

Kinetics of Thermal Interconversion between *cis,cis*-1,3,5-Octatriene, *cis,cis,cis*-2,4,6-Octatriene, and *cis,cis,trans*-2,4,6-Octatriene

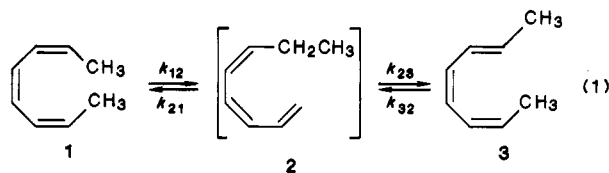
John E. Baldwin* and V. Prakash Reddy

Department of Chemistry, Syracuse University, Syracuse, New York 13244

Received July 27, 1987

The thermal equilibration between *cis,cis,cis* and *cis,cis,trans* isomers of 2,4,6-octatriene at 111 °C occurs both by an indirect route, with *cis,cis*-1,3,5-octatriene as reactive intermediate, and by a direct path.

In some of the earliest and most influential quantitative kinetic and stereochemical work related to thermal electrocyclic isomerizations of 1,3,5-hexatrienes to 1,3-cyclohexadienes, two groups reported in 1965 that the *trans,cis,trans* isomer of 2,4,6-octatriene gave *cis*-5,6-dimethylcyclohexa-1,3-diene with high stereoselectivity, reflecting the disrotatory course of this allowed pericyclic conversion.^{1,2} The *cis,cis,cis* and *cis,cis,trans* isomers, however, interconverted with one another so rapidly that they could not be used to gain sure stereochemical evidence on the slower electrocyclic reactions.³ Marvell and co-workers⁴ postulated that this facile reversible isomerization between *cis,cis,cis*- and *cis,cis,trans*-trienes 1 and 3 occurred through [1,7] sigmatropic hydrogen shifts and an unstable, undetectable intermediate, *cis,cis*-1,3,5-octatriene (2).



The hypothetical intermediate 2 was prepared in 1975 by Jaenicke and Seferiadis;⁵ it was characterized by ultraviolet and infrared spectroscopy and by mass spectrometry. The triene 2 proved relatively unstable, and no study of its thermal chemistry was undertaken.⁵

An interest in the multifarious thermal chemistry of trienes has led us to a critical reconsideration of the

isomerization 1 \rightleftharpoons 3. That reactive intermediate 2 may be involved was viewed as a plausible hypothesis that ought to be tested as a qualitative and quantitatively sufficient proposition. Triene 2 has been synthesized and found to be amenable to quantitative kinetic studies at temperatures compatible with measurements of the 1 \rightleftharpoons 3 process. Triene 2 does indeed form as a reactive intermediate in the interconversion of 1 and 3 at 111 °C, as suggested by Marvell and co-workers,^{1,4} but the isomerization 1 \rightleftharpoons 3 also occurs directly, without intervention of intermediate 2.

Results

Syntheses. *cis,cis*-1,3,5-Octatriene (2) was prepared from *cis*-1,3-hexadien-5-yne⁶ through alkylation of the derived sodium salt with ethyl bromide, followed by reduction either with zinc dust and potassium cyanide in water/methanol⁷ or with hydrogen over Lindlar catalyst.⁸ Isolation of pure material by preparative gas chromatography was not achieved, for temperatures required for volatilization and elution through packed columns caused substantial thermal degradation of 2. A combination of flash chromatography and HPLC procedures did give solutions of isomerically pure 2 in 2-methylpentane or mixtures of 2 and *trans,cis*-1,3,5-octatriene suitable for kinetic studies.

The 2,4,6-trienes 1 and 3 were secured following ample literature precedent^{1,2,4,9} and could be purified by prepa-

(1) Marvell, E. N.; Caple, G.; Schatz, B. *Tetrahedron Lett.* 1965, 385-389.

(2) Vogel, E.; Grimme, W.; Dinné, E. *Tetrahedron Lett.* 1965, 391-395.

