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Hydrocarbon Degenerate Thermal Rearrangements.

III. Characterization of the Methylallene Dimers.

Stereochemistry of the 1,2-Dimethylenecyclobutane Ring Opening

Sir:

Tetramethyleneethane (TME), or the 2,2'-bisallyl di-radical, was indicated as being responsible for the thermally induced hydrogen-deuterium scrambling of 1,2-bis(dideuteriomethylene)cyclobutane.^{1a} Degradative

subjected to vapor phase pyrolysis in a well-conditioned static reactor at partial pressures less than 10 Torr. Extended pyrolyses at 260° revealed that the hydrogen-shifted materials, trienes **8** and **9**, especially the former, constituted major portions of the product. However, at lower temperatures and shorter reaction times it was possible to observe interconversion of the nongeminal dimethyl-1,2-dimethylenecyclobutanes. The data of Table II indicate the product distribution from the pyrolysis of **1** and **2** at 237.8° and 254.7° for the lengths of time indicated. It was possible to isolate and pyrolyze **3** which gave mostly **8**, and **5** and **6** which gave mostly **9** (90% in each case). The approximate relative rates of disappearance of **1**, **2**, **3**, **5**, and **6** at 254.7° are 1.5:1.2:11:5.6:3.9, respectively. These data indicate that a substantial portion of the hydrogen-shifted product, **8**, formed in pyrolysis of **2** was derived from **3** but that **9** probably did not have **5** or **6** as precursors in these short-term pyrolyses.

Table I. Percentage of Dimer Products^a from Methylallene at 170°

Reaction time, ^d hr							
	1	2	3	4	5	6 ^b	7 ^b
1	25	4	37	18	13	3	~0.5
13 ^c	10	2	32	14	29	11	2
20	4	0.6	25	7	46	15	2.5

^a All new compounds had satisfactory exact masses. ^b **6** and **7** are identical with the two 1,2-diethylidene-cyclobutanes (1:1 mixture) obtained from base-catalyzed isomerization of *cis*-1,2-divinylcyclobutane: P. Heimbach and R. Schimpf, *Angew. Chem. Intern. Ed. Engl.*, **8**, 206 (1969). We thank Dr. Heimbach for a generous sample of this mixture. ^c Recovered methylallene, 32% (minimum); dimer, 29%; less volatile material, 8%; nonvolatile material, 31%. ^d All dimerizations were conducted with 450 μ l of the allene in 5-ml Pyrex tubes.

Table II. Product Distribution from Vapor Phase Pyrolyses of **1** and **2**

Compd	Temp, °C	Time, sec	1 (<i>t</i>) ^a	2 (<i>c</i>)	3 (<i>s</i>)	4 (<i>a</i>)	5 (<i>ss</i>)	6 (<i>sa</i>)	7 (<i>aa</i>)	8 ^{2a}	9 ^{2a}
1	237.8	3600	86.0	0	0.05	13.2	0	0	0.7	<0.05	0.09
1	254.7	3600	60.0	0	0.4	37.4	0	Trace	1.7	0.8	Trace
2	237.8	3600	1.6	90	3.6	1.0	0	1.0	<0.1	2.8	<0.1
2	254.7	3600	Trace	70	7.6	1.5	0	2.0	0	15.2	3.0

^a Letters in parentheses are the first letters of the stereochemical designations of the dimethyldimethylenecyclobutanes.

experiments indicated that this species, if involved, had effectively or, in fact, mutually perpendicular allyl radical residues.^{1a} It was our intention 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-dimethylenecyclobutanes, **1** and **2**, respectively, were isolated from dimerization of methylallene (Table I).² These materials were

The fact that **1** and **2** gave the other nongeminal dimethyl-1,2-dimethylenecyclobutanes renders unlikely the hypothesis that reversible hydrogen shifts were responsible for the 1,2-dimethylenecyclobutane thermally induced self-interconversion,¹ since methyl groups are not known to transfer as efficiently as hydrogen.³ The data of Table II also confirm the fact that rotation about the central bond in the TME species occurs to give the single inversion⁴ Cope type products, **3** and **4**, in addition

(1) (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) see also W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967).

