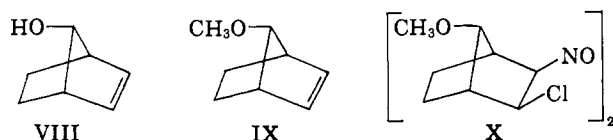


the known rigidity of the bicyclo[2.2.1]heptane ring system.¹¹ Furthermore, the model on which a $J_{3,4} \cong 0$ c.p.s. (80° angle) for VII is predicted does not include nonbonded interactions.

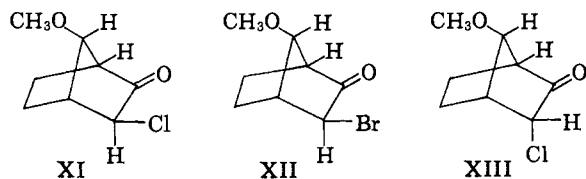
Alternatively, it is possible that $J_{3,4} \cong 0$ even in VI, and that the splitting of the *endo*-3 proton is due to interaction with a more distant proton. We have found this to be the case and would like to call attention to this previously unrecognized long-range coupling in the norbornyl system.

The logical candidates for long-range interactions in VI are the protons at C₁ and at C₇, present in VI but absent in VII. Of these, the *anti*-7 proton bears a geometrical relationship to the *endo*-3 proton rather similar to the relationship between the strongly coupled *endo*-5 and *endo*-6 protons of V. Evidence pointing to this particular interaction was readily obtained by preparing an analog of VI in which the *anti*-7 position was occupied by a methoxyl group, as described in the following section.

The readily available *anti*-7-norbornenol (VIII)¹² was converted by treatment with sodium hydride followed by methyl iodide into *anti*-7-methoxynorbornene (IX),¹³ which gave a crystalline dimeric nitroso chloride (X),¹³ upon treatment with isoamyl nitrite and hydrochloric acid. Levulinic acid-hydrochloric acid hydrolysis^{9,14} of this dimer gave *exo*-3-chloro-*anti*-7-methoxynorcamphor (XI).¹³ The n.m.r. spec-



trum of this compound showed the *endo*-3-proton as a *singlet* at 6.20 τ .¹⁵ The corresponding *exo*-3-bromo-*anti*-7-methoxynorcamphor (XII),¹³ prepared in an analogous way, again showed the *endo*-3 proton as a *singlet* (6.13 τ). As expected, the *endo* chloro epimer XIII,¹³ obtained by chromatography of the base-catalyzed equilibrium mixture derived from XI, showed the *exo*-3 proton as a doublet ($J_{3,4} \cong 4$ c.p.s., 6.00 τ).



We conclude that the n.m.r. spectra of α -haloketones of the general formula VI are characterized by a coupling ($J_{3,7} \cong 3-4$ c.p.s.) between the *endo*-3 and *anti*-7 protons. Whether this coupling is in part dependent on some specific feature of these molecules other than their geometry¹⁶ or whether it is quite general for norbornanes and norbornenes remains to be seen. However, the implications concerning the anticipation of *norbornane* spectra on the basis of *bornane* or other more substituted models are evident.

(11) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); D. A. Brueckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 799 (1962).
 (12) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).
 (13) All new compounds gave satisfactory elementary analyses.
 (14) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).
 (15) We are grateful to Dr. E. LeCoff for obtaining some of these spectra for us, using a Varian A-60 instrument at Mellon Institute.
 (16) The possibility that the electronegativity of attached groups plays a role in determining the value of coupling constants has been discussed recently by K. L. Williamson.¹¹

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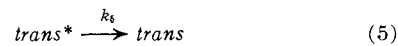
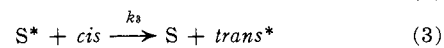
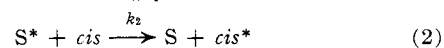
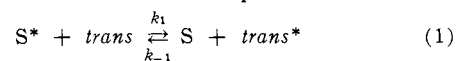
RECEIVED MAY 23, 1963

Mechanisms of Photochemical Reactions in Solution.

XVII. *cis-trans* Isomerization of the Stilbenes by Excitation Transfer from Low Energy Sensitizers

Sir:

We have reported that *cis-trans* isomerization of the stilbenes can be effected by photosensitizers.¹ Evidence is strong that the key step is transfer of triplet excitation from excited sensitizer molecules to the stilbenes. The following mechanism accounts for most of the available data. Asterisks indicate excited triplet states.



