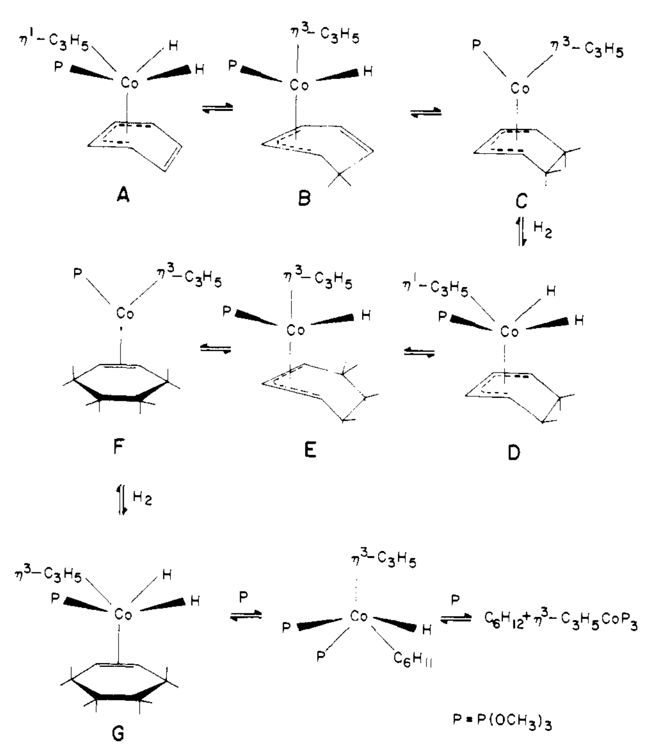


Figure 1. Possible reaction sequence for hydrogen transfer from cobalt to arene in the η^3-$C_3H_5Co[P(OCH_3)_3]_3$ catalyzed hydrogenation of aromatic hydrocarbons. Note the pervasive homofacial character of hydrogen addition to the ring. Sixteen-electron intermediates such as F will be in equilibrium with 18-electron intermediates through reaction with free trimethylphosphite.

present. The allylcobalt complex was recovered in near quantitative yield from the hydrogenation system and propylene (or propane) was not detected, at least in a 24-hr reaction period. In the absence of an arene, the dihydride does slowly evolve propylene (a small amount of which is hydrogenated to propane). This clearly indicates a significant interaction of arene with the dihydride (α), or an intermediate derived from the dihydride (*vide infra*), thereby inhibiting cis elimination. Also, we have shown that the hydride, $HCo[P(OCH_3)_3]_3$, derived from cis elimination is not the active arene hydrogenation catalyst. Closely related to the allylcobalt complex is η^3-$C_6H_5CH_2Co[P(OCH_3)_3]_3$.[9] This π-benzyl complex catalyzes arene hydrogenation but cis elimination of toluene is so rapid even in an arene solution *that hydrogenation ceases* very quickly with the formation of $HCo[P(OCH_3)_3]_3$. This monohydride which possesses a low stability, with decomposition to an intractable solid, appears to be a very active catalyst for HD exchange in H_2-D_2 mixtures[10] but it does not significantly catalyze arene hydrogenation.

The above studies clearly indicate a significant interaction of arene with the dihydride but we have not succeeded in gaining spectroscopic evidence of the interaction. We suggest that the dihydride (α) interacts with the arene in the manner outlined in eq 4–6. We further suggest that an important intermediate state is η^1-$C_3H_5CoH_2P(OCH_3)_3$-η^4-C_6H_6 since the reactivities of cyclohexadiene and benzene are so similar (*vide supra*); there is precedent for such η^4-arene metal complexes.[11] The compelling evidence for nondissociation of ring after initial reduction suggests the sequence in Figure 1. Note that the last step is irreversible; cyclohexane does not interact with the cobalt complex even in the presence of hydrogen (D_2). The sequence in Figure 1 also neatly accounts for the pervasive all cis stereochemistry[1] of the cyclohexanes derived from xylenes and mesitylene since the sequence requires addition of hydrogen atoms to one face of the arene.

$$\eta^1 - C_3H_5CoH_2[P(OCH_3)_3]_3 \rightleftharpoons \eta^3 - C_3H_5CoH_2[P(OCH_3)_3]_2 + P(OCH_3)_3 \quad (4)$$

$$\eta^3 - C_3H_5CoH_2[P(OCH_3)_3]_2 \rightleftharpoons \eta^3 - C_3H_5CoH_2P(OCH_3)_3 + P(OCH_3)_3 \quad (5)$$

$$\eta^3 - C_3H_5CoH_2P(OCH_3)_3 + C_6H_6 \rightleftharpoons \eta^1 - C_3H_5CoH_2P(OCH_3)_3 - \eta^4 - C_6H_6 \quad (6)$$

Final and conclusive demonstration of this reaction sequence rests on synthesis of the unknown η^3-C_3H_5Co-η^6-C_6H_6 and conversion of this complex to the proposed intermediates in Figure 1 through reaction with $P(OCH_3)_3$ and subsequent hydrogen titration. We are also attempting electronic and steric modification of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ to achieve a very high selectivity for arenes.[12]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation, Grant No. GP-39306X.

