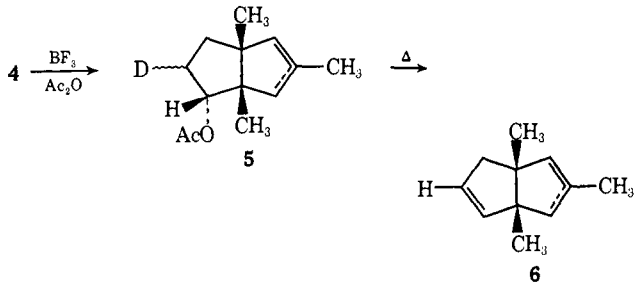


more remarkable since it is exactly the opposite of the result found by Nickon in the opening of nortricyclanol.[3] The two systems differ, of course, in that the carbanionic center and ketone leaving group probably cannot escape interaction in the bicyclo[2.2.1] ring system, while during the cleavage of **1** to **2** they must move apart a considerable distance. Both systems demonstrate, however, that in SEl reactions in which the carbon leaving group remains in the same molecule as the carbanion, structural effects can be far more important than solvent effects in determining the stereochemical course of reaction.[14]

Although the enforced proximity of carbanion and ketone in the nortricyclanol opening might be expected[2] to produce inversion, the structural features responsible for the observed retention of configuration in the cleavage of **1** are less obvious. One possibility is that the cage structure of **1** excludes solvent from part of one face of the developing carbanion. Protonation of the carbanion from the backside to give inversion would then generate an ion pair separated by a cavity of low dielectric constant and would be energetically less favorable than protonation from the same side as the departing carbonyl group, a process leading to retention.[15] Experiments to test this and other[16] hypotheses are in progress.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

(14) For another example in a less rigid system, see T. D. Hoffmann and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 1009 (1969).

(15) A similar explanation based on inefficient solvation of the cation on the endo face of the bicyclic system studied by Wharton[4] could rationalize why the endo alcohol, in contrast to the exo, gives predominant retention in ethylene glycol.

(16) A referee has suggested that in the cleavage of **1** "the geometry is such that the departing carbonyl group moves away from the carbanion but cannot escape completely; it does, however, distinguish between polar and nonpolar sides of the fixed (nonrotatable) carbanion, the polar side probably aggregating more available solvent and certainly lowering the energy of activation of protonation." Although it may well be that protonation occurs from a solvent molecule bound to a cation coordinated at the carbonyl[14] or aggregated by the carbonyl itself, it is not clear how this explanation would be applied to other systems[4] in which only one isomer gives an anomalous amount of retention.

Weston Thatcher Borden,* Vijaya Varma
Mayo Cabell, T. Ravindranathan
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received April 28, 1971

A Model of the Methylmalonyl Isomerase Reaction

Sir:

Several years ago, a mechanism was proposed[1] for the vitamin B_{12} catalyzed methylmalonyl isomerase reaction which involves ionic cleavage of an organocobalt intermediate and subsequent rearrangement of the resulting carbanion. This mechanism is supported by the statistical partitioning of deuterium between substrate and product,[2] but there has been no organic analog of the reaction. Now that a method for ionic cleavage of the carbon–cobalt bond has been found,[3] we have been able to show the rearrangement of an organocobalt compound comparable to the methylmalonyl isomerase reaction.[4] A solution of 0.52 mmol of 1-carbethoxy-2-oxocyclopentylmethyl(pyridinato)bis(dimethylglyoximato)cobalt(III) (I) (*Anal.* Calcd: C, 49.16; H, 6.00; N, 13.03. Found: C, 49.11; H, 5.98; N, 13.20) prepared by the method of Schrauzer and Windgassen[5] from ethyl 1-bromomethyl-2-oxocyclopentanecarboxylate[6] in 10 ml of dimethylformamide and 10 ml of absolute alcohol at 50° was allowed to react with 4.6 mmol of 1,4-butanedithiol for 48 hr. Product isolation was accomplished by dilution with water, extraction with petroleum ether, and washing with 2% aqueous KOH, 1 *N* HCl, and finally water. Gas chromatograms of this mixture were compared to those of known esters on four analytical columns with different stationary phases (SE-30, Carbowax 20M, LAC-446, and DEGS). On each column, peaks corresponding to 5% of the unrearranged ester, ethyl 2-oxo-1-methylcyclopentanecarboxylate (II),[7] 0.3% of the rearranged ester, ethyl 3-oxocyclohexanecarboxylate (III),[8] and none of the other possible rearranged ester, ethyl 2-oxocyclopentaneacetate (IV)[9] were obtained. Using gas chromatography followed by mass spectrometry, mass spectrograms of components of the reaction mixture were found to be identical with those of authentic II and III. (Peaks with *m/e* greater than 102 were: II, 170 (m^+), 142, 125, 115, 114, 113; III, 170 (m^+), 142, 128, 127, 125, 124, 114, 113.) The reaction sequence in Scheme I appears reasonable. In a similar reaction of cobaloxime I in ethanol, smaller yields were observed and in dimethylformamide only a trace of the rearranged product, III, was observed. The low yield of rearranged ester may result from the addition of 1,4-butanedithiol to a ketene intermediate. In methanol, neither ethyl nor methyl 3-oxocyclohexanecarboxylate was observed.

