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THERMAL CONVERSION OF 1,5,9-TRIYNES

[2+2+2]CYCLOADDITIONS OR [3.3]SIGMATROPIC SHIFTS?

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Abstract—The gas phase pyrolyses of variously labeled 1,5,9-decatriynes (**1**) and 1,5,9-cyclododecatriynes (**2**) were investigated to determine possible modes of thermal isomerizations. Conditions included temperatures in the range 400–600°, pressures of 40–10^{-4} Torr, and contact times of *ca* 1 ms to 15 s. The labeling patterns in **1** and **2** were chosen such as to be able to distinguish direct intramolecular [2+2+2]cycloadditions of the alkyne units to form an aromatic ring (perhaps with subsequent rearrangements), and [3.3]sigmatropic shifts of the 1,5-diyne moieties. Methods for synthesizing the isotopically (particularly ^{13}C) labeled triynes were devised and implemented. The route to 5,6-$^{13}C_2$-1,5,9-decatriyne (**1c**) made use of a new procedure for the synthesis of symmetrically disubstituted alkynes involving coupling between two equivalents of an alkyl copper reagent and diiodoacetylene-$^{13}C_2$. The synthesis of 1,10-$^{13}C_2$-1,5,9-cyclododecatriyne (**2b**) was accomplished starting with K^{13}CN, elaboration to labeled diethyl succinate, a crucial bis-Wittig condensation to labeled 1,5,9-cyclododecatriene **10**, and bromination–dehydrobromination of the latter (NaOH–ethylene glycol). Products from the pyrolysis of unlabeled **1a** included [1,2:4,5]dicyclobutabenzene, naphthalene, and 3,4-dimethylidene-1-(but-3-ynyl)cyclobutene. Pyrolysis of **1b** gave 3,6-dideuterio[1,2:4,5]dicyclobutabenzene and partially deuterated naphthalene, that of **1c** produced 1,2-$^{13}C_2$-[1,2:4,5]dicyclobutabenzene and 9,10-$^{13}C_2$-naphthalene. While the pyrolysis of **2a** resulted in hexamethylidenecyclohexane (hexaradialene), **2b** furnished 1,4-$^{13}C_2$-hexaradialene. The results rule out the occurrence of [2+2+2]cycloadditions of the alkyne units, but are consistent with the intervention of a series of [3.3]sigmatropic shifts which connect starting materials with products.

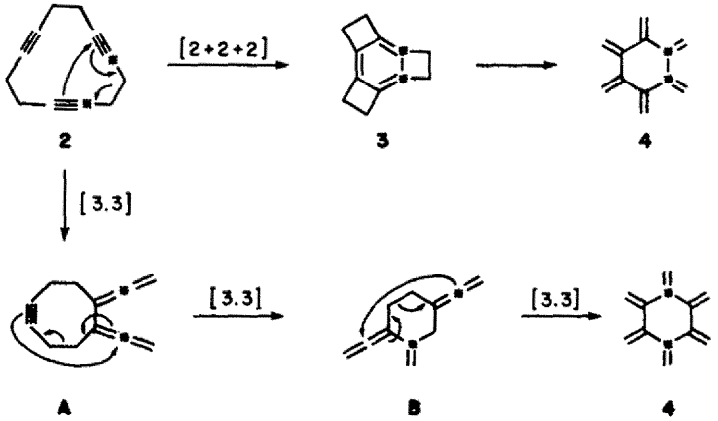
As early as 1866, Berthelot reported that acetylene, when heated to 600°, converted to a variety of products, including small amounts of benzene.[1] Considering the high exothermicity of this reaction (−143 kcal mol^{-1}),[2] the low yield and poor selectivity are quite surprising! Although symmetry-allowed and seemingly endowed with an aromatic transition state, recent calculations have predicted a substantial barrier to the thermal [2+2+2]cycloaddition of three alkynes to an aromatic nucleus.[3] The present work investigates the thermal rearrangements of two triynes chosen as potential models for points on the potential energy manifold of such a transformation and as substrates on which to obtain an estimate of its activation energy: 1,5,9-decatriyne (**1**)[4] and 1,5,9-cyclododecatriyne (**2**).[5]

This study was also of interest in connection with our observation that **2** on flash vacuum pyrolysis[6] converted to the theoretically interesting hexaradialene **4**.[5b,7] We postulated the 1,2:3,4:5,6-tricyclobutabenzene (**3**)[8] as an attractive intermediate but could not rule out a series of sigmatropic shifts

2a (no label)
2b (1,10-$^{13}C_2$)

1a (no label)
1b (1,10-D_2)
1c (5,6-$^{13}C_2$)

ΔHf (kcal mol^{-1}):[2] **1a**, 145.1.



Scheme 1. ΔHf (kcal mol^{-1}):[5b,14] **2**, 137; **3**, 93–114; **4**, 80; **A**, 152.8; **B**, 110.

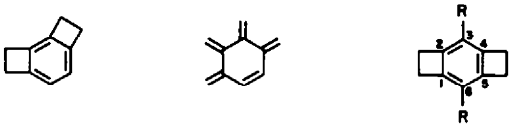
connecting starting material with product (Scheme 1). The ring opening of 3 to 4 is energetically favorable, the loss of ring strain overriding the loss of aromaticity[5b] and therefore the intervention of 3 seemed plausible. On the other hand, independently synthesized 3[8] and a perfluoro derivative[9] were shown to be thermally quite stable, and this, in conjunction with the theoretical work,[3] suggested the consideration of other alternatives, such as that shown in Scheme 1.

There is precedence for the [3.3]shifts depicted in this scheme. The Cope-like rearrangement of 1,5-hexadiynes to bisallenes (as in the conversion of 2 to A) is well known.[10] The transformation of A to B has an analogy in the degenerate rearrangement of hexa-4,5-diene-1-yne.[11] Finally, the last reorganization of B to 4 is well modeled by the thermal chemistry of 1,2,5,6-octatetraene[12] and, even better, of 1,4-bis(ethenylidene)cyclohexane.[13] Group equivalent calculations[2] also suggest the thermodynamic feasibility of intermediates A and B (Scheme 1). Therefore, at the outset of this study there was nothing but the bias of chemical intuition to make one pathway appear more reasonable than another in the synthesis of 4 from 2.

RESULTS AND DISCUSSION

The thermal chemistry of 1,5,9-*decatriyne* (1)[15]

The triyne 1 was chosen as the initial substrate for study because, unlike 3, the product of intramolecular [2+2+2]cycloaddition, the 1,2:3,4-dicyclobutabenzene (5),[16] was deemed to be thermodynamically stable to the pyrolysis conditions,[2] perhaps in equilibrium with the ring-opened isomer 6,[17] but potentially isolable.