References and Notes

(1) Paper I in this series: E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, **96,** 4063 (1974).

(2) Initial equimolar mixtures of benzene-d_6 and cyclohexene; no inert solvent was employed. Reactions run at 25° and ~760 mm.

(3) This statement applies to all reaction systems in which the hydrogen reactant is not exhausted. Analysis was gc–mass spec.

(4) Rate of this process is low with respect to the nmr time scale.

(5) K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Recl. Trav. Chim. Pays-Bas*, **85,** 1077 (1966).

(6) E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, in press.

(7) Nmr and electronic spectra are not detectably different for the allylcobalt complex in cyclohexane and in benzene.

(8) Alternatively, the observed hydride may be η^3-$C_3H_5CoH_2[P(OCH_3)_3]_2$ (see eq 4) where there would be three stereoisomers with cis hydride ligands (no resonances that could be attributed to the trans stereoisomer were detected).

(9) E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, **95,** 5419 (1973).

(10) Reaction of H_2, D_2, and benzene in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ yields HD and $C_6H_nD_{12-n}$ molecules with n odd and even numbers. This is tentatively ascribed to catalysis of H–D exchange by trace amounts of $HCo[P(OCH_3)_3]_3$.

(11) M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A, 292,* 61 (1966); G. Huttner, S. Lange, and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **10,** 556 (1971).

(12) NOTE ADDED IN PROOF. The conjugated, noncyclic olefin, 1,3-hexadiene, was hydrogenated at a rate 2–3 times lower than that of benzene to form only the internal olefin. We have prepared η^3-$C_3H_5Co[P(OCH_3)_3]_2[P(O$-$i$-$C_3H_7)_3]$ and find it is a more active catalyst; the increase in rate over η^3-$C_3H_5Co[P(OCH_3)_3]_3$ is a factor of 3.

F. J. Hirsekorn, M. C. Rakowski, E. L. Muetterties*
Spencer T. Olin Chemistry Laboratory, Cornell University
Ithaca, New York, 14853

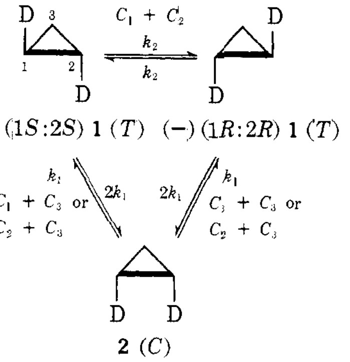
Received September 26, 1974

Thermal Stereomutation of Optically Active *trans*-Cyclopropane-*1,2-d*$_2$[1]

Sir:

Pyrolysis of cyclopropane or its substituted derivatives causes two major reactions:[2] hydrogen shift to an olefin (*e.g.*, cyclopropane → propylene)[3] and stereomutation (*e.g.*, *trans*- → *cis*-cyclopropane-*1,2-d*$_2$).[4] The trimethylene biradical, first proposed[3] as an intermediate in the olefin-forming reaction, more recently has also been invoked[5] to explain the stereomutation. In the case of cyclopropane itself, thermochemical estimates suggest that rotations about the C–C bonds of trimethylene would be fast relative to cyclization, a relationship that would result in a *stereorandom intermediate*.[5b-d,6]

Scheme I



A widely discussed alternative by-passes trimethylene and consists of the stereochemical equivalent of a 180° rotation of one of the methylene groups of cyclopropane.[7] Theoretical objection[5a] to this *single methylene rotation* mechanism gradually has become less severe,[8,9] and the process is at least formally consistent with (but not required by) the experimental results in the case of tetramethylcyclopropane-d_6.[10]

A third alternative, proposed by Hoffmann,[8] and based upon extended Hückel calculations, suggests that reaction might occur *via* a trimethylene in which the three ring carbons and four of the hydrogens occupy a common plane. The calculations indicate that this "0,0" species should have an antisymmetric highest occupied molecular orbital and hence should be formed and recyclized by synchronous conrotations of the two terminal methylene groups[8] (Scheme I). Experimental attempts[6,10-15] to detect this *double methylene rotation* process in substituted cyclopropanes have failed consistently.[16] It is disturbing that, nevertheless, a variety of later theoretical calculations[17-19] persist (although with now diminished force) in the prediction that the 0,0 form of unsubstituted trimethylene should lie on the favored stereomutation pathway.

