Recrystallization of **7** (β-carbomethoxy-1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane) from methanol–dichloromethane gave a white solid, mp 150–153°, whose mass spectrum gave a molecular ion at *m/e* 436. *Anal.* Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.54; H, 6.32.

The uv spectrum of **7** very closely resembled that of 1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane (**5**) in shape and the positions of the absorption bands except that in the 250-nm region where **5** has a minimum, **7** showed increased indistinct absorption due to the α,β-unsaturated ester absorption superimposed on that of the ring system. The nmr spectrum of **7** contained five sharp methyl ester singlets, a fact that points to a mixture of diastereomers.

Molecular distillation of **8** (1,2-dehydro-3,4,5-tricarbomethoxy-[6.2]paracyclophane) at 200° and 1.6 mm gave a glass whose mass spectrum exhibited a molecular ion at *m/e* 436. *Anal.* Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.70; H, 6.24.

The uv spectrum of **8** very closely resembled that of 1,2-dehydro-4,5-dicarbomethoxy[6.2]paracyclophane (**6**). The nmr spectrum exhibited six different methyl ester singlets, a fact that points to the presence of both diastereomers and cis–trans isomers in the mixture.

Control Run That Demonstrated Stability of *cis*-2,3-Dehydro[4.2]-paracyclophane (3) to the Conditions of Run 5. When 63 mg of **3** and 0.4 ml of dimethyl maleate were submitted to the reaction conditions of run 5, 62 mg of **3** was reisolated, mp 100–101°, pure by nmr analysis.

Control Run That Demonstrated Stability of β-Carbomethoxy-1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane (7) to the Conditions of Run 7. Triester **7** (41 mg) and 0.5 ml of dimethyl maleate were subjected to the conditions of run 7. The nmr spectrum of the reisolated **7** (38 mg) was superimposable on that of the starting sample.

Hydrocarbon Thermal Degenerate Rearrangements. V. Stereochemistry of the 1,2-Dimethylenecyclobutane Self-Interconversion and Its Relation to the Allene Dimerization and the Rearrangements of Other C_6H_8 Isomers[1a–c]

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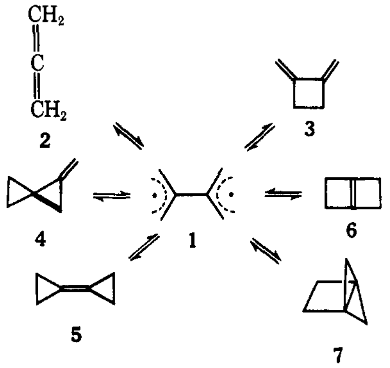
Contribution No. 2009 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received June 15, 1971*

Abstract: The thermally induced degenerate rearrangement of 1,2-bis(dideuteriomethylene)cyclobutane (**8a**) has been studied. Degradative experiments indicate that two products, 4,4-dideuterio-2-dideuteriomethylene-1-methylenecyclobutane (**8c**) and 3,3,4,4-tetradeuterio-1,2-dimethylenecyclobutane (**8b**), are formed in a ratio of ~2:1. This result suggests that the rearrangement proceeds *via* a perpendicular tetramethylenethane diradical (2,2′-bisallyl), **1**. Rotation about the central bond in **1** has been confirmed by observation of the stereospecific thermal rearrangement of *trans*- and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutane (**14** and **15**). The trans compound **14** gives almost exclusively 3-methyl-2-methylene-*anti*-ethylidenecyclobutane (**17**) and *anti,anti*-1,2-diethylidenecyclobutane (**20**). The cis isomer **15** gives almost exclusively 3-methyl-2-methylene-*syn*-ethylidenecyclobutane (**16**), *syn,anti*-1,2-diethylidenecyclobutane (**19**), and **17**, and the subsequent rearrangement product of **16**, namely, 3-methylene-4-methyl-*trans*-1,4-hexadiene (**21**). These results are consistent with a mechanism in which conrotatory ring opening of the cyclobutane ring occurs to form the orthogonal dimethyl **1**, which then closes to the respective products. The origin of this specificity is discussed as well as the energy surface relating various C_6H_8 isomers and two molecules of allene.

Tetramethyleneethane (TME), or 2,2′-bisallyl diradical (**1**), has been postulated as an intermediate in the thermal dimerization of allenes;[2] it also could be a potential intermediate for the interconversions of allene (**2**), 1,2-dimethylenecyclobutane (**3**), methylenespiropentane (**4**), biscyclopropylidene (**5**), $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**6**), and tricyclo[2.1.1.0^{1,4}]hexane (**7**). Therefore, it has been the subject of numerous, recent investigations.[1,3–6]



The allene dimerization has been shown by Moore to involve either a concerted $_{\pi}2_s + {}_{\pi}2_a$ cycloaddition or stereospecific formation of the bisallyl diradical followed by stereospecific closure of the diradical.[5] This latter interpretation has some support from Dolbier[7] who found that the rate-determining transition state did not respond to deuterium substitution but the product distribution was influenced by isotopic substi-

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(1) For preliminary communications of these results, see (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) *ibid.*, **91**, 5900 (1969); (c) taken in part from the Ph.D. Thesis of C. N. Shih, Indiana University, March 1971; (d) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

(2) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).

(3) W. von E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967).

(4) P. Dowd, *ibid.*, **92**, 1066 (1970).

(5) W. R. Moore, A. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969).

(6) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

(7) W. R. Dolbier, Jr., and S.-H. Dai, *J. Amer. Chem. Soc.*, **92**, 1774 (1970).

Table I. Deuterium Distribution of the Products of Pyrolysis of 1,2-Bis(dideuteriomethylene)cyclobutane (**8a**) at 278° (Chart I)

Reaction time, hr	% of total protium on *exo*-methylenes by nmr	*m/e* 222:223:224	**12**-d_2, **12**-d_3, **12**-d_4, %[a]	% of total protium on *exo*-methylenes by mass spectra, **12**-d_3/2 + **12**-d_4	**12**-d_3/**12**-d_4
3.25	17.4	109:41.5:18	74.3, 17.4, 8.3	17.0	2.1
12.33	41.5	100:91.5:50.5	46.6, 35.8, 17.5	35.4	2.04
19[c]	55	87:105:53	40.1, 42.5, 17.4	38.6	2.44
3.25[b]	30 ± 3		58.0, 27.7, 14.3	28.2	1.94

[a] Synthesized pure **12**-d_2 was used as a standard for correction. [b] Initial experiment.[1a] [c] There were extra peaks in the mass range examined which were not removed by repeated distillation.

tution which, therefore, implies a two-step process with the first being rate determining.

