, the proton n.m.r. spectrum of each of these three dimethylamides would be expected to show a single methyl absorption.

On the other hand, in the dimethylamide of isomer II, there are three distinctly different magnetic environments for the dimethylamino groups. Two of these dimethylamino groups are in the same environment, while the other two are in second and third environments. Thus the proton n.m.r. spectrum of this dimethylamide would be expected to show three methyl absorptions having an area ratio of 2:1:1.

It is well known that the tetrameric phosphonitrilic ring in the solid state is not planar, but rather is puckered. $(\text{PNCl}_2)_4$ exists in the boat form,⁵ and $(\text{PNF}_2)_4$ in the chair form.⁶ On the other hand, in solution $(\text{PNCl}_2)_4$ is planar.⁷

If discrete chair or boat forms of the tetrameric phenylphosphonitrilic chlorides exist in solution, then the proton n.m.r. spectra of the derived tetrakisdimethylamides would be expected to show a multiplicity of absorptions, and the more simple arguments given above would not be valid.

Experimentally we have found that the proton n.m.r. spectrum of the tetrakisdimethylamide B, melting at 136–138°, in carbon tetrachloride solution does exhibit three methyl absorptions. Each methyl absorption consists of a doublet having additional structure between the two peaks. Two of these doublets overlap and have not as yet been separated. The ratio of the area of these three doublets is approximately 2:1:1, and the ratio of the area of the two overlapping doublets to that of the separate doublet is approximately 3:1.

Further, dimethylamination of the mixture of tetrameric phosphonitrilic chlorides, m.p. 248–254°, followed by careful recrystallization of the products, has given compound B, m.p. 136–138°, and still a third tetrakisdimethylamide (C), m.p. 176–178°. *Anal.* Calcd. for $\text{C}_{32}\text{H}_{44}\text{N}_8\text{P}_4$: C, 57.80; H, 6.68; N, 16.86. Found: C, 57.65; H, 7.03; N, 16.52. The proton n.m.r. spectra of compounds A and C in carbon tetrachloride solution both show a single methyl absorption, each having a different chemical shift. This indicates that compounds A and C are derivatives of a different one of the isomers I, III, or IV. These n.m.r. data confirm the identity of compound B as *cis*-2,4,6-*trans*-8-tetrakisdimethylamino-*trans*-2,4,6-*cis*-8-tetraphenyl-1,3,5,7,2,4,6,8-tetrazatetraphosphocine. The corresponding chloro isomer, melting at 148–150.5°, thus is identified as *cis*-2,4,6-*trans*-8-tetrachloro-*trans*-2,4,6-*cis*-8-tetraphenyl-1,3,5,7,2,4,6,8-tetrazatetraphosphocine.⁸

(5) J. A. A. Ketelaar and T. A. deVries, *Rec. trav. chim.*, **58**, 1081 (1939).

(6) N. L. Paddock, *Endavour*, **19**, 137 (1960).

(7) L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).

(8) A. M. Patterson, L. T. Capell, and D. Walker, "The Ring Index," 2nd Ed., Supplement I, American Chemical Society, Washington, D. C., 1963, p. 8.

In addition, the n.m.r. data are interpreted as evidence that, if chair and boat forms of the tetrameric phenylphosphonitrilic ring do exist in solution, they are rapidly interconverting. The simplest tetrakisdimethylamide chair or boat isomer would be expected to have a proton n.m.r. spectrum exhibiting two methyl doublets, whereas two isomeric tetrakisdimethylamides have been isolated, each having only a single methyl doublet.

Finally, if chair and boat forms of compound B are present and are not rapidly interconverting in solution, the proton n.m.r. spectrum would be expected to be considerably more complex.

Low temperature n.m.r. studies are in progress to investigate the conformation of the ring. Work is also continuing to separate and identify the other isomers of $(\text{C}_6\text{H}_5\text{PNCl})_4$ and their derivatives. Detailed results will be reported separately.