A solution of the cobaloxime, I, in ethanol containing 10% of toluene was exposed to sunlight for 6 hr. This photolysis gave 0.2% of unrearranged ester, II, but no (<0.01%) rearranged products, III and IV, by gas chromatographic analysis.

These results support an ionic but not a radical mechanism for the methylmalonyl isomerase reaction. Attempts to show similar rearrangements in acyclic sys-

(1) L. L. Ingraham, *Ann. N. Y. Acad. Sci.*, **112**, 713 (1963).

(2) W. W. Miller and J. H. Richards, *J. Amer. Chem. Soc.*, **91** 1498 (1969).

(3) J. W. Sibert and G. N. Schrauzer, *ibid.*, **92**, 1421 (1970); G. N. Schrauzer and J. W. Sibert, *ibid.*, **92**, 3509 (1970).

(4) This study shows that a carbanion intermediate will account for the rearrangement regardless of the method of generation.

(5) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **88**, 3738 (1966).

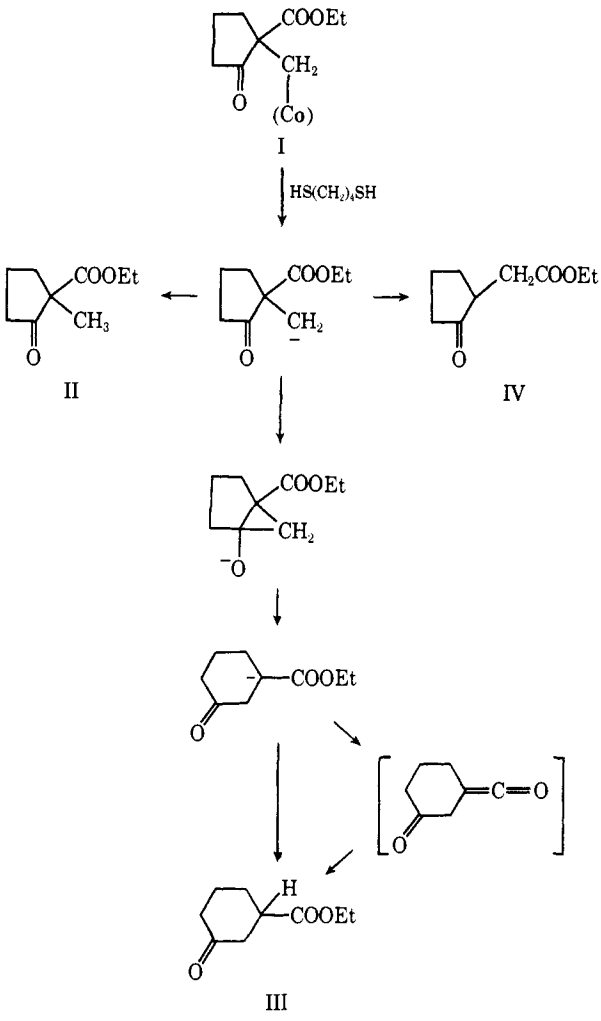
(6) R. Mayer and E. Alder, *Chem. Ber.*, 1866 (1955).

(7) Ya. I. Denisenko and A. D. Naber, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 35 (1945).

(8) (a) W. A. Perkin, Jr., and G. Tattersall, *J. Chem. Soc.*, **91**, 480 (1907); (b) the corresponding acid was prepared following the procedures of R. Grewe, A. Heinke, and C. Sommer, *Chem. Ber.*, **89**, 1978 (1956).

(9) R. Granger, P. F. G. Nau, and J. Nau, *Bull. Soc. Chim. Fr.*, 1807 (1959).