A fourth conceivable mechanism, *triple methylene rotation,* at present has no theoretical support but is considered here for the sake of completeness.

The present paper describes the pyrolysis of optically active *trans*-cyclopropane-*1,2*-d_2 (**1**), an experiment that provides the closest possible approach to an unperturbed test for the double methylene rotation and permits a decision among the mechanisms proposed.

As in the tetramethylcyclopropane-d_6 case,[10] the test depends upon a comparison of the measured rate constant for approach to the cis-trans (C/T) equilibrium mixture, $k_i = -(1/t)\ln[(T - C)/(T_0 - C_0)]$, with that for the loss of optical activity (α), $k_\alpha = t^{-1}\ln(\alpha_0/\alpha)$. In each mechanism, reaction at any site would be equiprobable by symmetry, if the secondary kinetic isotope effect of deuterium were negligible. However, such isotope effects usually cause a decrease of about 10% per deuterium in the rate of a thermal bond cleavage reaction,[4c,20] and Table I shows the k_i/k_α values predicted for each mechanism assuming either possibility, *i.e.*, isotope effects (k_H/k_D) of 1.00 or 1.10.

The synthesis of optically active **1** from (+)-*trans*-2-phenylcyclopropanecarboxylic acid[21] (**3**, absolute configuration shown) is achieved by the indicated steps (Scheme II), approximately 1.5 g of **1** being obtained from 2 kg of racemic **3**.

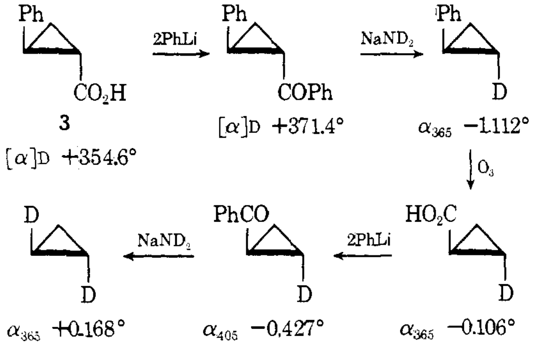
The synthetic sample of **1** consists of 62.6% d_2, 32.7% d_1, 3.7% d_0, and 1% d_3 (mass spectrometric analysis). The d_2 component contains 2.3% *cis*-cyclopropane-*1,2*-d_2 (**2**) and 97% trans (infrared spectrophotometric analysis[4b,d] on a gaseous sample measured at 35 Torr with a Perkin-Elmer Model 421 instrument, using the 846 cm^{-1} absorption). The analytical infrared absorption band obeys the Beer-Lambert law in the pressure range 15-70 Torr, and the estimated accuracy of 1% in the analysis for isomer composition is further validated by empirical calibration using known mixtures.

Table I. Predicted Ratios of Rate Constants for Stereomutation of **1**

Mechanism	Kinetic form of k_i/k_α	k_i/k_α if k_H/k_D = 1.00	if k_H/k_D = 1.10
Single CH_2 rot	2.00	2.00	2.00[a]
Random int	$(2k' + k'')/(k' + k'')$[b]	1.50	1.53
Double CH_2 rot	$2/(1 + (k_2/k_1))$[b]	1.00	1.05
Triple CH_2 rot	$0/k_\alpha$	0.00	0.00

[a] No significant isotope effect would be expected, since the only observable reaction involves a CHD group. [b] k_1 and k' measure reactions at monodeuterated C-C bonds, k_2 and k'' at dideuterated (see Scheme I).

Scheme II



The optical rotations are measured to 0.001° with a Rudolf Model 80 polarimeter on the neat liquid at 3°. Since cyclopropane has bp −33°, we use a special 1-dm cell of design[22a] and construction[22b] sufficient to maintain about 2 atm pressure above the liquid phase.