5 6 7a R = H; 7b R = D

ΔHf (kcal mol^{-1}):[2] 5, 68.8; 6, 67.4; 7a, 65.6.

Surprisingly, flash pyrolysis (10^{-3} Torr, contact time 1–5 ms, 450–600°)[6,18] of 1a yielded not 5 but rather the linear dicyclobutabenzene 7a, in addition to naphthalene 8. Independently prepared 5[17b] wa shown to be stable under these conditions, and its absence in the reaction mixture ascertained by GC.

Similar pyrolysis in a flow system (1–100 mm N_2 carrier gas, contact times 1–5 s, 350–475°), also gave 7a, but not naphthalene. Moreover, another product formed, the butynyldimethylenecyclobutene 9. Best yields were obtained at low conversion (11 mm N_2, 10 ml min^{-1}, 350°; 10% conversion, 30% 7a, 60% 9a).

8 9a R = H; 9b R = D

ΔHf (kcal mol^{-1}):[2,14] 8, 36; 9a, 118.

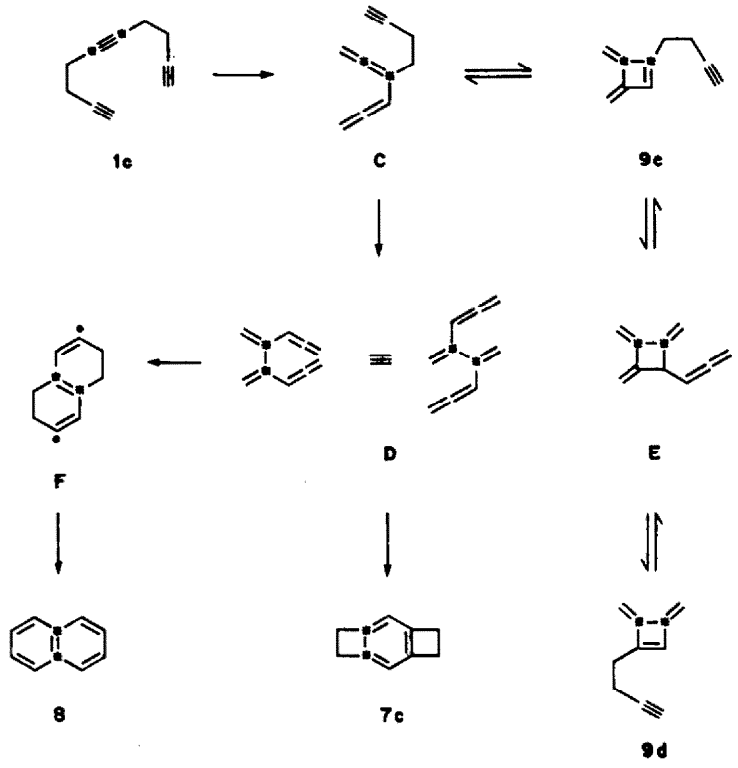
Typical yields at near complete conversion were 40%, the ratio of 7a to 9a changing from 1:4 at higher pressure (50 Torr) to 3:1 at lower pressures (1 Torr). Repyrolysis (flow or flash) of 7a gave only starting material. However, flash pyrolysis of 9a furnished 7a and naphthalene 8 in the same ratio (1:3) as that obtained from 1a. Thus, 9a is either in equilibrium with 1a or it is a direct precursor to 7a and 8. At very high temperatures (10^{-3} Torr, 950°) 7a converted to 8 and *m*- and *p*-divinylbenzene, probably by mechanisms related to other benzocyclobutene–styrene rearrangements.[19]

In order to shed further light on these observations, 1a was deuterated to 1b (>95% D_2), which could be pyrolyzed to give 7b and 9b. The naphthalene formed from 1b had lost H_2, HD, and D_2 but not in a random manner (calculated for a random process: d_0, 3.6%; d_1, 31%; d_2, 66%; found: d_0, 13.3%; d_1, 17.7%; d_2, 69%), favoring apparent H_2 and D_2 extrusion at the expense of that involving HD. Moreover, ^{1}H-NMR analysis showed slightly more deuterium located at the α-positions (6% over statistical) and a not quite random distribution of label over both aromatic rings. The latter conclusion was drawn after oxidative degradation[20] of labeled 8 to phthalic acid, methylesterification, and mass spectral analysis of the product (d_0, 40%; d_1, 43.1%; d_2, 16.9%; calculated for equal label distribution over both rings: d_0, 37%; d_1, 48.2%; d_2, 14.8%). We have no explanation for these deviations but the aromatization of 1 to 8 is obviously complex.

Schemes 2 and 3 suggest two mechanistic possibilities consistent with the observed results and indicating a potential way to distinguish between them. Thus, a [3.3]shift of one of the 1,5-diyne units[10] would result in C (Scheme 2) which would (reversibly)[21] close to 9, one of the products. At the same time C could rearrange[11] to D which is readily envisaged[12] to give the product 7 or naphthalene via F. A potentially complicating degenerate equilibration of 9 is also shown in Scheme 2, and would proceed through E. Because of the high energy content of 1, all postulated intermediates are energetically feasible.

The alternative depicted in Scheme 3 invokes biradicals F, G and H, the latter to rationalize the deuterium scrambling in the labeled naphthalene arising from 1b. Intermediate F might close to Dewar benzene I which would then result in 7d. The topological differences of these pathways can be used to advantage in a ^{13}C-labeling experiment involving 5,6-$^{13}C_2$-1,5,9-decatriyne 1c (stars in schemes). In particular, the [3.3]shift sequence maintains the connectivity of the labeled carbons; the Dewar benzene I leads to rupture of that bond. Both mechanisms predict the ^{13}C-label in 8 to emerge at the 9,10-positions.

An expedient synthetic method was developed to the required 1c taking advantage of the availability of commercial acetylene-$^{13}C_2$ (90% label). Since alkylation of the corresponding dianion with a homopropargyl halide was bound to lead to elimination, the crucial connections were planned to arise by a reverse polarization strategy. The latter took its inspiration from the known ethynylation of alkyl copper species with iodoacetylenes.[22] In our case this approach required the efficient synthesis of labeled diiodoacetylene, avoiding the reported[23] use of a large excess of acetylene. The problem of the reactivity of diiodoacetylene to overiodination[24] could be circumvented by

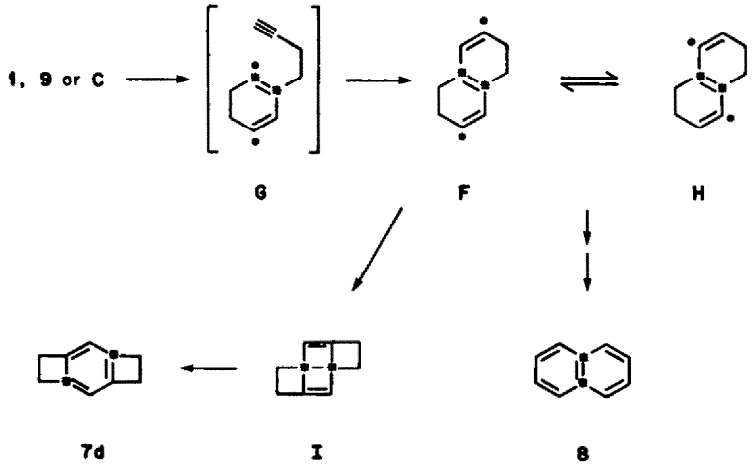


Scheme 2. ΔHf (kcal mol^{-1}):[2,14] C, 141.6; D, 121.7; E, 121.9; F, 150.1.