Reactions 1, 2, and the reverse of reaction 1 are of the type commonly suggested for energy transfer.² The excitation and deexcitation acts in eq. 1 and 2 involve the same transitions as are observed in emission and absorption spectroscopy.³ Occurrence of reaction 4 is suggested by our observation that, whereas excitation of either of the isomeric stilbenes produces an excited state which can be deactivated to *trans*-stilbene by the reverse of reaction 1 or by other quenching reactions (*vide infra*), the reverse of reaction 2 cannot be detected. Reaction 5 is an ordinary radiationless transition. Reaction 6 is at first startling; however, there is no reason to expect that conversion of electronic excitation to thermal energy will preserve faithfully the geometry of the excited states.⁴

Reaction 3 is demanded by our data. *cis*-Stilbene is a moderately effective acceptor of energy from sensitizer triplets having insufficient excitation energy to promote the substrate to its spectroscopic triplet state.⁵ The process must involve some transformation of the acceptor that does not conform to the Franck-Condon principle.

Sensitizers have been characterized by measurement of the photostationary states established in their presence. Data are presented in Fig. 1 in which photostationary ratios are plotted against triplet excitation energies of the sensitizers. Since results with sensitizers having excitation energies less than that of fluorenone are sensitive to the concentration of the sensitizer, the data plotted are extrapolated values for infinite dilution. Measurements were made in benzene solution at 28°.

If reaction 3 is omitted, the mechanism predicts the photostationary condition

$$\frac{[trans]_s}{[cis]_s} = \frac{k_2(k_5 + k_{-1}[S])}{k_1k_6} \quad (7)$$

High energy sensitizers show no concentration effects indicating that $k_6 \gg k_{-1}[S]$. This condition holds at infinite dilution with sensitizers which show activity as energy acceptors. Under such circumstances, reflected by the data in Fig. 1, eq. 7 reduces to 8.

$$\frac{[trans]_s}{[cis]_s} = \frac{k_2k_5}{k_1k_6} \quad (8)$$

Variation in the stationary state ratio as the sensitizer is changed should depend on the values of k_2/k_1 . Since

- (1) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).
- (2) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).
- (3) Emission and absorption refer to phosphorescence and $S_0 \rightarrow T_1$ absorption, respectively.
- (4) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).
- (5) Temperature variation shows that reaction 3 has no appreciable activation energy.

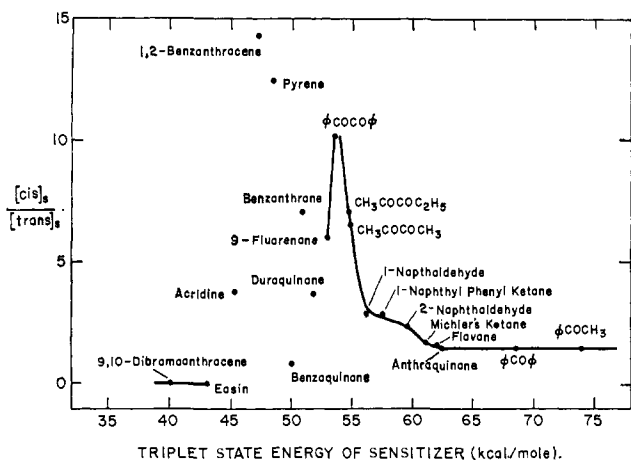


Figure 1.

the spectroscopic transition energy of *cis*-stilbene is about 57 kcal./mole and that of *trans*-stilbene is 50 kcal./mole,⁶ one would expect the value of k_2/k_1 to decrease as the energy of the sensitizer is lowered toward 57 kcal.⁹ This accounts for production of *cis*-rich mixtures with sensitizers having excitation energies of 54–62 kcal. However, we cannot account for the fact that the value k_2/k_1 apparently increases and finally becomes immeasurably large with sensitizers of still lower energy. We suggest that reaction 3, or some other process requiring less energy than transition to the spectroscopic *cis* triplet, must predominate. Since the ground state of *cis*-stilbene is unstable with respect to that of the *trans* isomer by 6 kcal./mole,¹¹ in any pair of processes in which two isomers undergo transitions to a common state, the reaction involving the *cis* isomer will be favored on energetic grounds. Figure 1 can be rationalized by the mechanism including reaction 3.

$$\frac{[trans]_s}{[cis]_s} = \frac{(k_2 + k_3)(k_5 + k_{-1}[S])}{k_1 k_6} \quad (9)$$