(3) Pace Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Structure and Mechanism*, 2nd ed.; Plenum: New York, 1984; Part A, p 532.

(4) Marvell, E. N.; Caple, G.; Schatz, B.; Pippin, W. *Tetrahedron* 1973 29, 3781-3789.

(5) Jaenicke, L.; Seferiadis, K. *Chem. Ber.* 1975, 108, 225-232.

(6) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: New York, 1971; pp 131, 132. Sondheimer, F.; Ben-Efraim, D. A.; Gaoni, Y. *J. Am. Chem. Soc.* 1961, 83, 1682-1685. Ben-Efraim, D. A.; Sondheimer, F. *Tetrahedron* 1965, 25, 2837-2843.

(7) Naf, F.; Decorzant, R.; Thommen, W.; Willhalm, B.; Ohloff, G. *Helv. Chim. Acta* 1975, 58, 1016-1037.

(8) Baldwin, J. E.; Reddy, V. P. *J. Am. Chem. Soc.* 1987, 109, 8051-8056.

(9) Kim, J. H.; Thornton, E. R. *J. Am. Chem. Soc.* 1975, 97, 1865-1871. Rennekamp, M. E.; Hoffman, M. K. *Org. Mass Spectrom.* 1975, 10, 1075-1083. Schuster, D. I.; Wang, L.; Van der Veen, J. M. *J. Am. Chem. Soc.* 1985, 107, 7043-7053.

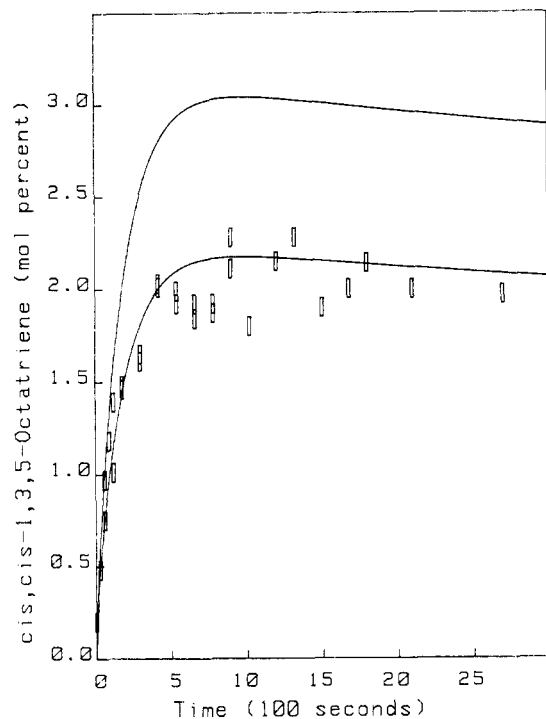


Figure 1. Formation of *cis,cis*-1,3,5-octatriene (2) from *cis,cis*-2,4,6-octatriene (1) at 111 °C: 29 experimental points from separate sealed-tube runs (rectangles) and theoretical profiles for [2(t)] with $k_{13} = 0$ (upper line) and $k_{13} = 0.4 \times 10^{-4} \text{ s}^{-1}$ (lower line).

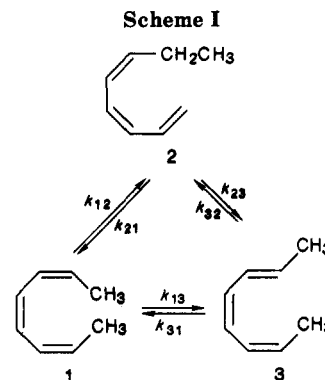
rative gas chromatography without difficulty.

