

A plot of  $\log \tau_{d\bar{e}}$  vs.  $1/T$  ( $^{\circ}\text{K}.$ ) is shown in Figure 3; the slope of the best fit straight line through the experimental points leads to an activation energy of 9.1 kcal. mole $^{-1}$  for the interconversion.

The more complicated line shape formula derived for  $mF_2$  is a function of the two rate parameters  $k$  and  $\beta$ , defined as

$$k = k_1 + k_2 \quad (3a)$$

$$\beta = (k_2 + k_3)/(k_1 + k_2) \quad (3b)$$

The parameter  $\beta$  is assumed to be approximately constant over the temperature range of interest.

A computer program was used to construct plots of  $\log k$  vs. the calculated peak positions for given values of  $\beta$ . By interpolation, these plots yielded values of  $k$  corresponding to the temperatures of the observed peak positions (Figure 4). Values of  $\beta$  ranging from 6 to 20 gave essentially linear plots of  $\log k$  vs.  $1/T$  (Figure 5) corresponding to activation energies<sup>5</sup> from 9.4 to 9.6 kcal. mole $^{-1}$ .

From eq. 2, 3a, and 3b it is possible to show that the relation

$$1/(k\tau_{d\bar{e}}) = 0.5(3 + \beta) \quad (4)$$

should hold if, indeed,  $k_1$ ,  $k_2$ , and  $k_3$  are the same for  $mF_2$  and  $mF_3$ . For  $\beta = 10$ ,  $1/(k\tau_{d\bar{e}}) = 5.0$  (at a common temperature), whereas from eq. 4  $1/(k\tau_{d\bar{e}})$  should equal 6.5. However, the analysis is sufficiently insensitive to the value of  $\beta$  chosen that we consider the identity of  $k_1$ ,  $k_2$ , and  $k_3$  for  $mF_2$  and  $mF_3$  to have been demonstrated. Further, the correctness of the model conformations and interconversion scheme is supported by the identity of the derived activation energies for  $mF_2$  and  $mF_3$ . The large value of  $\beta$  (6 to 20) indicates that the three-ring flip probability,  $k_3$ , is much larger than  $k_1$  or  $k_2$ . A detailed report of this work will be published, along with an analysis of the proton n.m.r. spectra of these compounds.

**Acknowledgment.** We wish to thank the National Science Foundation for financial support.

(4) The more general formula for the line shape of  $mF_3$  obtained under the assumption that the chemical shifts between  $d$  and  $e'''$  and between  $e'$  and  $e''$  are 0.4 c.p.s. yields similar results.

(5) Calculated energies of activation are considered accurate to about  $\pm 0.5$  kcal. mole $^{-1}$ .

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### Thermal Rearrangement of Cyclopropyl Ketones to Homoallylic Ketones. Relationship to the "Abnormal Claisen Rearrangement"

Sir:

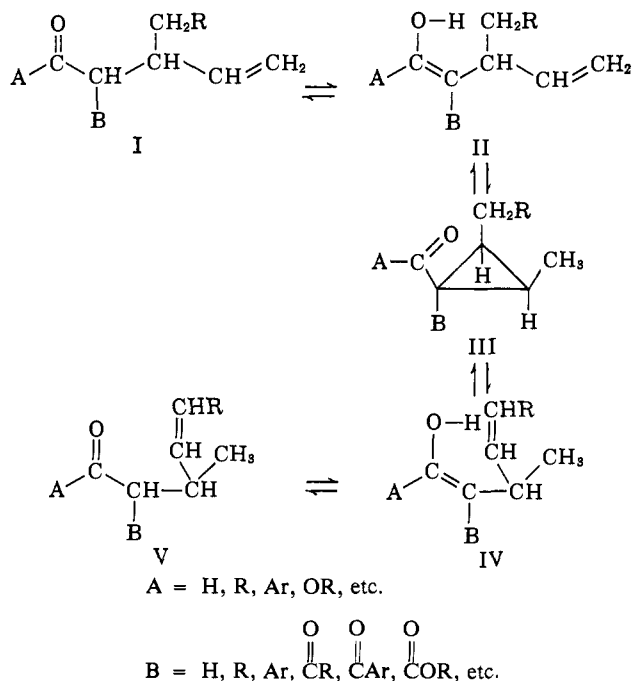
The "abnormal Claisen rearrangement"<sup>1</sup> has now been quite clearly identified as the result of two consecutive processes: the normal *ortho* Claisen rearrangement of a  $\gamma$ -alkylallyl phenyl ether to an *o*-( $\alpha$ -alkylallyl)-phenol, followed by an isomerization of the side chain of this phenol.<sup>2</sup> The mechanism of the secondary

(1) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, **58**, 1388 (1936), and later papers.

(2) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1109 (1962).

