synthesized using procedures developed by Nagata.[19] Hydrocyanylation of 6,6-dimethyl-$\Delta^{1,9}$-2-octalone[11,20] with potassium cyanide and ammonium chloride in dimethylformamide gave two cyano ketones, mp 66–66.5°[11] and mp 83–83.5°,[11] in a ratio of 5:2 after separation by preparative tlc. Hydrocyanylation using triethylaluminum and hydrogen cyanide gave the same products in a ratio of 17:1 by vpc analysis. On the basis of the close analogy of these results to those obtained by Nagata with $\Delta^{1,9}$-2-octalone, the major product, mp 66–66.5°, is assigned the trans configuration **8**. The cyano ketones were converted to the trans ketoacid **10**, mp 85–86°,[11] and cis ketoacid **11**, mp 120–121°,[11] by alkaline hydrolysis using the procedures reported by Nagata.

Ozonolysis of ketone **6** followed by oxidation of the ozonide with Jones reagent[21] gave a ketoacid, mp 85–86°, identical (melting point, ir, and nmr) with the authentic trans acid **10**. A sample consisting predominantly of a 50:50 mixture of ketones **6** and **7** was ozonized and the acidic product was esterified with diazomethane. Vapor phase chromatography of this material showed two peaks with retention times identical with those of the methyl esters of acids **10** and **11**.

The absence of dehydration–reprotonation reactions in the cyclization was shown by conducting the cyclization in the presence of deuterium. Ketones **6** and **7** isolated from a cyclization with deuteriotrifluoroacetic acid at −78° were shown by mass spectrometric analysis (comparison of P, P + 1, and P + 2 ions) to contain no more deuterium than material isolated from a similar cyclization with trifluoroacetic acid.

The results obtained with alcohol **5** show that generation of a decalin ring system by intramolecular attack of a monosubstituted double bond on a conformationally rigid cyclohexyl ring system with one sp^2-hybridized carbon is highly stereoselective. It should be noted that cyclizations in which the double bond is a nonterminal double bond or in which axial substituents are present on the six-membered ring should exhibit even greater stereoselectivity than shown in the present case.[8b,22]

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[19] W. Nagata, I. Kikkawa, and M. Fujimoto, *Chem. Pharm. Bull.*, **11**, 226 (1963).

[20] We thank Mr. Chung-ye Tseng for preparing this compound from the pyrollidine enamine of 4,4-dimethylcyclohexanone and methyl vinyl ketone.

[21] A. S. Narula and Sukh Dev, *Tetrahedron Lett.*, 1733 (1969).

[22] Our results suggest that formation of cis fused products in relatively high proportion in some previous studies[23] may be a result of elimination to a cyclohexenyl system from which concerted protonation–cyclization leading to cis products[3] competes with reprotonation to the cation.[8b]

[23] *Inter alia* R. E. Ireland, S. W. Baldwin, and S. C. Welch, *J. Amer. Chem. Soc.*, **94**, 2056 (1972); P. T. Lansbury, P. C. Briggs, T. R. Demmin, and G. E. DuBois, *ibid.*, **93**, 1311 (1971); P. T. Lansbury and G. E. DuBois, *Chem. Commun.*, 1107 (1971).

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Mechanisms of Photochemical Reactions in Solution. LXXVII. A New Method for the Determination of Intersystem Crossing Yields[1]

Sir:

We describe a new technique for the determination of intersystem crossing quantum yields in fluid solution and report some preliminary results obtained with this technique. The method is a combination of two previously reported procedures: the sensitized cis–trans isomerization method of Lamola and Hammond[2] and the flash spectroscopic method of Wilkinson and coworkers which utilizes heavy-atom enhancement of intersystem crossing.[3] While the method described here is applicable to most aromatic compounds, it is especially useful for substituted benzenes, compounds for which the two previously mentioned techniques are only marginally applicable.[4]

Our experimental procedure involves measurement of relative fluorescence intensities of an aromatic compound A and relative yields for isomerization of a "triplet counter" C in solutions with constant concentrations of A and C but with varying concentrations of heavy-atom fluorescence quencher H. The processes of interest are shown in the kinetic scheme below.