Kinetics. Thermal interconversion of 1 and 3 in dilute dodecane solutions at 111 °C was followed from either isomer, using fused silica capillary column gas chromatography as the analytical method. Considered as a two-component, reversible first-order isomerization (eq 2), a



standard treatment of the interconversion, with $K = [3]/[1]$ at equilibrium and concentrations expressed as mole fractions, shows that for kinetic runs starting with 1 a plot of $\ln([1](1+K) - 1)$ against time should be linear, with slope equal to $-(k_1 + k_2)$; for runs starting with 3, a plot of $\ln([3](1+K) - K)$ should be linear and have the same slope.¹⁰ At 111 °C, values of $(k_1 + k_2)$ determined accordingly from four kinetic runs, three starting from the *cis,cis* isomer 1 and one from the more stable isomer 3, were 1.57×10^{-4} , 1.60×10^{-4} , 1.64×10^{-4} , and $1.58 \times 10^{-4} \text{ s}^{-1}$; each run had 8–12 points and was followed to between two and three half-lives. At equilibrium at 111 °C, $[3]:[1] = 86:14$, corresponding to $K = 6.14$. With $(k_1 + k_2) = (1.60 \pm 0.03) \times 10^{-4}$, $k_1 = (1.38 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$ and $k_2 = (0.22 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$.

The growth of [2] to a low steady-state level in reaction mixtures derived from isomer 1 was followed by gas chromatography. The component identified as 2 through retention time comparisons on two capillary columns of differing polarity and through GC/MS comparisons with an authentic sample built up rapidly, reaching a maximum concentration of about 2% at approximately 10^3 s ($\sim 17 \text{ min}$). Figure 1 shows the experimentally defined concentrations of 2 in mixtures of 1, 2, and 3 as rectangular data points. The mole fractions of the three trienes at time = 0 were 0.939, 0.002, and 0.059, respectively.



Data Reduction. Recognition that there could theoretically be a direct, kinetically competitive path between isomers 1 and 3, as well as interconversion by way of 1,3,5-octatriene 2 as reactive intermediate, prompts consideration of the kinetic situation summarized in Scheme I. This framework for analysis includes the simpler case of eq 1; it presupposes nothing about the relative magnitudes of the six rate constants.

From the differential equations appropriate to Scheme I and application of the steady-state hypothesis to triene 2, it is easy to show that

$$d[1]/dt = -(k_{13} + k_{12}k_{23}/(k_{21} + k_{23}))[1] + (k_{31} + k_{32}k_{21}/(k_{21} + k_{23}))[3] \quad (3)$$

The relationships of eq 4 and 5 follow.

$$k_1 = k_{13} + k_{12}k_{23}/(k_{21} + k_{23}) \quad (4)$$

$$k_2 = k_{31} + k_{32}k_{21}/(k_{21} + k_{23}) \quad (5)$$

Earlier work⁸ associated with a study of primary and secondary deuterium kinetic isotope effects on [1,7] hydrogen shifts provides values of k_{21} and k_{23} at 111 °C; $k_{21} = (9.3 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$ and $k_{23} = (42.1 \pm 1.5) \times 10^{-4} \text{ s}^{-1}$. One is left then with a single independent variable, since microscopic reversibility requires that $k_{12}k_{23}k_{31} = k_{21}k_{13}k_{32}$. For any selected value of k_{13} , the consistent set of values for k_{12} , k_{31} , and k_{32} may be easily deduced, and the concentration versus time dependence of the isomer set 1, 2, and 3 may be calculated exactly from the known integrated rate expressions.^{11,12} There is, then, only one variable to be set so as to best match the experimental concentration profile shown in Figure 1.

For the simple kinetic situation of eq 1, which is identical with Scheme I when $k_{13} = k_{31} = 0$, the theoretical profile of [2] as a function of time calculated with the aid of a programmable calculator or a computer program is shown as the upper line in the figure: when $k_{13} = 0$, [2] is predicted to rise to a maximum of just over 3% in about 10^3 s , then decline gradually, maintaining a steady-state concentration. While this theoretical plot approximates reasonably well the general shape of the experimentally defined [2] versus time dependence, it fails to get the scale right: it badly overestimates the maximum concentration of 2.

