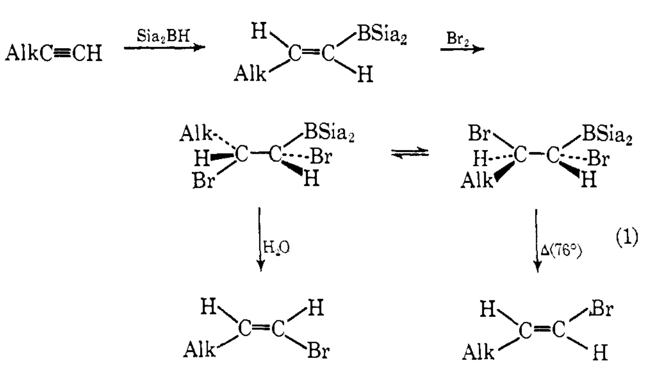
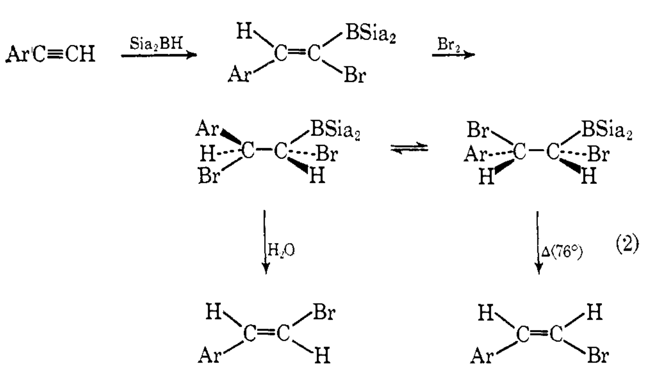


geometrical isomers formed with the 1-alkynes. This observation was checked repeatedly.

We have not attempted to investigate the precise cause of this inversion in the structure of the geometrical isomers produced. However, it is possible that addition of bromine to phenyl-substituted vinylborane results in a *cis* addition, rather than the usual *trans* (2).



Such a change has been observed previously in additions of chlorine, where the electron-deficient intermediate involves a benzylic center.[5]

The experimental results are summarized in Table I.

Table I. Vinyl Bromides from Acetylenes *via* Hydroboration

		Solvolysis		Thermal decompn	
Acetylene	Product	Yield, %[a]	*cis*: *trans*[a]	Yield, %[a]	*cis*: *trans*[a]
1-Pentyne	1-Bromo-1-pentene	65	97:3	40	0:100
1-Hexyne	1-Bromo-1-hexene	67	95:5	75	12:88
1-Heptyne	1-Bromo-1-heptene	76	97:3	60	12:88
1-Octyne	1-Bromo-1-octene	68	98:2	50	6:94
Phenylacetylene	β-Bromostyrene	88	4:96	78	82:18

[a] Yield and isomer distribution by glpc analysis.

The experimental procedure follows. A 100-ml, three-necked flask fitted with a reflux condenser, a thermometer, a rubber septum, and a pressure-equalized addition funnel was flushed with nitrogen. Fifty mmoles of disiamylborane, in tetrahydrofuran, was prepared as previously described,[2] and the solvent was then removed under vacuum. Carbon tetrachloride, 30 ml, was added to dissolve the reactant, and 50 mmoles of the acetylene was added at a rate such that the temperature did not rise above 5°. Then a solution of 52.5 mmoles of bromine in 30 ml of carbon tetrachloride was added, maintaining the temperature at 0–5°. The product underwent hydrolysis practically instantaneously upon the addition of 2 *M* sodium hydroxide. The carbon tetrachloride solution was separated, dried, and analyzed by glpc, using a tricresyl phosphate column, with comparisons using authentic samples. In the thermal decomposition procedure, the carbon tetrachloride solution of the dibromide was refluxed for 6 hr under nitrogen.

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(5) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956); R. E. Buckles and D. F. Knaak, *J. Org. Chem.*, **25**, 20 (1960).

(6) Research assistant, 1961–1963, on a project supported by the Ethyl Corporation at Purdue University.

(7) Postdoctorate research associates, 1963–1964, on Grant GM 10937 from the National Institutes of Health.

