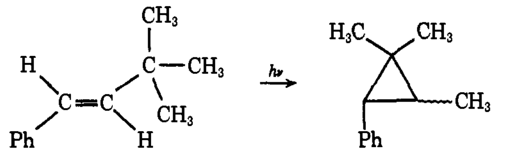
Acknowledgment. We thank Johnson-Matthey (United Kingdom) for a loan of platinum metal salts.

M. A. Bennett,* T. Yoshida
Research School of Chemistry, Australian National University
Canberra, ACT 2600, Australia
Received January 22, 1973

Photochemical Rearrangement of β-*tert*-Butylstyrenes. Stereochemistry

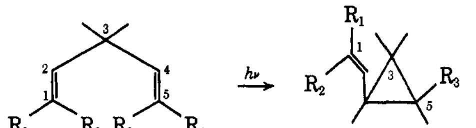
Sir:

The photochemical rearrangement of β-*tert*-butylstyrene (**1**) to trimethylphenylcyclopropane (**2**), a reaction discovered by Griffin[1] some years ago, is an intriguing one for several reasons. From one point of view the process may be looked upon as a 1,2 migration of a methyl group to the (presumably) radical-like β carbon of the excited state styryl group, a transformation which has little analogy in ground-state chemistry where migration of saturated carbon occurs only to cationic centers.[2] From another aspect, the reaction is formally analogous to the di-π-methane rearrangement,[3] in which unsaturated carbon undergoes a similar photochemical 1,2 shift. Both are formally ${}_{\sigma}2 + {}_{\pi}2$ cycloadditions and may proceed in a concerted fashion in the excited state with either ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ or ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ stereochemistry.[4]



1 **2** (1)

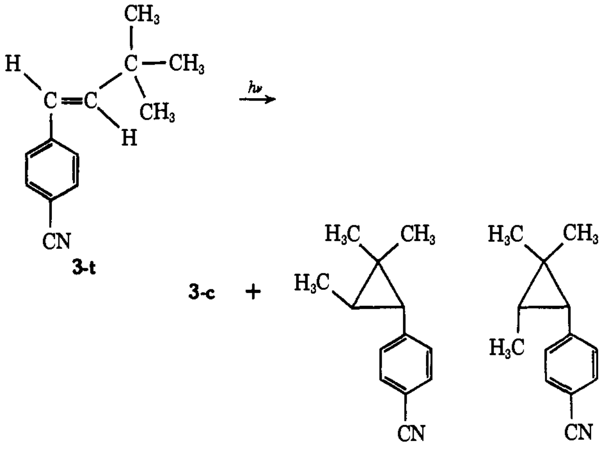
The stereochemistry of the divinylmethane rearrangement, a particular case of the di-π-methane, has been investigated in some detail.[3,5,6] Of the three centers of stereochemistry involved, the reaction has been found to proceed with inversion at C-3[5,6] and retention at C-1[3] and C-5,[6] consistent with a concerted ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ excited state process (eq 2).



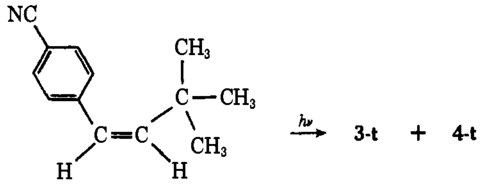
(2)

However, it seems likely that the divinylmethane rearrangement is not a simple ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ reaction, but rather use is made of both systems in a ${}_{\sigma}2_{a} + {}_{\pi}2_{a} + {}_{\pi}2_{a}$ process.[7] This cannot be true for **1**. Thus, an investigation of the stereochemistry of process 1 was inviting. We present here an analysis of the stereochemistry at C-1.