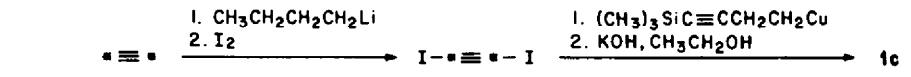
careful treatment of dilithioacetylene-$^{13}C_2$ with iodine in toluene at −78° (Scheme 4). After an aqueous workup, filtration through alumina gave labeled diiodoacetylene which was then exposed to 4-trimethylsilyl-3-butynyl-1-copper[25] and the resulting bis(trimethylsilylated) **1** protodesilylated to give **1c** in 12% overall yield.

The results of the subsequent pyrolysis experiments were gratifyingly clean, only **7c**, **9c**, and 9,10-labeled **8** being formed. The position of the label was ascertained by high field ^{1}H- and ^{13}C-NMR experiments including homo- and heteronuclear decoupling and spectral simulations. Thus, the coupling constants between H-3 and H-6 (~0.5 Hz), C-1 and H-3 (~0.7 Hz), and C-1 and H-6 (~7.0 Hz) are available from natural abundance spectra of **7a** and are as expected.[13] With these data in hand it is possible to simulate† the expected ^{13}C-spectral patterns for the carbons in **7c** and **d** (decoupled from the saturated hydrogen at δ 3.03 ppm) by using literature[26] values for $J_{C_1-C_2}$ ~ 56 Hz and $J_{C_1-C_4}$ ~ 8 Hz. The calculated spectra predict a four line spectrum for **7d** (and also 7-1,5-$^{13}C_2$), but only three lines for **7c**. Such a spectrum was cleanly observed. The undecoupled proton spectrum also shows a triplet at δ 6.71 for the aromatic nuclei, as expected.

† Spectra were calculated using an ITRCAL program on a Nicolet 1280 computer.



Scheme 3. ΔHf (kcal mol^{-1}):[2] G, 184.9.



Scheme 4.

Identification of the fate of the label in the dimethylene cyclobutene **9c** was accomplished by ^{13}C-NMR spectroscopy. Formation of any of the isotopomers of **9** via **E** (Scheme 2) involves the formation of **9d**: therefore, absence of this material proves the inoperability of the suggested label scrambling. The ^{13}C-NMR spectra of **9c** and **d** should be distinct: C-3 and C-4 should show signals near 150 ppm, whereas C-1 is expected to resonate near 160 ppm.[27] The proton-decoupled spectrum of labeled **9** exhibited two doublets (J_{CC} = 41.8 Hz) at 159.2 and 150.4 ppm. Had there been more than a few percent of **9d**, there would have been an additional four line pattern near the peaks at 150.4 ppm.

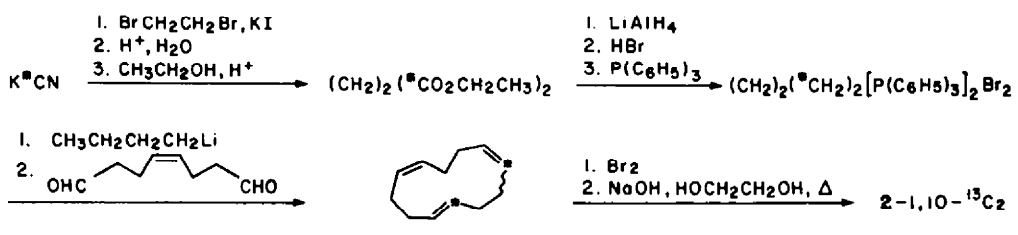
The ^1H-NMR spectrum of unlabeled **9** revealed a broad singlet at 6.8 ppm due to the vinyl hydrogen of the ring carbon, and a three line pattern (integration 1:2:1) at δ 4.67–4.49 ppm assigned collectively to the alkylidene protons. In labeled **9** the latter gives rise to four sets of broadened doublets with coupling constants from 7.5 to 14.2 Hz. Unfortunately, due to the lack of an NMR spectrometer capable of ^{13}C decoupling and the uncertainty in the assignment of the resonances of the unlabeled compound, it was not possible to analyze these spectra completely. However, the observed patterns are totally consistent with the above assignments of the ^{13}C label and the generally observed coupling constants[26] and inconsistent with the scrambling sequences. Finally, the proton-decoupled ^{13}C-NMR spectrum of labeled naphthalene exhibited a prominent peak at 133.9 ppm assigned to the 9 and 10 positions. The remaining resonances did not indicate any label enrichment beyond natural abundance, a finding corroborated by a ^{13}C-satellite proton spectrum.

In summary then, it appears that Scheme 2 most accurately describes the fate of **1** on pyrolysis. It is characterized by [3.3]sigmatropic shifts (or their topological, perhaps nonconcerted, equivalents), no sign of a [2+2+2]process being detectable. It could be argued that the (presumably) preferred *anti* conformation of **1** and entropy play a role in this chemistry. Such an effect would not be operating in 1,5,9-cyclododecatriyne (**2**), and therefore it became of prime interest to more closely investigate the mechanistic details of the conversion of **2** to hexaradialene **4**.

