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Mechanism of the Isomerization of 1,5,9-Cyclododecatriyne to Hexaradialene: 1,2:3,4:5,6-Tricyclobutabenzene Is Not an Intermediate

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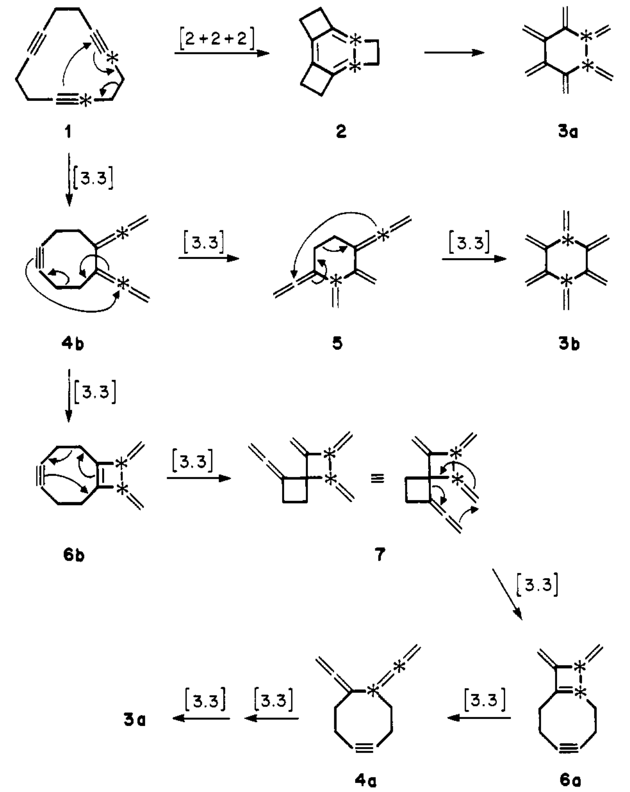
Ever since our discovery of the remarkable rearrangement of 1,5,9-cyclododecatriyne (**1**) to hexaradialene **3**,[1,2] we have puzzled over its mechanistic details. The conceptually simplest pathway (albeit unprecedented) seemed to be a [2 + 2 + 2] cycloaddition of the three alkyne units to give the postulated intermediate tricyclobutabenzene (**2**),[3] which would undergo sequential four-ring opening to product, estimated to be thermodynamically favorable.[4] However, several findings appeared at odds with this explanation: (a) independently synthesized **2**[3] and a dodecafluoro derivative[5] are quite thermally stable; (b) a theoretical study[6] has calculated a very high barrier for the cyclotrimerization of ethyne to benzene; (c) we have recently found[7] that the open-chain analogue of **1**, 1,5,9-decatriyne, converts to the linear 1,2:4,5-dicyclobutabenzene through a series of [3.3] shifts involving the 1,5-diyne moieties, instead of forming the angular isomer predicted by the direct cycloaddition mechanism. This suggested to us that an alternative connection between **1** and **3** deserved more serious attention, namely, a sequence of rearrangements,[8] proceeding through **4** and **5** to **3** (Scheme I).[9]

A labeling experiment (stars in Scheme I) was designed in order to distinguish between these pathways. It involved the projected synthesis of [1,10-$^{13}C_2$]cyclododecatriyne **1** and its pyrolysis. Inspection of the fate of the label according to the two mechanistic options allows for the following predictions: cyclization by the [2 + 2 + 2] mode should place the labeled carbons in adjacent positions as in **3a**; the sigmatropic shift sequence, however, would let the ^{13}C label emerge as in **3b**. A potential complication could be reversible[10] closure of **4b** to **6b**, followed by a degenerate label scrambling manifold[9] involving **7**.

