in the past by obtaining the NMR spectrum of the compound in which the free rotation of the molecule is restricted so that a particular orientation of the molecule with respect to the external field is maintained during the time of the NMR measurements. These measurements on solids and nematic phases have yielded useful information; however, there are many instances where the values of $\sigma_{\parallel}$ and $\sigma_{\perp}$ in a solution are desired. We have derived some equations which permit one to obtain $\sigma_{\parallel}$, $\sigma_{\perp}$, and, additionally, the correlation time τ from NMR measurements on solutions. This communication will use these equations on ^{15}N NMR data obtained on the molecule pyridine which has an aromatic nitrogen of the type found in porphyrin and related compounds (hemes, chlorophyll, and vitamin B_{12}) in order to obtain the molecular level information.

The nuclei for which the derived equations are applicable are those nuclei whose observed spin-lattice relaxation time, T_{1obs}, has components from the chemical shift anisotropy (csa) and spin-rotational (sr) modes of relaxation and therefore is a function of six parameters: $\sigma_{\parallel}$ and $\sigma_{\perp}$ which are the $\parallel$ and $\perp$ components of the chemical shift tensor, $C_{\parallel}$ and $C_{\perp}$ which are the $\parallel$ and $\perp$ components of the spin rotational tensor, and τ_c and τ_j which are the rotational angular position and velocity correlation times. Six constraints can be placed on the relations between the various parameters so analytic expressions can be obtained for the various parameters. The six constraints are as follows: the definition of $T_{1csa}{}^{-1}$, the definition of $T_{1sr}{}^{-1}$, Hubbard's equation relating τ_c and τ_j,[1] Ramsey's relation between $\sigma_{\parallel}$ and $C_{\parallel}$ and between $\sigma_{\perp}$ and $C_{\perp}$,[2] and the definition of σ, i.e., $\sigma = \frac{1}{3}\sigma_{\parallel} + \frac{2}{3}\sigma_{\perp}$. When these expressions are combined, closed equations for all the parameters can be determined three of which are shown below.

$$\sigma_{\perp} = \sigma - \tfrac{1}{3}\Delta\sigma \text{ and } \sigma_{\parallel} = \sigma + \tfrac{2}{3}\Delta\sigma \text{ where}$$

$$(\Delta\sigma)^2 = -\frac{9}{4}(\sigma^{sr})^2 \times \left\{1 \pm \sqrt{1 + 20\left(\frac{\beta_e}{\hbar H_0}\right)^2 \frac{T_{1sr}{}^{-1} T_{1csa}{}^{-1}}{(\gamma\sigma^{sr})^4}}\right\}$$

$$\tau_c{}^{-1} = -\frac{3}{10}\frac{(\gamma H_0 \sigma^{sr})^2}{T_{1csa}{}^{-1}} \times \left\{1 \pm \sqrt{1 + 20\left(\frac{\beta_e}{\hbar H_0}\right)^2 \frac{T_{1sr}{}^{-1} T_{1csa}{}^{-1}}{(\gamma\sigma^{sr})^4}}\right\}$$

The experimental measurements which are required for these expressions are as follows: $T_{1obsd}(H_A)$ the observed T_1 at one field strength, $T_{1obsd}(H_B)$ the observed T_1 at a second field strength, and σ, the chemical shift on the absolute chemical shift scale. The first two measurements are used to separate the csa component of the observed T_1. If only csa and sr modes are present, then T_{1sr} is obtained by difference. If dipolar relaxation is present as well, then additional experimental data are required to resolve $T_{1sr}{}^{-1}$ and $T_{1csa}{}^{-1}$. The ^{15}N chemical shift scale has been referenced by molecular beam measurements on $^{15}N_2$ so the value of σ can be determined by difference from the $\sigma(^{15}N_2)$ which is -101 ppm.[3]