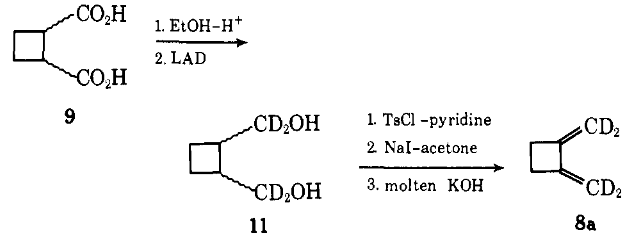
Recently, the olefin **5** has been found to give **4** irreversibly at 210° presumably *via* a trimethylenemethane type diradical and not the bisallyl one.[8] Crandall suggested the same type of intermediates for the thermal interconversion of 2,2,2′,2′,3′,3′-hexamethylbiscyclopropylidene and 4,4,5,5-tetramethylisopropylidenespiropentane and their irreversible conversion to 2,2,4,4-tetramethylisopropylidenespiropentane.[9] Dolbier has shown that diene **3** is formed by pyrolysis of **4** at 300° presumably *via* **1**, which then closes to the product; also formed in this pyrolysis is 12.5% of 1,3-dimethylenecyclobutane.[10] The strained bicyclic olefin **6** appears to give the diene **3** and the adduct of **6** and **3** in the pyrolysis of the sodium salt of spiro[2.3]-hexanone-4-tosylhydrazone.[11] Peripheral to these considerations, but important in a general sense, is the isolation of a bis(iron carbonyl) complex of **1** by the reaction of allene with iron dodecacarbonyl[12] and diiron nonacarbonyl.[13] Further, it should be noted that evidence for the triplet state of **1** has been obtained by Dowd who examined its esr when derived by low-temperature photolysis of 3,4-dimethylenecyclopentanone and possibly of **3** itself.[4]

Some questions concerning the transformations involving **1** need to be answered. Is the diradical **1** a molecular configuration of the energy surface for the dimerization of **2**? If so, what are the relative directions of rotation about bonds in **1** to form **3**? Can the diradical **1** revert to **2**? Can the same diradical be generated from **3**? If so, what is its geometry and by what set of bond rotations is it formed? What are the relative rates of bond rotations and ring closure? Does the pyrolysis of **3** give or involve **4**, **5**, **6**, and **7**? In this work we attempt to answer these questions by investigating the behavior of isotopically and stereochemically labeled 1,2-dimethylenecyclobutanes upon pyrolysis.

Results and Discussion

Synthesis of 1,2-Bis(dideuteriomethylene)cyclobutane (8a). In order to determine if **3** could be a precursor to **1**, **8a** was prepared and pyrolyzed. The synthetic sequence for preparation of **8a** is shown in Scheme I.

Scheme I

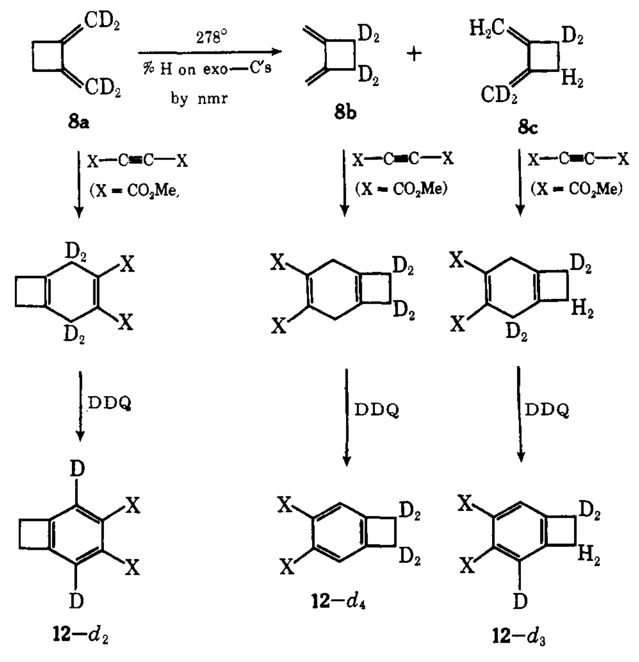


The route is similar to that used by Blomquist who first prepared **3** independent of the allene dimerization.[14]

The material was synthesized from predominantly *trans*-1,2-dicarboxycyclobutane (**9**) by esterification in acidic ethanol giving 1,2-cyclobutanedicarboxylic acid diethyl ester (**10**) which was reduced with lithium aluminum deuteride, treated with excess tosyl chloride in pyridine, doubly displaced with iodide ion in acetone, and doubly dehydroiodinated with molten potassium hydroxide.[15]

Pyrolysis of 1,2-Bis(dideuteriomethylene)cyclobutane (8a). Pyrolysis of **8a** in the vapor phase (2 Torr) for 3–13 hr at 278° gave a mixture of tetradeuterio-1,2-dimethylenecyclobutanes in 75–80% recovery. No

Chart I



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(8) P. LePerchec and J. M. Conia, *Tetrahedron Lett.*, 1587 (1970).

(9) J. K. Crandall, D. R. Paulson, and C. A. Bunnell, *ibid.*, 4217 (1969).

(10) W. R. Dolbier, Jr., *ibid.*, 393 (1968).

(11) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Amer. Chem. Soc.*, **93**, 246 (1971).

(12) A. Nakamura, *Bull. Chem. Soc. Jap.*, **39**, 543 (1966).

(13) R. Benshoshan and R. Pettit, *Chem. Commun.*, 247 (1968).

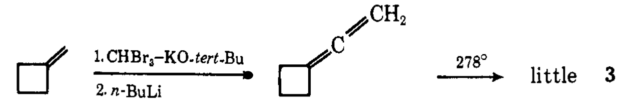
(14) A. T. Blomquist and J. A. Verdol, *J. Amer. Chem. Soc.*, **77**, 1806 (1955).

(15) E. A. Dorko, *ibid.*, **87**, 5518 (1965). The authors thank Professor R. Cargill for the details of this procedure.

additional peaks were visible in the pmr spectrum (100 MHz) of the recovered pyrolysate, except that protium was present on the exocyclic methylene groups (Table I). In order to determine the distribution of deuterium in the mixture, the recovered tetradeuterio-1,2-dimethylenecyclobutane was treated with excess dimethyl acetylenedicarboxylate followed by dehydrogenation with excess dichlorodicyanobenzoquinone (DDQ). Each reaction was carried to completion to avoid complications due to isotope effects. The product, 3,4-dicarbomethoxybicyclo[4.2.0]octa-1,3,5-triene (**12**), from a number of runs had the deuterium distribution shown in Table I. Since at low conversion the nmr and mass spectral analyses are in good agreement, the dehydrogenation must have occurred without hydrogen or deuterium shifts.

Origin of Deuterium Scramble. To prove that the isomerization was not due to a cleavage reaction to form allene followed by redimerization, a 50:50 mol % mixture of **3** and **8a** was pyrolyzed as above, and the mass spectrum of the recovered material in the region of *m/e* 75–85 was examined. Little, if any, dideuterated material was present, indicating that allene was not an intermediate. Further, a threefold change in pressures did not affect the fraction of the observed isomerization; thus the isomerization could not be a result of an allene dimerization or of a rapid, reversible cleavage of any dimeric (C_{12}) products.

It is conceivable that homolysis of the C-1–C-4 or the C-2–C-3 singly allylic bonds of **3** could form allenylcyclobutane (**13**) reversibly and would result in hydrogen–deuterium exchange. Therefore, **13** was prepared from methylenecyclobutane[16] by treatment with bromoform and potassium *tert*-butoxide,[17] followed by debromination with excess *n*-butyllithium in pentane,[18] and was subjected to pyrolysis. Under the pyrolysis conditions of **8a**, **13** gave at most 1% of **3**. This result excludes the possibility of deuterium scramble, at least initially, through reversible formation of **13**.