Pyrolysis of a sample of (+)-**1** at 422.5 ± 0.5° and 631 Torr is monitored on material separated by gas chromatography from small amounts of propylene. The first-order rate constants (± standard deviations) obtained from six points during two half-lives are[23] $k_i = (6.75 \pm 0.14) \times 10^{-5}$ sec^{-1} and $k_\alpha = (6.33 \pm 0.14) \times 10^{-5}$ sec^{-1}, so that k_i/k_α = 1.07. A set of comparisons of the k_i/k_α values calculated for each data point is more significant, since the history of the sample used for both infrared and polarimetric analysis is necessarily identical. Measurements at times of 10^3 sec × 4, 8, 12, 16, 20, and 24 give k_i/k_α values of 1.07, 1.03, 1.01, 1.12, 1.08, and 1.08, respectively, for an average of 1.07 ± 0.04.

Formally, the experimental ratio might be interpreted with a blend of mechanisms. This would require admixture of the random intermediate and/or single methylene rotation processes with a large fraction of triple methylene rotation (see Table I). It is certainly simpler and, in our opinion, sounder, to say that the double methylene rotation mechanism operates to the virtual exclusion of any other pathway.

In the double methylene rotation (Scheme I), isomerization of trans to cis (**1** ⇌ **2**) occurs only by rotations of the C_1-C_3 and C_2-C_3 pairs of methylenes. Rotations of the C_1-C_2 pair interconvert (+)-**1** and (−)-**1** but have no effect on **2**.

The present experiment does not distinguish conrotation from disrotation and therefore is incapable of a full definition of the reaction pathway. Nevertheless, the observed behavior adheres to the requirement for synchronous pairwise motion in the opening and reclosure of a 0,0 trimethylene. In the absence of an alternative rationale, the results may be viewed as confirmation of a remarkable theoretical prediction.

References and Notes

(1) The support of this work by the National Science Foundation (GP-33909X) and the Hoffmann-LaRoche Fund is gratefully acknowledged.

(2) For reviews, see (a) R. G. Bergman, "Free Radicals," Vol. I, J. Kochi, Ed., Wiley, New York, N.Y., Chapter 5, 1973; (b) M. R. Willcott, R. L. Cargill, and A. B. Sear, *Progr. Phys. Org. Chem.*, **9**, 25 (1972); (c) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966); (d) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(3) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934), and references cited therein.

(4) (a) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); (b) E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **82**, 5996 (1960); (c) D. W. Setser and B. S. Rabinovitch, *ibid.*, **86**, 564 (1964); (d) E. W. Schlag, Ph.D. Dissertation, University of Washington, 1958.

(5) (a) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (c) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," U.S. Department of Commerce, National Bureau of Standards, 1970; (d) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1971, p 83.

(6) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(7) (a) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958); (b) In the context of the present experiment, the "continuous diradical" hypothesis of Doering and Sachdev (ref 13) is the functional equivalent of the Smith single methylene rotation.

(8) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(9) H. Kollmar, *J. Amer. Chem. Soc.*, **95**, 966 (1973).

(10) J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, **90**, 7343 (1968).

(11) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

(12) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 7344 (1968).

(13) W. v. E. Doering and K. Sachdev, *J. Amer. Chem. Soc.*, **96**, 1168 (1974).

(14) M. R. Willcott, III, and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); **91**, 4310 (1969).

(15) A. Chmurny and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 4237 (1973).

(16) In most of these cases, interpretation of the experimental results as antithetical to the Hoffmann theory requires the so far untested hypothesis that reaction occurs preferentially at the most heavily substituted C–C bond. In the case of tetramethylcyclopropane-d_6, steric destabilization of the 0,0 intermediate has been mentioned as a possible obstacle to the Hoffmann mechanism.[10]

(17) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972); L. Salem, *Accounts Chem. Res.*, **4**, 322 (1971).

(18) P. J. Hay, W. J. Hunt, and W. A. Goddard, Jr., *J. Amer. Chem. Soc.*, **94**, 638 (1972).

(19) A. K. Q. Siu, W. M. St. John, III, and E. F. Hayes, *J. Amer. Chem. Soc.*, **92**, 7249 (1970).

(20) *Cf. inter alia* (a) S. Seltzer, *J. Amer. Chem. Soc.*, **85**, 1360 (1963); (b) S. H. Dai and W. R. Dolbier, Jr., *ibid.*, **94**, 3946, 3953 (1972); (c) R. J. Crawford and K. Takagi, *ibid.*, **94**, 7406 (1972); (d) S. E. Schepple, W. H. Rapp, D. W. Miller, D. Wright, and T. Marriott, *ibid.*, **94**, 539 (1972); (e) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970); (f) K. Humski, R. Malojcic, S. Borcic, and D. E. Sunko, *ibid.*, **92**, 6534 (1970); (g) W. R. Dolbier and J. H. Alonso, *ibid.*, **95**, 4421 (1973).

