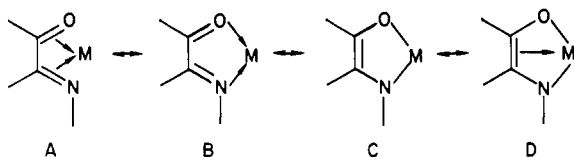


Figure 2. ORTEP view of $(Ar'O)_2Zr[OC(CH_2Ph)C(CH_2Ph)N(C_6H_5)]$ (**3**) emphasizing the central coordination sphere. Important bond distances (Å) and angles (deg): Zr–O(2) = 1.967 (5); Zr–O(17) = 1.929 (5); Zr–O(32) = 2.004 (5); Zr–N(35) = 2.038 (6); Zr–C(33) = 2.549 (8); Zr–C(34) = 2.581 (8); O(32)–C(33) = 1.377 (9); C(33)–C(34) = 1.348 (11); C(34)–N(35) = 1.434 (10); O(2)–Zr–O(17) = 117.4 (2); Zr–O(32)–C(33) = 96.1 (4); O(32)–C(33)–C(34) = 118.8 (7); C(33)–C(34)–N(35) = 119.0 (7); Zr–N(35)–C(34) = 94.4 (5); O(32)–Zr–N(35) = 84.2 (2).

we believe this compound to contain an enediolate ligand formed by the coupling together of two η^2 -acyl functions,¹⁰ although the exact nature and molecularity of this compound is as yet unknown.

In contrast the monoalkyl complex $Zr(OAr')_2(\eta^2$ -xyNCCH₂Ph)(CH₂Ph) (**1b**, xy = 2,6-dimethylphenyl) smoothly inserts CO at 200 psi and is quantitatively converted to complex **3** (Scheme I). Spectroscopic data for **3** are consistent with its formulation as containing an enamidolate ligand formed by a coupling reaction in a presumably intermediate mixed acyl, iminoacyl complex.¹¹ A single-crystal X-ray diffraction study of **3** confirmed this, but with an interesting structural feature (Figure 2).¹² It can be seen that although the $Zr(OAr')_2$ coordination is unremarkable, the enamidolate ligand is distorted from a planar coordination that has typically been observed for chelating enediolates.¹³ It is possible to write four resonance forms for the interaction of this group with zirconium. Resonances involving an α -keto imine form (A, B) would involve a formal



oxidation state of +2 on zirconium and seem unreasonable. The

(10) A solution of $Zr(OAr')_2(CH_2Ph)_2$ in benzene/pyridine reacts over a period of 24 h with 900 psi of CO to give a sparingly soluble product. Mass spectroscopic analysis shows a strong molecular ion at 818 (Zr-91). IR (Nujol mull) $\nu(C=C)$ 1620 cm^{-1} .

(11) **3**: ¹H NMR (200 MHz, C₆D₆) δ 3.51 and 3.99 (s, CCH₂Ph), 1.93 (s, C₆H₃Me₂N), 1.40 (s, OC₆H₃-*t*-Bu₂), 6.8–7.3 (m, Ar); IR (Nujol mull) $\nu(C=C)$ 1650 cm^{-1} .

(12) Crystal data for $Zr(OAr')_2[OC(CH_2Ph)C(CH_2Ph)N(C_6H_5)]$ (**3**) at $-160^\circ C$: space group $P1$, $a = 20.445$ (9) Å, $b = 11.750$ (4) Å, $c = 10.059$ (3) Å, $\alpha = 93.63$ (1) $^\circ$, $\beta = 88.56$ (1) $^\circ$, $\gamma = 88.73$ (1) $^\circ$, $\zeta = 2^\circ$, $d_{calc} = 1.173$ g cm^{-3} . Of the 6318 unique intensities collected by using Mo $K\alpha$ radiation, $6^\circ \leq 2\theta \leq 45^\circ$, the 5100 having $F > 3.00\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R_F = 0.0802$, $R_w = 0.0799$.