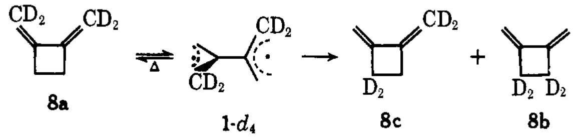
13

Deuterium scramble resulting from reversible formation of **5**, or from initial ring closure to **6** followed by reopening in the opposite direction, can account for only the 3,3,4,4-tetradeuterio-1,2-dimethylenecyclobutane product (**8b**, the precursor to **12**-d_4, the double-inversion Cope-type product[19]). However, if **5** were formed and equilibrated with **4**, subsequent rearrangement of **4** to **3** would form both **8b** and the single-inversion product, **8c**. This possibility is ruled out on the grounds of energetics (see below).

The fact that pyrolysis of *trans*- and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutane (**14** and **15**) gave the other nongeminal dimethyl-1,2-dimethylenecyclobutanes possible from the methylallene dimers[1] (see below) renders unlikely the hypothesis that reversible, forbidden 1,3-hydrogen shifts were responsible for the self-interconversion, since methyl groups are not known to transfer as efficiently as hydrogen.[20]

The observations can be rationalized by a simple mechanism shown in Scheme II. Here the doubly allylic C-3–C-4 bond breaking occurs with consequent or subsequent rotation around the C-1–C-2 bond to give an orthogonal TME species, **1**-d_4, which may collapse *via* four equivalent pathways: (a) one leading back to **8a**; (b) another to **8b**; (c) the other two to **8c**. This mechanism requires that the ratio of **8c** to **8b** be 2; and the ratio of **12**-d_3 to **12**-d_4 found at low conversions was ~2. If there was no rotation about the C-1–C-2 bond, then only **8a** and **8b** could be interconverted. Unanswered here is the question of the relative rates of central bond rotation and ring closure in **1**-d_4.

Scheme II



8a **1**-d_4 **8c** **8b**

2 : 1

Preparation and Pyrolysis of *trans*- and *cis*-3,4-Dimethyl-1,2-dimethylenecyclobutane. In order to provide further proof that a thermally induced skeletal rearrangement occurred with rotation about the central bond in the TME species and to provide information on the mode of opening of the cyclobutane ring, *trans*- and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutane (**14** and **15**) were prepared and subjected to vapor phase pyrolysis. The synthesis of **14** and **15** and the structural assignments of all their rearranged products, namely, 3-methyl-2-methylene-*syn*-ethylidenecyclobutane (**16**), 3-methyl-2-methylene-*anti*-ethylidenecyclobutane (**17**), *syn,syn*- and *syn,anti*-1,2-diethylidenecyclobutane (**18** and **19**), *anti,anti*-1,2-diethylidenecyclobutane (**20**), 3-methylene-4-methyl-*trans*-1,4-hexadiene (**21**), and 2-ethyl-3-methylene-1,4-pentadiene (**22**), have been reported previously.[1b,21]

Vapor phase pyrolyses of **14**, **15**, **16**, **18**, and **19** were conducted in a well-conditioned static reactor at pressures less than 10 Torr. Extended pyrolysis at 260° revealed that the hydrogen-shifted materials, trienes **21** and **22**, especially the former, constituted the major portions of the product as determined by vpc separation and nmr. However, at lower temperatures and shorter reaction times, it was possible to observe the interconversions of the nongeminal dimethyl-1,2-dimethylenecyclobutanes possible from the dimerization of methylallene.[1b] The data of Table II indicate the product distribution from the pyrolysis of **14**, **15**, **16**, **18**, and **19** at 237.8 and 254.7° for the lengths of time indicated. Pyrolysis of **16** gave mostly **21**, and pyrolysis of **18** and **19** gave mostly **22**. The first-order rate constants for all these pyrolyses are given in Table III. In addition, at 260° **16** isomerizes at a rate 3.5–4 times faster than **17**, and **20** is relatively inert compared to **18** and **19**. The data indicate that substantial amounts of the hydrogen-shifted product, **21**, formed in pyrolysis of **15** was probably derived from **16** and **22** may have **18**

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(16) J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949).

(17) (a) J. A. Landgrebe and D. E. Applequist, *ibid.*, **86**, 1536 (1964); (b) L. Skattebol, *J. Org. Chem.*, **29**, 2951 (1964).

(18) (a) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958); (b) L. Skattebol, *Tetrahedron Lett.*, 167 (1961); (c) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

(19) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5019 (1964).

(20) See, for example, J. W. DeHann and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **84**, 1594 (1965).

(21) J. J. Gajewski and C. N. Shih, *J. Org. Chem.*, **37**, 64 (1972).

Table II. Product Distribution from Vapor Phase Pyrolyses of **14, 15, 16, 18,** and **19**

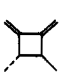
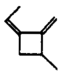
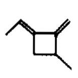
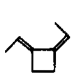
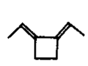
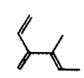
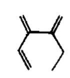
Compd	Temp, °C	Time, sec	 14	 15	 16	 17	 18	 19	 20	 21	 22
14	237.8	3600	86.0	0	0.05	13.2	0	0	0.7	<0.05	0.09
14	254.7	1800	79.5	0	Trace	19.3	0	0	0.7	0.4	0
14	254.7	3600	60.0	0	0.4	37.4	0	Trace	1.7	0.8	Trace
14	254.7	5400	45.0	0	0.3	45.9	0	Trace	4.4	3.0	1.5
15	237.8	3600	1.6	90	3.6	1.0	0	1.0	<0.1	2.8	<0.1
15	254.7	1800	Trace	81.8	4.2	0.4	0	0.9	0	11.3	1.4
15	254.7	3600	Trace	70	7.6	1.5	0	2.0	0	15.2	3.0
15	254.7	7200	Trace	40	8.4	8.4	0	4.2	0	33.7	5.1
16	254.7	1800	0.2	0.4	14.1	4.7	0	0.9	0	75.3	4.1
16	254.7	3600	0	Trace	1.0	2.1	0	0.8	0	90.0	5.9
18	254.7	1800	0	0	1.0	0	36.2	1.9	0	1.9	58.0
18	254.7	3600	0	0	0	0	13.8	3.5	0	1.8	80.6
19	254.7	1800	0	0	0.2	0	0.6	49.7	0.9	0.3	48.2
19	254.7	3600	0	0	0	0	0	23.6	1.6	1	73.8

Table III. First-Order Rate Constants for the Disappearance of **14, 15, 16, 18,** and **19** upon Pyrolysis[a]

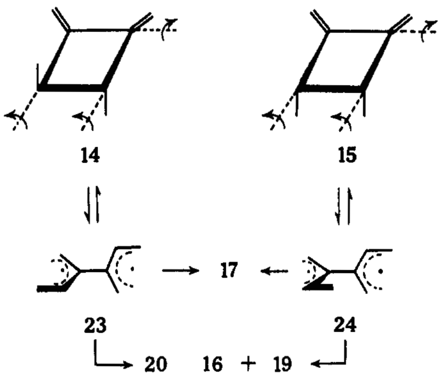
Compd	Temp, °C	k, sec^{-1}
14[b]	237.8	4.2×10^{-5}
14[b]	254.7	$1.5 \times 10^{-4} \pm 0.05$
15[b]	237.8	2.9×10^{-5}
15[b]	254.7	$1.2 \times 10^{-4} \pm 0.05$
16[c]	254.7	$1.1 \times 10^{-3} \pm 0.05$
18[c]	254.7	$5.6 \times 10^{-4} \pm 0.1$
19[c]	254.7	$3.9 \times 10^{-4} \pm 0.1$