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The Effect of Viscosity on the Internal Deactivation Modes of the Triplet State¹

Sir:

In a study concerning the effects of temperature and viscosity on the unimolecular deactivation modes of the triplet state, we have observed an interesting and unique result: the decrease of the rate constant, k_0 , of the radiative process with increasing viscosity. Phosphorescence from fluid solution has been previously observed.^{2,3} We have measured both lifetimes and relative quantum yields of phosphorescence for palladium(II) mesoporphyrin IX dimethyl ester dissolved in methyl phthalylethylglycolate over the temperature range 0 to -150° . Between 20 and -45° , the solvent, methyl phthalylethylglycolate, undergoes a viscosity change of 10^2 to 10^3 cp.; at $\approx -50^\circ$ a meniscus appears, indicating the formation of a rigid system. Extreme care has been employed to eliminate oxygen (the partial pressure was reduced to less than 10^{-5} mm.) and other quenching impurities from the solutions.

In order to eliminate the effects of concentration quenching, measurements were made at several different concentrations and the data extrapolated to infinite dilution.

Figure 1 shows the variation of the lifetime of the decay of the triplet state with the temperature of the solution at infinite dilution, as well as the variation of the relative quantum yield of phosphorescence with temperature for a 10^{-4} M solution. Measurement of

(1) Taken in part from a dissertation by S. J. Ladner, to be submitted to the faculty of the Department of Chemistry, University of Houston, in partial fulfillment of the requirements for the Ph.D. degree.

(2) R. S. Becker and S. J. Ladner, unpublished work, 1960.

(3) C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **66**, 2506 (1962).

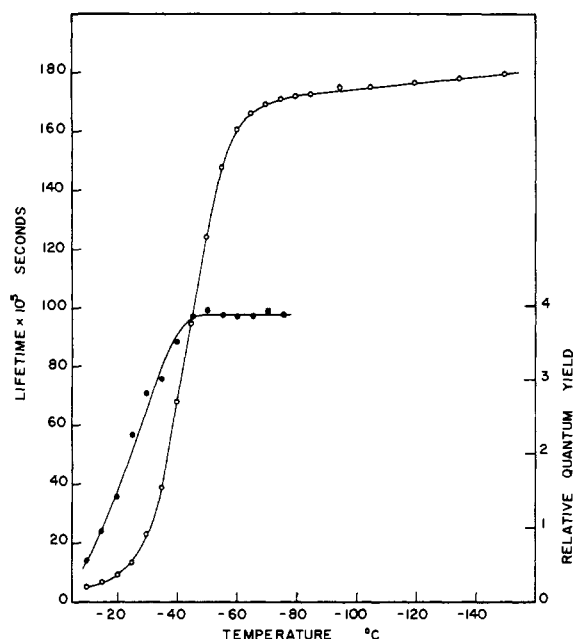


Fig. 1.—Intrinsic lifetime at infinite dilution and relative quantum yield for the decay of the triplet state of palladium(II) mesoporphyrin IX dimethyl ester vs. temperature.

the relative quantum yield at a different concentration and by a *different method* has yielded a parallel result, including the temperature at which the quantum yield levels off. Figure 1 shows that at approximately -50° the relative quantum yield becomes constant, while the lifetime continues to increase rapidly until about -80° , where it levels off to a slow rise. The interpretation of this result allows the conclusion stated at the beginning.

Palladium porphyrin exhibits a totally phosphorescent emission.⁴ The rate constants for fluorescence and internal degradation from the singlet state, k_F and k_{ID} , are known to be relatively small compared to the rate constant for intersystem crossing, k_i .⁴ Thus, the expression for the relative quantum yield can be written

$$\phi_p = K \left(\frac{k_i}{k_F + k_{ID} + k_i} \right) \left(\frac{k_1}{k_0 + k_1} \right) = K' \left(\frac{k_0}{k_0 + k_1} \right) \quad (1)$$

