Acknowledgment. This work was supported by the National Institutes of Health and Hoffmann-La Roche, Inc.

[21] National Institutes of Health Predoctoral Fellow, 1966–1969.
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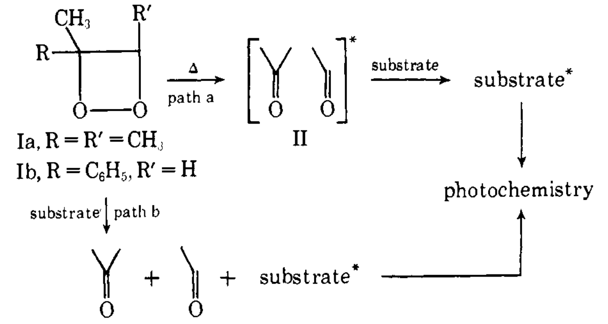
Received January 10, 1970

Utilization of Chemically Generated Excited States

Sir:

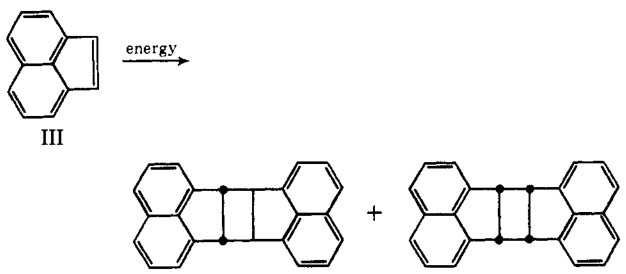
We have shown recently that it is possible to effect "photochemistry without light"[1] by using chemically produced electronically excited states. We now report that this method can lead to quantum yields in the useful range, that the excited states formed appear identical with those arrived at by means of photon absorption, and that triplet states are involved in all the cases studied with the additional implication of triplet-energy transfer in the dioxetane-driven dimerization of acenaphthylene (III).

Energy Sources. In most reactions studied, trimethyl-1,2-dioxetane (Ia)[1,2] was used as the energy source. By working at −5°, omitting the solvent, and distilling the product *in vacuo*, dioxetane Ia has been obtained as a pure liquid[3] **(Caution: potential explosive).** Dioxetane Ib has also been prepared, but appears to give lower yields of photoproducts than Ia.



Energy transfer from the dioxetane appears to involve path a (and exciplex II[2]) since fluorescent acceptors do not increase the rate of the decomposition of Ia[2] and since considerable light emission is seen in the absence of substrates, especially in the gas phase (emission at *ca.* 435 mμ).[4] This point warrants further examination, however.[5]

Acenaphthylene (III). In the photochemical dimerization of acenaphthylene it has been reported that the singlet state of III, in addition to undergoing intersystem crossing, yields the pure *cis* dimer (V) of acenaphthylene[6]



III

IV

V

or yields the *cis*-dimer V contaminated with only a trace of the *trans*-dimer IV.[7] The triplet state leads to a ratio of *cis* to *trans* dimers that is solvent dependent,[6] but in methanol values of 0.44 to 0.58 were found for low-energy sensitizers.[8]

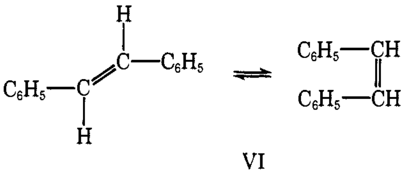
When a benzene solution of Ia (1.8 *M*) and III (0.7 *M*) is heated to 100° for 10 min, then cooled, crystals of dimers IV and V separate. This ready synthesis of IV and V illustrates the usefulness of the new procedure. The dimerization in benzene (Table I) is largely quenched by cyclooctatetraene;[6] the small amounts of *cis* and *trans* dimers still formed remain in the ratio of about 0.3–0.4, however. Both results, as well as the *cis*/*trans* ratio in the absence of quenchers, when compared with the photochemical counterparts,[6–8] show that the triplet state of III is largely responsible for the dimerization.