[a] Vapor phase at pressures of compounds less than 10 Torr with no added gas. [b] Determined from the data of Table II using zero time as a point. [c] Determined from three points including zero time as a point.

or **19** as precursors in these short-term pyrolyses. The data of Table II also confirm the fact that rotation about the central bond in the TME species occurs to give the single-inversion Cope-type products, **16** and **17**, in addition to the double-inversion products, **18, 19,** and **20**. Most important, however, are the facts that (a) interconversion of **14** and **15** occurs relatively slowly in short-term thermolyses; (b) **14** gives almost exclusively **17** and **20**; and (c) **15** gives almost exclusively **16, 17,** and **19** and the subsequent rearrangement product of **16**, namely **21**.

Mechanistic Interpretation. If the reasonable assumption that rotation about bonds occurs slowly relative to ring closure in the nearly, or completely, developed allylic radicals during the rearrangement, then the relative ratios of the double-inversion products, **18, 19, 20,** and **22,** indicate that conrotatory over disrotatory opening of the cyclobutane ring is favored by a factor of at least 10 from **14** and **15** kinetically. Further, if it is assumed that the intermediate responsible for the double-inversion product is also responsible for the single-inversion product, then orthogonal, or effectively so, Me$_2$TME species must be involved, and the one which must be produced from **14** is **23**, and the one which is produced from **15** is **24** by the conrotatory motions indicated above (Scheme III).

Scheme III



By virtue of the bidentate nature of the allyl radical, **23** can give **20, 17** (two ways), and **14** (by the microscopic reverse of its formation), and **24** can give **19, 16, 17,** and **15**. Thus, the conrotatory mode of ring opening deduced from the double-inversion product distribution is qualitatively in accord with the distribution of single-inversion products since little **16** is found in the trans (**14**) thermolysis. It is interesting that **24** must give five to six times as much **16** as **17** if it is the sole intermediate in the thermolysis of **15**. A third Me$_2$TME species can be formed by conrotatory opening of **14**, namely one in which the two methyl groups are directed to the interior of the system. However, **16** and **18** are the expected products from this species, and these are formed only to a limited extent, if at all, from **14**. This observation might be due to the increasing steric hindrance in the transition state for this mode of conrotation. Further support for conrotatory ring opening derives from the rates of reaction of **14** and **15**. The trans material **14** rearranges 1.3 times as fast as the cis compound **15**. This probably reflects a small increase of steric hindrance in the transition state of **15** for conrotation. Interestingly, *trans*-1,2,3,4-tetramethylcyclobutene isomerizes 22.5 times faster than its cis isomer at 250°.[22] In the latter case, the steric hindrance seems more serious in the transition state for conrotatory ring opening. In the former, the transition state is apparently a twisted TME, and thus, steric effects become less significant.

That opening of 1,2-dimethylenecyclobutanes to the orthogonal bisallyl diradical is conrotatory follows from theoretical considerations as well. Hoffmann and also Baldwin indicate that the highest occupied MO of the orthogonal diradical will correlate with the σ MO of

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[22] (a) R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959); (b) G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966); (c) E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 257 (1964).

the ring-closed product *via* conrotation. The reason for the HOMO being of this particular symmetry follows from consideration of spiroconjugation.[6,23] Some support for long range interaction between the allyl radicals in orthogonal **1** derives from the observation that levorotatory **14** gives dextrorotatory **17** upon pyrolysis.[24] Thus, there cannot be rapid rotation about the central bond in **23**, relative to ring closure.

Enthalpy Relationship among Compounds 1–7. In order to discuss the relationship and possible intervention of **1–7**, an estimate of the relative heats of formation of these compounds is most enlightening. Central to this study is 1,2-dimethylenecyclobutane (**3**), whose heat of formation is unknown; however, its 1,3 isomer has ΔH_f = 53.5 kcal/mol.[25a] To a zeroth approximation the ΔH_f of **3** should be similar. The only difference between these two is the conjugation in the former, but whatever stability is gained through conjugation is probably lost in the cisoid arrangement of π systems. The transition state for formation of the bisallyl diradical **1** lies 46.8 kcal/mol higher than **3** from Doering and Dolbier's work.[3] However, an estimation of the ΔH_f of **1** by conventional means gives a surprising result. Following Benson's[25b] arguments, $\Delta\Delta H_f$ of **1** and **3** is 55 kcal/mol ($\Delta\Delta H_f$ between cyclobutane and tetramethylene) − 25 kcal/mol (2 × allyl radical resonance energy) = 30 kcal/mol. Thus, to the extent this estimate is correct, the singlet ground state of **1** should lie about 16.8 kcal/mol lower than the transition state forming it, ignoring any spiroconjugation.

The heat of formation of allene (**2**), is known[25c,d] and that of two allenes is 95.4 kcal/mol, a value only slightly lower than that for the transition state enthalpy in the degenerate rearrangement of **3** and substantially higher than that calculated for **1**. The transition state for the allene dimerization must lie substantially higher than 95.4 kcal/mol; it is estimated to be about 15 kcal/mol based on very crude rate data and the assumption of a preexponential term of 10^7 M^{-1} sec^{-1}.[24] Therefore, **1** can be an intermediate in the allene dimerization on the grounds of energetics.

Hoffmann[6] has pointed out that methylenespiropentane (**4**) and biscyclopropylidene (**5**) could inhabit the energy surface for this degenerate rearrangement of **3** and that for the allene dimerization. However, the heat of formation of **4** can be estimated from spiropentane (ΔH_f = 44.23 kcal/mol)[26] by subtracting the contribution due to one methylene group (−5 kcal/mol),[27] adding the contribution of a $>C{=}CH_2$ group in a strainless situation (16.9 kcal/mol),[27] and adding the extra strain introduced in the spiropentane system (13.5 kcal/mol, the difference in heats of formation of a methylenecyclopropane and a cyclopropane with a strain-free *exo*-methylene)[28] and is equal to 79.6 kcal/mol. Thus, **4** is substantially less stable than **3** and, since it gives **3** only slowly at 300°,[10] it cannot be an intermediate in either the dimerization of **2** or the degenerate rearrangement of **3**. By the same token **5** gives exclusively **4** when heated at 200°; therefore, it must lie at least 5 kcal/mol higher in enthalpy than **4** and cannot be an intermediate in the aforementioned reaction. Further experimental support for these conclusions derives from the fact that **4** can be only a minor component (<1%) in the equilibrium between **4** and **3**. Therefore **4** is at least 5 kcal/mol less stable than **3**. Since the free energy of activation (and probably the enthalpy) for conversion of **4** to **3** is ~50 kcal/mol, the transition state for conversion of **3** to **4** must be >55 kcal/mol higher than **3**.