$$A_0 \xrightarrow{h\nu} A^{*(1)} \tag{1}$$

$$A^{*(1)} \xrightarrow{k_2} A_0 + h\nu' \tag{2}$$

$$A^{*(1)} \xrightarrow{k_3} A_0 \tag{3}$$

$$A^{*(1)} + C \xrightarrow{k_4} A_0 + C \tag{4}$$

$$A^{*(1)} \xrightarrow{k_5} A^{*(3)} \tag{5}$$

$$A^{*(1)} + H \xrightarrow{k_6} A^{*(3)} + H \tag{6}$$

$$A^{*(3)} \xrightarrow{k_7} A_0 \tag{7}$$

$$A^{*(3)} + C \xrightarrow{k_8} A_0 + C^{*(3)} \tag{8}$$

$$C^{*(3)} \xrightarrow{k_9} C \tag{9}$$

$$C^{*(3)} \xrightarrow{k_{10}} T \tag{10}$$

We carried out experiments with 0.05–0.10 *M* *cis*-2-pentene as the triplet counter and monitored the appearance of *trans*-2-pentene (T) by glpc. The heavy-atom fluorescence quencher was xenon, which has been shown to quench singlets by inducing intersystem crossing.[3]

The effect of fluorescence quenching by C in the absence of H is given by eq 11.[6,7] Equation 12 de-

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[1] Part LXXVI: G. F. Vesley and G. S. Hammond, *J. Amer. Chem. Soc.*, submitted for publication.

[2] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[3] A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **306**, 257 (1968), and references cited therein.

[4] The limitations of the Lamola–Hammond method have been discussed.[5] The procedure of Horrocks and Wilkinson[3] cannot be used for benzene derivatives because they generally do not show triplet–triplet absorption in flash spectroscopy.

[5] W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971), and references cited therein.

[6] Values of k_4 ranged from *ca.* 10^7 M^{-1} sec^{-1} (mesitylene) to *ca.* 10^8 M^{-1} sec^{-1} (anisole).

[7] F' and F^0 are the fluorescence intensities of A with and without C; τ_f' and τ_f^0 are the corresponding singlet lifetimes. Y_T' is the yield of T in the absence of H. F, τ_f, and Y_T refer to quantities with both C and H present.

$$F^0/F' = \tau_f^0/\tau_f' = 1 + k_4\tau_f^0[\mathrm{C}] \quad (11)$$

$$F'/F = \tau_f'/\tau_f = 1 + k_6\tau_f'[\mathrm{H}] \quad (12)$$

scribes the relative fluorescence intensities of solutions containing constant concentrations of A and C but varying concentrations of H.[7] The ratio of quantum yields for the appearance of T in the presence of H to that without H, at constant light dose, is given by eq 13. Since the second term in both numerator and

$$Y_T/Y_T' = \frac{(k_5 + k_6[\mathrm{H}])\tau_f\left(\dfrac{k_8[\mathrm{C}]}{k_7 + k_8[\mathrm{C}]}\dfrac{k_{10}}{k_9 + k_{10}}\right)}{k_5\tau_f'\left(\dfrac{k_8[\mathrm{C}]}{k_7 + k_8[\mathrm{C}]}\dfrac{k_{10}}{k_9 + k_{10}}\right)} \quad (13)$$

denominator is unaffected by xenon, the ratio of these terms in eq 13 is unity. Combining eq 11–13 gives eq 14, which predicts that a plot of $(F^0/F')(F'/F - 1)$

$$(F^0/F')(F'/F - 1) = \Phi_{\mathrm{isc}}[(Y_T/Y_T')(F'/F) - 1)] \quad (14)$$

vs. $(Y_T/Y_T')(F'/F) - 1$ should be linear with slope Φ_{isc}. An important advantage of the present method over previous methods employing sensitized isomerization[2,8] is that neither the efficiency of energy transfer nor the triplet counter decay ratio need be known. In addition, only relative measurements with the same sensitizer are required if all samples are irradiated under identical conditions.[9]