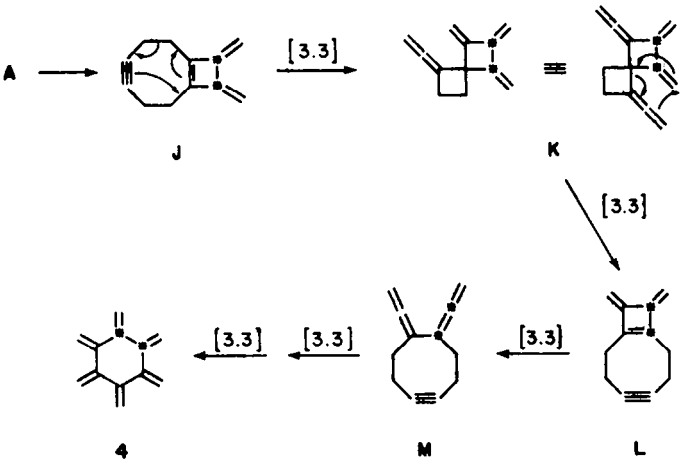
Synthesis and pyrolysis of 1,10 - $^{13}C_2$ - 1,5,9 - *cyclododecatriyne*[28]

Scheme 1 indicates how a labeling experiment might narrow the mechanistic options invoked to explain the behavior of **2** on pyrolysis (stars). It was chosen, in part, because of synthetic expediency but nevertheless required a new strategy to the construction of the cyclic triyne framework through labeled 1,5,9-cyclododecatriene **10** (Scheme 5). The sequence starts with the commercially available (and relatively cheap) potassium ^{13}C-cyanide which is converted into $^{13}C_2$-diethyl succinate according to literature procedures.[29] Reduction to the diol, transformation to labeled 1,4-dibromobutane, and treatment with triphenylphosphine gave the bis(phosphonium) salt.[30] The subsequent step in the strategy was crucial: a bis-Wittig reaction[31] with *cis*-oct-4-enedial.[32] As expected,[31] it proved to be fairly inefficient, giving a mixture of *c,c,t*-(10%) and *c,t,t*-(25%)-1,5,9-cyclododecatrienes (**10**) with the appropriate label in place. The next two synthetic manipulations, bromination–dehydrobromination to give labeled **2**, were viewed with trepidation in view of the problems encountered in the original synthesis of **2**[5a,b] which could only be effected starting from all-*cis*-1,5,9-cyclododecatriene. Indeed, **10** could not be converted into **2** using the conditions developed earlier. Fortunately, this problem was solved by employing hot basic ethylene glycol in the dehydrobromination of the mixture of hexabromides derived from **10**, which gave **2**, albeit in poor yield (14%). The use of potassium t-butoxide in hydrocarbon solvent[33] gave poorer yields (< 10%).

With **2c** in hand, the two sequences depicted in Scheme 1 should be readily discerned: the [2+2+2]pathway generates **4** with two adjacent labels; the [3.3]shifts result in "*para*"-labeled hexaradialene. Complications can be envisaged, however, which could significantly obscure the observed results. One such complication is related to that considered also for the rearrangement of **1c**, namely the equilibration of **9c** and **d** via **E** (Scheme 2). Applied to **A** this could generate the (thermodynamically well-accessible)[2] intermediates and scrambling indicated in Scheme 6. Because of the intervention of spiro-intermediate **K** we will label the mechanism involving this species spiro[3.3], as opposed to the sigmatropic pathway outlined in Scheme 1 (labeled [3.3]), and the direct cyclization of the alkyne units to **3** (labeled [2+2+2]). It is apparent that the spiro[3.3] sequence may furnish "*ortho*"-labeled **4** to a varying degree. The extent of scrambling will depend on the ability of **M** to equilibrate with 1,2-$^{13}C_2$-**2** and of the starting labeled **2** to equilibrate with 1,6-$^{13}C_2$-**2** via the alternative mode of the [3.3]shift involving only one labeled alkyne. To simplify our predictions we will only consider a spiro[3.3] mode



Scheme 5.

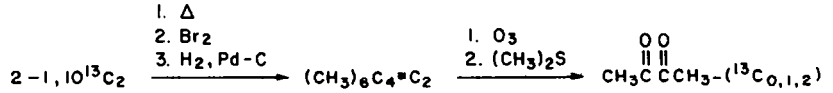


Scheme 6. ΔHf (kcal mol^{-1}): J, 129;[14] K, 147.[34]

which involves complete equilibration before product formation (2:1 ratio "*ortho*":"*para*"-$^{13}C_2$-4). Finally, for our calibration, as another complication we will also consider an unspecified process which would randomly interconvert sp-hybridized carbon atoms ("random").

Regardless of these considerations, in labeled 4 the symmetry and complexity of the spin system as well as the reactivity of hexaradialene and the relatively poor yields in its generation from 2 was thought to preclude a simple NMR analysis of the pyrolysis mixtures resulting from 2-1,10-$^{13}C_2$. Instead, a degradative method was designed which would convert 4 into three stable four-carbon fragments presumably readily analyzed by GC–MS. At first, it was planned to subject labeled 4 to catalytic hydrogenation,[5b] followed by Birch reduction of the resulting hexamethylbenzene[35] and ozonolysis. Discouraged by the irreproducibility of the first, and the low yields in the second step, we instituted slight changes in strategy which gave more satisfactory results. Thus, the crude 4 produced from 2 was efficiently brominated to hexa(bromomethyl)benzene, which in turn was exposed to hydrogenolysis over Pd[36] to give hexamethylbenzene. This compound was ozonized directly to 2,3-butanedione, ready for mass spectral analysis (Scheme 7). This procedure yielded consistent, albeit small amounts of product (~5%). In order to rule out that any potential and not readily detected impurities in the labeled hexaradialene (and therefore the resulting hexamethylbenzene) were responsible for a significant portion of the butanedione, a control experiment was run. In this experiment, unlabeled 2 was pyrolyzed, brominated, and hydrogenolyzed. The total hexamethylbenzene content was determined by quantitative GC and an equivalent quantity of hexakis(trideuteriomethyl)benzene was added. This mixture was subjected to ozonolysis and found to contain as much perdeuterated butanedione as unlabeled butanedione. Had a molecule other than hexamethylbenzene served as the source of a significant amount of dione, then the ratio of deuterated to nondeuterated product should not have reflected the ratio of deuterated to nondeuterated hexamethylbenzenes.

What kind of label distribution is to be expected according to the various mechanisms? A simple statistical analysis predicts the following ratios of $^{13}C_2$:$^{13}C_1$:$^{13}C_0$-butanedione: 1:2:3 if 3 is the only intermediate; 0:2:1 for the simple [3.3]shift; and 1:4:4 for the spiro[3.3] pathway. The randomization of all ring carbons predicts a ratio of 1:8:6. Corrected for the 90% ^{13}C label distribution, the presence of natural abundance ^{13}C and for the fragmentation pattern measured on unlabeled 2,3-butanedione generates the values depicted in Table 1. The actually observed values are reported in the last column, clearly



Scheme 7.

