The Cyclotrimerization of 2-Butyne-1,1,1-d₃ by Triphenyltris(tetrahydrofuran)-chromium(III)

The Cyclotrimerization of 2-Butyne-1,1,1- d_3 by Triphenyltris(tetrahydrofuran)chromium(III)1

Sir:

The cyclotrimerization of substituted acetylenes to benzene derivatives using organometallic catalysts is a transformation of considerable synthetic usefulness. 2.3 A controversial area in mechanistic discussions of this reaction centers around the importance of metal-cyclobutadiene complexes as reaction intermediates. The observation that various isolable transition metal complexes of cyclobutadienes react with acetylenes only in the presence of oxidizing agents or donor ligands has been interpreted as evidence against cyclobutadiene intermediates.2,4 However, the reactivity of these stable compounds does not bear directly on that of less stable and presumably more reactive complexes which might be formed under the cyclotrimerization conditions. Labeling and product studies have provided on support for cyclobutadiene intermediates in these reactions, but these experiments are amenable to a number of interpretations.6 We wish to report the results of deuterium-labeling experiments which provide clear evidence excluding a chromium-tetramethylcyclobutadiene intermediate in the cyclization of 2-butyne-1,1,1- d_3 (1) to hexamethylbenzene- d_9 by triphenyltris(tetrahydrofuran)chromium(III).3

If the mechanism of this cyclotrimerization involves dimerization of 1 to a tetramethylcyclobutadienechromium complex, the initial stages in the cyclization must produce head-to-head and head-to-tail configurations of the labeled cyclobutadienes 2 with equal probability.7 Further, ample experimental precedent supports the assumption that a cyclobutadiene moiety complexed with a transition metal will adopt a square geometry in which the carbon-carbon bonds of the ring are chemically equivalent.3 In consequence, reaction of a tetramethylcyclobutadiene-containing inter-

mediate with another molecule of 1, either directly or following dissociation of the cyclobutadiene from the metal, will lead to a statistically determined distribution of the labeled hexamethylbenzenes 4, 5, and 6 (relative yields 1:5:2). In contrast, cyclotrimerization proceeding in a concerted manner through an intermediate

in which three molecules of 1 are simultaneously coordinated with the metal (represented schematically by 3), or through a metal heterocycle of the type proposed by Blomquist and Collman, should lead only to 5 and 6 in 3:1 relative yield.

We have distinguished experimentally between these two alternative paths by determining the yield of 4 produced in the cyclization, relative to the combined yields of 5 and 6. Compound 4 is unique among the labeled

(5) J. C. Sauer and T. L. Cairns, ibid., 79, 2659 (1957); G. N. Schrauzer, Angew. Chem. Intern. Ed. Engl., 3, 185 (1964).

(6) For example, T. I. Bieber, Chem. Ind. (London), 1126 (1957). See also E. M. Arnett and J. M. Bollinger, J. Am. Chem. Soc., 86, 4729

(7) We assume that any kinetic isotope effects in the formation and subsequent degradation (eq 1) of the hexamethylbenzenes can be ne-

(8) R. P. Dodge and V. Schomaker, Acta Cryst., 18, 614 (1965); J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, Helv. Chim. Acta, 45, 647 (1962); C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, J. Am. Chem. Soc., 89, 2833 (1967). (9) J. P. Collman and J. W. Kang, ibid., 89, 844 (1967).

⁽¹⁾ Supported in part by the U.S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

⁽²⁾ P. M. Maitlis, Advan. Organometal. Chem., 4, 95 (1966). (3) H. Zeiss in "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, p 380.

⁽⁴⁾ A. T. Blomquist and P. M. Maitlis, J. Am. Chem. Soc., 84, 2329 (1962); L. Watts, J. D. Fitzpatrick, and R. Pettit, ibid., 87, 3253 (1965); 88, 623 (1966).

hexamethylbenzenes in having three *adjacent* labeled methyl groups. Degradation of a mixture of **4**, **5**, and **6** to corresponding isotopically substituted 3-methyl-2,4-pentanediones (7) by reduction with sodium in hexamethylphosphoramide-t-butyl alcohol, followed by ozonolysis, isolates sets of three adjacent methyl groups in separate molecules (eq 1). This degradation does not scramble or exchange methyl groups; hence, mass spectral determination of the proportion of 7 having three labeled methyl groups, followed by appropriate statisti-

$$d_{9} \xrightarrow{\text{Na-HMPA}} H$$

$$d_{9} \xrightarrow{\text{1.0}_{0}} H$$

$$(1)$$

cal corrections to account for the distribution of labeled methyl groups expected on reduction of each of the hexamethylbenzenes, provides a method of determining the relative yield of 4.