(13) To date the solid-state structure of a simple, chelating enediolate coordinated to M(IV) (M = Ti, Zr, Hf, Th, U) has not been determined. However, that of a number of substituted derivatives formally containing the

(M–OC=CO) chelating backbone have been reported. (a) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393. (c) Moley, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1983**, *105*, 5696.

solid-state structure is best accommodated into resonance form D involving σ -coordination of oxygen and nitrogen and then π -interaction to the olefinic function of the metallacycle. The distances to these ring carbons, 2.55–2.58 Å, although outside the range of typical Zr–C σ -bonds, is similar to that found between zirconium and the carbon atoms of Cp (C₅H₅) rings.¹⁴ The coordination of the enamidolate fragment in **3** is strikingly similar to that characterized recently by Erker for a substituted butadiene coordinated to zirconium where the situation was also described as σ^2, π -coordination.¹⁵

We hence conclude that coupling of acyl and iminoacyl groups appears to be a facile reaction on zirconium–aryl oxide metal centers and, furthermore, that a ground state, nonplanar, σ^2, π -coordination of metallacycles $Zr(XC(R)=C(R)Y)$ (X, Y = O, NR, CR₂) is a general possibility.¹⁶

Acknowledgment. We thank the National Science Foundation (Grant CHE-821906 to I.P.R.) for support of this research.

Supplementary Material Available: Listings of atomic coordinates and temperature factors (8 pages). Ordering information is given on any current masthead page.

(14) Compare distances of 2.25 (2) Å found in $Zr(OAr')_2(CH_2Ph)_2$ from ref 4 and "typical" Zr– η^2 -C₅H₅ distances of 2.48–2.55 Å; see ref 13a and references therein.

(15) Erker, G.; Engel, K.; Kruger, C.; Muller, G. *Organometallics*, **1984**, *3*, 128.

(16) It is possible that simple enediolates may adopt this ground state; those listed in ref 3 contain substituents on the chelate carbons that can interact with the olefinic π -cloud, favoring a planar geometry.

Dynamic Isotope Dilution as a General Method for Ascertaining Partition of Photochemical Pathways Potentially Utilizing Nondiscernible Intermediates: Application to a New Reaction^{1,2}

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In pursuing our objective of finding new photochemical reactions, we searched for a second example of the homo-di- π -methane rearrangement; the case in which a three ring and an aryl group are bonded to the central (i.e. "methane") carbon was unknown and of particular interest.³

In this study we encountered a problem which has provided an obstacle in several of our investigations. Thus, in dealing with a new photochemical reaction one often finds that a starting material (e.g., A) may reasonably be formulated as proceeding directly to product (C) or, alternatively, proceeding totally or partially via an intermediate B. A particularly important case is where the intermediate proceeds onward photochemically.

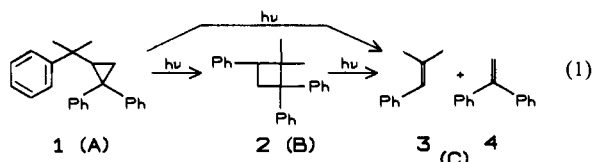
Where the intermediate is isolable or readily discernible, one can simply extrapolate the B/C ratio to zero conversion to obtain the partition of the direct A \rightarrow C and indirect A \rightarrow B \rightarrow C routes. Where the reasonable intermediate B is either not detectable or is present in minute quantities, another approach is needed. The arylcyclopropylmethane reaction proved to be such a case, and the method of dynamic isotope dilution described below proved ideal in solving the dilemma.

(1) Mechanistic and Exploratory Organic Photochemical Series. 142.

(2) Part 141: Zimmerman, H. E.; Ramsden, W. D. *Can. J. Chem.* **1984**, *62*, 2592–2611.

(3) (a) Our only previous example consists of a vinylcyclopropyl-type system.^{3b} (b) Zimmerman, H. E.; Samuel, C. J. *J. Am. Chem. Soc.* **1975**, *97*, 4025–4036.

Our investigation began with the photochemistry of reactant 1 as shown in eq 1.⁴ Direct irradiation of reactant 1 led to

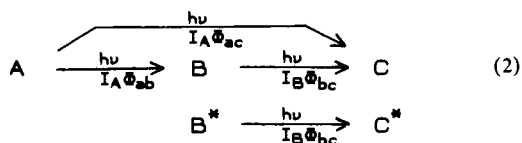


photoproducts 3 and 4. Consideration of the reaction mechanism (vide infra) suggested the possibility of cyclobutane 2 as a reaction intermediate. However, normal spectral analysis of the reaction mixture did not reveal the presence of this potential intermediate (i.e., 2). Still, independent photolysis of cyclobutane 2 did afford phenylisobutylene 3 and diphenylethylene 4. This result provided necessary but not sufficient evidence for cyclobutane 2 being an intermediate in the homo-di- π -methane reaction.

At this point in our research we therefore were faced not only with the normal questions of reaction multiplicity and efficiency, but also with the A-B-C vs. A-C partition. We deal with the latter first.