Table 1. Calculated and experimental[a] relative peak intensities (%) 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	51.4	38.5	47.0	43.9	41.5
87	4.0	34.1	59.5	42.6	48.9	58.5
88	0.0	14.5	2.0	10.4	7.2	<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.

incompatible with the operation of any of the mechanisms considered other than [3.3]. This result certainly lends credence to the theoretical estimate that purely thermal [2+2+2] alkyne cycloadditions are obstructed by unusually high barriers, in this case enforcing the intermediacy of alternative structures by a different pathway. We believe that an uncatalyzed cycloaddition of this type remains to be observed.[37]

EXPERIMENTAL

General. ^{1}H- and ^{13}C-NMR spectra were obtained on a Varian Associates T60, EM360 or a "home built" UCB-250 or UCB-200 spectrometer: both the UCB instruments used a Nicolet 1180 data system and a CryoMagnet Systems 5.7-T magnet. Chemical shifts are reported in ppm downfield of TMS, or referenced to the residual proton signal at 7.20 ppm, or the center C resonance at 77.0 ppm, of $CDCl_3$.

Mass spectral data were collected on an AEI-MS-12 (low resolution) or DuPont CEC 21-110B (high resolution) instrument by the Mass Spectral Services of the University of California, Berkeley. Elemental analyses were carried out by the Microanalytical Laboratory. Analytic gas chromatography was performed on a Shimadzu GC-mini 2 flame ionization detector instrument with a 30 m × 0.25 mm J&W fused silica column with a 0.25 μm SE30 coating. Preparative gas chromatography was carried out on a Varian 920 instrument with a 5 ft × 1/4 in 10% SE30 on Chromosorb W stainless steel column. Coupled GC–MS data were undertaken with a Finnigan 4000 machine in conjunction with an Incos data system.

THF was distilled from sodium benzophenone ketyl; $CDCl_3$ was purified over alumina to remove residual acid and degassed immediately before use. Other solvents were purified by standard procedures.

Pyrolyses were accomplished using a Hoskins FD303A electric tube furnace regulated by an Omega 4001KC temp controller and heating a 1.8 × 45 cm quartz tube. Temps were measured at the center of the oven and varied less than 5° for the center segment (25 cm) of the pyrolysis tube.

Flash pyrolysis of 1,5,9-*decatriyne* (1). A sample of dioxane (3 mg) was placed in an NMR receiving tube fitted with a ground glass joint, attached to the pyrolysis apparatus and frozen at −196°. The sample holder was charged with 1 (78 mg, 0.67 mmol) and cooled to −196° while the system was evacuated to 10^{-3} Torr and the oven was heated to 575°. The apparatus was allowed to reach equilibrium and the trap was filled with liquid N_2. The sample was then allowed to warm to room temp and sublimed through the quartz tube. When the sublimation was complete (*ca* 2 h), the oven was cooled and a layer of degassed $CDCl_3$ was deposited on the frozen pyrolysate by vacuum transfer. The liquid N_2 was then removed from the trap by syphon, the sample was allowed to warm to room temp and drip into the NMR sample tube, and then refrozen at −196°. The tube was sealed and the sample subjected to analysis. Preparative GC (oven temp 195°, flow rate 32 ml min^{-1}) gave first naphthalene (9 mg, 12%): retention time 10 min; *m/e* (rel. intensity) 129 ($M^+ + 1$, 3.6), 128 (M^+, 100), 127 (14), 126 (9), 102 (11); ^{1}H-NMR (CCl_4) δ 7.65 (dd, J = 3, 6 Hz, 4H), 7.28 (dd, J = 3, 6 Hz, 4H) and subsequently [1,2:4,5]dicyclobutabenzene (3 mg, 4%) as colorless crystals: retention time 11 min; m.p. 101° (lit.[17] m.p. 101°); *m/e* (rel. intensity) 130 (M^+, 100), 129 (80), 128 (75), 115 (85), 77 (20), 64 (23), 63 (32), 51 (49); ^{1}H-NMR δ 3.03 (s, 8H), 6.74 (s, 2H); ^{13}C-NMR ($CDCl_3$) 29.5, 117.5, 143.6.

Flow pyrolysis of 1: 3,4 - *dimethylene* - 1 - (3 - *butynyl*)*cyclobutane* (9a). In an apparatus similar to that described above, the sample holder was charged with 1 (95 mg, 0.73 mmol) and cooled to −78°. The system was evacuated to 10 Torr and pentane (10 ml) was degassed in a solvent reservoir by alternate freezing and thawing. The pentane was then vacuum transferred onto the cold finger trap and frozen at −196°. Attached needle valves were set to provide a flow of N_2 (measured at 760 Torr) of 10 ml min^{-1} (pressure in the oven: 40 Torr), and the oven was heated to 475°. When the system had equilibrated, the sample was warmed to 40° and allowed to sublime through the oven (*ca* 5 h). Subsequently, the oven was allowed to cool and the liquid N_2 was removed from the trap by syphon. The product was isolated by allowing the pentane to melt and be collected in a 25 ml pear-shaped flask. The solvent was removed under reduced pressure, the sample was covered with N_2, and then subjected to purification by preparative GC (to avoid possible rearrangement, the injector and detector temps were lowered to 260°, the oven temp was 185°; the flow rate was 32 ml min^{-1}). The product was collected in two fractions: (A) [retention time 8 min] contained two components which were separated by HPLC (reversed phase conditions; C_{18} stationary phase on ODS microspheres, eluted with 12.5% H_2O–MeOH at 1 ml min^{-1}). Fraction A1 (no strong UV absorptions) was extracted into pentane (2 ml) and the solvent removed to give crystals of recovered 1 (2 mg, 2%): retention time 5 min; colorless crystals, m.p. 45°; ^{1}H-NMR (CCl_4) δ 2.24 (br s, 8H), 1.80 (br s, 2H). Fraction A2 was taken immediately for UV spectral analysis: retention time 6 min; UV λ_{max} (12.5% H_2O–MeOH) 244, 208 nm (absolute intensities not calculated due to the air sensitivity and small quantity available; relative intensities: 0.70, 0.11); cf. 1-methyl-2,3-dimethylenecyclobutene;[10b] λ_{max} (EtOH) 245 (log ε 3.76), 210 (4.49) nm. Fraction (B) consisted of 7a (8 mg, 8%).

A second reduced pressure flow pyrolysis was performed as above, starting with 1 (107 mg, 0.82 mmol), at an oven temp of 575° to total conversion (no signals due to 1 were detectable in the NMR spectrum of the crude pyrolysate). Preparative GC (conditions as above) gave 9a (37% by GC thermal conductivity response, 7a internal standard): retention time 8 min; ^{1}H-NMR (CCl_4) δ 1.81 (bs, 1H), 2.15–2.45 (m, 4H), 4.50 (br s, 1H), 4.59 (br s, 2H), 4.68 (br s, 1H), 6.84 (br s, 1H).