Figure 1 shows plots of eq 14 for anisole, mesitylene, and toluene. The lines shown were calculated by the method of least squares and linear correlation coefficients are 0.995 or greater in each case. Values of Φ_{isc} obtained from the slopes are listed in Table I, along with the corresponding fluorescence quantum yields. While the sum of Φ_{isc} and Φ_f is unity within experimental error for anisole, it is much less for mesitylene and toluene. We conclude that a significant fraction of excited singlets of mesitylene and toluene decay through pathways other than fluorescence and intersystem crossing.

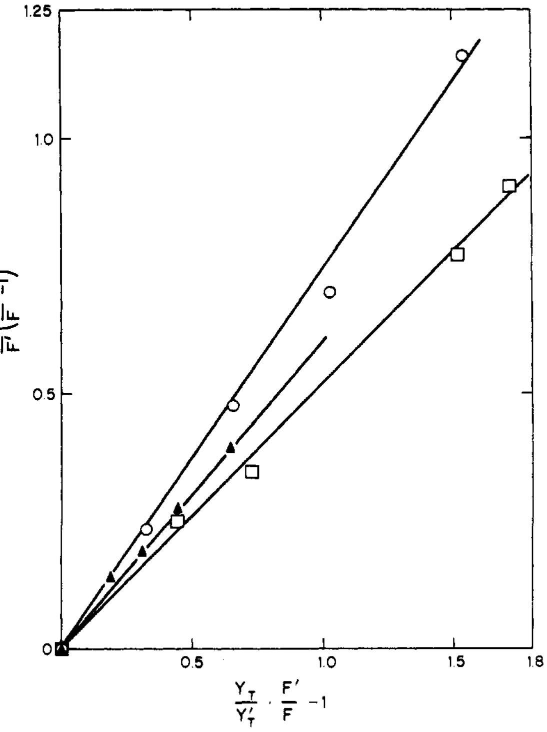

Figure 1. Determination of intersystem crossing quantum yields for anisole (○), mesitylene (▲), and toluene (□).

Table I. Intersystem Crossing and Fluorescence Quantum Yields in Deoxygenated Isooctane Solution

Compound	Φ_{isc}[a]	Φ_f[b]	Φ_{isc} (lit.)
Anisole	0.74 ± 0.04	0.24 ± 0.01	
Mesitylene	0.60 ± 0.03	0.13 ± 0.01	
Toluene	0.52 ± 0.03	0.14 ± 0.01	0.53,[c] 0.46,[d] 0.34[e]

[a] Determined from the slopes in Figure 1. The estimated errors primarily reflect uncertainties in relative fluorescence yields. [b] Quantum yields of fluorescence (254-nm excitation) determined relative to cyclohexane solutions of equal optical density: J. B Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, pp 98, 122. [c] Dilute cyclohexane solution: K. Sandros, *Acta Chem. Scand.*, **23**, 2815(1969). [d] Neat toluene.[8] [e] Reference 5.

We are currently determining intersystem crossing yields for other benzene derivatives by this technique. The method should also be useful in elucidation of the mechanisms of photochemical reactions which give products by both singlet and triplet pathways. In this case the products could function as singlet or triplet monitors.

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(8) R. B. Cundall and W. Tippett, *Trans. Faraday Soc.*, **66**, 350 (1970).

(9) Irradiations were conducted simultaneously at 254 nm in a merry-go-round apparatus[10] and were stopped at less than 4% conversion of C to T. Corrections for back reaction are small at such low conversions.

(10) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(11) (a) National Science Foundation Predoctoral Fellow, 1969–1972; (b) National Science Foundation Trainee, 1968–1971.

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Additions and Corrections

The Determination of Double-Bond Character in Cyclic Systems. VI. Anthracene. Evidence for Benzenoid Terminal Rings [*J. Amer. Chem. Soc.*, **87**, 1247 (1965)]. By JOHN L. FERRARI,* I. MOYER HUNSBERGER, and