In one previous study⁵ a solution was provided by using radioactive starting reactant (i.e., A) admixed with the potential intermediate (i.e., B*⁶), however nonradioactive. The reasoning was that if A proceeded via radioactive B, then B (i.e., B + B*) recovered after partial reaction would be radioactive. If A, instead, proceeded directly to form product C without intervention of B, then the B isolated would be nonradioactive. This test is useful only in the extreme case where reisolated B contains no activity thus signifying that the mechanism involves direct conversion of A to C. In that previous study, the isolated B was nonradioactive and the A-B-C pathway could be excluded.

Where all of the reaction proceeds via B as an intermediate, or where both mechanisms intervene, the kinetics are complex since the rates are not linear with the concentrations of the compounds involved. Thus, each compound has a unique extinction coefficient, and the light captured competitively (i.e., I_A , I_B , I_C) by each will vary in a nonlinear fashion as concentrations vary during the reaction. The general problem is outlined in eq. 2.



Nevertheless, the kinetics are subject to solution and are found to afford a general means of solving the A-B-C problem. Solution of the kinetics leads to eq 3,^{4a}

$$F = \ln \left[\frac{B^*_0(B^*A_0 - B^*_0A)}{B^*(B^*_0B - B^*_0B_0)} \right] = L \ln(A_0/A) + \ln(1-L)/M \quad (3a)$$

$$L = \phi_{bc}\epsilon_b / (\phi_{ab} + \phi_{ac})\epsilon_a \quad (3b)$$

and

$$M = \phi_{ab} / (\phi_{ab} + \phi_{ac}) \text{ or } \phi_{ab} / \phi_{ac} = M / (1 - M) \quad (3c)$$

(4) (a) Full synthetic and other experimental details will be provided in our full paper. Similarly, the mathematical derivations will be provided.⁷ (b) The present method is especially useful where $\phi_{bc} \gg \phi_{ab}$ is not compensated for by a low extinction coefficient of B. Here $\epsilon_A = 850$ and $\epsilon_B = 700$.

(5) Zimmerman, H. E.; Diehl, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 1841-1857.

(6) The asterisk is used to designate the different labeling of added intermediate compared with reactant A. Also, note that B is often used to connote B + B* for brevity.

(7) The technique used for the ABC photochemical problem is applicable to thermal reactions as well, which is simpler due to lack of involvement of extinction coefficients. Here $L = k_{bc}/(k_{ab} + k_{ac})$ and $M = k_{ab}/(k_{ab} + k_{ac})$.

(8) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932-3933. (b) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718-1727. (c) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531-551. (d) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

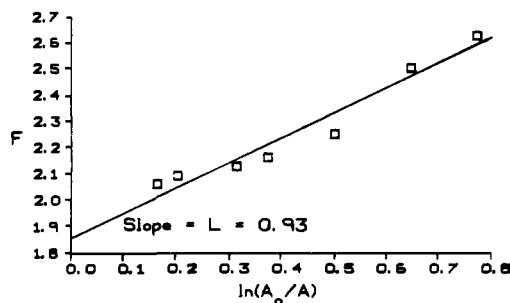
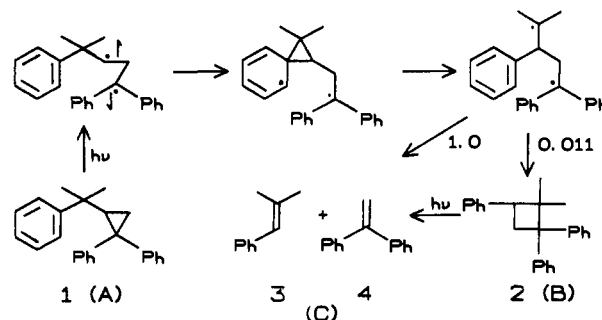


Figure 1. Plot of the mixing function F vs. $\ln(A_0/A)$ for the arylcyclopropylmethane rearrangement of eq 1.

Scheme I. Mechanism of the Homo-Di- π -Methane Rearrangement of Phenylcyclopropylmethane 1



where A, B, B*, etc. are the concentrations of the corresponding species. This form of eq 3 proves particularly useful. Thus the "mixing function" F is linear with the logarithm of (A_0/A) . By running a series of photolyses to differing conversions, the slope L is obtained and used in the intercept to derive M . M , in turn, by using eq 3c, affords the ratio of the utilization of path AB to path AC.