(2) (a) Only seven dimers were found in the reaction; all were *cisoid* conjugated dienes (uv λ 245–252 $m\mu$); nmr could easily distinguish between the sets (1, 2), (3, 4), and (5, 6, 7), and indeed between all of them; **6** is unique in the nmr; **2** was synthesized from the 2-butyne-maleic anhydride photoadduct^{2b} in a manner that would ensure a *cis*-dimethyl relationship; the inside vinyl hydrogens of **4**, **6**, and **7** were at δ 5.35–5.63 ppm while the outside hydrogens of **3**, **5**, and **6** were at δ 4.98–5.18 ppm; ultimate proof of the stereochemistry about the double bonds rests on the fact that **3** underwent a rapid 1,5-hydrogen shift^{2c} at 260° to give ultimately 3-methylene-4-methyl-*trans*-1,4-hexadiene (**8**),^{2d} while **4** did so much slower; **5** and **6** gave 2-ethyl-3-methylene-1,4-

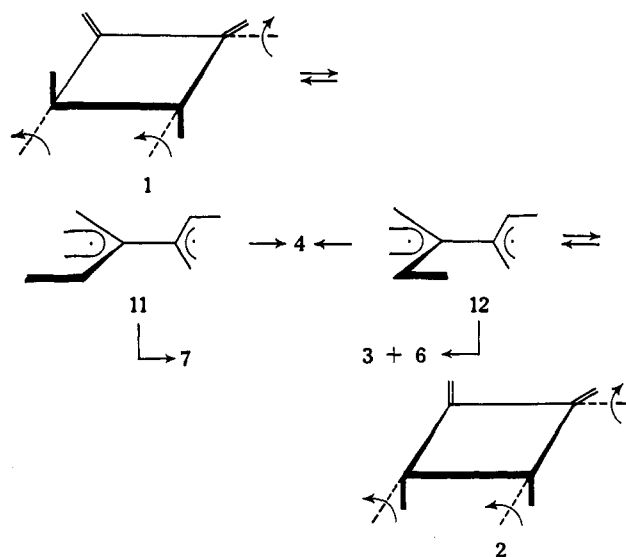
pentadiene (**9**), also *via* the hydrogen shift at 260°, while **7** was relatively inert.^{2f,g} (b) R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freud, *Chem. Ber.*, **97**, 2942 (1964). (c) J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962). (d) The *trans* stereochemistry was assigned in analogy to Frey's results with the thermal polymerization of 1,4-dimethylcyclobutene.^{2e} (e) H. M. Frey, D. C. Marshall, and R. F. Skinner, *Trans. Faraday Soc.*, **61**, 861 (1965). (f) See E. F. Kiefer and J. Y. Fukunaga, *Tetrahedron Lett.*, 933 (1969), and E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969), for analogous reactions. (g) The significance of these and similar results will be discussed in a forthcoming publication.

(3) See, for example, J. W. De Haan and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1594 (1965).

(4) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5019 (1964), and references contained therein.

tion to the double-inversion products, 5, 6, and 7. More striking, however, are the facts that (a) interconversion of 1 and 2 occurs relatively slowly in short-term thermolyses; (b) 1 gives almost exclusively 4 and 7; (c) 2 gives almost exclusively 3, 4, and 6 and the subsequent rearrangement product of 3, namely 8.

If the reasonable assumption that rotation about bonds occurs slowly relative to ring closure in the nearly, or completely, developed allylic radicals at the higher reaches of the energy surface for the rearrangement, then the relative ratios of the double-inversion products, 5, 6, and 7, indicate that conrotatory over disrotatory opening of the cyclobutane ring is favored by a factor of at least 100 from 1 and at least 10 from 2. 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_2TME species must be involved, and the one which must be produced from 1 is 11, and the one which is produced from 2 is 12 by the conrotatory motions indicated above.⁵⁻⁷