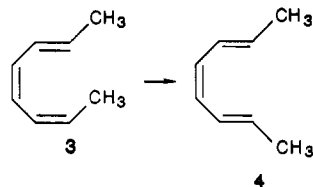
Theory and experiment may be brought into agreement by including a direct path between 1 and 3. With $k_{13} =$

(11) Szabó, Z. G. In *Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1969; Vol. 2, pp 1–80.

(12) For related kinetic analyses, see: Swain, C. G. *J. Am. Chem. Soc.* 1944, 66, 1696–1700. Alberty, R. A.; Miller, W. G. *J. Chem. Phys.* 1957, 26, 1231–1237. Kallo, D.; Schay, G. *Acta Chim. Acad. Sci. Hung.* 1963, 39, 183–211. Hijazi, N. H.; Laidler, K. J. *J. Chem. Soc., Faraday Trans.* 1972, 1235–1242. Jakeš, J.; Štokr, J.; Elkwil, S. R.; Schneider, B. *Collect. Czech. Chem. Commun.* 1978, 43, 2142–2153.

$0.40 \times 10^{-4} \text{ s}^{-1}$, for instance, and thus $k_{12} = 1.20$, $k_{32} = 0.87$, and $k_{31} = 0.064$, all $\times 10^{-4} \text{ s}^{-1}$, the second, lower theoretical [2] versus time profile of Figure 1 results. The steep rise is reproduced again, and the maximum and steady-state levels of [2] are much more closely approximated.

trans,cis,trans-2,4,6-Octatriene. When analysis suggested a direct path $1 \rightarrow 3$ the possibility that *trans*-, *cis*-, *trans*-, 2,4,6-octatriene (4) might form from triene 3 under the reaction conditions became an issue. An au-



thentic sample was prepared, its gas chromatographic retention times on two capillary columns were determined, and the chromatograms recorded for the isomerization of 3 to the equilibrium mixture of 1, 2, and 3 were reexamined.

A sample of 3 heated at 111 °C for 14 h gave nearly equilibrium proportions of 1, 2, and 3, as well as *trans*-, *cis*-, *trans*-, 2,4,6-octatriene (4) (22% of mixture of the four trienes).

Discussion

The mobile equilibrium between 1 and 3 was assumed by Marvell and co-workers^{1,4} to involve [1,7] hydrogen shifts leading to and from *cis*-, *cis*-, 1,3,5-octatriene as an intermediate (eq 1). Neither direct nor indirect evidence for this intermediate was adduced: it was not detected by gas chromatography, nor was 5-ethylcyclohexa-1,3-diene formed in reaction product mixtures.^{1,4}

Thanks to the advent of higher resolution capillary gas chromatography, the hypothetical reaction intermediate 2 has now been conclusively detected and identified, and kinetic studies of its formation as 1 and 3 interconvert have demonstrated that it is involved in the major, but not the exclusive, pathway linking 1 and 3. The hypothesis of Marvell and co-workers is thus unambiguously confirmed as a qualitative proposition, and a second reaction path has been implicated.

The thermal *cis*-*trans* interconversion of conjugated trienes is ordinarily seen only at higher temperatures. The first-order rate constant estimated for k_{13} , $4 \times 10^{-5} \text{ s}^{-1}$ (or $2 \times 10^{-5} \text{ s}^{-1}$ on a symmetry corrected basis) at 111 °C, corresponds to ΔG^\ddagger of only 31 kcal/mol; the thermal isomerizations of *trans*-, 1,3,5-hexatriene to cyclohexa-1,3-diene, with formation of *cis*-, 1,3,5-hexatriene as the rate-determining step, takes place at 111 °C with $\Delta G^\ddagger = 44 \text{ kcal/mol}$.^{13,14} Thermal isomerizations about the terminal double bond of conjugated trienes have been observed by Doering and Beasley¹⁴ and by Egger and James,¹⁴ starting from *trans*-, *trans*-, *trans*-, 2,4,6-octatriene and *trans*-, *trans*-, 1,3,5-heptatriene, respectively, but these isomerizations have not been accessible to detailed study: other reactions under the temperatures employed dominated the overall chemistry.^{14,15}