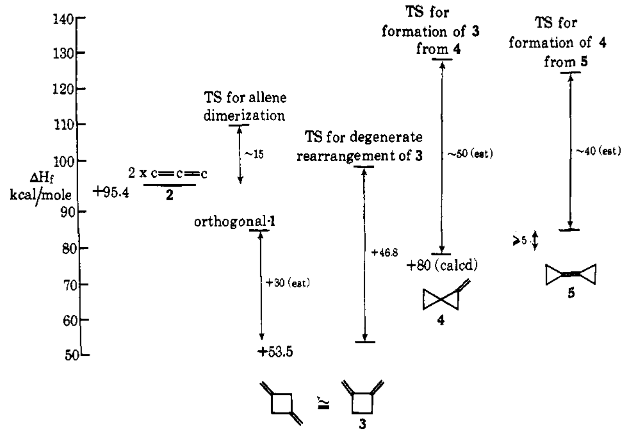

Figure 1. Energy surface for relating compounds **1–5**.

It is unknown precisely where $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**6**) resides on the energy surface, since its heat of formation is impossible to estimate by virtue of the unknown strain of the internal double bond. However, it is clear that the degenerate rearrangement of **3** cannot proceed exclusively *via* **6**, or else no single-inversion Cope-type products corresponding to **8c**, **16**, and **17** could be formed. Thus, the transition-state enthalpy for interconversion of **3** and **6** must be at least as large as that for the degenerate rearrangement of **3**.

Although it is impossible to estimate the heat formation of tricyclo[2.1.1.0^{1,4}]hexane (7) at present, 7 is probably not involved in the degenerate rearrangement of **3**, since no reasonable mechanism can be drawn to account for the deuterium exchange.

Finally, all of these calculations and estimates can be used to construct the energy surface shown in Figure 1. It must be admitted that further work is in order to refine some of the estimates, but the zeroth order numbers are probably not grossly in error and provide a meaningful framework for subsequent experimentation and discussion.

Relationship between the 1,2-Dimethylenecyclobutane Rearrangement and the Allene Dimerization. The energy surface constructed above allows the bisallyl diradical (**1**), the intermediate in the degenerate rearrangement of the 1,2-dimethylenecyclobutanes, to also be an intermediate, albeit formed long after the rate-determining step, in the allene dimerization. Dolbier's isotope effects are consistent with this view.[7]

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(23) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).

(24) J. J. Gajewski and C. N. Shih, unpublished results. At present the optical purities and relative configurations of **14** and **17** are unknown.

(25) (a) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Colburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (c) M. Coperthwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962); (d) APIRP Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," gives ΔH_f allene = +45.92 at 298.2°, Table 23-2-(5.2202)-W.

(26) F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stand.*, **54**, 143 (1955).

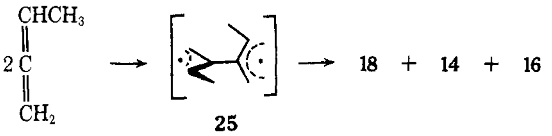
(27) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(28) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

However, the remarkable stereospecificity of the 1,2-cyclononadiene dimerization observed by Moore suggests that allene dimerizations are concerted in a ${}_\pi 2_s + {}_\pi 2_a$ sense.[5] Moore also indicated that a two-step mechanism is possible in which conrotation about allene bonds occurs in the formation of the bisallyl diradical and that the biradical then closes disrotatory; alternatively, a path involving disrotatory motions about the allene bonds in the formation of the bisallyl diradical followed by conrotatory closure will also account for the experimental facts.[5] No theoretical rationale for stereospecificity of either of the two-step pathways was given, although if the same bisallyl diradical is involved in the dimerization as in the degenerate rearrangements studied here, only the two-step pathway terminating in conrotatory closure of the biradical is possible.

Unfortunately, none of the data reported here can directly resolve the question save for perhaps a comparison of the isotope effects in the product-forming step in the allene dimerization and the degenerate rearrangement of **8a**. If the **8c**/**8b** ratio from **8a** were the same at low conversions as was formed in the dimerization of 1,1-dideuterioallene, at low conversions, including temperature corrections, thus a necessary but insufficient condition for identity of intermediates could be established. However, at low conversions of **8a** to **8b** and **8c** in the range of 4–10% conversion, the **12**-d_3/**12**-d_4 ratio is quite uncertain due to the large $m + 1$ and $m + 2$ contributions from **12**-d_2, and we have been unable to obtain reliable, that is, internally consistent, percentages. Thus, the question must remain unanswered.

A final point concerns the relationship between the methylallene dimerization and the rearrangements of the dimethyl-1,2-dimethylenecyclobutanes reported here. The product distributions from the dimerization, particularly those of **16**–**20**, are substantially different than those obtained from pyrolysis of **14** or **15** or a mixture of the two.[1b] Most prominent among the differences is the fact that the *syn,syn*-1,2-diethylidenecyclobutane (**18**) is a substantial product (13% at low conversion of methylallene to dimer) but is not formed at all from either **14** or **15**. We suggest that **18** should be formed from the *trans,trans*-1,1′-dimethyl-2,2′-bisallyl species (**25**) if bisallyl species are involved in the allene dimerization and if **25** closes conrotatory; **14** and **16** can also be formed. Since **14** does not open to **25**, the formation of **18** in the dimerization suggests that the transition state for dimerization controls the relative rates of formation of biradicals **23**–**25** (if they are, in fact, involved), and these species are not interconnected in the dimerization. If biradicals **23**–**25** are involved in the methylallene dimerization, then the ratio of **16** to **18** produced from **25** must be ~1.5,[21] a ratio of mono- to diethylidene compounds that is substantially different from that from **23** (20:1) and **24** (7:1) (Table II).



25

in addition to **23** + **24**

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on Varian A-60 and HA-100 spectrometers. Carbon tetrachloride was used as a solvent with TMS as an internal lock in frequency sweep mode; chemical shifts are reported in δ values in parts per million downfield from TMS. Infrared spectra were obtained with Perkin-Elmer Model 137 and 137G spectrophotometers in the indicated phase. Vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using dibutyl tetrachlorophthalate (DBTCP) as liquid phase, unless otherwise specified. For separation and purification, a 15 ft × 0.25 in. column with 30% DBTCP on 60–80 Chromosorb W was used and operated at 80°, 40 psi, and 60 ml/min of helium flow. A 200-ft DBTCP capillary column operated at 90°, 30 psi, was used for analysis. Exact masses were taken on an AEI MS-9 mass spectrometer operating at 70 eV. Melting points were measured with a Thomas-Hoover capillary melting point apparatus without correction.

1,2-Bis(tosyloxymethyl)cyclobutane (26). A solution of 4.9 g (0.423 mol) of 1,2-cyclobutanedimethanol[14] in 150 ml of pyridine and 177 g (0.93 mol) of recrystallized *p*-toluenesulfonyl chloride in 450 ml of pyridine was stirred for 5.5 hr at 0°. To the light brown reaction mixture was added slowly 15 ml of ice water, and this was stirred for 0.5 hr to decompose the excess *p*-toluenesulfonyl chloride. This mixture was then poured into ice water and extracted repeatedly with ether. The ether layer was washed with a 5% hydrochloric acid until the washings were acidic, then with an aqueous sodium bicarbonate solution. After drying over anhydrous sodium sulfate, the ethereal solution was concentrated *in vacuo* to give 153 g (85.5% yield) of a light brown viscous oil which was used without further purification: nmr ($CDCl_3$, 60 MHz) δ 1.85 (m, 4 H), 2.3 (m, 2 H), 2.4 (s, 6 H), 3.9 (m, 4 H), 7.55 (A_2B_2, J = 8 Hz, 8 H); ir (neat) 3.38 (m), 3.48 (sh), sharp 6.23 (m), broad 7.35 (vs), sharp 8.4, 8.5 μ (vs).

