

Table II. The *cis-trans* Isomerization of Stilbene<sup>a</sup>

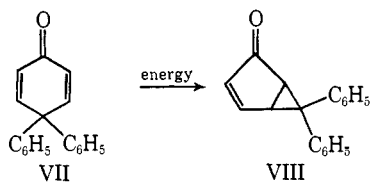
Solvent	Temp, °C	Starting concentrations, <i>M</i>		% <i>cis</i> isomer <sup>b</sup>	Apparent quantum yield (10 <sup>3</sup> ) <sup>c</sup>
		Ia	VI		
Benzene	95-100	0.3	0.25 <i>trans</i>	5	4
	95-100	0.3	0.05 <i>trans</i>	10	1.7
	95-100	3	0.05 <i>trans</i>	30	0.6
	95-100	<i>d</i>	0.05 <i>trans</i>	41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

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

isomerization appreciably. Phenanthrene was not detected in the aerated runs.<sup>10</sup> The quenching by cyclooctatetraene suggests isomerization from the triplet state.

Using chemically produced excited states, a photo-stationary 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



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

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

(11) H. E. Zimmerman 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<sup>9</sup> as an energy source (H. Güsten and E. F. Ullman, *Chem. Commun.*, **28**, (1970)).

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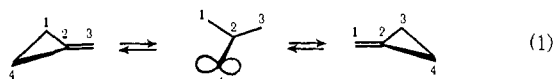
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## Degeneracy in the Methylene-cyclopropane Rearrangement<sup>1</sup>

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.<sup>2</sup> Attractive alternatives for molecular geometries of hypothetical intermediates and/or transition states have been suggested.<sup>3</sup> 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,<sup>4</sup> phenyl,<sup>5</sup> and possibly alkoxy,<sup>6</sup> 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.



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

(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).

(3) J. P. Chesick, *ibid.*, **85**, 2720 (1963).

(4) T. Sanjiki, H. Kato, and M. Ohta, *Chem. Commun.*, [9] 496 (1968).

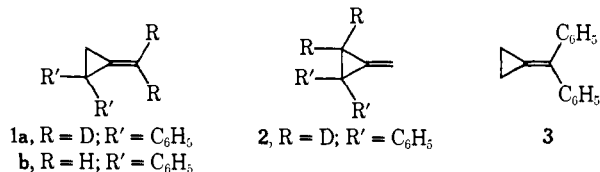
(5) R. Noyari, H. Takaya, Y. Nakanisi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969).

(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<sup>8a</sup> by reduction with LiAlD<sub>4</sub>, tosylation of the resulting bromoalcohol,<sup>8b</sup> 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*<sub>2</sub> 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).

equilibrium mixture of **1a** and **2** in which a ratio of the integrated areas for the vinyl and cyclopropyl absorptions of 1.04:1.00 is established. A quantitative evaluation of the dependence upon temperature of the rate of the equilibration results in the expression  $\log(k_1 + k_{-1}) = 10.77 - (22,800/2.303RT)$ .



The remarkably facile exchange<sup>9</sup> of the vinylic and allylic methylene groups of **1a** occurs to the exclusion of formation of **3**,<sup>11</sup> which is anticipated to be thermodynamically the more stable isomer.<sup>12</sup> Attempts to set **1b** and **3** into equilibrium fail even under conditions considerably more drastic than those required for the degenerate isomerization. Thus, heating of **1b** for 9.5 hr at 140°, the temperature at which an irreversible rearrangement to 2-methyl-3-phenylindene (**4**) assumes kinetic significance,<sup>13</sup> produces no **3** (as little as 5% could have been detected). Approach of the equilibrium from the other side is equally unsuccessful; isomer **3** is stable up to 190°, at which temperature it rearranges to 1-phenyl-3,4-dihydronaphthalene (**5**),<sup>14</sup> with neither **1b** nor **4** being detectable.

The observation that no more than 5% of **3** is formed under the conditions stated, coupled with the reasonable assumption that the preexponential factor for the hypothetical first-order isomerization of **1b** to **3** would be at least as great as that for the degenerate isomerization, allows the conclusion that the energy of activation for the former process is at least 6.5 kcal/mol greater than that of the latter reaction. This difference represents a conservative estimate of the selectivity accorded to the methylenecyclopropane rearrangement by the phenyl groups.

