tion. The low conversions of **3-t** and **3-c** to the other isomer and to product (as well as the respective quantum yields) ensure that the reactions observed are from the starting isomer only and that **4-c** was not being destroyed as rapidly as it was formed in either case.

The striking result is that the methyl migration of **3** is not stereospecific. This is in marked contrast to the divinylmethane process which proceeds stereospecifically with retention at C-1.[3] Some basic difference between the two processes is indicated.[12]

Such nonspecificity could arise from (a) a stepwise process leading to long-lived biradical **5** which closes

5
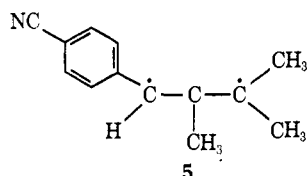
preferentially to **4-t**; (b) reaction of **3-t** and **3-c** from a common (twisted) excited state; (c) a concerted $_\sigma 2_s + _\pi 2_s$ reaction from **3-c** and a $_\sigma 2_a + _\pi 2_a$ reaction from **3-t**.[13] While no evidence is available to allow us to make a firm choice among these, a point against choice c is the result in the divinylmethane case where retention at C-1 is observed[3] with both cis and trans starting materials and where the steric requirements are quite similar to those in the present case. Nothing at present favors a over b though we feel more comfortable with a than b since we suspect that the twisting mentioned in the latter would be accompanied or closely followed by rapid deactivation to ground-state olefin.

We note that while the divinylmethane rearrangement and the methyl migration show a basic difference in mechanism or timing of bonding, at least by this stereochemical criterion, the present results are similar to those found in the phenyl migration variation of the di-π-methane rearrangement,[14,15] where stereochemistry is apparently not retained and a common biradical intermediate seems likely.[14,16] A further similarity is seen in the effect of substituents on the two processes.[17]

(12) Starting with either pure cis-1 or trans-1 we obtain only trans-2 at low conversion. However, due to the very low absorbance of cis-1 and its rapid isomerization to trans-1 as well as the fact that the cyclopropanes elute from the gc on the tail of the cis-1 peak we cannot accurately determine a quantum yield for cis-1 → cyclopropane and eliminate the contribution from trans-1 to the total amount of cyclopropane formed. However, it appears here, too, that the reaction is not stereospecific, and the results with 3 are not peculiar to the cyano substituent.

(13) Combinations of a–c are also possible.

(14) E. W. Valyocsik and P. Sigal, J. Org. Chem., **36**, 66 (1971).

(15) S. S. Hixson, J. Amer. Chem. Soc., **94**, 2507 (1972).

(16) However, it should be noted that time dependence studies, which show that the lack of stereospecificity was truly a result of kinetic control, were not presented in ref 14.

(17) S. S. Hixson and T. P. Cutler, J. Amer. Chem. Soc., **95**, 3032 (1973).

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## Substituent Effects on π–π* Rearrangements. Methyl Migration in β-tert-Butylstyrenes

Sir:

In a previous communication[1] we reported the effect of polar substituents on the photochemical rearrangement of 1,3-diarylpropenes to 1,2-diarylcyclopropanes[2] proceeding *via* aryl migration[3] (eq 1). We noted[1] that
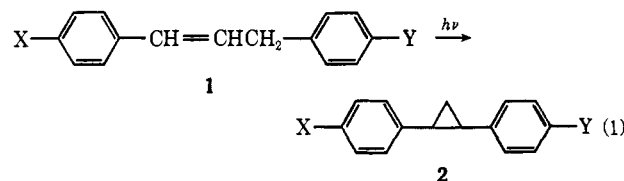
when the migration terminus is substituted with a strongly electron withdrawing group (X = CN; Y = H), the reaction proceeds rapidly ($k_{rel} = 41$) relative to the unsubstituted compound (X = Y = H). However, substitution by an electron donating group (X = OCH$_3$; Y = H) drastically curtails the rate ($k_{rel} \leqslant 0.04$). Such a polar effect was striking and unexpected; it indicated that the electron density at the migration terminus was a very important factor in determining the rate of phenyl migration, much as in the ground-state migration of phenyl to an adjacent carbon.