If further study confirms that $1 \rightarrow 3$ directly and $3 \rightarrow 4$ are indeed unimolecular processes involving rotations

Table I. Equilibrations of *cis*-, *cis*-, *cis*- and *cis*-, *cis*-, *trans*-Trienes 1 and 3 at 111 °C

1		2		3		4	
T^a	[1] ^b	T^a	[1] ^b	T^a	[1] ^b	T^a	[3] ^b
0.057	93.0	0	96.3	0.06	91.5	0	97.8
0.18	90.7	0.057	95.1	0.18	90.4	0.3	97.2
0.3	90.1	0.3	92.4	0.30	90.8	0.9	96.2
0.42	88.2	0.9	85.1	0.42	87.6	2.1	94.3
0.6	85.8	1.68	78.4	0.60	86.0	3.0	93.5
0.9	81.7	3.6	60.4	0.96	82.0	4.8	91.9
1.2	81.0	5.46	47.9	1.38	75.8	6.9	90.7
1.74	72.6	9.0	33.7	2.10	70.6	12.6	87.5
2.4	67.9			3.30	59.2		
7.2	38.6			4.86	51.1		
10.98	28.4			7.86	35.9		
				10.86	27.1		

^a Time ($\times 10^{-3}$), s. ^b Concentrations in mole percent; [1] + [3] = 100.

about a terminal double bond occurring with surprisingly low free energies of activation, it may be supposed that the triene reactants have substantially higher heats of formation than related isomers having *trans* geometry at the central double bond: the relatively low ΔG^\ddagger for these isomerizations may in large measure be associated with ground-state effects. While thermochemical data needed to assess this possibility directly are not available, $\Delta_r H^\circ$ values for *E* and *Z* isomers of 1,3-pentadiene are known and they differ by 5.3 kcal/mol.¹⁶ Large cumulative ground-state effects in 1 and 3 leading to high heats of formation, and relatively fast rotations about terminal double bonds, seem a definite possibility.

Experimental Section

Dodecane was distilled from CaH_2 . 2-Methylpentane was 99+% pure (Aldrich Chemical Co). All reactions were carried out under a nitrogen atmosphere unless otherwise indicated. Proton NMR spectra were recorded for CDCl_3 solutions on Bruker 360 or GE QE 300 spectrometers. Mass spectral data were secured with Hewlett-Packard (HP) 5890, 5970B, and 9836 instruments and computer. Analytical gas chromatographic analyses were done with a 0.2-mm i.d. 25-m cross-linked 5% phenyl methyl silicone fused silica capillary column, a 0.2-mm i.d. 25-m methyl silicone capillary column, a HP 5780 instrument with FID detectors, and HP 3390A and 3392A reporting integrators. Preparative gas chromatographic (GC) separations were accomplished with a Varian A-90-P3 instrument using a SE-30 on Chromosorb W 60/80 (0.6 cm \times 11 m) column.

cis,cis-1,3,5-Octatriene (2) was prepared and characterized as described earlier.⁸

cis,cis,cis-, **cis,cis,trans**-, and **trans,cis,trans-2,4,6-octatrienes (1, 3, and 4)** were prepared by Lindlar reductions of the corresponding octa-2,6-dien-4-yne and were purified by GC. The retention times of these trienes at a column temperature of 80 °C on the preparative SE-30 column were 8, 9, and 10 min respectively for 4, 3, and 1. A very pure sample of *cis*-, *cis*-, *cis*-, 2,4,6-octatriene, required for the kinetic work, was obtained by GC followed by flash chromatography on a small silica gel column.

cis,cis,cis-2,4,6-Octatriene (1). ¹H NMR (300 MHz) δ 1.78 (dd, 6 H, $J = 7.1 \text{ Hz}$, 1.4 Hz, CH_3), 5.6 (dt, 2 H, $J = 10.7 \text{ Hz}$, 3.6 Hz, C2-H, C7-H), 6.29 (apparent d, 2 H, C3-H, C6-H), 6.43–6.51 (m, 2 H, C4-H, C5-H); MS, m/z 108 (M^+).