A GC–MS of the unpurified pyrolysate showed all parent masses to be at *m/e* 130 indicating the absence of fragmentation during pyrolysis. By comparison of the relative intensities and retention times, the two major peaks in the GC–MS were identified as 9a: *m/e* (rel. intensity) 130 (M^+, 39), 129 (40), 128 (100), 127 (34), 115 (38), 65 (92); and 7a.

1,10-*Dideuterio*-1,5,9-*decatriyne* (1b). Compound 1 (200 mg, 1.54 mmol) was dissolved in dry distilled THF (100 ml) and cooled to −78°. A soln of MeLi (2.2 ml of a 1.4 M soln in hexane, 3.1 mmol) was added and the mixture was allowed to warm to 0°, then cooled to −78°. A portion of D_2O (1.0 ml, 50 mmol) was added, the soln was warmed to reflux for 5 min, and poured into a separatory funnel containing ether (10 ml) and H_2O (5 ml). The organic layer was dried over $MgSO_4$. Evaporation of the solvent under reduced pressure gave colorless crystals of 1b (180 mg, 90%): m.p. 45–46° (from pentane); *m/e* (rel. intensity) 132 (M^+, 86), 131 (100), 117 (75), 92 (91); IR (neat) 3340, 2950, 2610, 1990, 1442 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.29 (br s, 8H), 1.80 (br s, 0.01H).

Flash pyrolysis of 1,10 - *dideuterio* - 1,5,9 - *decatriyne* (1b). Flash pyrolysis of 1b (100 mg, 0.77 mmol) (>95% 1,10-d_2 by ^{1}H-NMR) in the usual fashion followed by preparative GC (oven temp 195°, flow rate 32 ml min^{-1}) gave a mixture of deuterated naphthalenes (10 mg, 10%): retention time 10 min; *m/e* (rel. intensity) 132 (2), 131 (14), 130 (100), 129 (41), 128 (32), 127 (7); ^{1}H-NMR (CCl_4) δ 7.65 (m, 1.2H), 7.28 (m, 1.0H); and 7b (4 mg, 4%): retention time 11 min, *m/e* (rel intensity) 132 (M^+, 100), 131 (90), 130 (71), 117 (64), 116 (36), 65 (19); ^{1}H-NMR ($CDCl_3$) δ 3.04 (s, 8H), 6.75 (br s, 0.01H).

Flow pyrolysis of 1b. Flow pyrolysis of 1b (61 mg, 0.47 mmol) as described above was performed at 510°, with a N_2 flow of 14 ml min^{-1} at 40 Torr. Collection of the pyrolysate in pentane followed by removal of the solvent under reduced pressure and preparative GC (injector and detector temp 260°, oven temp 185°, flow rate 32 ml min^{-1}) gave 9b: retention time 8 min; ^{1}H-NMR (CCl_4) δ 2.15–2.45 (m, 4H), 4.49 (br s, 1H), 4.58 (br s, 2H), 4.79 (br s, 1H); and 7b.

Oxidation of partially deuterated naphthalene. The partially deuterated naphthalene (10 mg, 0.07 mmol) from the pyrolysis

of **1b** was dissolved in $CHCl_3$ (10 ml), and added to a stirred mixture of CF_3CO_2H (0.3 ml) and 30% H_2O_2–H_2O (0.3 ml). To this purple soln was added H_2SO_4 (0.1 ml). The mixture was heated to 30° for 1 h, a tip of a spatula of PtO_2 was added, and the suspension was stored overnight at 5°. The volatiles were removed under reduced pressure and anhyd MeOH (10 ml) was added. After heating to reflux for 2 hr, the soln was cooled, extracted with ether (10 ml) and H_2O (10 ml) and the organic phase was submitted for GC–MS to detect deuterated dimethyl phthalate: *m/e* (rel. intensity) 195 (1.4), 194 (2.4), 165 (46), 164 (100), 163 (89), 79 (24), 78 (52), 77 (64), 76 (23).

Trimethylsilylation of 1,5,9-*decatriyne* **1** *to* 1,10-*bis*(*trimethylsilyl*)-1,5,9-*decatriyne*. A sample of **1** (260 mg, 2 mmol) was dissolved in dry THF (100 ml). After cooling to −78°, n-BuLi (3 ml of a 1.4 M soln in hexane, 4.1 mmol) was added, the soln was allowed to warm to room temp, and then cooled to −78°. A portion of chlorotrimethylsilane (0.6 ml, 4.8 mmol) was added and the soln was heated to a gentle reflux for 15 min. After cooling, the mixture was washed with H_2O and brine (50 ml portions) and dried over $MgSO_4$. Filtration followed by removal of solvent under reduced pressure gave colorless crystals (0.466 g, 85%): m.p. 44°; *m/e* (rel. intensity) 274 (M^+, 0.9), 259 (5), 171 (16), 155 (13), 119 (10), 73 (100); ^{1}H-NMR (CCl_4) δ 0.13 (s, 18H), 2.30 (s, 8H). (Found: C, 69,64; H, 9.32. Calc for $C_{16}H_{26}Si_2$: C, 70.0; H, 9.54%.)

1,5,9-*Decatriyne* **1** *by protodesilylation*. To a stirred soln of KOH (0.8 g) in EtOH (100 ml was added the bissilyltriyne (0.50 g, 1.8 mmol). Stirring was continued for 15 min. The soln was added to a separatory funnel along with pentane (10 ml) and H_2O (50 ml). The aqueous layer was washed with pentane (20 ml) and the combined pentane fractions were dried over $MgSO_4$. After filtration, the pentane was removed under reduced pressure to give colorless crystals of **1** (0.20 g, 84%).

1-*Trimethylsilyl*-4-*bromo*-1-*butyne*. The preparation of this compound was accomplished by the method of Hammond and Descoins,[38] with the following modification. In acetone (450 ml) was dissolved 4-trimethylsilyl-3-butynyl 1-*p*-toluenesulfonate (44.4 g, 150 mmol) and LiBr (33 g, 300 mmol). The suspension was heated to reflux overnight and then poured into a separatory funnel containing ether (400 ml) and H_2O (200 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated to an oil. Purification with a Kugelrohr apparatus (10 Torr, oven temp 55°) gave product (28.3 g, 92%): *m/e* (rel. intensity) 206 (M^+, 3.7), 204 (3.7), 191 (100), 189 (100), 139 (54), 137 (54), HRMS calc for $C_7H_{13}Si^{79}Br$, 203.9977; found, 203.9977; ^{1}H-NMR (CCl_4 δ 3.25 (t, J = 14 Hz, 2H), 2.62 (t, J = 14 Hz, 2H), 0.12 (s, 9H).