Little is known about the nature of the electronic interactions that bring about rearrangements in π–π* systems and, in particular, the effect of π-electron distribution on these rearrangements. Thus, we have extended the studies noted above on the migration of *unsaturated* carbon in an excited styryl system to include a study of substituent effects on the migration of *saturated* carbon occurring upon photolysis of β-tert-butylstyrene[4] (eq 2). Such a study promised to pro-

3a, X = H
b, X = CN
c, X = OCH$_3$

4a, X = H
b, X = CN
c, X = OCH$_3$
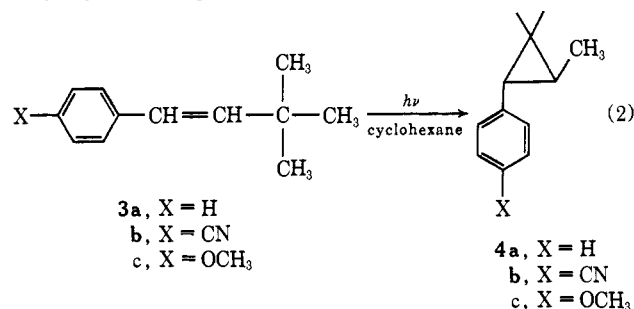
vide a further[5] comparison of the two types of rearrangement, one which can proceed *via* bridging between two π systems, the other which cannot. In addition, though, it would provide an indication of whether the effects noted above were general and applied to different sorts of migration processes.

The irradiation[6] of **3a** was followed closely by gas chromatography. As reported by Griffin in his original study of **3a**,[4] small amounts of **4a** (cis and trans) were initially formed but did not accumulate due to their rapid further transformation. In the present case the

(1) S. S. Hixson, J. Amer. Chem. Soc., **94**, 2507 (1972).

(2) G. W. Griffith, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965).

(3) S. S. Hixson, Tetrahedron Lett., 1155 (1972).

(4) H. Kristinsson and G. W. Griffin, J. Amer. Chem. Soc., **88**, 378 (1966).

(5) S. S. Hixson and T. P. Cutler, J. Amer. Chem. Soc., **95**, 3031 (1973).

(6) Synthetic and experimental details will be reported in a full paper.

photolysis was stopped when the amount of **4a** appeared to be at a maximum. Olefins were then removed by permanganate oxidation; **4a** (cis and trans) was isolated by column chromatography and identified by comparison (nmr and ir spectra; gc retention times) with an authentic sample of **4a** (cis and trans). We point out that this is the first isolation of **4a** from **3a** although the work of Griffin[4] left little doubt as to its being formed. Similarly, cyclopropanes **4b** (cis and trans) could be isolated from the photolysis of **3b**.[5] Strikingly, however, irradiation of **3c** led to no observable formation of **4c** or of any other product. Indeed, prolonged irradiation gave solely trans–cis isomerization with only a very slow disappearance of starting material being noted. Triplet sensitization of **3a–c** with xanthone gave only cis–trans isomerization indicating the observed migrations are singlet state processes.

Quantum yield studies of the rearrangements of the trans olefins were carried out on a merry-go-round apparatus using 254-nm light. At the low conversions (<1%) of these irradiations only trans cyclopropanes were formed.[5] The results are shown in Table I. To

Table I. Quantum Yield and Relative Rate Data for Olefins **1a–c**

Compd	$10^{-3}\varphi_r{}^a$	$k_t(rel)^b$	$\varphi_t(rel)^{b,c}$	$k_r(rel)^b$
3a	0.0010	1.0	1.0^d	1.0
3b	0.0026	1.4	1.2^e	3.0
3c	<0.0001	1.2	1.7^f	$\leqslant 0.07$

^{a} ±15–20%. ^{b} Computed as in ref 1. ^{c} λ(excitation) 265 nm; solutions $\sim 10^{-5}$ M in cyclohexane. ^{d} λ_{max} 313 nm. ^{e} λ_{max} 318 nm. ^{f} λ_{max} 329 nm.

ensure that the differences in quantum yields found really reflected differences in singlet state reactivity rather than large rate differences in other singlet deactivation processes the quantum yields were converted to relative rates as done previously.[1,7] These are also listed in Table I.