Experimental measurements of the pyridine ^{15}N T_1 values at two different field strengths have been made[4] and at -41 °C a $T_{1csa}{}^{-1}$ of 1.3×10^{-2} s^{-1} is calculated. In this molecule both dipolar (inter- and intramolecular) and sr modes of relaxation are present. At -41 °C a minimum in the observed T_1 exists and the customary procedure of assuming $T_{1sr} = T_{1csa}$ at the minimum gives a $T_{1sr}{}^{-1}$ of 4.4×10^{-3} s^{-1}. For liquid pyridine σ is found to be -93 ppm of which $+324$ ppm is the free atom part of the diamagnetic contribution and -417 ppm is the spin-rotational part of the paramagnetic contribution. When these values are used in the previously given equations, one obtains a $\sigma_{\parallel}$ of 565 ppm, a $\sigma_{\perp}$ of -422 ppm, and a τ_c of 2.8 ps. This $\Delta\sigma$ value is 987 ppm which is larger than that observed in the solid state. It is possible that the ring currents from the immobilized solid may contribute more to the chemical shift of one element of the tensor than to the other producing a smaller $\Delta\sigma$ in the solid than in the rotationally averaged solution molecules. However, the difference between the solid and solution values may have its origin in the fact that the method for determining the relative amounts of T_{1dd} and T_{1sr} was not the Overhauser enhancement approach but instead the minimum in the temperature dependence of T_1 method. This method is valid only if the activation energies for both the dipolar and sr processes are the same which is not generally the case. When $T_{1sr}{}^{-1}$ is taken to be 2.0×10^{-3} s^{-1}, then $\Delta\sigma$ becomes 758 ppm, and τ_c is 4.8 ps.

This communication demonstrates the fact that for aromatic nitrogens it is possible to obtain a measure of the chemical shielding of the nitrogen atom along different axes of the molecule and of the mobility of the molecule in solution from NMR data. Thus, the means are now available to treat problems such as the dimerization of chlorophyll a which may involve changes in the directional shielding of the aromatic nitrogen of the porphyrin. More details on the derivation of the equations will appear elsewhere.[5]

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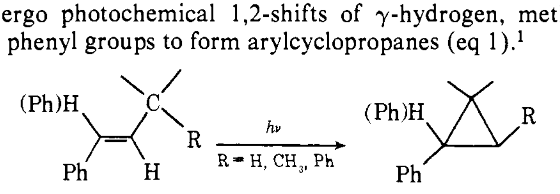
Relative and Absolute Rate Constants for Photochemical 1,2-Migration of Hydrogen, Methyl, and Phenyl in *trans*-β-Substituted-Styrenes

Sir:

Appropriately substituted styrenes or diphenylethylenes undergo photochemical 1,2-shifts of γ-hydrogen, methyl, and phenyl groups to form arylcyclopropanes (eq 1).[1]



(1)

The rates of these migrations are markedly and similarly affected by para substitution in the styrene or diphenylethylene chromophores.[2] Until now no direct comparison of the migratory aptitudes of the three groups—methyl, phenyl, and hydrogen—in the processes shown in eq 1 has been made, nor to our knowledge has a quantitative measure of the photochemical migratory abilities of these three fundamentally different moieties been carried out in any system.[3] In this communication we present a study of the relative and absolute rates of photochemical 1,2-migration of the three groups in β-substituted styrenes. Importantly, we make use of compounds which are identical but for the migrating species. We also show how substitution at the migration origin can markedly affect the migration process.

Scheme I

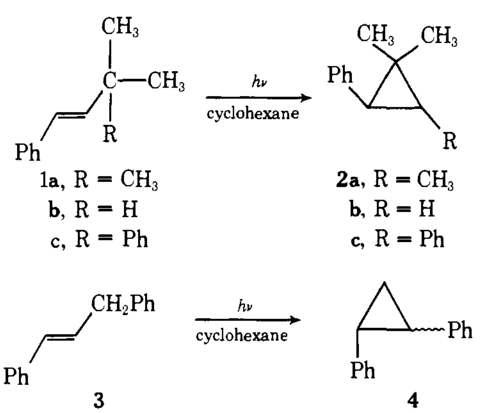


Table I. Singlet Lifetimes, Quantum Yields, and Rate Constants for Rearrangement of **1a–c** and **3**

Reactant	Product	ϕ_r[a,b]	ϕ_f(rel)[a,c]	τ_s, ns[a]	k_r, s^{-1}
1a	**2a**	0.001	0.95[d]	9.7[e,f]	1.0×10^5
1b	**2b**	0.014	1.0	9.6[e]	1.4×10^6
1c	**2c**	0.42	0.086	0.65[g]	6.5×10^8
3	**4**	0.005	0.83	6.3[e]	7.9×10^5

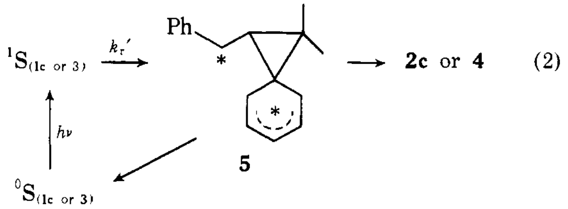
[a] Nitrogen-purged cyclohexane solutions of the olefins were used. [b] Determined via ferrioxalate actinometry, 254-nm irradiation. [c] Fluorescence quantum yields relative to that of **1b.** [d] $\phi_f = 0.155$.[7] [e] Determined by single photon counting. [f] Crosby and Salisbury[7] have reported τ_s(**1a**) = 12.5 ns. [g] Determined from fluorescence quantum yield relative to that of **3**.

