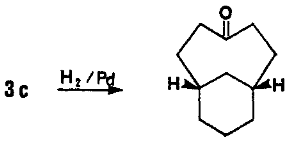
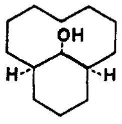
the saturated ketone **10**[14] (semicarbazone,[4] mp 187-188 °C) whose symmetry is revealed by its seven-line ^{13}C NMR spectrum.



10



9

Several aspects of the chemistry of the bridgehead olefins **3a-c** are under investigation.[15]

Registry No. 1a, 77080-00-3; **1b**, 65173-72-0; **1c**, 41597-04-0; **2a**, 77080-01-4; **2a**·K, 77080-02-5; **2b**, 77080-03-6; **2c**·K, 77080-04-7; **3a**, 77080-05-8; **3b**, 77080-06-9; **3c**, 77080-07-0; **4**, 77080-08-1; **5**, 77080-09-2; **7**, 77080-10-5; **8**, 884-36-6; **9**, 77080-11-6; **10**, 77080-12-7; **10** semicarbazone, 77080-13-8; vinyl bromide, 593-60-2; methyl cyclohex-2-enecarboxylate, 25662-37-7; ethyl 5-bromopentanoate, 14660-52-7.

---

(13) The anionic oxy-Cope rearrangement of **2c** to **3c** has very recently been carried out as a model reaction for the key step in a prospective synthesis of the antibiotic pleuromutilin. M. Kahn, *Tetrahedron Lett.*, 4547 (1980).

(14) IR (CS_2) 1690 cm^{-1}; ^{13}C NMR ($CDCl_3$) 215.4, 43.0, 31.9, 30.5, 29.6, 28.8, 16.6 ppm; mass spectrum (70 eV), *m/e* 166 (66%), 67 (100%).

(15) A comprehensive review by Kenneth J. Shea of recent developments in the synthesis, structure, and chemistry of bridgehead olefins is scheduled for publication in *Tetrahedron*. We thank Professor Shea for sending us a prepublication copy of his manuscript.

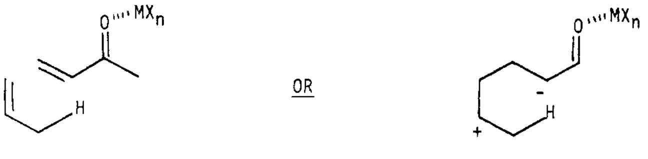
Samuel G. Levine,* Roger L. McDaniel, Jr.
Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27650

Received December 23, 1980

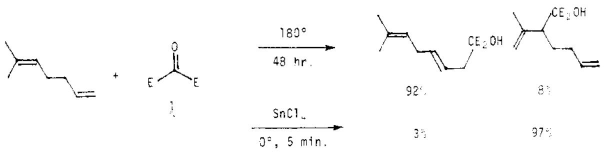
Changes in Ene Reaction Mechanisms with Lewis Acid Catalysis

Summary: Inter- and intramolecular isotope effects for both thermal and $SnCl_4$-catalyzed ene reactions of oxomalonic esters have been measured. Primary isotope effects are high (~3.3) in thermal reactions and negligible (~1.1) in $SnCl_4$-catalyzed cases, even where intramolecular competitions are available. A concerted mechanism with variations in C-C bond formation and C-H(D) bond breaking is proposed. A potentially useful cyclization reaction is also described.

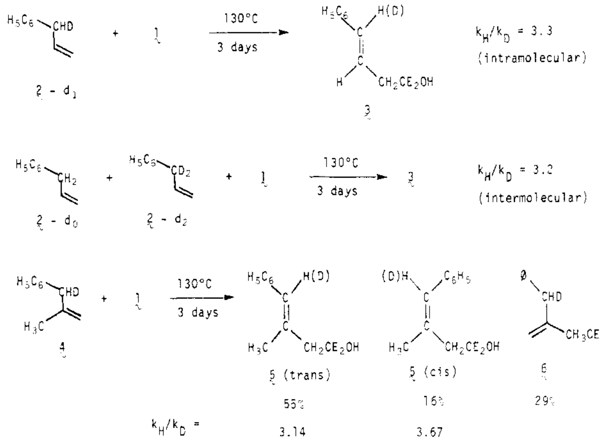
Sir: Interest in synthetic applications of the ene reaction has increased substantially with the demonstrations by several groups that Lewis acid catalysis can be dramatic. In many cases, additions of less than molar amounts of aluminum or tin halides have made it possible to reduce reaction times and temperatures to points where conditions are quite mild.[1] In a recent review, Snider[1] has summarized evidence related to the two limiting mechanisms in these catalyzed cases, namely, the concerted and dipolar pathways. This present study compares deuterium isotope effects for thermal and tin chloride catalyzed ene reactions of dimethyl and diethyl oxomalonates **1**. We conclude, even in this extreme case, that dipolar intermediates are not fully formed.