The observed isotopic composition of 7 obtained by degradation of the hexamethylbenzenes from cyclization of 1 with triphenyltris(tetrahydrofuran)chromium(III)³ is given in Table I, together with the isotopic distribution

Table I. Calculated and Observed Isotopic Compositions (%)

	7, (CH ₃) ₃	7, (CH ₃) ₂ - (CD ₃)	7, (CH ₃)- (CD ₃) ₂	7, (CD ₃);
Calcd: concerted Calcd: cyclobutadiene Obsd: (C ₆ H ₂) ₂ Cr(III)	0.0	48.9	50.5	0.5
	4.0	44.9	46.4	4.6
3THF	0.0	47.4	52.0	0.6
Obsd:* AlCla	3.7	43.7	48.1	4.5

^a The starting 2-butyne had isotopic composition corresponding to $98.9^{\circ,\circ}_{0}$ CD₃CH₃ and $1.1^{\circ,\circ}_{0}$ (CD₃)₂. The experimental compositions include contributions to the spectra from the approximately $1.1^{\circ,\circ}_{0}$ isotopic impurity (CHD₂) in the CD₄ groups. ^b Experimental error in these values is estimated to be $\pm 0.2^{\circ,\circ}_{0}$.

calculated assuming that the reaction proceeds through a tetramethylcyclobutadiene intermediate and that calculated assuming a concerted cyclotrimerization (or some geometrically equivalent path). ¹⁰ Experimental results obtained by a parallel degradation of the hexamethylbenzene from cyclotrimerization of 1 using aluminum chloride in benzene are also included in this table. ¹¹ Comparison of the observed and calculated values shows that no 7, (CD₃)₃ was formed in the chro-

mium-catalyzed reaction beyond that attributable to the isotopic composition of the starting 2-butyne and consequently indicates that within our experimental error no 4 was formed in this cyclization. The close agreement between the isotopic composition observed for the aluminum chloride catalyzed reaction and that calculated on the basis of a cyclobutadiene intermediate provides assurance that the degradation yields reliable results. Taken together, these results exclude a cyclobutadiene intermediate in the cyclotrimerization of 2-butyne over triphenylchromium(III).

We have used a similar approach to demonstrate that a tetramethylcyclobutadiene-chromium complex is not an intermediate in the production of 1,2,3,4-tetramethylnaphthalene (8) in the chromium-catalyzed cyclization of 2-butyne. In particular, isolation of sets of two adjacent methyl groups from 8, using the degradation outlined in eq 2, and mass spectral determination of the isotopic composition of 9 have established that no 1,2-dimethyl-3,4-di(methyl- d_3)naphthalene (10) is formed

in the reaction of triphenyltris(tetrahydrofuran)chromium(III) with 1. 10,14

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(12) The aluminum chloride catalyzed cyclizations were carried out at 100°. Since hexamethyl(Dewar benzene) can be isolated from this reaction under milder conditions, this result is expected. Whether tetramethylcyclobutadiene is actually an intermediate in this reaction is presently a moot question since, e.g., a cyclobutenyl cation of type i offers an equally satisfactory rationalization of our labeling results. However, the mass spectral data do indicate that no appreciable scrambling of deuterium between labeled and unlabeled methyl groups takes

place during this cyclization. Hence cation it is not an intermediate.

- (13) H. Hart and R. K. Murray, J. Org. Chem., 32, 2448 (1967).
- (14) This degradation was checked using an authentic sample of 10. (15) National Science Foundation Trainee. 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1968.

George M. Whitesides, William J. Ehmann¹⁵

Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts Received November 14, 1967

⁽¹⁰⁾ Mass spectra were obtained using a nominal ionizing voltage of 8.3 eV: K. Biemann, "Mass Spectrometry—Organic Chemical Applications," McGraw-Hill Book Co. Inc., New York, N. Y., 1962, p 223 ff.

⁽¹¹⁾ W. Schäfer and H. Hellmann, Angew. Chem. Intern. Ed. Engl., 6, 518 (1967).