The results are quite revealing. It is noted that—as in the rearrangement of diarylpropenes[1]—(1) substitution in the styryl group of hydrogen by a para methoxy moiety drastically curtails the rate of methyl migration, and (2) substitution by a para cyano group increases the rate though the effect here is, very interestingly, much less than with the diarylpropenes.[1] Once again we find that 1,2 migration in a π–π* state becomes less and less favorable as the electron density at the reaction terminus increases. This is notably similar to the case with ground-state 1,2 shifts of alkyl (and aryl) groups to an adjacent carbon where there is little evidence for migration of saturated carbon to other than an adjacent *cationic* center.[9] A simple picture of the photochemical case is that the reactive π–π* systems, in which a bonding orbital has lost an electron to a less stable antibonding orbital, are electrophilic in these migrations. Substituents decreasing this electrophilicity also decrease reactivity and *vice versa*.

While we are exploring the generality of the effects

(7) This is essentially the procedure of Zimmerman and Baum[8a] and of Dalton and Turro.[8b]

(8) (a) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, 93, 3646 (1971); (b) J. C. Dalton and N. J. Turro, *ibid.*, 93, 3569 (1971).

(9) Reference 5, footnote 2.

noted here, it is worthwhile to point out their interesting connection to the relation between the reactivity of cyclohexenones and their methylene analogs.[10] 4,4-Dimethyl-2-cyclohexenone (**5**) rearranges *via* alkyl migration to bicyclic isomer **6**.[11] However, neither the singlet nor the triplet state of the methylene analog **7**

5   **6**   **7**
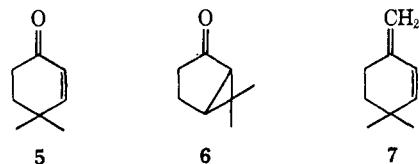
of the ketone undergoes any similar sort of rearrangement.[10b] This implies[10b] (a) an ^3n–π* state is necessary for the rearrangement or (b) it is the difference in electron distribution of the excited π–π* states that is important, that of the ketone being polarized toward oxygen. Since **5** and similar enones most likely rearrange *via* alkyl migration from $^3\pi$–π* states,[12] differences in enone and olefin excited state polarities would seem to be a possibly important factor in determining their relative reactivities.[13–15] Indeed our results with rearrangements of π–π* singlets are consistent with this and show that excited state electron distribution is very important in determining rates of migration of π–π* states.

(10) (a) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967); H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969); (b) W. G. Dauben and W. A. Spitzer, *ibid.*, **90**, 802 (1968).

(11) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(12) W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3674 (1971), and references therein.

(13) A "free rotor" effect[14] could explain the nonreactivity of the diene triplet, but most likely not that of the singlet.

(14) (a) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **92**, 1411 (1970); (b) J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *ibid.*, **93**, 4808 (1971).

(15) 1,2-Alkyl shifts have been observed with acyclic diene singlets. Here, the migrating group is benzyl: E. C. Sanford and G. S. Hammond, *ibid.*, **92**, 3497 (1970).

(16) Undergraduate honors research participant.

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The Oxidation of Cinnamic Acid by Permanganate Ion. Spectrophotometric Detection of an Intermediate

Sir:

Permanganate ion reacts rapidly with cinnamic acid in aqueous perchloric acid solutions to form an intermediate which appears yellow and which exhibits an absorption maximum at 415 nm. The intermediate then decomposes at a slower rate to give benzaldehyde and manganese(III) as products. Although this intermediate has only transitory existence, it has been possible to identify it and to study its rate of formation and subsequent decomposition by stopped-flow techniques.

The rate of the first step of the reaction can be determined either by following the disappearance of the permanganate ion absorption maximum at 530 nm or