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(5) All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given in our full publication.

(6) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

(7) All of the incident light was absorbed by the diphenylcyclopropene ring in these irradiations; λ_{max} (95% ethanol) 337 and 319 nm (ϵ 21 000 and 2800).

(8) 1,2-Diphenylcyclopropenes have been reported to undergo dimerization from the triplet state of the cyclopropene, see C. D. DeBoer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967); C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Am. Chem. Soc.*, **95**, 861 (1973).

(9) It should be noted that the formation of **4** in the presence of piperylene has a much lower quantum yield than that for the formation of **2** in the direction irradiation of **1**.

(10) (a) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964); (b) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

(11) Further discussion of the regioselectivity of bond cleavage of unsymmetrical disubstituted cyclopropenes will be given in a forthcoming publication, see A. Padwa, T. Blacklock, D. Getman, and N. Hatanaka, unpublished results. Similar studies have also been carried by H. E. Zimmerman and S. M. Aasen, manuscript in press.

(12) For coupling constants in the tricyclo[2.2.0.0^{2,6}]hexane system, see C. Y. Ho and F. T. Bond, *J. Am. Chem. Soc.*, **96**, 7355 (1974).

(13) Our failure to detect reaction from the singlet state of cyclopropene **1** on direct irradiation can be reasonably attributed to a decrease in the rate of single bond cleavage relative to intersystem crossing. Introduction of an alkyl or phenyl substitutent on the 3-position of the cyclopropene will increase the rate of singlet ring opening relative to intersystem crossing. For a related substituent effect in ketone photochemistry, see P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Am. Chem. Soc.*, **96**, 924 (1974).

(14) Methoxy ether **13** was prepared by treating 3,4-diphenyl-3-buten-2-one with allyl magnesium bromide followed by reaction with sodium hydride and methyl iodide. Treatment of ether **12** with acidic methanol gave structure **13**.[5]

(15) An alternate mechanism involving protonation of the excited cyclopropene double bond, followed by a cyclopropyl → allyl cation rearrangement and methanol trapping has been suggested by one of the referees and cannot necessarily be eliminated at this time.

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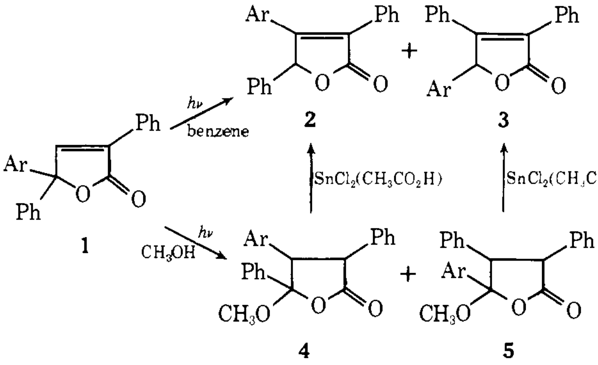
Solvent Control of Migratory Aptitudes in the Photochemical Rearrangement of 2(5*H*)-Furanones[1]

Sir:

During the course of our studies dealing with the photochemical rearrangement of 5,5-diaryl-2(5*H*)-furanones,[2] we uncovered a striking and rare[3] crossover in the competitive migratory aptitudes[4] of aryl groups which arises from a solvent alteration. We report here the results of this study which show that, in certain instances, excited-state migratory aptitudes can be controlled by stabilization of the nonmigrating aryl group.

We had previously studied the photochemical rearrangement of 5-(4′-anisyl) (**1a**) and 5-(4′-cyanophenyl)-3,5-diphenyl-2(5*H*)-furanone (**1b**) in benzene.[2] In both cases, rearrangement is a triplet derived reaction and the substituted aryl group was found to migrate in preference to the unsubstituted phenyl group. The rate constants of aryl group migration for furanones **1a**–**1c** were estimated from quenching studies using piperylene as a quencher. These were found to be 0.18 × 10^{10}, 1.3 × 10^{10}, and 0.9 × 10^{10} s^{-1} for migration of phenyl,[5] *p*-anisyl, and *p*-cyanophenyl in benzene[6,7] (Table I). Thus, *p*-An and *p*-CNPh are more reactive migrating groups than phenyl by factors of 7.2 and 5.0, respectively. Zimmerman and Levin[4,8] found that a nonmigrating *p*-CNPh group increased the rate constant for phenyl migration in 4,4-diarylcyclohexenones by a factor of 1.3. We found that, relative to phenyl migration with nonmigrating phenyl, the rate of phenyl migration is accelerated 1.4-fold by nonmigrating *p*-CNPh and decreased 2.0-fold by a nonmigrating *p*-An group when benzene is used as the solvent.