where k_0 is the rate constant for the radiative process, phosphorescence, k_1 is the rate constant for internal conversion from the triplet state, and K and K' are constants. The ratio $k_i/(k_F + k_{ID} + k_i)$ is considered to be constant, since k_F and k_{ID} are small compared to k_i . Any change in these constants large enough to affect the ratio detectably would have been detected experimentally, such as the observation of fluorescence which, in fact, was not detected. Since the lifetime, τ , equals $1/(k_0 + k_1)$, we may write

$$\phi_p = K' k_0 \tau \quad (2)$$

If, for the sake of argument, trivial, pseudo-first-order quenching by a trace impurity, Q , was occurring, as has been shown to be quite frequent by Helpfern, Porter, and Stief⁵ and Livingston and Ware,⁶ the term

(4) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2662 (1963).

(5) J. W. Helpfern, G. Porter, and L. J. Stief, *Proc. Roy. Soc. (London)*, **A227**, 437 (1964).

(6) R. Livingston and R. W. Ware, *J. Chem. Phys.*, **39**, 2593 (1963).

$(k_0 + k_1)$ in the above expressions would be replaced by $(k_0 + k_1 + k_d[Q])$. However, the form of eq. 2 would remain the same. This situation is unlikely, though, since a simple calculation, employing the Debye expression to obtain a value for k_d (the rate constant for a diffusionally limited bimolecular process), suggests that a concentration of 0.3 mole/l. of a quenching agent, capable of unit encounter efficiency, would be necessary to account for the data.

Reference to eq. 2 shows that for ϕ_p to remain constant while τ increases, k_0 must decrease. Moreover, for ϕ_p to be exactly constant, k_1 must be zero or decrease according to the expression $k_1 = Ck_0$ where C is a constant equal to ϕ_1/ϕ_p and ϕ_1 is the quantum yield for internal conversion. In any event, k_0 must be large relative to k_1 and decrease with increasing viscosity and decreasing temperature.

The implications of these results are important for two reasons: (1) they provide strong evidence that viscosity change has a significant effect on the true unimolecular deactivation modes; and (2) they may, upon further examination, shed new light on the problem of the nature of the mechanism involved in internal degradation of the triplet state. These considerations will be discussed more thoroughly along with presentation and discussion of additional results in a forthcoming publication.

(7) NASA trainee, Sept., 1963 to Sept., 1964.

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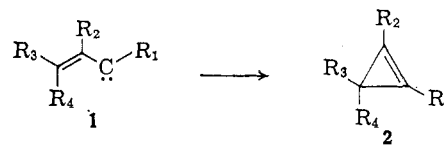
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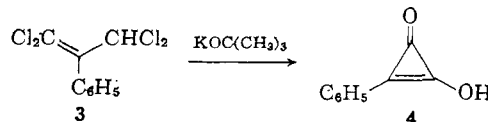
α -Elimination in 2-Phenyltetrachloropropene. Synthesis of Phenylhydrocyclopropenone

Sir:

The concept of the rearrangement of a vinyl carbene to a cyclopropene has been applied with great success by Closs to the synthesis of a number of cyclopropenes.¹



We wish to describe the synthesis of phenylhydrocyclopropenone (4) by the conceptually related reaction of 2-phenyltetrachloropropene (3) with potassium *t*-butylate.



Thus, 3² (m.p. 45–46°, lit. m.p. 45–46°; n.m.r., τ (CCl₄) 2.6 and 2.9, area ratios 5:1) dissolved in dry ether was added dropwise to a rapidly stirred slurry of potassium *t*-butylate (4 molar equiv.) in ether, maintained at

(1) G. I. Closs, I. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(2) Ch. Granacher, E. Usteri, and M. Gieger, *Helv. Chim. Acta*, **32**, 703 (1949). In the preparation of the precursor 1,1,2,3,3-pentachloro-2-phenylpropane, we found it necessary to stir the crude product in carbon tetrachloride with additional aluminum chloride (1.1 equiv.) at room temperature for 2 hr. in order to complete conversion of the alcohol to the chloride.