Salomon and co-workers[2] have reported that diethyl oxomalonate (**1**, E = carboethoxy or carbomethoxy) undergoes clean ene reactions both thermally and with $SnCl_4$ catalysis. It is obvious from the example given below that the $SnCl_4$ catalysis is profound and that the reactive species in the catalytic reaction is very much more electrophilic than is oxomalonate alone. Regiospecificity changes such as that shown are consistent with this increase in electrophilicity.



Isotope effect measurements suggest that the uncatalyzed ene reaction of oxomalonate is unremarkable. Both intra- and intermolecular isotope effects are high. These high, primary isotope effects are consistent with those found in a variety of other concerted ene fractions.[3] Even without a detailed stereochemical study, we are confident that this represents a one-step ene reaction with C-H bond breaking and C-C bond making occurring at about the same time. Recent isotope effect measurements by Achmatowicz and Szymoniak[4] and an accompanying detailed analysis support this point of view.



Catalysis of this reaction with small amounts of $SnCl_4$ results in a substantial reduction in the magnitude of the isotope effect. Both inter- and intramolecular competitions are affected to a very similar degree.

These data suggest that C-H or C-D bond breaking is a much less significant aspect of transition-state structure in catalyzed relative to uncatalyzed cases. The most economical explanation is that a concerted reaction continues to prevail but that C-H(D) bond breaking may have only slightly progressed at the transition state. These data allow a rigorous elimination of a mechanism in which formation of a dipolar intermediate is followed by C-H(D) bond breaking with a significant activation energy. In the

---

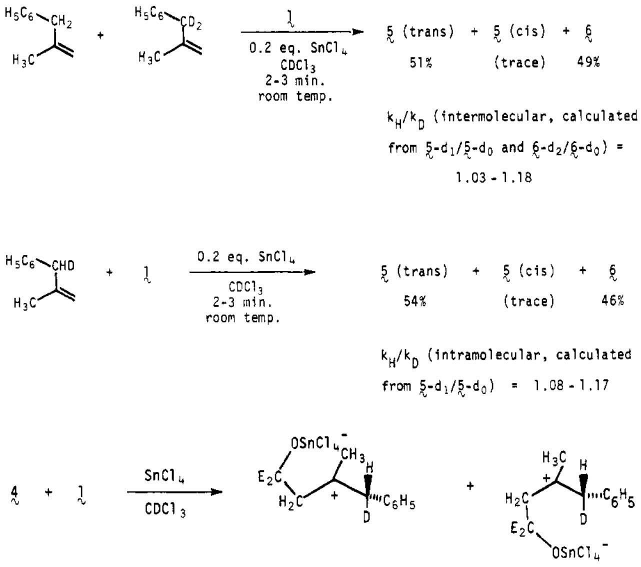
(1) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426-432.

(2) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2473.

(3) Stephenson, L. M.; Mattern, D. L. *J. Org. Chem.* **1976**, *41*, 3614.

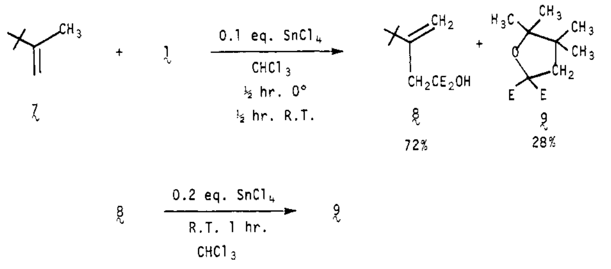
(4) Achmatowicz, O., Jr.; Szymoniak, J. *J. Org. Chem.* **1980**, *45*, 1228; *Ibid.* **1980**, *45*, 4774.

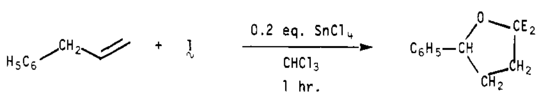
0022-3263/81/1946-2200$01.25/0



two dipolar species shown below, for example, one would normally expect an isotope fractionation at the CHD grouping since H is competing with methyl CH in the left-hand species, while D is competing with methyl CH in the geometrically equivalent right-hand species. If a fully developed dipolar species is involved in this reaction, the subsequent removal of H or D must proceed essentially without activation energy.[5]

Attempts to measure isotope effects in several other catalyzed reactions have been thwarted by a novel cyclization which may be synthetically useful. In the reaction of 7, for example, it is obviously possible for $SnCl_4$ to catalyze addition of the OH proton to the olefin in product 8. In cases where subsequent alkyl (or hydride; see below) shift is favorable, five-membered-ring products, e.g., 9 and 10, are the only significant species which can be detected by NMR.





10

The previously unrecognized cyclization extends the synthetic usefulness of at least selected reactions in this series and is being actively explored.

Acknowledgment. Professor Harry S. Mosher has provided considerable encouragement to us and financial support for M.O. We also acknowledge support of NSF Grant CHE-80-12233 (to L.M.S.).