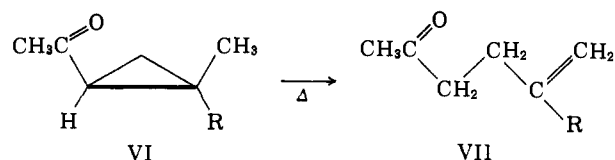
isomerization has been formulated as involving a cyclopropyldienone intermediate.<sup>2,3</sup> Assuming this mechanism is correct, we anticipate that such a mechanism may not be restricted to phenols but may represent quite a general, and so far unnoticed, type of intramolecular rearrangement.

In simplest form, it may be outlined as the conversion of one homoallylic carbonyl compound (I) to another (V) via the allylic enols II and IV and the cyclopropyl



carbonyl compound III. We now wish to report the thermal rearrangement of two cyclopropyl ketones to homoallylic ketones (e.g., III  $\rightarrow$  I) and, in the following communication,<sup>4</sup> we supply evidence for the whole reversible sequence I  $\rightleftharpoons$  V.<sup>5</sup>

1-Acetyl-2,2-dimethylcyclopropane (VI, R = Me) smoothly rearranged to ( $\beta$ -methylallyl)acetone (VII, R = Me) at temperatures above 150 $^{\circ}$ . First-order rate constants of  $3.86 \times 10^{-5}$  sec. $^{-1}$  (152 $^{\circ}$ ) and  $9.00 \times$



$10^{-5}$  sec. $^{-1}$  (163 $^{\circ}$ ) and an activation energy of 33 kcal./mole were calculated. The reaction mixtures were analyzed by vapor phase chromatography, and ( $\beta$ -methylallyl)acetone was found to be the only product that developed. A sample of the product was isolated from a rearrangement mixture by preparative scale v.p.c. and identified through its semicarbazone (m.p.

(3) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

(4) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *J. Am. Chem. Soc.*, **87**, 2282 (1965).

(5) D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel [*Proc. Chem. Soc.*, 415 (1964)] recently observed thermal isomerizations of several esters, which they explained in terms of the mechanism represented by the sequence III  $\rightarrow$  I, where A = OCH $_3$ . R. J. Ellis and H. M. Frey [*ibid.*, 221 (1964)] described a similar rearrangement of *cis*-1-methyl-2-vinylcyclopropane. None of these compounds was structurally capable of showing rearrangement of the type I  $\rightarrow$  V.

137.5–138.5°, lit.<sup>6</sup> m.p. 136.5–137.5°). The n.m.r. and infrared spectra were consistent with the structural features of ( $\beta$ -methylallyl)acetone.

A *cis* relationship between the carbonyl and alkyl groups in the cyclopropyl carbonyl compound is inherent in the intramolecular mechanism proposed for these rearrangements.<sup>2,3</sup> To test the applicability of this requirement to the rearrangement of substituted acetylcyclopropanes, the *cis* and *trans* isomers of 1-acetyl-2-methylcyclopropane were prepared and subjected to rearrangement conditions. Infrared, n.m.r., and mass spectral analyses of the starting materials were indicative of their isomeric relationship. At 160° the *cis* isomer (VI, R = H) rearranged almost entirely in 12 hr. to allylacetone (VII, R = H), identified by comparison with v.p.c. retention time and infrared spectrum of the authentic material. The *trans* compound was stable under these conditions.<sup>7</sup> Over a period of 24 hr. at 180°, the *trans* isomer decomposed slightly, but no allylacetone was formed. All rearrangements were carried out on samples sealed in Pyrex tubes at 0.1 mm.

Brown<sup>8</sup> has described a similar rearrangement under photolytic conditions, obtaining ( $\beta$ -methylallyl)acetophenone from 1-benzoyl-2,2-dimethylcyclopropane. We found that 1-acetyl-2,2-dimethylcyclopropane rearranged to ( $\beta$ -methylallyl)acetone under irradiation at room temperature.<sup>9</sup> Experiments are in progress to determine if steric factors are determinative for the photolytic process.

**Acknowledgments.** We gratefully acknowledge assistance from the Robert A. Welch Foundation, the National Science Foundation, and the University of Texas Research Institute.

(6) W. Kimel and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1992 (1943).

(7) Chemical proof of the geometric configuration of the *cis* and *trans* isomers is in progress. There seems no doubt as to which isomer rearranged and which did not, however, and the nearly identical mass spectrometric fragmentation patterns of the two show them unequivocally to be stereoisomers.

(8) W. G. Brown, *U. S. Govt. Res. Rept.*, **38**, (22) 25 (1963).

(9) Irradiation by a high-pressure Hg arc lamp in a Pyrex flask.

(10) University of Texas Fellow, 1964–1965.