Scheme I



tems have been unsuccessful,[10] presumably because the carbanion adds a proton before the groups are rotated into a position for the carbanion to attack the carbonyl group and rearrange. The orientation is favorable in the cyclic ester. In the enzymatic reaction, the substrate is probably held in the proper position by the enzyme to favor rearrangement through a stabilized homoenolate ion.[11]

Acknowledgment. We gratefully acknowledge the assistance of Drs. Roy Teranishi and Robert Lundin at the Western Regional Research Laboratory. This work was supported by the National Institutes of Health (GM 08285).

(10) (a) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **89**, 1999 (1967); (b) J. Fox, Dissertation, University of California at Davis, 1970.

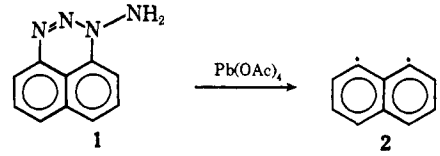
(11) A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **88**, 1905 (1966).

James N. Lowe, Lloyd L. Ingraham*
Department of Biochemistry and Biophysics
University of California
Davis, California 95616
Received April 21, 1971

Addition of 1,8-Dehydronaphthalene to Cyclopentadiene

Sir:

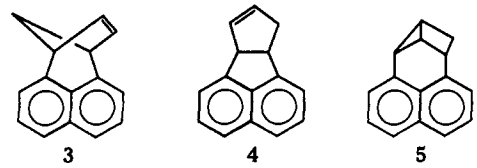
In 1965 Rees and Storr reported that oxidation of 1-aminonaphtho[1,8-*de*]triazine (**1**, eq 1) provides a convenient source of the highly reactive intermediate, 1,8-dehydronaphthalene (**2**).[1] At the same time these



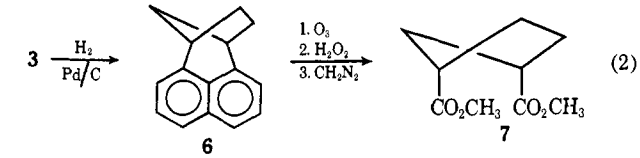
(1)

authors demonstrated that **2** adds 1,2 to olefins, in a stereospecific manner. In contrast, *o*-benzyne undergoes nonstereospecific 1,2 cycloadditions,[2] and prefers to react as a dienophile.[3,4] Recent calculations by Hoffmann and coworkers suggest that the antisymmetric combination of 1,8-dehydro orbitals in **2** is of lower energy than the symmetric combination, and that 1,2 addition to olefins should be favored over 1,4 addition to conjugated diene systems.[5] We wish to report the first study of the reactions of 1,8-dehydronaphthalene (**2**) with a conjugated diene.

When **2** was generated[6,7] by lead tetraacetate oxidation of **1** in a methylene chloride solution of cyclopentadiene, a mixture of three 1:1 adducts was isolated in *ca.* 20% yield. These were purified by chromatography on basic alumina, followed by preparative glpc (5 ft × 1/4 in. HMDS-treated column of 10% SE-30 on 60–80 mesh Chromosorb W at 180°), and identified as **3**, **4**, and **5** on the basis of the evidence presented below.[8]



The component of shortest glpc retention time, **3** (9% of the 1:1 products), had the following nmr spectrum (60 MHz): aromatic protons, τ 2.60 (6 H, m), olefinic protons, 3.92 (2 H, broad s), a broad, complex doublet ($J \sim 9$ Hz, 2 H) at 6.28, and a multiplet at 7.7 (2 H). Upon hydrogenation (5% Pd/C), **3** afforded a new compound **6** whose nmr spectrum (60 MHz) consisted of aromatic hydrogens, τ 2.75 (6 H), a broad singlet at 6.67 (2 H), and a broad multiplet (7.7–8.5, 6 H). Ozonolysis of **6**, followed by esterification of the resulting acid with diazomethane, afforded *cis*-1,3-dicarbomethoxycyclopentane (**7**, eq 2),[9] as de-



(2)

(1) C. W. Rees and R. C. Storr, *Chem. Commun.*, 193 (1965).

(2) See M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969), and references cited therein.

(3) G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

(4) R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963).

(5) R. Hoffmann, A. Imamura, and W. J. Hehre, *ibid.*, **90**, 1499 (1968).

(6) C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 760 (1969).

(7) R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittrich, *ibid.*, 769 (1969).

(8) Mass spectra of samples of **3**, **4**, and **5** confirmed the $C_{16}H_{12}$ formulation. These products were also shown to be stable under the separation and purification conditions.

(9) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).