We then turned to the homo-di- π -methane rearrangement outlined in eq 1. However, in this instance unlabeled reactant 1 (i.e., A) was used and the intermediate 2 was labeled with deuterium atoms replacing the four-ring methylene hydrogens. Analysis was by FT NMR using 1024 scans. The plot shown in Figure 1 resulted. Use of the slope (L) and the intercept afforded the partition of the two mechanisms. ϕ_{ab}/ϕ_{ac} was determined to be 0.011.^{4b} Hence, the mechanism in Scheme I may be formulated showing 99.0 \pm 0.4% of the reaction proceeding by direct 1,4-(2,3)-fragmentation of the 1,4-diradical. Knowledge of the partition permitted determination of the quantum efficiencies as $\phi_{ab} = 0.00019$ and $\phi_{ac} = 0.018$. Independent determination gave $\phi_{bc} = 0.025$. With the efficiency $\phi_{bc} \gg \phi_{ab}$ the necessity of the method is apparent. Additionally, we note that all of the reactions are singlet processes; this was indicated by the lack of reactivity with acetone or acetophenone sensitization.

One interesting point is the preference for fragmentation rather than four-ring formation. In the case of cyclopropyldicarbonyl diradicals encountered in the di- π -methane⁹ and bicycle⁹ rearrangements, evidence has been presented that it is S_0 , formed by internal conversion of the intermediate diradicals, which undergoes 1,4(2,3)-fragmentation.¹⁰

Not only did this study provide a test of the method of dynamic isotope dilution but also afforded evidence that the homo-di- π -methane rearrangement may be general.

(9) (a) Zimmerman, H. E.; Juers, D. F.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1970**, *92*, 3474-3476. (b) Zimmerman, H. E.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3662-3674. (c) Zimmerman, H. E.; Cutler, T. P. *J. Chem. Soc., Chem. Commun.* **1978**, 232-234. (d) Zimmerman, H. E.; Cutler, T. P. *J. Org. Chem.* **1978**, *43*, 3283-3303. (e) Zimmerman, H. E.; Armesto, D.; Ameza, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367-6383. (f) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538-3548.

(10) A correlation diagram treatment of the present 1,4-diradical suggests that the fragmentation is S_0 allowed and S_1 forbidden, while the converse is true for cyclobutane formation. This will be discussed in our full paper.

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

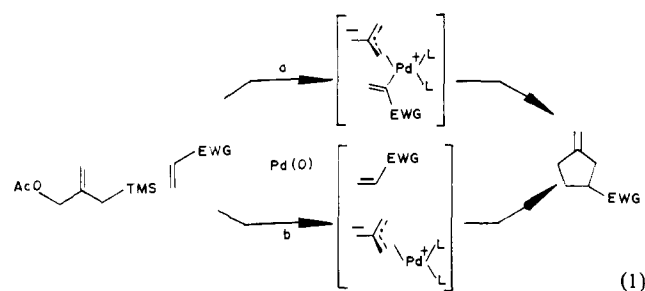
Donor Stereospecificity of Pd-Mediated Cycloadditions. A Case of Distal Attack of Acceptor on Donor

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Transition-metal-mediated reactions are frequently viewed as associations of ligands on the surface of the metal. Excellent examples are carbonylations, reductions, and the oligomerization of olefins.¹ The cooligomerization of a methylenecyclopropane with a simple olefin may also involve just such a process.² When the Pd-mediated cycloaddition of 2-[(trimethylsilyl)methyl]allyl acetate (donor) with electron-deficient olefins (acceptors)³ is considered, an analogous process can be envisioned (eq 1, path a). The result of this prior coordination of the acceptor to the



metal would be to deliver the acceptor olefin to the same face of the trimethylenemethane-palladium complex (TMM-Pd) as the metal (proximal attack). In spite of the precedent that suggests the likelihood of this pathway, an alternative in which the acceptor reacts directly with the carbanion center on the face of the TMM-Pd complex away from the metal (distal attack) should be considered (eq 1, path b).

Differentiation of these pathways requires determining the stereochemistry of bonding to the TMM fragment. Thus, a substituted TMM unit with a stereochemical marker is required. Our initial attempts were thwarted when the acetate **3a**, easily available from *cis*-carveol⁴ by the direct metalation approach (eq 2),^{3a,5} failed to react with Pd(0) catalysts.⁶ Ancillary studies in

(1) For reviews, see: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. Parshall, G. W. "Homogeneous Catalysis"; Wiley: NY, 1980. Su, A. C. L. *Adv. Organomet. Chem.* **1979**, *17*, 269. Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: NY, 1975. Also see: Larock, R. C.; Burkhart, J. P.; Oertle, K. *Tetrahedron Lett.* **1982**, *23*, 1071.