Table I. The Dimerization of Acenaphthylene[a]

Solvent	Ia, *M*	III, *M*	Temp, °C	Ratio,[b] V:IV	Total yield of IV + V, wt %	Total apparent quantum yield (10²)[c]
Benzene	1.8	0.7	95–100	0.30	8	2−
Benzene[d]	1.8	0.7	95–100	0.30	7	1+
Benzene[e]	1.8	0.7	95–100	0.4	0.2	0.04
Methanol	1.3	0.6	40	0.7	2	0.4

[a] All solutions degassed, except where noted. [b] Determined by ultraviolet spectra of the products separated on a tlc plate (silica gel developed with cyclohexane at 40°). [c] Mol of dimer/mol of Ia. [d] Solution saturated with oxygen. [e] 0.16 *M* in cyclooctatetraene.

Stilbene (VI). Data for the chemically sensitized isomerization of stilbene are given in Table II. The



VI

yields of *cis* isomer are somewhat solvent dependent and they are improved by higher temperatures (a similar effect has been noted for the photochemical isomerization[9]); high stilbene concentrations and low dioxetane concentrations also increase the yield. Oxygen was not found to be an efficient quencher, nor was it found to influence the corresponding photochemical

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[1] E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

[2] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).

[3] $\nu_{max}^{CCl_4}$ 1393, 1380, 1156, 1069, 884 cm^{-1}; nmr (CCl_4) τ 4.78 (quartet, J = 6.5 Hz, 1 H), 8.47 (singlet, 3 H), 8.53 (singlet, 3 H), 8.65 (doublet, J = 6.5 Hz, 3 H); mol wt 100 (freezing point depression of C_6H_6). *Anal.* Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.49; H, 10.35 (full purification not achieved because of the explosive nature of Ia; traces of acetone seen in the ir and nmr spectra).

[4] A value of 430–440 mμ has been reported for the decomposition of Ia in benzene.[2]

[5] Rate acceleration has been found in a related case (M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969)).

[6] I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967).

[7] D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967).

[8] R. L. Drisko, Ph.D. Thesis, The Johns Hopkins University, 1968.

[9] G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

Table II. The *cis–trans* Isomerization of Stilbene[a]

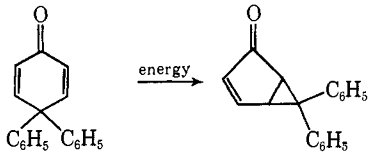
Solvent	Temp, °C	Starting concentrations, M Ia	VI	% *cis* isomer[b]	Apparent quantum yield (10^2)[c]
Benzene	95–100	0.3	0.25 *trans*	5	4
	95–100	0.3	0.05 *trans*	10	1.7
	95–100	3	0.05 *trans*	30	0.6
	95–100	*d*	0.05 *trans*	41	
	95–100	*d*	0.05 *cis*	41	
e	95–100	3	0.05 *trans*	2	0.04
Acetone	95–100	3	0.05 *trans*	26	0.4
f	80	3	0.05 *trans*	17	0.3
Methanol	23	3	0.05 *trans*	16	0.3

[a] Solution degassed (except where noted) and heated in sealed tubes. [b] By glpc (% *cis* found/% recovered olefin). [c] Mol of *cis*/mol of Ia (minimum value because of reversibility). [d] Fifty molar equivalents of Ia added slowly. [e] 0.4 M in cyclooctatetraene. [f] Saturated with air (effectively the same results degassed).

isomerization appreciably. Phenanthrene was not detected in the aerated runs.[10] The quenching by cyclooctatetraene suggests isomerization from the triplet state.

Using chemically produced excited states, a photostationary state of stilbene was readily reached with about 50 equiv of Ia (Table II); a value of 59% *trans*–41% *cis* was found for 0.05 M solutions of VI in benzene at 100°.

4,4-Diphenyl-2,5-cyclohexadienone (VII). Solutions in benzene of Ia (1 M) and VII (0.02 M) heated to 100° for 10 min gave the photoproduct VIII in 19% yield



VII VIII

(apparent quantum yield = 0.004). Zimmerman and Swenton[11] have reported that the rearrangement of VII to VIII occurs from the triplet state, and presumably that is the case here as well. It was also reported[11] that the triplet energy of VII is 69 kcal; thus quanta of at least this energy are available from the decomposition of Ia.