The systems studied are illustrated in Scheme I. In all cases only the pure trans isomers of the styrenes were investigated.

Quantum yields for the transformations of **1a** (to *trans*-**2a**)[2b] and of **3** (to *cis*- and *trans*-**4**)[5] have been published previously. The conversion of **1b** to **2b** has been noted by Mazzocchi, but no quantum yield was determined.[1e] We have now measured the efficiency of this reaction at very low conversion of **1b** both to **2b** and to the cis isomer of **1b** (Table I). Upon irradiation **1c** is converted to **2c**, the product expected by analogy with the reaction of **3**. In contrast to the reaction of **3**, however, only the trans cyclopropane isomer **2c** was detected from **1c**. Most strikingly, the reaction of **1c** is highly efficient, much more so than that of **3** or of **1a** or **1b**: $\phi_{2c} = 0.42$. Benzophenone sensitization studies with **1b** and **1c** showed that the observed hydrogen and phenyl migration reactions, like the migrations of **1a**[2b] and **3**,[2a] are singlet-state processes.

Since the reactions of **1a–c** and **3** do proceed from the singlet states, the apparent rate constants for reaction (k_r) may be obtained directly from the measured quantum yields and the singlet lifetimes (τ_s): $k_r = \phi_r/\tau_s$. The singlet lifetimes of **1a, 1b,** and **3** were measured directly using the single photon counting technique (Table I). The lifetime of **1c** was determined indirectly by comparing the fluorescence quantum yield of **1c** with that of **3**. This latter determination makes use of the relationship $\tau_s = \phi_f/k_f$ and the reasonable assumption that the k_f's of **1c** and **3** are the same.

The increased migratory aptitude of hydrogen with respect to methyl which we find here (**1a** vs. **1b**) has also been found in thermal pericyclic reactions.[6] The migrations of **1a** and **1b** arise via interaction of the styryl π system with the σ bond to the migrating group, possibly leading to a concerted $2_\pi + 2_\sigma$ process. The dramatic increase in reaction rate found on proceeding from **1a** and **1b** to the phenyl migration reaction of **1c** shows how the ability of a phenyl group to migrate utilizing its π electrons substantially enhances its migratory ability relative to that of hydrogen and methyl which have no π electrons. Clearly the phenyl group is not migrating by a $\sigma + \pi$ interaction mechanism, for the phenyl-C-3 bond in **1c** is stronger than the methyl-C-3 bond in **1a.** Were both the methyl and the phenyl migrations going by $\sigma + \pi$ mechanisms, one would expect methyl to migrate faster. A similar conclusion about the mechanism of the divinylmethane rearrangement has been made by Zimmermann and Little.[8] Equation 2 illustrates a likely mechanism for phenyl migration.



(2)

The dramatic difference in k_r's between **1c** and **3** is revealing. Consider the mechanism in eq 2 in which bridged species **5** is formed irreversibly.[9] Assuming this mechanism is operative, we see that the k_r measured for **1c** and for **3** is actually the product of two terms: k_r', the rate constant for phenyl-vinyl bridging, and f, the fraction of bridged species **5** which goes on to form product; i.e., $k_r = k_r'f$. The rate-enhancing effect of the *gem*-dimethyls in **1c** could then reflect an enhanced value for k_r' and/or f, and from our data we conclude that both factors are most likely affected. For **1c** and **3** we have $1/\tau_s = k_r' + k_f + k_d$, where k_f is the fluorescence rate constant and k_d represents the sum of the rate constants, other than $k_r' + k_f$, for all processes leading from ^1S. We reasonably assume that $k_f + k_d$ is about the same for all four *trans*-β-substituted-styrenes studied (**1a–c, 3**)[11a] and that this sum is approximately $1/\tau_s$ for **1a** or **1b,** where $1/\tau_s = k_r + k_f + k_d \simeq k_f + k_d = 1.0 \times 10^8\ s^{-1}$. Then we calculate for **1c**, in which case $1/\tau_s$ is substantially greater than $10^8\ s^{-1}$ ($1/\tau_{s(\mathbf{1c})} = 1.5 \times 10^9\ s^{-1}$), that $k_r'_{(\mathbf{1c})} = 1.4 \times 10^9\ s^{-1}$. In the case of **3**, for which $1/\tau_s$ is on the order of $10^8\ s^{-1}$ ($1/\tau_{s(3)} = 1.6 \times 10^8\ s^{-1}$), the value determined for $k_r'_{(3)} \simeq 6 \times 10^7\ sec^{-1}$ must be regarded as an approximate one; however, it is clearly much lower than $k_r'_{(\mathbf{1c})}$. Thus one effect of the *gem*-dimethyl substitution is to enhance by more than an order of magnitude the rate of phenyl-vinyl bonding.[11a-c] On the other hand, analogy with the divinylmethane version of the di-π-methane rearrangement[1f,10] indicates that the *gem*-dimethyl group in **1c** almost certainly increases the value of f relative to that of **3**. Indeed, for **1c** we calculate $f = k_r/k_r' = 0.46$, whereas for **3** f is estimated to be ~0.01. The increase in the phenyl-vinyl bonding rate constant, k_r', brought about by the *gem*-dimethyls is most likely a manifestation of the well-known Thorpe-Ingold effect.[12] The increase in f is ascribed to the added stabilization by the methyls of the odd-electron density developing at C-3 during the transformation of bridged species **5** to product.[1f] We note that a major source of inefficiency in phenyl migration reactions appears to be reversion of the bridged intermediates to starting olefin.