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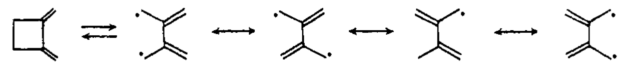
Tetramethyleneethane. The Degenerate Thermal Rearrangement of 1,2-Dimethylenecyclobutane

Sir:

Our interest in the pyrolyses of unsaturated hydrocarbons which may proceed *via* orbitally degenerate diradical intermediates led to the suspicion that the intermediate postulated in the allene dimerization,[1] namely, the tetramethyleneethane diradical[2] (**2**), could be responsible for a thermal self-interconversion of 1,2-dimethylenecyclobutane (**1**).



1 2

To test this hypothesis, 1,2-bis(dideuteriomethylene)-cyclobutane (**3a**) was prepared from predominantly *trans*-1,2-dicyanocyclobutane by a standard synthetic sequence[3] with the deuterium atoms being incorporated at the stage of reduction of the corresponding bis-(N,N-dimethylamide). Pure **3a** (99+% by capillary vpc) was obtained in moderate yield upon vacuum pyrolysis of the bis(dimethylamine oxide) and passage of the pyrolysate through a calcium chloride trap; nmr of **3a**: singlet at δ 2.58 (the two two-proton resonance singlets at δ 4.61 and 5.05 present in the perprotio derivative **1** were absent in **3a**), mass of **3a**: 84.0873 (calcd for $C_6D_4H_4$, 84.0877).

Pyrolysis of **3a** in the gas phase (15 μl in a 100-ml carefully neutralized tube sealed at −78° under nitrogen at 120 mm) for 2 hr at 275° gave tetradeuterio-1,2-dimethylenecyclobutane in 35% recovery (relative to benzene internal standard); no other materials of near-comparable volatility were observed. The remainder of the product consisted of less volatile compounds, as indicated by their much-delayed emergence from gas

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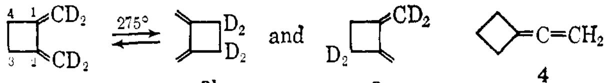
(1) For a brief review see J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

(2) (a) Hückel molecular orbital theory[2b] predicts orbital energies for this diradical of 2.0β, 1.0β, 0.0β, 0.0β, −1.0β, and −2.0β and a total π energy of $6\alpha + 6\beta$. Its delocalization energy relative to two double bond and two radical fragments is 2β; relative to two allylic radicals the DE is 0.35β. (b) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1, Pergamon Press, New York, N. Y., 1965, p 7.

(3) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **82**, 3619 (1960).

chromatographic columns relative to starting diene. These less volatile materials appeared to result from dimerization[4] since their rate of formation decreased with decreasing starting pressures of 1,2-dimethylenecyclobutane. The pmr spectrum of the pyrolysis product indicated that 26–31% (range from a number of runs) of the total *protium* was present on the exocyclic methylene groups of the recovered tetradeuterio-1,2-dimethylenecyclobutane.



3a **3b** **3c** **4**

To prove that the isomerization was not due to a cleavage reaction to form allene followed by redimerization, a 50:50 mole % mixture of the tetradeuterio material **3a** and perprotio compound **1** was pyrolyzed as above, and the mass spectrum of the volatile product 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, the rate of the observed isomerization was not dependent on the pressure of **3a** over a threefold range of pressures (at 20 mm of **3a** 75% **3** was recovered and 26% isomerization took place upon heating **3a** at 275° for 2 hr); thus the isomerization could not be a result of an allene dimerization or of a rapid, reversible cleavage of any dimeric (C_{12}) products.

