from an authentic sample.[12] The surprisingly efficient lactonization–migration step[13] is an intriguing aspect of this synthesis and is the subject of current investigation. The utility of this approach in preparing further analogs of rosenonolactone, *e.g.*, the 11β-hydroxy derivative, Rosein III,[9] is also under examination.

Supplementary Material Available.—Complete experimental details on all compounds described in this communication will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-4090.

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[12] We are grateful to Professor R. W. Rickards, Australian National University, for this compound.

[13] *Cf.* W. Herz and H. J. Wahlborg, *J. Org. Chem.*, **30**, 1881 (1965).

DEPARTMENT OF ORGANIC CHEMISTRY,
UNIVERSITY OF ADELAIDE,
ADELAIDE, SOUTH AUSTRALIA,
AUSTRALIA, 5001
W. S. HANCOCK
L. N. MANDER*
R. A. MASSY-WESTROPP

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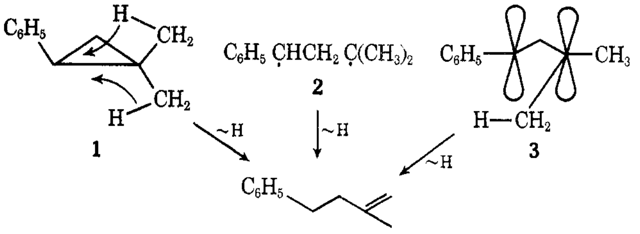
The Photoisomerizations of 2-Methylphenylcyclopropanes. Isotope Effects and Stereochemistry

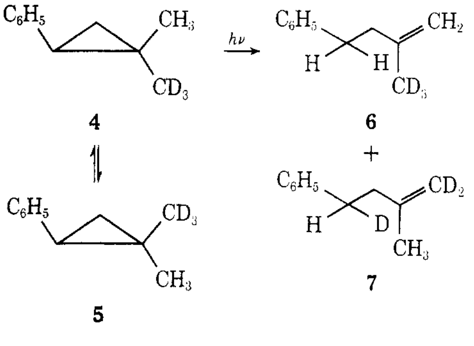
Summary: A deuterium-labeling study on 2,2-dimethylphenylcyclopropane has resulted in the determination of secondary and rather small primary isotope effects for the photochemical reaction and has shown that hydrogen migration in this system takes place preferentially from the methyl group trans to the benzene ring.

Sir: The photochemistry of phenylcyclopropanes has been the subject of intensive investigation recently.[1-6] In particular the isomerizations of 2-alkylphenylcyclopropanes to 4-phenyl-1-butenes[7-11] are of interest since they could represent an example of the allowed $[{}_\sigma 2_s + {}_\sigma 2_s]$ concerted[12] photochemical cycloaddition. Alternatively the reaction could proceed *via* preliminary opening to a classical diradical (**2**) or a π cyclopropane-like[13] intermediate (**3**) resulting from disrotatory or conrotatory opening of **1** with subsequent hydrogen migration affording the observed product. *A priori* one expects equivalent migration from *cis*- and *trans*-methyl groups *via* the ${}_\sigma 2 + {}_\sigma 2$ route with steric factors possibly causing a slight preponderance of migration from the *trans*-methyl group, whereas, if **2** is the intermediate, stereochemical information on the initial locus of the migrating hydrogen must be lost. Preferred disrotatory opening to **3** for electronic or steric reasons requires migration from the *trans*-methyl group, whereas migration from the *cis*-methyl group would result from conrotatory opening. Stereochemical information is thus of value in elucidating the mechanism of this rearrangement.



In principle the problem could be solved by examining the relative rates of rearrangement of *cis*- and *trans*-2-methylphenylcyclopropane; however, this system is complicated by the fact that the ground-state conformations and energies of the isomers differ significantly[14] and photochemical cis → trans isomerization[4] is so fast that it completely dominates terminal olefin formation.

The problem can be solved by examining the products from photolysis of labeled materials such as **4**. The cis to trans migration ratio is simply the **6**:**7** ratio obtained on photolysis of **4**,[15] and this ratio is amenable to mass spectroscopic analysis; *i.e.*, whereas **6** affords a normal tropylium ion at *m/e* 91, the tropylium ion from **7** (C_7H_6D) appears at *m/e* 92. The **6**:**7** ratio is obtained from the suitably corrected[16] *m/e* 91/92 peak intensity ratio (H/D). As expected geometrical isomerization (*i.e.*, **4** → **5**) is slower in this system than in the 2-methylphenylcyclopropanes and the experimental **6**:**7** ratios from **4** were obtained by determining



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[13] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968). Hoffmann's calculations suggest that there is no distinct energy minimum in the singlet or triplet excited states of the trimethylene diradical.

[14] J. J. Rocchio, Ph.D. Thesis, University of Maryland, 1970.

[15] Details of the synthesis of the labeled compounds used will be presented elsewhere.