By virtue of the bidentate nature of the allyl radical, 11 can give 7, 4 (two ways), and 1 (by the microscopic reverse of its formation), and 12 can give 6, 3, 4, and 2. 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 3 is found in the *trans*-1 thermolysis.^{8,9} It is interesting that 12 must give 5 to 6

(5) (a) It is possible that the double inversion product results from initial closure to a $\Delta^{1,4}$ -bicyclo[2.2.0]hexene which reopens in the opposite direction. The single inversion product then must result from 1,3-sigmatropic rearrangements^{5b} proceeding *via* species which would not have D_{2d} symmetry as would the TME species envisioned here, *sans* methyl groups. It is difficult to imagine such species, however, since they would differ from the D_{2d} species by only a stretching vibrational motion. (b) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

(6) A third Me_2TME species can be formed by conrotatory opening of 1, namely one in which the two methyl groups are directed to the interior of the system. However, 3 and 5 are the expected products from this species, and these are formed only to a limited extent, if at all, from 1.

(7) (a) SCF π -electron calculations with extensive configuration interaction^{7b} suggest that the orthogonal and planar TME species are nearly equivalent in energy; thus, steric interactions may control the relative energies, and EHT calculations suggest that the D_{2d} geometry is favored over the D_{2h} geometry by 4 kcal/mol.^{7b} (b) R. Hoffman, private communication.

(8) If 11 is solely responsible for product from 1, there are two possible rotations about the C-1-C-2 bond with respect to the other bond

times as much 3 as 4 if it is the sole intermediate in the thermolysis of 2.

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rotations. At the point of intersection of the rotation axes in the above figure, the relative rotations are as meshed bevel gears. However, an "antibevel" pathway is also possible which gives exactly the same stereochemical results.

(9) Disrotatory ring opening to form 3 and 4 cannot be ruled out by these experiments, as has been implied above and stated by a referee; however, conrotatory ring opening is sufficient to explain all the observations with a minimum number of assumptions and apparent contradictions.

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Low-Temperature Hydrogenation over Borohydride-Reduced Catalysts. A New Convenient Procedure for Improving the Selectivity of Reduction

Sir:

In the course of a systematic study of the uses of the new borohydride-reduced metal catalysts,¹ we found that the observed rates of hydrogenation of a representative olefin, 1-octene, were remarkably insensitive to temperature decreases.² This unexpected insensitivity of the reaction (run under preparatively useful conditions) suggested a convenient technique for affecting the course of hydrogenations merely by lowering the temperature. This communication reports that such reductions at low temperature are eminently feasible and, in fact, examples chosen at random show considerable improvements in the selectivity of hydrogenation.

The feasibility of the technique was demonstrated with the hydrogenation of a series of increasingly substituted ethylenes over $\text{Pt}(\text{BH}_4^-)\text{-C}^3$ at 25, 0, and -25° , using a low (0.005:1) metal:olefin ratio. The times for total hydrogenation increased appreciably from 1-hexene, to 2-methyl-1-pentene, to 2-methyl-2-pentene, to 2,3-dimethyl-2-butene. However, even the tetra-substituted olefin was completely reduced in 4 hr at -25° with the low amount of catalyst. It is clear that, if desired, reaction times could be considerably shortened

Table I. Effect of Temperature upon Hydrogenation of Four Representative Olefins^a

Substrate	25°	0° $T_{100\%}$, min ^b	-25°
1-Hexene	10	14	24
2-Methyl-1-pentene	10.5	13.5	46
2-Methyl-2-pentene	12	29	152
2,3-Dimethyl-2-butene	14	52	240

^a Hydrogenation of 40.0 mmoles of distilled substrate over 0.20 mmole of Pt on 1.0 g of Darco G-60 carbon at 1 atm. ^b Time for complete reduction. The time for 50% reduction was 40-50% of this. Temperatures were held to $\pm 1^\circ$ except $-25^\circ (\pm 3^\circ)$.

(1) H. C. Brown and C. A. Brown, *Tetrahedron, Suppl.* 8, Part I, 149 (1966).

(2) C. A. Brown, unpublished observations.

(3) The borohydride-reduced carbon-supported catalyst,