1a, Ar = *p*-$CH_3OC_6H_4$
1b, Ar = *p*-CNC_6H_4
1c, Ar = C_6H_5
1d, Ar = *m*-$CH_3OC_6H_4$
1e, Ar = *p*-$CH_3C_6H_4$

Irradiation of furanones **1a**–**e** in methanol gave lactones **4** and **5**. The structures of **4** and **5** were established by treatment with stannous chloride in refluxing acetic acid to give furanones **2** and **3**, respectively. Compounds **2a**–**e** and **3a**–**e** were identified by comparison with authentic samples prepared by independent syntheses.[9] Table I lists quantum yields, rate data, and migratory aptitudes for compounds **1a**–**c** in both benzene and methanol. Although no quantitative studies were performed on the related furanones **1d** and **1e**, product ratios were measured in benzene and methanol. Rearrangement of furanone **1d** in benzene indicated the *m*-anisyl had migrated with slight preference over phenyl (ratio **2d**/**3d** = 1.5/1). When methanol was used as the solvent, both groups had migrated with the same ease (i.e., ratio **4d**/**5d** = 0.95). With *p*-toluyl furanone **1e**, irradiation in benzene afforded lactones **2e** and **3e** (ratio 3.5/1), whereas photolysis in methanol resulted in preferential phenyl migration (ratio **4e**/**5e** = 0.81).

The striking feature of these rearrangements is that a substantial crossover in migratory aptitude occurs upon changing the solvent from benzene to methanol. The reversal of the migratory aptitude of *p*-anisyl vs. phenyl when the reaction of **1a** is carried out in methanol is of special interest. The quantum yield for the reaction of **1a** in methanol is much lower than for the reaction in benzene. The triplet sensitized reaction in methanol, however, is quite efficient (Φ = 0.40). The product distribution for the sensitized reaction was found to be virtually identical with that for the direct irradiation. These results indicate either that the product distribution for rearrangement in the singlet manifold is identical with that for the triplet, or, more plausibly, that rearrangement occurs only in the triplet manifold. Assuming the latter, the efficiency of intersystem

Table I. Rate Constants for Reaction and Decay from the Triplet States of 3,5,5-Triaryl-2(5H)-Furanones[6,7]

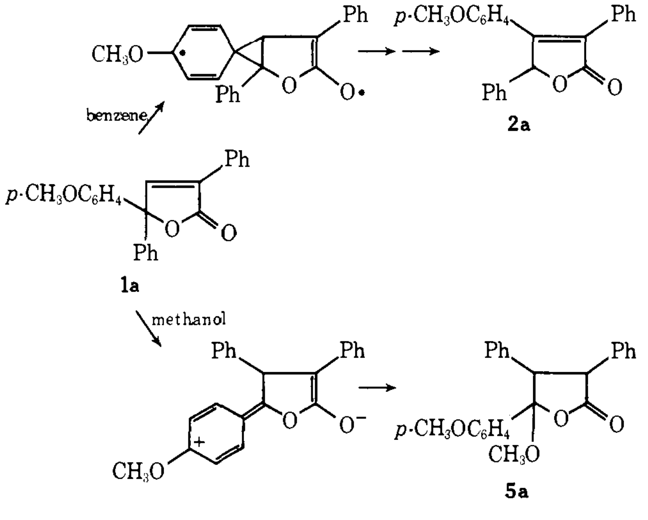
2(5H)-Furanone derivative	Solvent	Φ_{direct}[a]	τk_q[b]	$10^{10}k_d$,[c] s^{-1}	k_r Ar/k_r Ph[d]	$10^{10}k_r$ (net),[e] s^{-1}	$10^{10}k_r$ (Ar),[f] s^{-1}	$10^{10}k_r$ (Ph),[g] s^{-1}
3,5,5-Triphenyl(**1c**)	Benzene	0.37	0.52	0.6	—	0.36	—	0.18
3,5-Diphenyl-5-p-anisyl(**1a**)	Benzene	0.36	0.12	2.75	16	1.4	1.3	0.09
3,5-Diphenyl-5-p-cyanophenyl (**1b**)	Benzene	0.48	0.21	1.25	3.5	1.15	0.9	0.25
3,5,5-Triphenyl(**1c**)	Methanol	0.37	0.53	0.6	—	0.35	—	0.17
3,5-Diphenyl-5-p-anisyl(**1b**)	Methanol	0.06	0.056[h]	5.4	0.72	3.6	1.5	2.1
3,5-Diphenyl-5-p-cyanophenyl(**1b**)	Methanol	0.43	0.55	0.51	4.5	0.39	0.32	0.07