It should be emphasized that the above analysis of k_r for **1c** and **3** does assume irreversible bridging, and that the ease of C-3-phenyl bond cleavage does not affect the rate constant k_r' and thus the initial excited-state lifetime of **1c** or **3**. While this assumption is in accord with what is felt to be the case with other di-π-methane systems,[1f,10] our results are equally compatible with a mechanism in which the facility of C-3-phenyl bond cleavage does affect reactant excited-state lifetime; e.g., appreciable bond-breaking occurs simultaneously with bridging. Should this be the case, then the odd-electron stabilizing effect of the methyls could be of greater relative importance. In any case our data clearly demonstrate a dramatic enhancement of phenyl migration by the *gem*-dimethyls and point out the importance of the structure of the nonmigrating group in migratory aptitude studies.

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(3) (a) There have been several cases involving intramolecular comparisons of photochemical migratory aptitudes.[1c–e,4] However, these studies have not afforded a true measure of relative migratory abilities since in each case the nonmigrating moiety would be different depending on which species migrated. Furthermore, in general only one group migrated so that only an upper limit of migratory aptitudes (with the previous qualification) was obtained. (b) In one intermolecular comparison of methyl and hydrogen migratory abilities in which the nonmigrating group was the same, only quantum yields, not rates, were determined. See the discussion in ref 4a.

(4) (a) See, e.g., K. A. Burdett, F. L. Shenton, D. H. Yates, and J. S. Swenton, *Tetrahedron*, **30**, 2057 (1974); (b) K.-W. Shen, W. E. McEwen, and A. P. Wolf, *Tetrahedron Lett.*, 827 (1969); (c) C. B. Jones and V. Jones, *J. Am. Chem. Soc.*, **89**, 1880 (1967).

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(9) Zimmermann[10] has presented strong arguments that bridging is rate limiting in the divinylmethane version of the di-π-methane reaction.

(10) H. E. Zimmermann, D. P. Werthemann, and K. S. Damm, *J. Am. Chem. Soc.*, **96**, 439 (1974).

(11) (a) Using $\phi_{f(1a)} = 0.155$ (ref 7), we calculate from the data in the table that $k_{f(1a)} = 1.6 \times 10^7\ s^{-1}$ ($k_{d(1a)} = 8 \times 10^7\ s^{-1}$) while $k_{f(3)} = 2.1 \times 10^7\ s^{-1}$, a difference of 31%. (b) If the sum $k_f + k_d$ for **3** is 30% larger than that for **1a** or **1b** then $k_r'_{(3)} = 3 \times 10^7\ s^{-1}$. (c) The maximum possible value of $k_r'_{(3)}$ is found by assuming $1/\tau_{s(3)} = k_f + k_r'$, i.e., that k_d is negligible; $k_r'_{(3)max} = 1.4 \times 10^8\ s^{-1}$.

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Tris(η^5-cyclopentadienyl)tricarbonyltricobalt. An Exceptionally Deformable Molecule

Sir:

Stereochemical nonrigidity has been widely investigated in a variety of compounds in recent years using NMR spectroscopy.[1] While in most cases the barriers to the intramolecular rearrangements responsible for the nonrigidity have been in the range of 8-20 kcal/mol, there are a few cases in which the barriers are much lower. Of particular interest is the type of molecule in which there is a continuous range of configurations over which the free energy changes by only a few kilocalories, so that many, or even a virtually continuous range, of molecular configurations may coexist in solution. An example already known is $Fe_3(CO)_{12}$.[2,3] Another such readily deformable molecule, a type for which we propose the designation *fictile*, is reported here.

