

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 Helpen, 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. Helpen, 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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF HOUSTON
HOUSTON, TEXAS

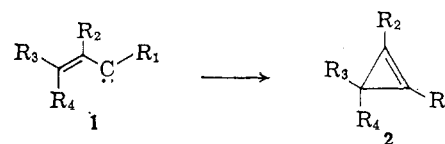
S. JULES LADNER⁷
RALPH S. BECKER

RECEIVED AUGUST 27, 1964

α -Elimination in 2-Phenyltetrachloropropene. Synthesis of Phenylhydroxycyclopropenone

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 phenylhydroxycyclopropenone (4) by the conceptually related reaction of 2-phenyltetrachloropropene (3) with potassium *t*-butylate.



Thus, **3**² (m.p. $45-46^{\circ}$, lit. m.p. $45-46^{\circ}$; n.m.r., τ (CCl_4) 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. L. Closs, L. 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.

-10° . After further stirring at room temperature for 21 hr., the solids were removed by centrifugation and washed with pentane. Work-up of the liquid fraction afforded recovered starting material (11%), and, after treatment with dry HCl in ether at -20° , a low yield of phenylpyruvic acid (m.p. $147-150^{\circ}$, lit. m.p. $151-154^{\circ}$).³ The infrared spectrum of this substance exhibited peaks corresponding to those recorded for phenylpyruvic acid.

The solids were dissolved in dilute hydrochloric acid and extracted with ether. Concentration afforded 4 as a crystalline precipitate (10%). Evaporation of the filtrate and sublimation afforded phenylpropionic acid (m.p. $133-135^{\circ}$, lit. m.p. $133-135^{\circ}$; infrared, 3.4, 4.5, 5.9, 13.25, and $14.6 \mu^4$; n.m.r., $\tau -2.2$, multiplet at 2.6, area 1:5.2) in 11% yield.

Phenylhydroxycyclopropanone (C, 73.97; H, 3.96; neut. equiv. 147) was obtained as faint yellow needles, m.p. $244-245^{\circ}$ dec. with gas evolution at 250° , by recrystallization from acetonitrile. Although the acid appeared to be an associate dimer in dioxane (osmometric mol. wt. 274, calcd. 292), its sodium salt in water was monomeric and dissociated (osmometric mol. wt. 80, calcd. for monomer 84, for dimer 112). The compound is slightly soluble in water and soluble in methanol, aqueous sodium bicarbonate, and 12 *N* hydrochloric acid. It decolorized bromine and permanganate, reduced silver nitrate, and gave a positive test with ferric chloride and periodic acid. The ultraviolet spectrum exhibited absorption at 248 $m\mu$ in strong acid and 256 $m\mu$ in strong base, with a pK value of approximately 1. The infrared spectrum (KBr pellet) was disturbingly amorphous, undulating from 3 to 11 μ with rounded peaks or shoulders at 4, 5.4, 6.2, and 7.2 μ and strong peaks at 13.0 and 14.5 μ . The n.m.r. spectrum in dimethyl sulfoxide exhibited a sharp singlet at $\tau -0.1$ and a broadened singlet at $\tau 2.6$ in area ratios of 1.1 to 5. The structure (4) seems to be the only reasonable isomer of phenylpropionic acid consistent with all these facts.

The several rearranged products obtained in the reaction of olefin 3 with potassium *t*-butylate find an attractive explanation in the formation of a cyclopropane such as 2 ($R_1, R_3, R_4 = Cl$ or $(CH_3)_3CO$, $R_2 = C_6H_5$) by α -elimination and ring closure, conveniently abstracted as the rearrangement 1 ($R_1, R_3, R_4 = Cl$ or $(CH_3)_3CO$; $R_2 = C_6H_5$) to 2. Ring openings of halogenated and alkoxyated cyclopropanes in the presence of alkoxide to give olefinic and acetylenic esters have been reported in the literature.^{5,6} In fact, in a very closely related study, McElvain⁶ observed the ring opening of cyclopropane 2 ($R_1 = Cl$, $R_2 = C_6H_5$, $R_3 = R_4 = CH_3O$) with alkoxides to give esters of phenylpropionic acid and α -alkoxycinnamic acids. Apparently, their conditions of reaction and work-up were such that 4 was either not formed or not isolated.