The fundamental importance of the phenyl substituents in the isomerization also is evident in the magnitude of the activation parameters for the interconversion of **1a** and **2** ( $\Delta H^{\ddagger}_{52^\circ} = 22.1$  kcal/mol,  $\Delta S^{\ddagger}_{52^\circ} = -11.5$  eu) as compared to those calculated from Chesick's data<sup>3</sup> on the equilibration of 2-methylmethylenecyclopropane and ethylenecyclopropane ( $\Delta H^{\ddagger}_{52^\circ} = 39.8$  kcal/mol,  $\Delta S^{\ddagger}_{52^\circ} = 3.2$  eu). The negative entropy of activation for the isomerization can be associated, at least in part, with the requirement of a specific orientation of the phenyl rings in order to induce cleavage of

(9) It is of interest to note that a similar exchange through a methylenecyclopropane rearrangement is not detectable when the *exo*-carbon atom of **1** is substituted with either one or two methyl groups.<sup>10</sup> It is likely that methyl-phenyl interactions in the rearrangement products (**2**, R' = C<sub>6</sub>H<sub>5</sub>, R = R = CH<sub>3</sub> or R = CH<sub>3</sub>, R = H) markedly destabilize these isomers so that their concentrations at equilibrium are negligible.

(10) M. Jones, Jr., and M. E. Hendrick, unpublished results.

(11) Prepared according to the procedure of K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 3267 (1966).

(12) The expectation that **3** would be favored thermodynamically is supported by the observation that fluorenylidene cyclopropane is formed irreversibly upon thermolysis of 2-methylenespiro[cyclopropane-1,9'-fluorene], the product of addition of fluorenylidene to allene.<sup>10</sup>

(13) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, unpublished results.

(14) Identified by comparison of its ir and nmr spectra with those of an authentic specimen synthesized according to the method of H. Christol, C. Martin, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 1696 (1960).

the ring. The low enthalpy of activation tempts interpretation as requiring a concerted reaction mechanism, but the value can, in fact, be shown to be consistent with a stepwise process as well. This is accomplished by first noting that a decrease of *ca.* 18 kcal/mol in the dissociation energy of a carbon-carbon bond, cleavage of which generates a benzhydryl radical, is anticipated.<sup>15</sup> If the energy of the transition state for bond cleavage reflects a major portion of this decrease, as well as most of the stabilization available from release of ring strain and from allylic delocalization, factors evaluated previously,<sup>3</sup> a minimum enthalpy of activation of 19–22 kcal/mol can be derived.<sup>17</sup>

Whether the methylenecyclopropane rearrangement is characterized as a stepwise or a concerted process, the proposal that electron delocalization involving substituents is important in defining the energy of the transition state for rearrangement accounts most economically for the positional selectivity noted here.

(15) The decrease in the carbon-carbon bond dissociation energy afforded by the benzhydryl group can be estimated in the following way. The difference in the dissociation energies of the benzylic bonds of phenylacetic acid (55 kcal/mol) and diphenylacetic acid (52 kcal/mol) approximately reflects the energy difference expected upon formation of a primary benzylic *vs.* a secondary benzylic radical.<sup>16</sup> Thus, the stabilization available from delocalization at the transition state for bond cleavage is about the same whether one or two phenyl groups is present. The magnitude of benzylic stabilization is estimated at *ca.* 18 kcal/mol on the basis of the dissociation energies for the carbon-carbon bonds of butane (87 kcal/mol, C<sub>2</sub>-C<sub>3</sub> bond) and *n*-propylbenzene (69 kcal/mol, benzylic bond).<sup>16</sup>

(16) J. A. Kerr, *Chem. Rev.*, 66, 465 (1966).

(17) A slight decrease in this predicted value might result if buttressing effects present in **1** are relieved by ring opening.

(18) NDEA Title IV Fellow, 1967–1970.

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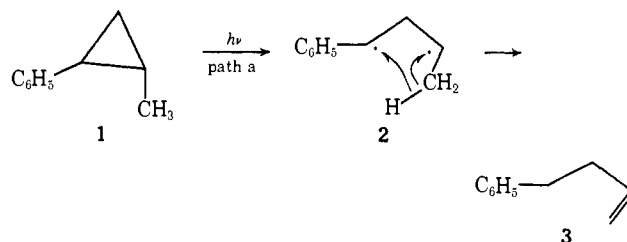
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## The Photoisomerizations of 2-Methylphenylcyclopropanes. Deuterium Labeling

Sir:

The photoisomerizations of various 2-methylphenylcyclopropanes to 4-phenyl-1-butenes have been described<sup>1,2</sup> and the reaction appears to be a common one for phenylcyclopropanes substituted in this manner. Mechanistic speculation has centered on the intermediacy of diradical **2** which would afford the observed product *via* migration of a methyl hydrogen to the benzylic position. An alternate mechanism, involving



initial hydrogen migration to the *ortho* position of the benzene ring, followed by rearomatization of the intermediate tetraene **4**, has also been suggested. The latter

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

(2) H. Kristinsson and G. W. Griffin, *Tetrahedron Lett.*, 3259 (1966).