cis,cis,trans-2,4,6-Octatriene (3). ¹H NMR (300 MHz) δ 1.76 (d, 3 H, $J = 7 \text{ Hz}$, *cis*(C1)- CH_3), 1.8 (d, 3 H, $J = 6.7 \text{ Hz}$, *trans*(C8)- CH_3), 5.53–5.61 (m, 1 H, C2-H), 5.73 (apparent sextet, 1 H, C7-H), 5.97 (t, 1 H, $J = 10.7 \text{ Hz}$, C6-H), 6.14 (t, 1 H, $J = 11 \text{ Hz}$, C3-H), 6.41–6.56 (m, 2 H, C4-H, C5-H); MS, m/z 108 (M^+).

trans,cis,trans-2,4,6-Octatriene (4). ¹H NMR (300 MHz) δ 1.8 (dd, 6 H, $J = 6.5 \text{ Hz}$, 1.4 Hz, CH_3), 5.7 (apparent sextet, 2

(13) Orchard, S. W.; Thrush, B. A. *J. Chem. Soc., Chem. Commun.* 1973, 14–15; *Proc. R. Soc. London, Ser. A* 1974, 337, 257–274. See also: Rose, T. L.; Seyse, R. J.; Crane, P. M. *Int. J. Chem. Kinet.* 1974, 6, 899–920.

(14) Doering, W. v. E.; Beasley, G. H. *Tetrahedron* 1973, 29, 2231–2243.

(15) Egger, K. W.; James, T. L. *Trans. Faraday Soc.* 1970, 66, 410–420.

(16) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986; p 90.

Table II. Formation of *cis,cis*-1,3,5-Octatriene (2) from *cis,cis,cis*-2,4,6-Octatriene (1) at 111 °C

<i>T</i> ($\times 10^{-2}$), s	[2], mol %	<i>T</i> ($\times 10^{-2}$), s	[2], mol %
0	0.2 ^a	7.8	1.92; 1.87
0.3	0.48	9.0	2.11; 2.28
0.6	0.75; 0.97 ^b	10.2	1.80
0.9	1.18	12.0	2.15
1.2	1.01; 1.39	13.2	2.28
1.8	1.46; 1.48	15.0	1.9
3.0	1.61; 1.65	16.8	2.0
4.2	2.01; 2.03	18.0	2.14
5.4	1.92; 1.99	21.0	2.0
6.6	1.84; 1.92	27.0	1.97

^a At time = 0, [1] = 93.9 mol %, [3] = 5.9 mol %. ^b Second value from independent run, here and below.

H, C2-H, C7-H), 5.83 (dd, 2 H, *J* = 6.5 Hz, C3-H, C6-H), 6.5 (m, 2 H, C4-H, C5-H): MS, *m/z* 108 (*M*⁺).

Kinetic Measurements. Kinetics of thermolyses were measured by using sealed 0.5-mm capillary tubes and an oil bath

maintained at 111 °C by a Bayley precision temperature controller (Model 253), and monitored by a Hewlett-Packard 2802A thermometer. While temperature at a fixed position in the bath was constant to ± 0.1 °C, temperature across the entire bath was constant only to ± 1 °C. Typically, 10 μ L of a dilute solution of triene 1 or 3 in dodecane, with 2-methylpentane of comparable GC area percent magnitude as internal standard, was filled in each capillary tube, chilled in dry ice-acetone under argon, and sealed. The sample tubes were immersed in the kinetic bath, then withdrawn from the bath at appropriate time intervals, cooled briefly in liquid nitrogen, allowed to reach room temperature, opened, and analyzed by capillary GC. Trienes 1-4 have distinctive retention times on the fused silica capillary columns employed.⁸ Kinetic data are summarized in Tables I and II.