With high energy sensitizers, k_1 and k_2 , the rate constants for energy transfer with vertical excitation of the acceptor, have the magnitude for diffusion-controlled processes and are larger than k_3 . The value of k_2 falls off as the excitation energy of sensitizers approaches and falls below the $S_0 \rightarrow T_1$ excitation energy of *cis*-stilbene. As the energy of the sensitizers is lowered further, the value of k_1 falls sharply. Since k_3 , the rate of transfer with nonvertical excitation of *cis*-stilbene, depends on factors other than the excitation energy of the acceptor, $(k_2 + k_3)/k_1$ may be large with low energy sensitizers. Behavior in the 45–52 kcal. region will require further documentation prior to detailed discussion.

Sensitizers having energies close to that of *trans*-stilbene show pronounced concentration effects. The data fit eq. 9, implying that transfer of energy to *cis*-stilbene produces a species which can transfer energy to sensitizer molecules in their ground states. Confirmation was provided by experiments in which azulene was included in the reaction mixtures. The stationary states became more *trans*-rich and data for various azulene

(6) The energies are estimated from the singlet-triplet absorption spectra as reported.^{7,8}

(7) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

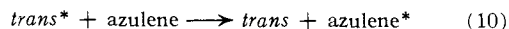
(8) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(9) Transfers exothermic by more than 3–5 kcal. appear to be diffusion-controlled.¹⁰

(10) (a) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961); (b) K. Sandros and H. L. J. Bäckström, *Acta Chem. Scand.*, **16**, 958 (1962); (c) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(11) R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942).

concentrations obeyed a law including reaction 10 in the mechanism.



The effect of azulene is observed irrespective of the energy of the sensitizers. Clearly, all energy transfer processes produce long-lived stilbene triplets which are quenched by azulene with the inevitable production of ground state *trans*-stilbene. This observation unequivocally demonstrates that reaction 3 does not deliver excitation to *cis*-stilbene as vibrational (thermal) energy.

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CONTRIBUTION No. 2992

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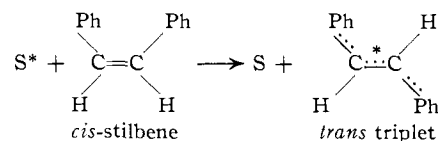
GEORGE S. HAMMOND

RECEIVED JUNE 17, 1963

Mechanisms of Photoreactions in Solution. XVIII. Energy Transfer with Nonvertical Transitions

Sir:

In the accompanying communication¹ we have given evidence for the occurrence of a process that was formulated as



The product of the excitation transfer may be a triplet having a transoid configuration or it may be some other triplet having a noncisoid configuration. If such a

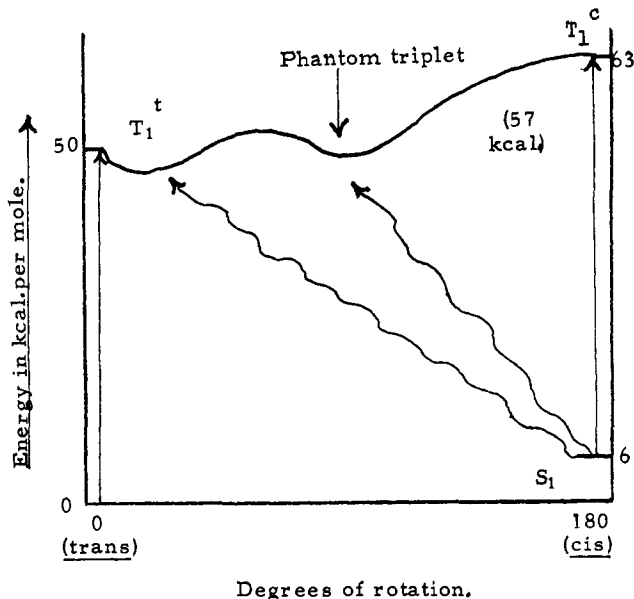


Fig. 1.—Possible potential function for rotation about the central bond in the stilbene triplet states.

“phantom” triplet is involved it must be both readily interconvertible with the *trans* triplet and rather close to isoenergetic with it. The potential function for twisting about the central bond might look as is shown in Fig. 1. However, we should stress the fact that the two possibilities, *trans* triplet only or *trans* triplet and phantom triplet in equilibrium, cannot be distinguished on the basis of presently available information.

(1) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963).