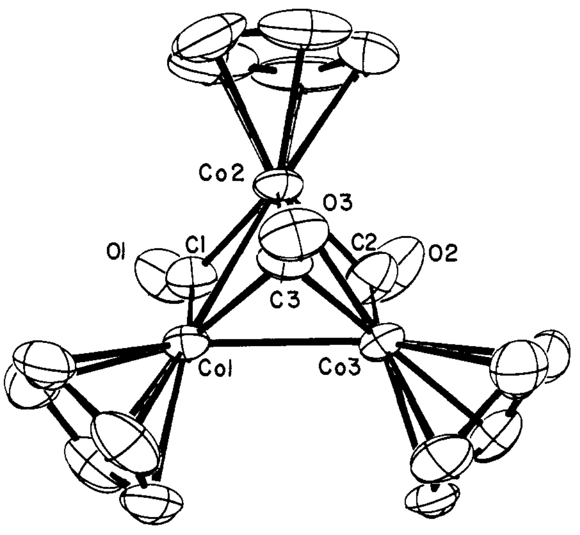

Figure 1. An ORTEP drawing of the $[\eta^5\text{-}C_5H_5)Co(CO)]_3$ molecule as it occurs in the crystal.

Table I. Summary of Pertinent Bond Lengths and Angles of $[CpCo(CO)]_3$

Co1–Co2	2.440 (4) Å	Co2–C1	1.99 (3) Å
Co2–Co3	2.458 (4) Å	Co2–C2	2.11 (4) Å
Co1–Co3	2.521 (4) Å	∠Co1–C1–01	148.6 (7)°
Co1–C1	1.78 (3) Å	∠Co3–C2–02	153.2 (7)°
Co3–C2	1.75 (4) Å		

As part of our current effort to prepare organometallic complexes containing metal-metal multiple bonds,[4] we have attempted to prepare compounds of the type $CpCo(\mu\text{-}R_2C_2)CoCp$ which would be expected to contain a cobalt-cobalt double bond by the photochemical reaction of $CpCo(CO)_2$ and di-*tert*-butylacetylene, $t\text{-}Bu_2C_2$. This reaction did not produce the desired $Cp_2Co_2(\mu\text{-}t\text{-}Bu_2C_2)$, but did provide $[CpCo(CO)]_3$ a substance earlier reported by King.[5] The inability of Uchtman and Dahl[6] to reproduce King's synthesis coupled with the recently reported work of Vollhardt et al.[7] who, along with King, have proposed incorrect structures for $[CpCo(CO)]_3$ prompted us to report a few results of our structural and spectral studies on this and related systems. A full report will appear later.

$[CpCo(CO)]_3$ crystallizes in the triclinic space group, $P\bar{1}$, with cell dimensions: $a = 9.128$ (4), $b = 11.691$ (5), $c = 7.948$ (4) Å; $\alpha = 105.45$ (4)°, $\beta = 100.70$ (4)°, $\gamma = 91.21$ (3)°. The structure, shown in Figure 1, was solved using 2738 reflections having $F_o^2 > 3\sigma(F_o^2)$ and $2\theta < 50°$. Data were collected at 21 ± 2 °C with monochromatized Mo Kα radiation using θ-2θ scans. Presently the structure is refined to convergence using isotropic temperature parameters for all non-hydrogen atoms; the conventional R value is 9.4%.

The structure of $[CpCo(CO)]_3$, like that of Uchtman and Dahl's $Cp_3Co_3(\mu_3\text{-}CO)$ (μ_3-O), is based upon a triangle of cobalt atoms each of which is bonded to a η^5-cyclopentadienyl ring, and it also contains a triply bridging carbonyl, C3-O3 (Figure 1). In addition $[CpCo(CO)]_3$ contains two semibridging carbonyls.[3,8] That C1-O1 and C2-O2 are indeed semibridges can be seen from the data summarized in Table I: C1 is 0.21 Å closer to Co1 than to Co2 while C2 is 0.36 Å closer to Co3 than Co2; these data together with the very low M-C-O angles clearly indicate the marked asymmetry of these carbonyl bridges.

In contrast to the equilateral triangle of cobalt atoms found in $Cp_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$, the cobalt atoms of