Calculations of theoretical values for [2] formed from triene 1 as a function of time, initial concentrations of 1-3, and six rate constants (Scheme I) were performed, first, with the aid of a Hewlett-Packard 11C calculator and, later, with a Pascal program; the two theoretical curves in Figure 1 utilized output from the latter and an HP 7470A plotter. The analytical expression for [2(*t*)] was taken from Szabó (p 31, eq 2).¹¹

Tautomerism in 2-Hydroxy-5,10,15,20-tetraphenylporphyrin: An Equilibrium between Enol, Keto, and Aromatic Hydroxyl Tautomers

Maxwell J. Crossley,* Margaret M. Harding, and Sever Sternhell

Department of Organic Chemistry, The University of Sydney, N.S.W. 2006, Australia

Received July 21, 1987

Tautomerism in free-base and metallo derivatives of 2-hydroxy-5,10,15,20-tetraphenylporphyrin (2) has been investigated. In the case of the free-base porphyrin 2, ¹H NMR experiments show the existence of three tautomeric forms, 2a-c, in solution. Each of these species maintains aromaticity in the macrocycle by an 18-atom 18- π -electron (i.e., [18]diazannulene) "inner-outer-inner-outer" delocalization pathway. Two of the forms, 2a and 2b, result from proton transfer processes on the inner periphery and retain the hydroxyl group, while the third form, 2c, results from tautomerism directly involving the substituent. This is the first observation of prototropic tautomerism at a porphyrin β -pyrrolic position. Other possible species, e.g., 2d and 2e, in which aromaticity is maintained by a 17-atom 18- π -electron delocalization pathway were not detected. The position of the tautomeric equilibrium in 2 is solvent dependent, with the hydroxyl forms, 2a and 2b, predominating in dimethyl sulfoxide and the keto form, 2c, the main species in less polar solvents. Infrared spectral studies on 2 show the presence of keto and hydroxyl tautomers in the solid state, as well as in solution. By comparison, 2-amino-5,10,15,20-tetraphenylporphyrin (4) exists in solution as a mixture of the two tautomers that retain the amino group; i.e., corresponding imino tautomers were not detected. The possibility that metalloporphyrins, like the free-base compounds, exist as a mixture of tautomeric species with 18-atom 18- π -electron delocalization pathways was probed by monitoring the extent of (the secondary) keto-enol tautomerism shown by the substituent. The zinc(II) and copper(II) 2-hydroxy-5,10,15,20-tetraphenylporphyrins, 5 and 6 respectively, exist almost entirely in hydroxyl forms in both solution and the solid state. However, in the zinc porphyrin 5, the β -pyrrolic hydrogen adjacent to the hydroxyl substituent undergoes base-catalyzed exchange showing the presence of low equilibrium concentrations of metalated species which have a keto chlorin structure.

A study of two tautomeric processes working in concert, one involving tautomerism in the porphyrin macrocycle and the other involving a β -pyrrolic substituent on the porphyrin periphery, is reported. In solution, simple tetraarylporphyrins exist in two tautomeric forms, each containing an 18- π -electron aromatic delocalization pathway with two isolated double bonds on the porphyrin periphery (Figure 1).¹ We have recently shown by high-field dynamic NMR studies that β -pyrrolic substituents alter the position of the tautomeric equilibrium 1a \rightleftharpoons 1b,²

and we have examined the kinetics of the process.³ Thus, 2-nitro- and 2-cyano-5,10,15,20-tetraphenylporphyrin exist in solution almost exclusively (>96%) in the form 1a, where the substituent resides on the carbon of an isolated double bond. In contrast, the tautomeric equilibrium in 2-isopropyl-5,10,15,20-tetraphenylporphyrin lies substantially in the direction of 1b, in which the substituent resides on a carbon in the aromatic delocalization pathway. Porphyrins, therefore, differ from simpler arenes in that additional tautomeric forms which directly involve the substituent are possible, e.g., arising from tautomer 1a,

(1) Storm, C. B.; Teklu, Y. *J. Am. Chem. Soc.* 1972, 94, 1745.

(2) Crossley, M. J.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* 1986, 108, 3608.

(3) Crossley, M. J.; Field, L. D.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* 1987, 109, 2335.