Scheme I



Labeled **1** was synthesized and degraded as depicted in Scheme II via [1,4-$^{13}C_2$]diethyl succinate[13] and [1,4-$^{13}C_2$]-1,4-bis(triphenylphosphonio)butane dibromide.[14] Bis-Wittig reaction[15] with *cis*-oct-4-enedial[16] gave [1,10-$^{13}C_2$]-1,5,9-cyclododecatriene as a 7:3 mixture of *cis,trans,trans* and *cis,cis,trans* isomers, converted as shown to [$^{13}C_2$]-**1**.[17] Reduced-pressure N_2-flow pyrolysis[1] onto Br_2–CH_2Cl_2 at −196 °C, followed by hydrogenolysis of thus formed labeled hexakis(bromomethyl)benzene[18] gave [$^{13}C_2$]-hexamethylbenzene, which was ozonized[19] to 2,3-butanedione. Small but sufficient quantities of product are generated from 15 mg of [$^{13}C_2$]-**1** to alow for unambiguous mass spectral analysis. The possibility that a source other than hexamethylbenzene gave rise to the final 2,3-butanedione was eliminated by a second experiment. Unlabeled **1** was converted to hexamethylbenzene as above, and its quantity in the mixture determined by GC. Two-thirds of this amount of perdeuteriohexamethylbenzene was added, and the mixture was ozonized and subjected to analysis. The ratio of undeuterated to deuterated dione was the expected 3:2.

A simple statistical appreciation of the label distribution arising from the three mechanisms outlined in Scheme I predicts the following ratios of double to single to unlabeled butanedione: 1:2:3

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(9) This sequence appears thermodynamically perfectly accessible:[4] ΔH_f (kcal mol^{-1}) **1**, 137; **4**, 156;[11] **5**, 110; **6**, 124;[11] **7**, 147.[12]

(10) The dimethylenecyclobutene ring closure is very likely reversible: T. J. Henry and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 5103 (1972).

(11) Ring strain in cycloocta-1-en-5-yne is ~18 kcal mol^{-1}: W. Leupin and J. Wirz, *Helv. Chim. Acta*, **61**, 1663 (1978); H. Meier, H. Petersen, and H. Kolshorn, *Chem. Ber.*, **113**, 2398 (1980).

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(17) Mass spectral analysis of this compound in comparison with unlabeled **1** confirmed 90% ^{13}C label incorporation.

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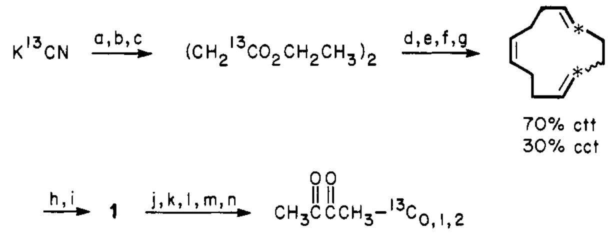
Scheme II



[a] $BrCH_2CH_2Br$, KI, CH_3CH_2OH, Δ. [b] H_2SO_4, Δ. [c] C_6H_6 ($-H_2O$), CH_3CH_2OH, Δ (50% overall). [d] $LiAlH_4$, THF (85%). [e] 40% HBr, H_2SO_4 (80%). [f] $(C_6H_5)_3P$ (82%). [g] *n*-BuLi, THF, *cis*-oct-4-enedial (35%). [h] Br_2, CH_2Cl_2, CH_3COOH (73%). [i] $NaOCH_2CH_2OH$, $HOCH_2CH_2OH$, THF, Δ (15%). [j] 500 °C, 45 torr of N_2, 10 mL/min flow. [k] Br_2, CH_2Cl_2. [l] H_2, Pd/C. [m] O_3, CH_3COCH_3. [n] $(CH_3)_2S$.

Table I. Calculated and Experimental[a] Relative Peak Intensities (in %) for the M^+ Peak of Butanedione according to Various Mechanisms

m/e	observed for unlabeled butanedione	[2 + 2 + 2]	[3.3]	predicted for spiro-[3.3]	random	obsd
86	96	51.5	39	47.2	44	41.5
87	4.0	34	59	42.4	49	58.5
88	0.0	14.5	2	10.3	7	<1.5

[a] Data averaged from four runs, standard deviation less than 1.5. The sum of the mass spectral line intensities *m/e* 87 and 86 was always greater than 30 000 counts.

if **2** is an intermediate ("[2 + 2 + 2]"), 0:2:1 if the rearrangement involves **4b** and **5** (but not **7**) ("[3.3]"), and 2:6:7 if **7** is readily accessible ("spiro[3.3]").[20] Should there somehow be scrambling of the label over all the ring carbons ("random"), that ratio would be 1:10:7.

Inspection of the parent peak envelope at *m/e* 86–88 for unlabeled butanedione[21] allows one to predict the peak ratios expected for the above options by taking into account 90% ^{13}C label incorporation and the presence of natural abundance label in the unenriched positions (Table I). Perhaps most obvious is the necessity for the formation of doubly labeled degradation product from any mechanism other than that proceeding directly through [3.3] shifts (e.g., **1** → **4b** → **5** → **3b**).