The apparent quantum yields (ϕ_{app}) found for compounds VI and VII in benzene are *ca.* 0.017 and 0.004. The corresponding triplet photochemical quantum yields (ϕ_{photo}) are about 0.4 for 0.05 M stilbene in benzene[9] and 0.77 for VII in benzene + 3% methanol.[11] Since $\phi_{app} = \phi_{I \rightarrow II}\phi_{transfer}\phi_{photo}$,[12] and the efficiency of transfer of triplet excitation at our concentrations is effectively 1,[9] $\phi_{I \rightarrow II}$ for the chemical excitations of VI and VII become 0.04 and 0.005.[13] Work is in progress on elucidating these differences of excitation yields, as well as other aspects of the reactions.

Acknowledgment. We thank the Public Health Service for its financial support (Research Grant No. 5R01 7868 from the National Institute of Neurological Diseases and Blindness).

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Received December 18, 1969

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[10] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 86, 3094 (1964).

[11] H. E. Zimerman and J. S. Swenton, *ibid.*, 89, 906 (1967).

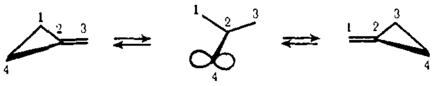
[12] Correction factors for nonideal conditions have not been included.

[13] Recently, photochemical processes at lower energies have been carried out using the oxalate ester–hydrogen peroxide system[5] as an energy source (H. Güsten and E. F. Ullman, *Chem. Commun.*, 28, (1970)).

Degeneracy in the Methylenecyclopropane Rearrangement[1]

Sir:

Understanding of the detailed mechanism of thermally induced methylenecyclopropane rearrangements has been extended by recognition that the isomerization does not involve a reactive species having the planar geometry of trimethylenemethane.[2] Attractive alternatives for molecular geometries of hypothetical intermediates and/or transition states have been suggested.[3] These geometries are related in that the developing p orbital of the pivoting carbon atom, *i.e.*, the atom that can be considered to be undergoing a 1,3 migration (C-4, eq 1), is coincident with the plane defined by the four carbon atoms of the trimethylenemethane skeleton, whereas the remaining incipient p orbitals are not in this plane. One important implication of this common feature is that appropriate substituents might influence, to a greater or lesser extent, the migratory aptitude of a carbon atom and thereby endow the methylenecyclopropane rearrangement with significant positional selectivity. To the qualitative support of this expectation for substituents such as carboalkoxy,[4] phenyl,[5] and possibly alkoxy,[6] we wish to add the quantitative confirmation available from evaluation of the high selectivity and acceleration of rate imparted by phenyl substituents to this rearrangement.



(1)

Thermolysis of 2,2-diphenyl-1-(dideuteriomethylene)cyclopropane (**1a**)[7] at 80° in carbon tetrachloride solution results in diminution of intensity of the broad singlet at δ 1.8 for the cyclopropyl hydrogens and in the appearance of broad singlets at δ 5.53 and 5.72, chemical shifts that correspond to those of the vinyl hydrogens of **1b**. Continued heating ultimately produces an

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[1] The support of this research by The Robert A. Welch Foundation is gratefully acknowledged. The HA-100 nmr spectrometer used in this work was purchased with funds provided by the National Science Foundation (Grant No. GP-6940).

[2] (a) E. F. Ullman, *J. Amer. Chem. Soc.*, 82, 505 (1960); (b) J. J. Gajewski, *ibid.*, 90, 7178 (1968).

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[6] T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *J. Amer. Chem. Soc.*, 87, 3026 (1965).

[7] Compound **1a** was prepared from 2,2-diphenyl-1-bromo-1-carbomethoxycyclopropane[8a] by reduction with $LiAlD_4$, tosylation of the resulting bromoalcohol,[8b] and treatment of the bromotosylate with magnesium. The isolated **1a** was characterized by its spectra and was shown by mass spectrometric analysis to consist of at least 98% of the d_2 isomer.

[8] (a) H. M. Walborsky, *et al.*, *J. Amer. Chem. Soc.*, 83, 2517 (1961); (b) H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, 86, 3283 (1964).