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### Reversible Intramolecular Hydrogen Transfers between Allylic Enol and Cyclopropyl Carbonyl Systems

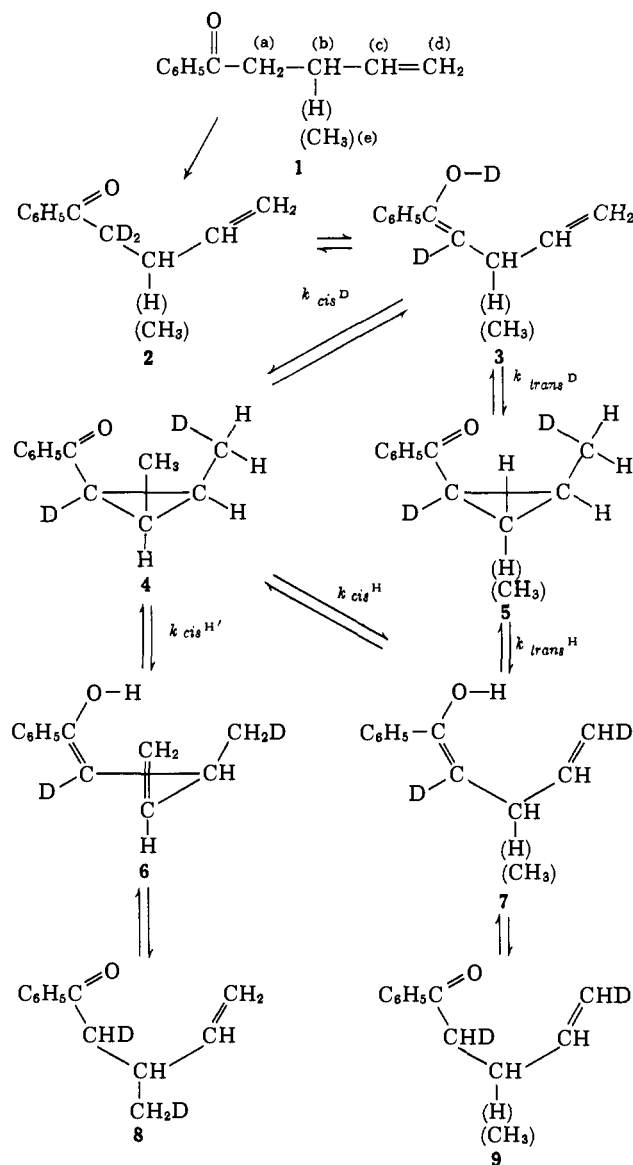
Sir:

In the preceding communication<sup>1</sup> we reported examples of a thermal rearrangement in which transfer of hydrogen from a methyl group to a *cis*-carbonyl oxygen of a ketone occurs, concerted with the opening of a cyclopropane ring. In order to substantiate a rearrangement mechanism in an aliphatic system analogous to the allylic phenol rearrangement of the "abnormal Claisen rearrangement," we must demonstrate the reversibility of this reaction, *i.e.*, the formation of a cyclopropyl carbonyl compound from an allylic enol, with concerted hydrogen transfer.

(1) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, **87**, 2281 (1965).

For the initial test of such a process, we chose a technique that is a modification of the elegant deuterium tracer experiments of Schmid.<sup>2</sup>

Allylacetophenone (1, H)<sup>3</sup> is ideally suited for this study because of the good separation of the n.m.r. absorptions of its hydrogens: C<sub>6</sub>H<sub>5</sub>, 2 H(*o*) multiplet,  $\tau$  2.1, 3 H(*m,p*) multiplet, 2.6; CH<sub>2</sub>(a) triplet, 7.1; CH<sub>2</sub>(b) multiplet, 7.6; CH(*c*) multiplet, 4.1; CH<sub>2</sub>(d) triplet, 5.0. It was deuterated by base-catalyzed exchange with D<sub>2</sub>O<sup>4</sup> to yield 2 (H) (n.m.r. identical with that of 1 (H) except for disappearance of the CH<sub>2</sub>(a) triplet and replacement of the CH<sub>2</sub>(b) multiplet by a doublet,  $J = 8$  c.p.s.). Intramolecular hydrogen exchange according to the scheme shown for 2 (H)  $\rightleftharpoons$  9 (H) could be followed by appearance of H n.m.r. absorption at  $\tau$  7.1 and decrease at  $\tau$  5.0. If equilibrium were reached, absorption at these regions should become equal.



The deuterated allylacetophenone (2, H) was heated at  $200 \pm 5^\circ$  (sealed tubes evacuated to  $<0.1$  mm.) for

(2) H. Schmid, *Oesterr. Chemiker-Ztg.*, **65** (4), 109 (1964); *Chem. Abstr.*, **61**, 2999 (1964); and private communication.

(3) (a) A. C. Cope, K. E. Hoyle, and D. R. Heyl, *J. Am. Chem. Soc.*, **63**, 1843 (1941); (b) prepared by the method of W. Kimel and A. C. Cope, *ibid.*, **65**, 1992 (1943).

(4) Professor V. J. Shiner, private communication.