The reactions of other polyhalopropenes with potassium *t*-butylate are under investigation. For example, 1,1,2,3,3-pentachloropropene (or tetrachloroallene) with excess potassium *t*-butylate in ether at -20° gives much

the same mixture of olefinic *t*-butyl esters as obtained from the reaction of tetrachlorocyclopropane with potassium *t*-butylate (cf. ref. 5).

Acknowledgment.—This work was supported by the Petroleum Research Fund (Grant 742A4).

- (7) Fellow of the Alfred P. Sloan Foundation.
(8) Fellow of the Danforth Foundation.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

DONALD G. FARNUM⁷
PAUL E. THURSTON⁸

The Helix Interruption Constant for Poly-L-glutamic Acid from the Pressure Dependence of Optical Rotation

Sir:

The cooperative nature of the helix-coil equilibrium in polypeptides leads one to expect the position of the equilibrium to be unusually sensitive to changes in conditions imposed on the system. No studies of the effects of applied pressure on the equilibrium have been reported, although the occurrence of volume changes^{1,2} in the helix-coil transformation suggests that such effects should be observable. We wish to report the first results of such a study and to show that the effect yields new information about the nature of the equilibrium. Poly-L-glutamic acid (PGA) was chosen for this study because sufficient data exist to determine its helix interruption constant and other thermodynamic quantities.

Changes in helix content were followed by optical rotation measurements, using a Rudolph spectropolarimeter, Model 80AQ6, whose detection system was modified to give routine reproducibility to 0.001° . The solution was contained in a specially constructed, water-jacketed, stainless steel polarimeter tube of 1-dm. length. "Zero-stress-optical" glass³ disks 8 mm. thick were used for windows. These windows exhibited no change in blank rotations under pressures up to 130 atm., which were supplied by a tank of compressed helium.

A 2% solution of PGA (Pilot Chemicals Lot G-34, degree of polymerization = 520, as determined from intrinsic viscosity) was prepared in 0.2 *M* NaCl. The pH was adjusted between 4.5 and 9.0 by addition of concentrated NaOH or HCl in order to vary the helix content or fraction of hydrogen bonds formed, *f*. The Moffitt parameter⁴ b_0 was determined at atmospheric pressure from the rotatory dispersion between 400 and 600 $m\mu$, and *f* was calculated as $-b_0/625$. The pressure derivative $(\partial f/\partial P)_T$ was obtained from the change in specific rotation with pressure, using the correlation of rotation with helix content.⁴ For this purpose, rotations were measured at 546 and/or 436 $m\mu$, the results for $(\partial f/\partial P)_T$ being the same within experimental error at both wave lengths. The calculation required a correction (amounting to about 6% near the center of the transition) for a pressure dependence of the rotation of the random coil, as determined on a solution at pH 9. No such correction was necessary for the helix rotation, as the latter was found to be independent of pressure in an experiment using dioxane-water (1:2 by volume)

(3) M. Josien, M. L. Jousset-Dubion, and J. Vizet, *Bull. soc. chim. France*, 1148 (1957).

(4) Cf. Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1959.

(5) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 56 (1964).

(6) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959).

(1) W. Kauzmann, *Biochim. Biophys. Acta*, **28**, 87 (1958).

(2) H. Noguchi and J. T. Yang, *Biopolymers*, **1**, 359 (1963).

(3) Type DEDF 845236 supplied by Chance-Pilkington Optical Works, St. Asaph, Flintshire, Great Britain.

(4) See, for example, P. Urnes and P. Doty, *Advan. Protein Chem.*, **16**, 401 (1961).