(21) (a) Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964). (b) The key steps are the highly stereospecific Haller–Bauer cleavages, which have precedent in the work of F. J. Impastato and H. M. Walborsky, *J. Amer. Chem. Soc.*, **84**, 4838 (1962).

(22) (a) A modification of the one described by G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957). (b) By Mr. Ralph Stevens, glassblower to the Department of Chemistry.

(23) The value for k_i is within experimental error of that extrapolated from data of Rabinovitch and Schlag.[4b,d] A separate determination on a small sample of (+)-**1** gives $k_i = (6.70 \pm 0.17) \times 10^{-5}\ \text{sec}^{-1}$.

Jerome A. Berson,* Larry D. Pedersen

Department of Chemistry, Yale University
New Haven, Connecticut 06520

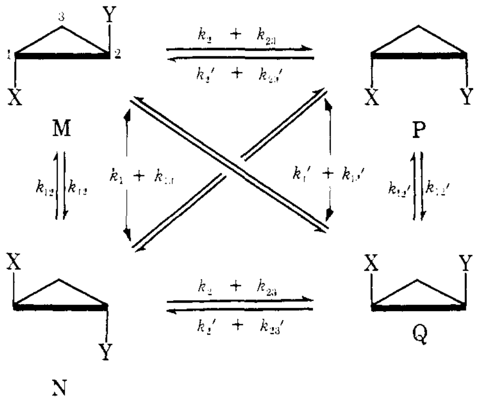
Received September 17, 1974

Synchronous Double Rotation in the Stereomutation of Optically Active 1-Phenylcyclopropane-*2-d*[1]

Sir:

A recent study[2] of the minimally perturbed case of *trans*-cyclopropane-*1,2-d_2* has confirmed the prediction[3] that stereomutation of cyclopropane should occur by synchronous rotation of two methylene groups. However, previous studies with a variety of cyclopropanes bearing true rather than isotopic substituents have failed to detect this process.[4-10] Although the theoretical calculations[3,11] have dealt only with cyclopropane itself, one might have hoped for a broader range of applicability of the results. Unless the predicted effect is substantial enough to survive minor structural changes in the substrate, there is reason to question whether the underlying theoretical basis has been identified properly. The present paper reports that a synchronous double rotation also is prominent in the stereomutation of 1-phenylcyclopropane-*2-d*.

Scheme I



Scheme I outlines a generalized version of an experimental system common to several of the previous studies, where X or Y are alkyl, alkenyl, phenyl, CO_2Me, CN etc.[6,7,9,10] It involves an unsymmetrically 1,2-disubstituted cyclopropane, in which both the trans and cis isomers are chiral. Six independent phenomenological rate constants characterize the network of epimerizations and enantiomerizations.

The most general analysis of Scheme I would permit any of the three ring carbons and their attached substituents to be involved in both unaccompanied single rotations (with single index mechanistic rate constants) and synchronous double rotations (with double index rate constants).[12] Note that single rotation of the unlabeled carbon C_3 results in no reaction.

For the special case of chiral 1-phenylcyclopropane-*2-d* (M, X = Ph; Y = D), the molecular symmetry would require that, to a very close approximation, all of the primed rate constants of Scheme I become equal to their unprimed counterparts, since the relevant kinetic isotope effects would be negligibly different from 1.00. Moreover, there is a unique benefit conferred by the symmetry in that the rate constant k_{13} for double rotation of C_1–C_3 is necessarily equal to the rate constant k_{12} for double rotation of C_1–C_2, modified by the isotope effect. The latter now might not be negligible and should lie in the range 1.00–1.10.[2] Thus, $k_{13} = k_{12}k_H/k_D$.

If k_1 has a finite value, the pyrolysis would include a contribution from single rotation of C_1, either in a Smith mechanism[13] or in a trimethylene biradical.[14] On the other hand, if $k_1 = 0$, the interconversions M $\rightleftharpoons$ Q and N $\rightleftharpoons$ P would be entirely characterized by the double rotation rate constant k_{13}. The problem thus reduces to devising an experimental estimate of the magnitude of k_1.

Conversion of (−)-*trans*-2-phenylcyclopropanecarboxylic acid (M, X = Ph; Y = CO_2H; configuration as shown[15]) to the nitrile and epimerization of the latter with KO-*t*-Bu-DMSO give a mixture of nitriles M and P (X = Ph, Y = CN), which after separation and treatment with PhMgBr gives ketones M and P (X = Ph, Y = COPh) of identical