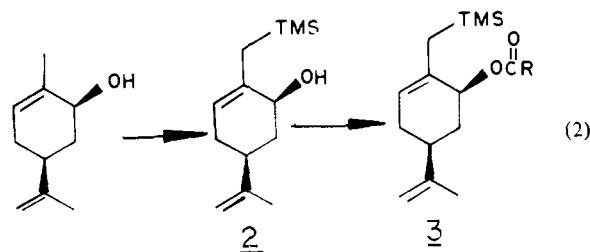
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(3) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326. (b) Trost, B. M.; Nanninga, T. N.; Chan, D. M. T. *Organometallics* **1982**, *1*, 1543. (c) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5972. (d) Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 5974.

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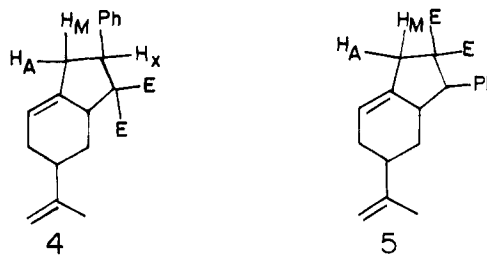
(6) Chan, D. M. T. Ph.D. Thesis, University of Wisconsin, Madison, 1982.



a) R = CH₃

b) R = OCH₃

the parent cyclohexenyl system suggested the greater reactivity of the carbonate may be beneficial. Indeed, reaction of **3b** with dimethyl benzylidenemalonate using 5 mol % of a Pd(0) catalyst generated in situ [1 equiv of Pd(OAc)₂, 2 equiv of *n*-C₄H₉Li, 5 equiv of Ph₃P] in refluxing THF gives an 86% yield of two products in a 4:1 ratio.⁸ The first question relates to regiochemistry (i.e., **4** or **5**). Both products show the presence of a

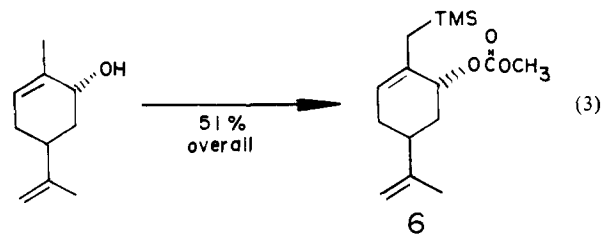


clean AM pattern for an isolated methylene group [major, δ 3.60 and 2.95, J = 19.1 Hz; minor, δ 3.45 and 2.66, J = 16.9 Hz], which is consistent only with **5**.

The critical question is stereochemistry. Four diastereomers (ignoring optical isomers) are possible (**5a-d**; see Chart I). Both isomers show a characteristic upfield absorption for 1 H as a quartet (major, δ 0.83, J = 12.0 Hz; minor, δ 1.05, J = 12.0 Hz), which has previously been shown to correspond to a *cis*-3,5-disubstituted cyclohexene—i.e., H_c in **5a** and **5b** in which $J_{bc} = J_{cd} = J_{ce}$.⁹ Double irradiation confirms this assignment. Furthermore, in the major isomer, the NMR spectrum taken in C₆D₆ reveals H_d at δ 1.62 as a ddd, J = 12.0, 5.0, and 2.3 Hz, in addition to H_c at δ 0.98 as a quartet, J = 12.0 Hz.

The benzylic proton appears as a doublet in both cases (major, δ 4.02, J = 7.4 Hz; minor, δ 3.52, J = 12.8 Hz)—a fact that reinforces the earlier conclusion regarding regioselectivity. Models reveal that the dihedral angle between H_a and H_b in **5a** is approximately 20°; whereas, it is approximately 180° in **5b**. Thus, the major isomer with the smaller J_{ab} is assigned as *cis*, *cis*.

To verify the stereospecificity, the epimeric carbonate **6** was prepared from *trans*-carveol¹⁰ in identical fashion with the *cis* series (see eq 3).¹¹ Cycloaddition as above produces a 7:3 ratio of two



(7) All new compounds have been fully characterized spectrally and elemental composition determined by high-resolution mass spectroscopy. Unless otherwise noted, NMR spectra were taken in CDCl₃.

(8) A trace amount of a third product could be detected in the NMR spectrum. It is not the alternative stereoisomers **5c** nor **5d** by comparison to authentic samples. Unfortunately, it was present in such low amounts it could not be obtained pure. From the NMR spectral data of mixtures, it is tentatively assigned as the alternate regioisomer.

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(10) Johnston, R. G.; Read, J. *J. Chem. Soc.* **1934**, 233.