1,2-Bis(iodomethyl)cyclobutane (27). A solution of 152 g (0.359 mol) of ditosylate **26** in 200 ml of acetone was added to 215 g (1.43 mol) of sodium iodide dissolved in 1 l. of hot acetone. After heating at reflux with stirring for 24 hr, the yellow mixture was filtered to remove sodium toxylate. The filtrate was concentrated *in vacuo*, dissolved in ether, and washed with water. The ether layer was washed with a saturated aqueous sodium bisulfite solution until it was colorless. After having been washed with water and dried over anhydrous sodium sulfate, the solvent was evaporated giving 96 g (80% yield) of a dark brown viscous liquid diiodide which was used without further purification: nmr ($CDCl_3$, 60 MHz) δ 1.2–2.5 (complex m, 6 H), 3–3.5 (complex m, 4 H); ir (neat) 3.4 (s), 3.5 (sh), 6.98 (sh), 7.02 (m), 8.02 (s), 8.45 (s), 8.6 μ (s).

1,2-Dimethylenecyclobutane (3). In a 100-ml four-necked flask equipped with a thermometer, a serum cap, an inlet, and an outlet for helium gas, was placed 35 g of potassium hydroxide. The flask was heated at 200° and agitation was provided by a magnetic stirrer. Into the molten potassium hydroxide was injected 7 g (20.8 mmol) of crude diiodide **27** in 200-μl shots under helium flow. The volatile product was trapped from the outgoing gas in a tube cooled with liquid nitrogen. In this way, 1.5 ml of a yellow liquid was obtained. This crude liquid was then distilled bulb-to-bulb at room temperature at 15 mm giving 0.72 g (43% yield) of a distillate and 0.2 g of a yellow polymeric material. The distillate was further purified by passage through a preparative DBTCP column. Analysis on a DBTCP capillary column indicated 99 + % purity: nmr (CCl_4, 60 MHz) δ 2.58 (s, 4 H), 4.61 (s, 2 H), 5.05 (s, 2 H); ir (CCl_4) 3.25 (m), 3.4 (s), 5.67 (m), 6.06 (m), 7.1 (m), 8.06 (m), 11.40 μ (s); uv (isooctane) 237.5 (sh), 246 (λ_{max}), 256 nm (sh); both ir and uv identical with published spectra;[14] m/e 80.0619 (calcd for C_6H_8, 80.0626).

1,2-Bis(hydroxydideuteriomethyl)cyclobutane (11). To 2.52 g (60 mmol) of lithium aluminum deuteride in 40 ml of anhydrous ether was added slowly with stirring a solution of 10 g (50 mmol) of 1,2-dicarbethoxycyclobutane[14] in 40 ml of anhydrous ether. The reaction mixture was stirred at room temperature and the extent of reaction was followed by ir on observing the disappearance of carbonyl groups. Overnight stirring led to only 90% conversion, so an additional 0.25 g of lithium aluminum deuteride was added to the incomplete reaction mixture which was stirred again overnight. After the reaction was complete, the reaction mixture was decomposed with a freshly prepared saturated aqueous solution of anhydrous sodium sulfate. The ethereal solution was filtered from the salts and the salts were washed thoroughly with tetrahydrofuran. The washings and original ether solution were combined and dried over anhydrous sodium sulfate. After evaporation of the solvent, 5.83 g (97.3% yield) of a viscous oil was obtained: nmr ($CDCl_3$, 60 MHz) δ 1.4–2.8 (complex m, 6 H), 4.3 (s, 2 H, concentration-dependent); ir (neat) 3.01 (broad, vs), 3.4 (s), 4.56 (m), 4.78 μ (m).

1,2-Bis(tosyloxydideuteriomethyl)cyclobutane (26-d_4). To a solution of 16.8 g (88 mmol) of recrystallized *p*-toluenesulfonyl chloride in 35 ml of pyridine at 0° was added a cold solution of 4.8 g (40 mmol) of tetradeuterio diol **11** in 15 ml of pyridine followed by stirring at 0° for 5.5 hr, followed by addition of 1 ml of ice water with 20 min of further stirring. This mixture was then poured into ice water. The same work-up procedures described above for the corresponding protio compound **26** were then followed, and 13.6 g (79.5% yield) of a light brown viscous oil was obtained: nmr ($CDCl_3$, 60 MHz) δ 1.5–2.6 (complex m, 6 H), 2.43 (s, 6 H), 7.55 (A_2B_2, J = 8 Hz, 8 H); ir (neat) 3.3 (sh), 3.4 (m), 3.5 (sh), sharp 6.23 (m), 7.3 (vs), 7.4 (sh), 8.35 (vs), 8.45 μ (vs).

1,2-Bis(dideuterioiodomethyl)cyclobutane (27-d_4). A solution of 13.6 g (31.8 mmol) of crude tetradeuterioditosylate (**26**-d_4) in 25 ml of acetone was added to 19 g (127 mmol) of sodium iodide dissolved in 75 ml of hot acetone. After reflux with stirring for 24 hr, the reaction mixture was worked up by the same procedures described above for the corresponding protio diiodide **27** giving 10.2 g (94.5% yield) of a viscous brown oil. Its nmr ($CDCl_3$, 60 MHz) indicated very complex pattern at δ 1.25–2.95: ir (neat) 3.4 (s), 3.5 (sh), 6.97 (w), 8.1 (m), 10.69 μ (vs).

1,2-Bis(dideuteriomethylene)cyclobutane (8a). The equipment and the technique described above for the preparation of the corresponding perprotio diene **3** were employed. By addition of 4.35 g (12.8 mmol) of crude tetradeuterio diiodide (**27**-d_4) to 35 g of molten potassium hydroxide, 1.5 ml of a yellow liquid was obtained. This crude liquid was then distilled bulb-to-bulb at room temperature at 15–0.5 mm giving 0.74 g of a yellow polymeric residue and 0.32 g (29.7% yield) of a colorless distillate. The latter was further purified by passage through a preparative DBTCP column. Analysis on a DBTCP capillary column indicated 99+% purity: nmr (CCl_4, 60 MHz) δ 2.58 (s); ir (CCl_4) 3.35 (s), 3.4 (s), 3.53 (w), 4.32 (w), 4.51 (w), 6.08 (m), 6.14 (m), 6.2 (w), 7.05 (m), 14.3 μ (vs); uv (isooctane) 237 (sh), 245 (λ_{max}), 255 nm (sh); *m/e* 84.0873 (calcd for $C_6D_4H_4$, 84.0877).