4-*Trimethylsilylbut*-3-*ynyl*-1-*copper*. To a 250 ml flask fitted with a condenser and dropping funnel was added THF (100 ml), Mg turnings (4.1 g, 0.18 mol), and one crystal of I_2. The dropping funnel was charged with THF (40 ml) and 1-trimethylsilyl-4-bromo-1-butyne (20.81 g, 0.1 mol) added to the flask at such a rate as to maintain a gentle reflux. When the addition was finished, the mixture was heated for another 30 min, cooled to 5° and decanted under N_2 into a dry 250 ml flask. More THF (100 ml) was added, the soln was stored under N_2 at 0° and titrated before use (0.4 M).

To a magnetically stirred suspension of dimethylsulfide–cuprous bromide[39] (2.26 g, 11 mmol) in THF (75 ml) under N_2 at −45° was added by syringe over 20 min a soln of 4-trimethylsilyl-3-butynyl magnesium bromide (27 ml of a 0.4 M soln in THF, 10.8 mmol). The resulting red suspension was used as described below.

5,6-$^{13}C_2$-1,5,9-*Decatriyne* (**1c**). The requisite acetylene-$^{13}C_2$ (100 ml, 4.5 mmol, 90% ^{13}C, Stohler Isotope Chemicals) was supplied in a breakseal flask at atmospheric pressure. The container was modified by the addition of a stopcock. A serum cap was wired onto the open end of the apparatus, the stopcock was opened, and the outer portion of the system was repeatedly evacuated and filled with N_2 to remove H_2O and O_2. With the outer portion of the apparatus under vacuum, the stopcock was closed and the seal broken by repeatedly lifting a glass encased magnet and dropping it onto the seal. The magnet was then raised into the wide part of the tube, the flask was cooled to −78°, the stopcock was opened, and n-BuLi (6.4 ml of a 1.4 M soln in hexane, 9.1 mmol) was added by syringe. After closing the stopcock, the flask was warmed to room temp and swirled. A needle which connected to a vacuum line was inserted, the stopcock was opened, and the hexane was removed under reduced pressure. The resulting white solid was cooled to −78° and a soln of I_2 (2.4 g, 9.4 mmol) in toluene (30 ml) was added by syringe with swirling over 10 min. Addition was stopped when the mixture maintained the purple I_2 color. The suspension was washed with H_2O (10 ml), the aqueous layer was extracted with ether (15 ml), and the combined organic fractions were dried over $MgSO_4$. This soln was purified by column chromatography on alumina (50 g) eluting with ether (75 ml). Solvent was removed on a rotary evaporator until the volume of soln was about 40 ml. This soln of $^{13}C_2I_2$ was added slowly to a stirred suspension of 4-trimethylsilylbut-3-ynyl-1-copper (see above) (11.1 mmol) in THF (100 ml) at −47°.

The red suspension gradually turned a muddy green as stirring continued for an additional 30 min at −40°. A 2% H_2SO_4–MeOH soln (10 ml) was added, the resulting mixture was poured into a separatory funnel and extracted four times with dilute aqueous ammonia (100 ml each) to remove Cu salts and unreacted $^{13}C_2I_2$. The organic phase was suction-filtered through filteraid, washed with dilute H_2SO_4, 10% $NaHCO_3$, and brine (100 ml each), and then dried over $MgSO_4$. Filtration followed by removal of the solvent under reduced pressure and purification by preparative GC (oven temp 150°, flow rate 55 ml min^{-1}) gave 1,8-bis(trimethylsilyl)-1,7-octadiyne[40] (270 mg, 1.8 mmol): retention time 7 min; ^{1}H-NMR ($CDCl_3$) δ 2.22 (m, 4H), 1.58 (m, 4H), 0.16 (s, 18H) and 1,10-bis(trimethylsilyl)-5,6-$^{13}C_2$-1,5,9-decatriyne (163 mg, 11.5%): retention time 14 min; ^{1}H-NMR ($CDCl_3$) δ 2.27 (br s, 8H), 0.16 (s, 18H).

This compound (163 mg, 0.6 mmol) was protodesilylated in EtOH–NaOH as described above to give **1c** (65 mg, 84%): *m/e* (rel. intensity) 132 (M^+, 14), 131 (93), 130 (100), 129 (52), 117 (89), 93 (57); ^{1}H-NMR ($CDCl_3$) δ 2.30 (br s, 8H), 1.79 (br s, 2H); ^{13}C-NMR ($CDCl_3$) 83.2 m, 79.4 (intense signal), 69.1, 18.9 (d, J = 8.5 Hz), 18.8 (d, J = 80 Hz).

Flash pyrolysis of 5,6-$^{13}C_2$-1,5,9-*decatriyne* (**1c**). A sample of **1c** (25 mg, 0.2 mmol) was subjected to flash pyrolysis (10^{-3} Torr, 600°) as described above. The pyrolysate was collected in $CDCl_3$ in an NMR tube and immediately taken for spectroscopic analysis. Identifiable in the mixture were 9,10-$^{13}C_2$-naphthalene: ^{1}H-NMR ($CDCl_3$) δ 7.78 (m, 4H), 7.42 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 133.4; and 1,2-$^{13}C_2$-[1.2.4.5]dicyclobutabenzene **7c** ^{1}H-NMR ($CDCl_3$) δ 3.04 (s, 8H) 6.72 (t, J = 4 Hz) ^{13}C-NMR ($CDCl_3$) 143.5; selective heteronuclear proton decoupling at δ 3.04: δ 143.5 (t, J = 3.9 Hz).

Preparative GC (oven temp 190°, flow rate 32 ml min^{-1}) gave naphthalene (*ca* 1 mg, 4%): retention time 9.8 min; and **9c** (< 1 mg): retention time 10.5 min.

Flow pyrolysis of **1c**. A sample of **1c** (35 mg, 0.27 mmol) was subjected to flow pyrolysis as described for the pyrolysis of **1a** (400°, 100 Torr, 10 ml min^{-1} N_2 carrier gas). The pyrolysate was dissolved in $CDCl_3$ and taken for spectroscopic analysis. Identifiable in the mixture were residual **1c**; **7c** and **9c**: ^{1}H-NMR ($CDCl_3$) δ 2.62–2.3 (m), 4.50 (d, J = 13.5 Hz), 4.59 (d, J = 7.5 Hz), 4.71 (d, J = 10 Hz), 6.78 (br d, J = 16.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 150.4 (d, J = 41.8 Hz), 159. 3(d, J = 40.9 Hz); selective heteronuclear decoupling at δ 3.3 in ^{1}H-NMR gives ^{13}C-NMR 159.1 (dm, J = 44 Hz), 150.3 (ddm, J = 43.5, 10.85 Hz); decoupling at δ 6.8 gives 159.1 (br d, J = 40.1 Hz), 150.3 (br d, J = 40.3 Hz).