If rapidly reversible, 1,3 hydrogen shifts of the necessarily suprafacial, symmetry-forbidden variety[5] (proceeding *via* 2-methyl-3-methylenecyclobutene) are excluded from consideration, the most economical explanation for the apparent deuterium shift in the pyrolysis of **3a** involves carbon–carbon bond fission followed by electron reorganization. Cleavage of the C-1–C-2 doubly vinylic bond in **3a** would be unexpected upon consideration of energetics; furthermore, no simple, precedented sequence of electron shifts after fission of this bond appears to account for the observations. Homolysis of the C-1–C-4 or the C-2–C-3 singly allylic bonds in **3a** could conceivably occur under the reaction conditions, and reversible formation of a resulting allylic rearrangement product, allenylcyclobutane (**4**-d_4), could be responsible for the deuterium scramble; however, the fact that a sample of **4** prepared independently[6] gave at most 3% 1,2-dimethylenecyclobutane relative to recovered **4** under the pyrolysis conditions tends to rule out this possibility. The only alternative left involves fission of the C-3–C-4 doubly allylic bond with consequent (or subsequent) formation of the tetramethyleneethane diradical (**2**-d_4) which, if rotation about the central bond is rapid, may close *via* four different paths to give the three different tetradeuterio isomers, **3a–c**. If rotation about the central bond in **2**-d_4 is slower than ring closure, then only two deuterium isomers, **3a** and **3b**, would be formed from **3a**, at least initially.[6f]

Considerations of allylic resonance energy and strain energy indicate[7] that cleavage of the doubly allylic bond in **1** (or **3**) should proceed with an activation free energy less than 35 kcal; moreover, if HMO calculations[2] on the diradical species **2** are valid, then the activation free energy for the ring opening should approach 30 kcal; yet, the experimental activation free energy for the isomerization is about 43.5 kcal. While it is possible that the rate of isomerization may be slower than that of ring opening, it would appear that the transition state for ring opening should resemble the diradical **2**, which is the most likely intermediate in the isomerization. If the rate of isomerization truly reflects the difficulty in opening the doubly allylic bond in **1**, then the stability of the resultant intermediate or transition state, presumably **2**, must be less than anticipated, or else the ground state of 1,2-dimethylenecyclobutane is more stable than expected. The latter explanation is at least partially valid in that the butadiene-type π-electron system in **1** may enjoy some resonance stabilization which must be lost to a certain extent in the ring opening; however, it is unlikely[8] that this stabilization approaches the ~10-kcal discrepancy noted above. The observations can be rationalized on the basis that isomerization must proceed *via* the singlet state of the diradical (in order to converve spin angular momentum[9]) and that the actual resonance energy of **2** with this electron multiplicity is substantially less than that calculated by simple HMO theory due to a large singlet–triplet splitting. This suggestion warrants experimental and theoretical verification.

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(4) For examples of similar reactions see (a) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 751 (1958); **81**, 2723 (1965); (b) K. Alder and O. Ackermann, *Ber.*, **87**, 1567 (1954).

(5) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(6) (a) This compound was prepared from 1,1-dibromospiro[2.3]-hexane[6b] by treatment[6c-e] with excess butyllithium in pentane at − 10° followed by vpc purification; infrared of **4**: 3050, 1960, 1040, 850 cm^{-1}; nmr of **4**: quintet, J = 7.5 Hz, at δ 1.90 (2 H); multiplet at δ 2.8 (4 H); quintet, J = 5 Hz, at δ 4.58 (2 H); (b) J. A. Landgrebe and D. E. Applequist, *J. Am. Chem. Soc.*, **86**, 1536 (1964); (c) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958); (d) L. Skattebol, *Tetrahedron Letters*, 167 (1961); (e) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

(6f) NOTE ADDED IN PROOF. Isomerized tetradeuterio material, **3**, having 30 ± 3% protium on the exocyclic methylenes gave, after reaction with dimethyl acetylenedicarboxylate followed by a dichlorodicyanobenzoquinone-induced dehydrogenation, 3,4-dicarbomethoxybicyclo[4.2.0]octa-1.3.5-triene with the following deuterium distribution: 58.0% d_2, 27.7% d_3, and 14.3% d_4. In addition to the internal consistency of the result, it was found that **3a** gave, *via* the same reaction sequence, the benzocyclobutene having no protium on the aromatic ring. Thus, **2**-d_4 is effectively or in fact two mutually orthogonal allylic fragments.

(7) (a) For example, *trans*-1,2-divinylcyclobutane undergoes isomerization with a free energy of activation of 34 kcal.[7b] Methylenecyclobutane undergoes a degenerate rearrangement *via* allylic bond cleavage with an activation free energy of 49 kcal,[7b] and substitution of one more double bond should stabilize the resulting diradical by at least 13 kcal[7d] even neglecting the extra ring strain in this case. (b) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964). (c) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **7**, 397 (1966). (d) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964).

(8) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692 (1965).

(9) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 256.

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