The observed ratios in Table I are clearly incompatible with the generation of **3a**, and hence **2** and/or **7**, but show admirable coincidence with the values calculated for the direct sigmatropic shift sequence. These results constitute a truly surprising experimental manifestation of the theoretical prediction that thermal [2 + 2 + 2] alkyne cycloadditions are prohibitively costly in kinetic terms. Since now disproven for **1**, the feasibility of a concerted thermal ethyne to benzene conversion remains to be demonstrated.

Acknowledgment. This work was supported by NIH-CA 20713. K.P.C.V. is a Camille and Henry Dreyfus Teacher–Scholar (1978–1983). We thank Professor E. L. Muetterties for a sample of perdeuteriohexamethylbenzene and Professor M. A. Darensbourg for details of its preparation.

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(20) With assumption of complete reversibility of **4** and **1**. Note that the scheme indicates only one of the several possible modes of undergoing [3.3] shifts, all of which have to be considered. Complete equilibration of **1** via **7** (and its isotopomers) furnishes an equimolar mixture of [1,2-$^{13}C_2$]- [1,6-$^{13}C_2$]-, and [1,10-$^{13}C_2$]-**1**, which in turn results in a 2:1 ratio of **3a**:**3b** and therefore the quoted ratio for the dione.

(21) These data were obtained under standardized conditions by GC mass spectrometry on a Finnigan 4000 instrument equipped with an Incos data system. Glass silica capillary columns coated with SE-54 served to separate product from solvent and impurities.

2-Bromo-3-(trimethylsilyl)propene. An Annulating Agent for Five-Membered Carbo- and Heterocycles

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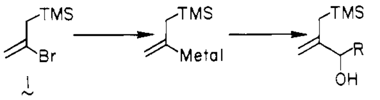
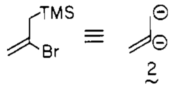
In conjunction with our program on the use of bifunctional conjunctive reagents for substrates for transition metals, we reported the synthesis of 2-bromo-3-(trimethylsilyl)propene (**1**) and


(1)

its addition to carbonyl groups according to eq 1, in order to generate precursors for substituted trimethylenemethanepalladium complexes.[1-4] By combination of the ability to effect transmetalation of the vinyl bromide with the nucleophilic properties of the allylsilane, this readily available reagent can become a synthon for the dianion **2**. In this communication we report the



realization of this proposal as a route to five-membered carbo- and heterocycles.

Lewis acid catalyzed addition of **1** to carbonyl groups[5] showed a sensitivity to the nature of the carbonyl partner. As Table I reveals, aldehydes react well even at concentrations of 0.1 M. Aliphatic ketones fail to react at all at such dilutions. Increasing the concentration to 1 M permits obtention of the desired adducts in excellent yields. Aromatic ketones fail to react at any concentration, although their corresponding ketals form the expected addition products. In each case where stereoisomers are possible, only one results. Most noteworthy is the case of the aldehyde **1** (entry 8), which provides only one isomer in this reaction in contrast to the addition of allylmagnesium bromide, which gives a 1:1 stereoisomeric mixture. In the case of entry 6, the stereochemical assignment was verified by reductive debromination and comparison to an authentic sample. For entries 7 and 8, the stereochemistry is based upon analogy in related systems and must be considered tentative at present.[6,7]

The second anion equivalent from the vinyl bromide was envisioned to involve metalation with a nickel complex in order to achieve carbonylation and thus an α-methylene-γ-butyrolactone synthesis.[8] Indeed, treatment with 1.5 equiv of $(Ph_3P)_2Ni(CO)_2$ in refluxing THF in the presence of 2 equiv of $(C_2H_5)_3N$ gave the α-methylene-γ-butyrolactones in high yields. The exclusive formation of a single stereoisomer from 4-*tert*-butylcyclohexanone is in contrast to other methods.[9] The example in entry 8 is most intriguing in terms of the synthesis of polyether ionophores.

Reversing the unmasking of the two pronucleophilic centers permits a methylenecyclopentane annulation. Copper-catalyzed

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(2) In addition to the copper coupling of (trimethylsilyl)copper with 2,3-dibromopropene, **1** also arises from reaction of this dibromide with trichlorosilane [$(C_2H_5)_3N$, CuCl] followed by methylmagnesium bromide; cf. ref 3.

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