2,2,5,5-Tetradeuterio-3,4-dicarbomethoxybicyclo[4.2.0]octa-1(6),3-diene (28-d_4). A solution of 40 μl (32 mg, 0.381 mmol) of tetradeuterio diene **8a** and 54 μl (62.5 mg, 0.44 mmol) of dimethyl acetylenedicarboxylate in 1 ml of benzene was heated under nitrogen in a sealed 5-ml tube for 12 hr at 82°. After the completion of reaction, the solvent was evaporated giving 90 mg of a low-melting solid. This crude mixture was distilled first at 50° (0.5 mm) to remove excess acetylenedicarboxylate and finally at 100–110° giving 75 mg (87.1%) yield of a waxy solid: nmr (CCl_4, 60 MHz) δ 2.55 (s, 4 H), 3.7 (s, 6 H).

3,4-Dicarbomethoxybicyclo[4.2.0]octa-1(6),3-diene (28). This compound was prepared in 88% yield by the same procedures described above for the corresponding tetradeuterio bicyclic diene **28**-d_4: mp 48–50°; nmr (CCl_4, 60 MHz) δ 2.55 (s, 4 H), 2.88 (s, 4 H), 3.7 (s, 6 H); ir (CCl_4) 3.4 (m), 3.53 (sh), 5.76 (s), 6.12 (m), 6.99 μ (s).

3,4-Dicarbomethoxybicyclo[4.2.0]octa-1,3,5-triene (12). To a solution of 75 mg (0.338 mmol) of crude bicyclic diene **28** in 3 ml of benzene was added 100 mg (0.44 mmol) of recrystallized 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), followed by refluxing for 22 hr and filtration. The filtrate was diluted with ether and successively washed twice with a saturated aqueous solution of sodium bisulfite to reduce excess DDQ, twice with 10 ml of 1 *N* sodium hydroxide to remove phenol, then twice with water and finally twice with saturated brine. After drying over anhydrous sodium sulfate and evaporation of the solvent, 60 mg of a viscous oil was obtained, which was distilled at 100–110° (0.5 mm) giving 40 mg (53.7% yield) of a waxy solid: mp 49°; nmr (CCl_4, 60 MHz) δ 3.2 (s, 4 H), 3.8 (s, 6 H), 7.28 (s, 2 H); ir (CCl_4) 3.38 (m), 3.5 (sh), 5.76 (s), 6.1 (w), 6.29 (m), 6.44 (sh), 6.98 μ (s); *m/e* 220.0073 (calcd for $C_{12}H_{12}O_4$, 220.0074).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.29; H, 5.62.

2,5-Dideuterio-3,4-dicarbomethoxybicyclo[4.2.0]octa-1,3,5-triene (12-d_2). A mixture of 40 mg (0.177 mmol) of crude tetradeuterio bicyclic diene **28**-d_4 with 55 mg (0.248 mmol) of recrystalliaed DDQ was refluxed in 1.5 ml of benzene for 19 hr. This reaction mixture was then worked up successively by the same procedures described above for the corresponding protio compound **12** giving 40 mg of an oil. After distillation at 100–110° (0.5 mm), 30 mg (76.5% yield) of a low-melting solid was obtained: nmr (CCl_4, 60 MHz) δ 3.2 (s, 4 H), 3.8 (s, 6 H). The mass spectral analyses indicated *m/e* 222.0862 (calcd for $C_{12}D_2H_{10}O_4$, 222.0861) and *m/e* 222:223:224 = 100:14.7:1.82 (taken on a Varian Mat CH-7, 10–12 eV). This ratio was served as a standard for correction in the mass spectral analyses of the rearranged products (see below).

Pyrolysis of 8a. A typical run is described below. Into each of two well-conditioned 5-l. flasks, equipped with two 0.25 in. × 15 in. side tubings, was placed 20 μl of pure **8a**. The flasks were evacuated at 0.5 mm and then sealed while the contents were frozen in liquid nitrogen. After the liquid was vaporized by removal of liquid nitrogen, the flasks (2 Torr) were set in an oven at 278° and heated for 3.25 hr. After cooling in air, the end of one side tubing of the flask was immersed in liquid nitrogen to condense pyrolysate and thus 15 μl of a liquid was recovered from each flask. The pmr (100 MHz) spectrum of the combined pyrolysate (30 μl) in carbon tetrachloride revealed a clean mixture of isomers without contamination of polymeric materials and 17.4% of total protium on *exo*-methylenes (*i.e.*, fraction of protons at δ 4.61 and 5.05) calculated from integration. To this nmr solution were added 1 ml of benzene and 40 μl (*ca.* 11.5% excess) of dimethyl acetylenedicarboxylate, and then the solution was heated at 82° for 12 hr under nitrogen in a sealed 5-ml tube. After the solvent was evaporated, 66 mg of a pale yellow oil was obtained, which was purified by molecular distillation at 40–50° (0.5 mm) to remove excess acetylenedicarboxylate and finally at 100–110° (0.5 mm) giving 60 mg of pure adducts: nmr (100 MHz, CCl_4) δ 2.55 (s), 2.88 (s, 17.3% of total protium excluding carbomethoxy groups), 3.7 (s). Into 1 ml of benzene was dissolved 40 mg of above purified adducts; the solution was then treated with 55 mg of recrystallized DDQ at reflux for 21 hr. After cooling and filtration, the filtrate was diluted with ether and successively washed twice with a saturated aqueous solution of sodium bisulfite, twice with 5 ml of 1 *N* sodium hydroxide, twice with water, and finally with saturated brine. After drying over anhydrous sodium sulfate and evaporation of the solvent, 38 mg of the crude product was obtained which was distilled at 100–110° (0.5 mm) giving 25 mg of a waxy solid whose nmr showed (CCl_4, 60 MHz) δ 3.2 (s), 3.8 (s), 7.28 (s). This purified isotope mixture was subjected to mass spectral analysis (Varian Mat CH-7, 10–12 eV) indicating *m/e* 222:223:224 = 109:41.5:18. After correction of natural abundance of ^{13}C by using pure synthesized **12**-d_2 as a standard, **12**-d_2:**12**-d_3:**12**-d_4 = 109:25.5:12.2 was found, a result which indicated that the mixture consisted of 74.3% **12**-d_2, 17.4% **12**-d_3, and 8.3% **12**-d_4. The ratio of **12**-d_3 to **12**-d_4 was 2.1. The percentage rearrangement was given by **12**-d_3/2 + **12**-d_4 = 17.0%, since the precursor to **12**-d_3 (**8c**) has only half the *exo*-methylene protium as the precursor to **12**-d_4 (**8b**). The results of four runs carried out at various extents of conversion are given in Table I.