Registry No. 1 ($E = CO_2Et$), 609-09-6; 1 ($E = CO_2Me$), 3298-40-6; 2, 300-57-2; 2-d_1, 63523-01-3; 3 ($E = CO_2Me$), 77028-62-7; 3 ($E = CO_2Et$), 77028-80-9; 3-d_1 ($E = CO_2Me$), 77028-81-0; 3-d_1 ($E = CO_2Et$), 77028-82-1; 4, 3290-53-7; 4-d_1, 77028-63-8; 4-d_2, 77028-64-9; *cis*-5 ($E = CO_2Me$), 77028-65-0; *cis*-5 ($E = CO_2Et$), 77028-66-1; *cis*-5-d_1 ($E = CO_2Et$), 77028-83-2; *cis*-5-d_1 ($E = CO_2Me$), 77028-84-3; *trans*-5 ($E = CO_2Me$), 77028-67-2; *trans*-5 ($E = CO_2Et$), 77028-68-3; *trans*-5-d_1 ($E = CO_2Me$), 77028-85-4; *trans*-5-d_1 ($E = CO_2Et$), 77028-86-5; 6 ($E = CO_2Me$), 77028-69-4; 6 ($E = CO_2Et$), 77028-70-7; 7, 594-56-9; 8 ($E = CO_2Me$), 77028-71-8; 8 ($E = CO_2Et$), 77028-72-9; 9 ($E = CO_2Me$), 77028-73-0; 9 ($E = CO_2Et$), 77028-74-1; 10 ($E = CO_2Me$), 77028-75-2; 10 ($E = CO_2Et$), 77028-76-3; 6-methyl-1,5-heptadiene, 7270-50-0; methyl 2-(carbomethoxy)-3-isopropenyl-2-hydroxy-6-heptenoate, 77028-77-4; ethyl 2-(carboethoxy)-3-isopropenyl-2-hydroxy-6-heptenoate, 73961-90-7; methyl 2-(carbomethoxy)-2-hydroxy-8-methyl-4,7-nonadienoate, 77028-78-5; ethyl 2-(carboethoxy)-2-hydroxy-8-methyl-4,7-nonadienoate, 77028-79-6.

L. M. Stephenson
Department of Chemistry and
Hydrocarbon Research Institute
University of Southern California
Los Angeles, California 90007

Michael Orfanopoulos*
Department of Chemistry
Stanford University
Stanford, California 94305

Received January 12, 1981

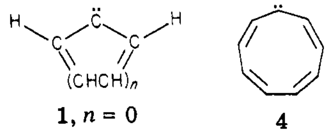
---

[5] A suitable example for comparison is provided by: Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848. Attack of $(RC{\equiv}O)^+$ on appropriately deuteriated methylenecyclohexane gives ene-like reaction products and shows negligible inter- but high intramolecular isotope effects, 1.0 ± 0.3 and 3.2 ± 0.7, respectively. Here it is clear that an intermediate is produced and that subsequent H(D) removal is an activated process.

Cyclononatetraenylidene

Summary: Cyclononatetraenylidene has been generated and is found to give a dimeric product via its triplet state.

Sir: The interest in cyclic, completely conjugated carbenes has been evident.[1] The potential for alternating properties (e.g., the electronic nature of the ground state, the electrophilicity or nucleophilicity of the singlet state) adds theoretical importance to the 1–3 series of carbenes. To date, the largest monocyclic conjugated carbene which has been approached is cycloheptatrienylidene, 3.[2] The generation of the C_9 carbene, cyclononatetraenylidene (4), is now reported.[3]



1, $n = 0$
2, $n = 1$
3, $n = 2$

4

The logical precurser of 4, diazocyclononatetraene (5), had been reportedly isolated from the reaction of lithium cyclononatetraenide (6) with *p*-toluenesulfonyl azide.[4] Actually, the isolated product of this reaction was 9-azidobicyclo[4.3.0]nonatriene (7).[5] It is now found that the use of 4-nitrobenzenesulfonyl azide with 6 all but eliminates the formation of 7 and a $C_{18}H_{18}$ hydrocarbon (8) is isolated in 33% yield. The proton and carbon NMR spectra and the UV spectrum are identical with the spectra

---

(1) Dürr, H. *Top. Cur. Chem.* **1973**, *40*, 103–142.

(2) (a) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391–6397. (b) It is quite possible that the chemistry of 3 is better ascribed to 1,2,4,6-cycloheptatetraene instead.

(3) The classical approach to 1,2,4,6,8-cyclononapentaene, which produces indene, has been reported. Waali, E. E.; Allison, N. T. *J. Org. Chem.* **1979**, *44*, 3266–3268.

(4) Lloyd, D.; Preston, N. W. *Chem. Ind.* (*London*) **1966**, 1039.

(5) Waali, E. E.; Taylor, J. L.; Allison, N. T. *Tetrahedron Lett.* **1977**, 3873–3874.

0022-3263/81/1946-2201$01.25/0