[a] Sum of both products. [b] Slope of Stern-Volmer plot. [c] $(1 - \Phi)/\tau$. [d] From product ratios. [e] Φ/τ. [f] $(\Phi_{\mathrm{Ar}}/\Phi_{\mathrm{total}})k_{r(\mathrm{net})}$. [g] $(\Phi_{\mathrm{Ph}}/\Phi_{\mathrm{total}})k_r(\mathrm{net})$. [h] ±40% as a consequence of the low magnitude of the slope.

crossing of **1a** in methanol based on $\Phi_{\mathrm{sens}} = 0.40$ is estimated to be only 15%. Intersystem crossing by each of the furanones, including **1a**, in benzene occurs with an efficiency indistinguishable from unity by sensitization studies. The marked decrease in intersystem crossing efficiency in methanol occurs only for **1a** and not for **1b** or **1c**.[10]

Furanones **1a**–**c** show phosphorescence spectra (MCIP or methanol-ethanol, 77 K, 0-0 band at 483 nm = 59 kcal, τ_p = 170 ms) which correspond closely to the low-lying $^3\pi,\pi^*$ state of 1-phenylcyclopentene[12] with little perturbation by the lactone carbonyl group. We assume from these measurements that the lowest lying styrene-type π,π^* triplet of **1a**–**c** is the excited state responsible for the rearrangement.

The foregoing results suggest that the photochemistry of the p-anisyl furanone system (**1a**) proceeds from a diradical state in benzene while in methanol the rearrangement occurs from a zwitterionic state.[13] Whereas the migration of p-anisyl in preference to phenyl in benzene is attributable to stabilization of the radical like free valence by the *migrating* group, the slight preference for migration of phenyl over p-anisyl in methanol may be attributed to stabilization of the electron deficiency which develops at C_5 by the *nonmigrating* p-anisyl group. As noted in Table I, the rate constant for p-anisyl migration in triplet **1a** is little affected by solvent while a nonmigrating p-anisyl group significantly accelerates the rate of phenyl migration in methanol. In furanone **1b**, both p-cyanophenyl and phenyl migration occur less readily in methanol than in benzene. The nonmigrating p-cyanophenyl retards phenyl migration by a factor of 3.5 in methanol whereas it aids it in benzene. These observations provide additional evidence that stabilization by the nonmigrating aryl group of the electron deficiency which develops at C-5 during aryl migration is of major importance in methanol. The above results serve to emphasize the important role that electron distribution plays in photochemical migratory processes.



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(3) See for example W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Am. Chem. Soc.*, **93**, 3674 (1971).

(4) For other examples of photochemical migratory aptitudes see H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Am. Chem. Soc.*, **87**, 1138 (1965); H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); H. E. Zimmerman and J. O. Grunewald, *ibid.*, **89**, 5163, 3354 (1967); H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).

(5) Since we are interested in the rate of migration of a single aryl group, for statistical reasons the rate constant for 3,5,5-triphenyl-2(5H)-furanone (**1c**) is halved.

(6) The rate constants listed in Table I are based on a common k_q value of 5×10^9 M^{-1} s^{-1} in benzene and methanol. Since these molecules possess a low triplet energy (ca. 59 kcal), energy transfer to piperylene may not be diffusion controlled and consequently the rate values listed may be somewhat high.

(7) It should be noted that the k_r's measured are net k_r's which are equal to the rates of formation of any intermediate species multiplied by the fractions of the intermediates which continue on toward product. Thus, the values listed are minimum values for k_r, although it is conceivable that there is no triplet decay and that $k_r = 1/\tau$. The relative k_r values listed in Table I are based on the assumption that there is either no return of an intermediate to ground state or else that all of the lactones undergo the same fraction of such return.

(8) For a review of the cyclohexenone results see H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

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(10) We presently consider the possibility that radiationless deactivation modes of the excited singlet state of the electron rich p-anisyl furanone **1a** in methanol are substantially larger than those of furanones **1b** and **1c**, thereby suppressing the intersystem crossing of this compound to the triplet state. Studies to clarify this substituent effect are under way. It should be noted, however, that a similar effect of solvent on the efficiency of intersystem crossing had been noted by Cohen in the p-aminobenzophenone system.[11] Apparently, some sort of intramolecular charge transfer interaction is common to both systems.

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