Experimental difficulties (*vide infra*) precluded an accurate assessment of the stereochemistry of the reaction of **1** itself. However, it was feasible to do so with the para cyano derivative **3**.[8] Under preparative irradiation conditions **3-t** produces rapidly a mixture of **3-c** and **3-t** and, more slowly, a mixture of cyclopropanes **4-t** and **4-c**. The cyclopropanes do not accumulate to any great extent due to their very efficient further transformation to olefins.[1,9] Nonetheless, it was possible to isolate the mixture of **4-t** and **4-c** by preparative gc and show they were identical (nmr and ir spectra; gc retention times) with a mixture prepared independently.[8,10]



3-t **4-t** **4-c**



3-c

Quantitative irradiations[8] starting with pure **3-c** and **3-t** were carried to very low conversions: 1–2% to the other isomer; <0.2% to cyclopropane. Remarkably, at these low conversions, both **3-c** ($\Phi = 0.0070$) and **3-t** ($\Phi = 0.0026$) gave **4-t** as the only observable cyclopropane. We could detect no **4-c** in either case; our separation and detection limits are such that we can say cyclopropane **4** is formed with at least 93% trans stereochemistry.

Both reactions are singlet state processes since xanthone sensitization results only in trans–cis isomeriza-

---

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

[2] (a) H. E. Zimmerman in "Molecular Rearrangements, Part One," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 394–399, and references therein. (b) Recently an example of an apparent radical rearrangement involving a 1,2-alkyl shift has been observed; see C. Walling and A. Cioffar, *J. Amer. Chem. Soc.*, **94**, 6064 (1972). As Walling notes, 1,2-alkyl rearrangements in biradicals are well-substantiated phenomena.

[3] H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972), and references therein.

[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 98–99.

[5] P. S. Mariano and J. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1971).

[6] H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969).

[7] (a) H. E. Zimmerman and R. D. Little, *ibid.*, **94**, 8256 (1971); (b) H. E. Zimmerman, P. Hackett, D. F. Jeurs, J. M. McCall, and B. Schroder, *ibid.*, **93**, 3653 (1971).

[8] Synthetic and experimental details will be presented in a full paper.

[9] (a) H. Kristinsson and G. W. Griffin, *Tetrahedron Lett.*, 3259 (1966); (b) P. H. Mazzochi, R. S. Lustig, and G. W. Craig, *J. Amer. Chem. Soc.*, **92**, 2168 (1970).

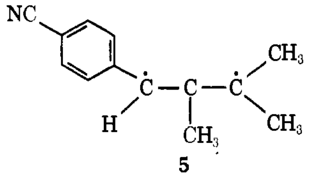
[10] Cyclopropane configurations were readily assigned by the method of Closs and Moss.[11] The signals due to the methyl groups in 3-c and 3-t are very similar to those in the unsubstituted cyclopropanes (2).

[11] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

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 $_\sigma2_s + {}_\pi2_s$ reaction from **3-c** and a $_\sigma2_a + {}_\pi2_a$ 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]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

[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, 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).

[18] Undergraduate honors research participant.

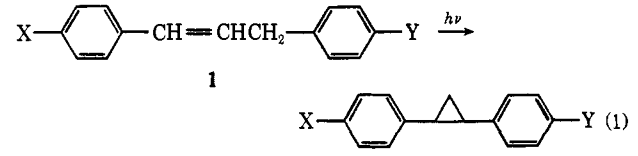
Stephen S. Hixson,* Timothy P. Cutler[18]
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

Received December 14, 1972

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

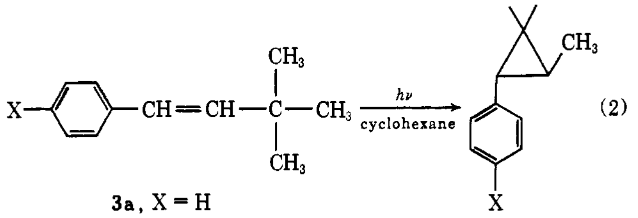


1

2

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 provide 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.



3a, X = H
b, X = CN
c, X = OCH_3

4a, X = H
b, X = CN
c, X = OCH_3

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.