1,1-Dibromospirohexane (29). The method of Skattebol was employed.[17b] To a well-stirred mixture of 3.8 g (55.9 mmol) of methylenecyclobutane, which was prepared by the method of Roberts and Sauer,[16] and 6.26 g (55.9 mmol) of potassium *tert*-butoxide in 50 ml of *n*-pentane at −10° under nitrogen was added with a syringe 14.68 g (58 mmol) of bromoform. The addition required 4 hr and the mixture was allowed to stir at room temperature overnight. Then the reaction mixture was treated with water and separated. The aqueous layer was extracted with *n*-pentane and the washings were combined with the original pentane layer. The combined solution was washed with water and saturated brine and dried over anhydrous sodium sulfate. The solvent was removed to give 10.2 g of a light brown liquid residue, which was distilled at 12 mm giving 8 g (59.6% yield) of a colorless liquid, bp 73–74° [lit.[17a] bp 74° (12 mm)]. This crude distillate was further purified by passage through a 10 ft × 3/8 in. XF 1150 column (30% on Chromosorb W 60–80), operated at 135° and 30 psi, giving the pure product from the second peak: nmr ($CDCl_3$, 60 MHz) δ 1.62 (s, 2 H), 1.83–2.67 (complex m, 6 H); ir (neat) 3.35 (m), 3.4 (m), 3.52 (sh), 7.09 (m), 8.06 (w), 9.45 (m), 9.7 (m), 9.93 (m), 14.58 μ (s).

Allenylcyclobutane (13). The method of Moore and Ward was used.[18c] Into a stirred solution of 5.4 g (22.6 mmol) of dibromide **29** in 10 ml of *n*-pentane was added dropwise at −10° under nitrogen 24 ml (2 g, 31.3 mmol) of *n*-butyllithium in *n*-pentane (12.9%, 0.65 g/ml). White precipitates were formed immediately. After 10 min, the reaction mixture was treated with a saturated aqueous solution of anhydrous sodium sulfate; then the pentane layer was decanted and dried over anhydrous sodium sulfate. After concentration by distilling off the solvent, about one-half of the pentane solution was passed through the above-mentioned XF 1150 column, operated at 85° and 16 psi, and 500 μl of pure allene was obtained:

nmr (CCl_4, 60 MHz) δ 1.9 (quintet, J = 7.5 Hz, 2 H), 2.8 (m, 4 H), 4.6 (quintet, J = 5 Hz, 2 H); ir (neat) 3.27 (sh), 3.34 (s), 3.38 (s), 3.41 (s), 3.52 (sh), 5.1 (s), 5.88 (w), 6.92 (m), 7.03 (m), 9.55 (m), 11.8 μ (s); m/e 80.0600 (calcd for C_6H_8, 80.0626).

Control Experiments. (a) A 50:50 mol % mixture of the tetradeuterio diene **8a** (8 μl) and perprotio diene **3** (7.6 μl) was pyrolyzed at 275° for 2 hr in a 100-ml carefully neutralized tube sealed at −78° under nitrogen at 120 mm. The mass spectrum of the recovered volatile pyrolysate in the region of m/e 75–85 was examined indicating that little, if any, m/e 82 material ($C_6H_6D_2$) was present.

(b) A threefold change in the pressure of diene **8a** was found to have no influence on the observed fraction of isomerization.

(c) Allenylcyclobutane (**13**) was pyrolyzed at 278° for 3.25 hr under the same condition described for the pyrolysis of diene **8a.** The recovered pyrolysate was analyzed on a capillary DBTCP column and by nmr indicating only unchanged starting material. At 315°, pyrolysis of **13** for 2.5 hr under the same condition gave 10% of a product whose retention time on a capillary DBTCP column was identical with that of diene **3**.

Pyrolysis of 14, 15, 16, 18, and 19. All starting materials and products were characterized previously.[1b,21] Pyrolyses were performed in a static reactor whose construction has been published.[29]

Each run utilized 3 μl of diene with 15–20% of distilled n-octane as a standard in a 200-ml well-conditioned reactor at the indicated temperatures. After the indicated lengths of time, the material was removed, collected from the vacuum line by condensing in a liquid nitrogen trap, and analyzed on a DBTCP capillary column. No loss of material for each run was found relative to the internal standard. The results are summarized in Table II.

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(29) J. J. Gajewski, *J. Amer. Chem. Soc.*, **93,** 4450 (1971).

Tricarbonyl(*trans*-π-pentadienyl)iron Cations. Solvolysis Stereochemistry

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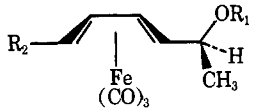
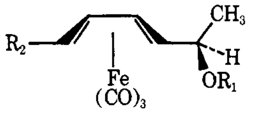
Abstract: The *ψ-exo-* and *ψ-endo*-tricarbonyl(*trans,trans*-4-methyl-3,5-heptadien-2-yl 3,5-dinitrobenzoate)iron esters, **12b** and **11b**, respectively, were prepared and solvolyzed in 80% aqueous acetone. The ψ-exo/ψ-endo rate ratio was 2500 ± 1000. Sodium borohydride reduction of *trans,trans*-dienone tricarbonyliron complexes gives ψ-endo alcohols in a highly stereoselective fashion. These data along with nmr vicinal coupling constants in the complexed dienols support previous assignments of ψ-exo and ψ-endo configurations and demonstrate unambiguously that the leaving group departs exo to iron in the solvolyses. The *exo-* and *endo*-tricarbonyl(3-*trans*-β-styryl)-2-cyclohexen-1-yl 3,5-dinitrobenzoate)iron esters gave a low exo/endo solvolysis rate ratio of 6. This anomalous behavior is discussed in terms of steric and conformational effects.

Analysis of nonbonded interactions in syn-substituted tricarbonyl(diene)iron compounds based on many known crystal structures gave the conformational model shown in Figure 1.[3] Assumption that the larger groups will avoid the very crowded position (c) led to our conclusion that the most stable conformations of several diastereomeric dienol complexes and their esters were those shown here as **1** and **2**. The corresponding dinitrobenzoates underwent S_N1 type solvolysis with retention of configuration and gave ψ-exo/ψ-endo rate ratios of *ca.* 90. Based on this we concluded that the leaving group preferred to depart exo to (away from) iron.[4]



ψ-exo

1a, $R_2 = CH_3$
b, R_2 = Ph



ψ-endo

2a, $R_2 = CH_3$
b, R_2 = Ph

The conformational analysis and resulting assignments of relative configuration and conformational preference upon which our conclusions about solvolysis stereochemistry are based are entirely reasonable and self-consistent. Nevertheless, such a treatment of organotransition metal molecules has little precedent. Thus further tests of our assumptions and conclusions were in order. This paper describes such work.

Synthesis

Two cyclic dienol complexes were prepared in a fashion which allowed unambiguous assignment of their stereochemistry. Key reactions are shown in Scheme I. Owing to the large size of the tricarbonyliron group, borohydride reduction of the dienone complex **3** should proceed by addition of hydride exo to iron[4a,5] to give *endo* alcohol, **5a**. In fact, only one alcohol with a high R_f on silica gel thin layers, indicative of a sterically shielded hydroxy group,[4a,6,7] was produced. Complexation of **4a** was nonstereospecific, as expected, pro-

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(3) N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92,** 3058 (1970).

(4) (a) N. A. Clinton and C. P. Lillya, *ibid.*, **92,** 3065 (1970); (b) N. A. Clinton and C. P. Lillya, *Chem. Commun.*, 579 (1968).

(5) D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.*, **72,** 5743 (1950); W. G. Dauben, G. J. Fonken, and D. S. Noyce, *ibid.*, **78,** 2579 (1956).

(6) D. H. R. Barton and G. A. Morrison, *Fortsch. Chem. Org. Naturst.*, **19,** 163 (1961).

(7) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83,** 4216 (1961).