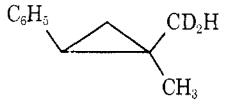
[16] An empirical correction factor was calculated from *m/e* 91/92 ratios obtained from synthetic mixtures of 2-methyl-4-phenyl-1-butene and 2-methyl-4-phenyl-4-d_1-1-butene. Scrambling of deuterium from the methyl and vinyl positions to the benzylic position in the mass spectrum was also considered. Examination of the mass spectra of suitable model compounds showed that this was not a major process. The error limits reflect our estimation of the magnitude of this process.

this ratio at various conversions and extrapolating back to zero conversion. The formation of **6** and **7** is also subject to primary and secondary isotope effects and knowledge of these values is necessary to make the data applicable to compound **1**. If we define π as the primary, α and β as secondary type I and type II isotope effects, respectively, and x as the fraction migration from the *cis*-methyl group, an expression relating the corrected m/e 91/92 (H/D) to the **6**:**7** ratio can be written; *i.e.*, hydrogen migration to give **6** occurs from the cis side (x) and is subject to three secondary type II effects (β^3), while **7** results *via* trans migration ($1 - x$) and is subject to a primary (π) and a pair of secondary type I effects (α^2) (eq 1).

$$\mathrm{H/D} = \frac{x/\beta^3}{(1-x)/\pi\alpha^2} = \frac{x\pi\alpha^2}{(1-x)\beta^3} \tag{1}$$

Similarly for systems **8** → **11** + **12** equations 2–5 can be written. These equations allow a solution for

$$\mathrm{H/D} = \frac{\pi\beta^2 x + (1-x)3\pi\alpha^2}{2x\alpha\beta^2} \quad \text{for} \tag{2}$$



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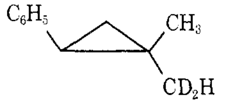
$$\mathrm{H/D} = \frac{3x\pi\alpha^2 + (1-x)\pi\beta^2}{2\alpha\beta^2(1-x)} \quad \text{for} \tag{3}$$



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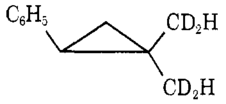
$$\mathrm{H/D} = \frac{\pi}{2\alpha} \quad \text{for} \tag{4}$$



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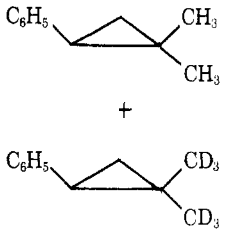
$$\mathrm{H/D} = \pi\alpha^2\beta^3 \quad \text{for} \tag{5}$$



x, π, α, and β[17] and substitution of the experimental H/D values (Table I) affords isotope effect values: $\pi = 1.96 \pm 0.22$; $\alpha = 1.10 \pm 0.05$; $\beta = 1.04 \pm 0.09$.[18,19]

The calculated value of x is 0.373 ± 0.054; *i.e.*, there is a distinct preference for migration from the methyl group trans to the benzene ring. The 63:37 ratio of trans to cis migration is significant and clearly rules out **2** as a viable intermediate. In addition, processes which proceed with exclusive disrotatory or conrotatory opening to an intermediate such as **3** are also excluded by these results.

Table I

System	**4**	**8**	**9**	**10**	**11 + 12**
H/D[a]	1.23 ± 0.12	5.68 ± 0.97	2.49 ± 0.25	0.893 ± 0.089	2.67 ± 0.27

[a] Corrected m/e 91/92 intensity ratio.

The data are consistent with mechanisms which either result from a mixture of disrotatory and conrotatory openings to **3** followed by hydrogen migration or a reaction which proceeds *via* a $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ transition state, or its equivalent,[20] subject to a slight steric discrimination.

It is inviting to attempt to interpret the isotope effects determined. Whereas the secondary effects are of the expected magnitude and direction for the hybridization changes involved,[21] the primary effect is low. In fact the magnitude of this effect is in the range predicted for a four-centered transition[22] state like that which would be involved in a $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ process. However, the lack of appropriate models for isotope effects in photochemical systems would make mechanistic interpretation of these data dangerous. Experiments on the stereochemistry at the migration terminus further elucidate the mechanism of this reaction.[23]

Acknowledgment.—We wish to thank the Research Corporation and the Center of Materials Research of the University of Maryland for partial support of this work.

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[17] S-H. Dai and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **94**, 3953 (1972). These authors use a similar method to calculate isotope effects.

[18] The validity of the use of eq 5 can be questioned; *i.e.*, these are intermolecular isotope effects as opposed to intramolecular effects in the other cases. In the case of **11** + **12** we could be seeing an effect which arises on formation of the reactive excited state. The use of five equations for the four unknowns allows a solution for x independent of eq 5. Furthermore the fact that the calculated values constitute a solution, well within experimental error, of eq 1–4 suggests that there is little, if any, isotope effect on formation of the reactive excited state.

[19] The inclusion of the secondary type 2 effect is actually mechanistically prejudicial suggesting that C_1–C_2 bond cleavage occurs in the rate-determining step in the reaction. We have no evidence on this point. Inclusion of a value $\beta = 1.00$ results in little change in the calculated values for π and α ($\pi = 2.11$, $\alpha = 1.05$) and the value for x is unchanged.

[20] We cannot at present differentiate a $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ process from one in which 1,2 bond cleavage has occurred *via* simple expansion of the C_1–C_3–C_2 bond angle followed by hydrogen migration.

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Department of Chemistry
University of Maryland
College Park, Maryland 20742

Paul H. Mazzocchi*
Robert S. Lustig

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Exceptionally High Regioselectivity in the Hydroboration of Representative Olefins with 9-Borabicyclo[3.3.1]nonane in a Simplified Rapid Procedure

Summary: Hydroboration–oxidation of olefins with stoichiometric amounts of 9-borabicyclo[3.3.1]nonane in refluxing tetrahydrofuran proceeds rapidly and gives the anti-Markovnikov alcohols in high isomeric purity, often >99.5%. The regioselectivity obtained surpasses that obtained with other hydroborating agents, especially in the case of internal olefins.

Sir: The hydroboration of even highly substituted olefins with stoichiometric quantities of 9-borabicyclo-