A GC–MS analysis of the pyrolysis mixture gave additional evidence for the presence of these compounds: **1c**: *m/e* (rel. intensity) 132 (M^+, 13.6), 131 (93.2), 130 (100), 129 (52), 117 (89); **9c**: *m/e* (rel. intensity) 132 (M^+, 1.9), 131 (29), 130 (100), 129 (59), 117 (76), 116 (27), 67 (60), 66 (84); **7c**: *m/e* (rel. intensity) 132 (M^+, 100), 131 (92), 130 (69), 129 (35), 117 (57), 116 (23), 65 (18), 52 (19).

1,4 - $^{13}C_2$ - 1,4 - *Bis(triphenylphosphino)butane dibromide.* $^{13}C_2$-Diethylsuccinate[29] (1.3 g, 3.3 mmol) was dissolved in THF (5 ml) and added dropwise to a soln of LAH (0.70 g, 20 mmol) in THF (50 ml) under N_2 at 0°. While stirring, the mixture was heated to reflux for 3 h. A soln of 3 M H_2SO_4 aq (2 ml) was added dropwise, and the suspension was heated to reflux overnight. After cooling and filtration, the solid was washed thoroughly with MeOH and the solvent of the combined filtrate was removed by rotary evaporation. The resulting viscous liquid was taken up in 40% aq HBr (7 ml), cooled to 0°, and conc H_2SO_4 (3 ml) was added dropwise with stirring. The flask was fitted with a reflux condenser and stirred at reflux for 6 h; the reflux condenser was replaced with a microstillhead and the product distilled until no more of the organic phase of the distillate was apparent (total distillate volume 5.2 ml). After extraction with two portions of ether (10 ml each), the distillate was dried over $MgSO_4$, filtered, and the ether was removed through a 3 in Vigreux column. Triphenylphosphine (1.70 g, 6.4 mmol) was added and the mixture heated to 190° in an oil bath without stirring. After 10 min stirring was started and crystals formed immediately. Stirring stopped and the oil temp was increased to 230° for 30 min. After cooling, the solid was recrystallized from $CHCl_3$ (15 ml) and acetone (10 ml) to give the phosphonium salt (1.00 g, 19%): white crystals, m.p. > 250° (lit.[30] 296°); ^{1}H-NMR ($CDCl_3$) δ 7.84–7.76 (m, 12H), 7.66–6.54 (m, 18H), 3.93 (br d, J = 133 Hz, 4H), 2.12 (br s, 4H); ^{13}C-NMR ($CDCl_3$) δ 134.5 (d, 1.5 Hz), 134.0 (d, J = 10 Hz), 130.25 (d, J = 13 Hz), 118 (d, J = 86 Hz), 21.9 (d, J = 52 Hz).

1,10-^{13}C-1,5,9-*Cyclododecatriyne* (**2b**). The above salt (1.00 g, 1.3 mmol) was ground with a mortar, dried overnight in a vacuum oven, suspended in THF (30 ml) under N_2, and cooled to −78° with magnetic stirring. A portion of n-BuLi (2.0 ml of a 1.4 M soln in hexane, 2.8 mmol) was added and the resulting red soln was stirred at room temp for 3 h. A soln of *cis*-5-octenedial[32] (0.2 g, 1.4 mmol) in THF (10 ml) was loaded into a syringe and both of the above solns were added by syringe pump to THF (250 ml) stirring at room temp under N_2. The simultaneous addition was carried out dropwise and was complete after 2 h. Care was taken to ensure that the mixture maintained a faint orange color. When the addition was complete, the soln was stirred at room temp for 2 h, and the mixture then extracted with 5% NH_4Cl and brine (250 ml each), and dried over $MgSO_4$. After filtration, the solvent was removed by rotary evaporation and the resulting oil was washed four times with pentane (5 ml). The combined extracts were concentrated and chromatographed on silica gel (10 g, pentane as eluent) to give an oil (74 mg). Analytical GC (oven temp 150°) showed two components with identical retention times compared to *c,c,t*- (3.25 min, 30% of mixture by FID response) and *c,t,t*-1,5,9-cyclododecatriene (3.13 min, 70% of mixture by FID response) by comparison with a commercial sample (Aldrich Chemical Co.).

The oil was dissolved in CH_2Cl_2 (25 ml), cooled to 15° and a soln of AcOH (0.1 ml) and Br_2 (1.0 g, 6.2 mmol) in CH_2Cl_2 (10 ml) was added dropwise over 1 h with stirring. The mixture was washed with $NaHSO_3$ aq (20 ml) four times, then with 2 portions of brine (15 ml), and dried over $MgSO_4$. Filtration and removal of the solvent gave an oil which was dissolved in THF (10 ml) and immediately taken on to the next step.

To ethylene glycol (150 ml) and H_2O (5 ml) was added Na (0.62 g, 27 mmol) and the mixture was heated to reflux overnight while purging with N_2. The soln was cooled to 30° and the THF soln from the above bromination reaction was added. This mixture was heated to reflux for 48 h, cooled, and poured onto ice (100 g). The aqueous layer was washed with pentane (100 ml) and ether (100 ml). The combined organic fractions were washed with 10% NH_4Cl aq (100 ml), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to give crystals of **2b** (8 mg, 7.7%): *m/e* (rel. intensity) 158 (M^+, 24), 157 (100), 156 (46), 155 (66), 154 (35); ^{1}H-NMR ($CDCl_3$) δ 2.35; ^{13}C-NMR ($CDCl_3$) δ 80.41; proton-coupled 80.41 (br s).

Pyrolysis of **2b**. A portion of **2b** was placed in the reduced pressure flow pyrolysis apparatus and cooled to 0°. The system was evacuated to 10 Torr and a soln of Br_2 (0.5 g, 3.1 mmol) in CH_2Cl_2 (20 ml) was vacuum transferred onto the cold finger trap and frozen at −196°. The reaction was then carried out under the following conditions: flow rate, 10 ml min^{-1} N_2 (measured at atmospheric press); temp, 575°; pressure in oven, 40 Torr. The sample was warmed to 60° and sublimed through the pyrolysis oven. When the sublimation was complete (1 h), the pressure was raised to 150 Torr, the oven was cooled and the trap allowed to warm to room temp. The resulting suspension was collected in a 50 ml flask and the solvent evaporated under reduced pressure to give a solid. After addition of CH_2Cl_2 (20 ml), 10% Pd–C (10 mg), and Na_2CO_3 (35 mg), the mixture was saturated with H_2. Stirring under a H_2 atmosphere for 10 h was followed by filtration and removal of the solvent under reduced pressure. The resulting solid was dissolved in acetone (0.5 ml), filtered through a plug of glass wool and evaporated under reduced pressure to a solid. A second portion of acetone (0.5 ml) was added, the soln was again filtered through glass wool and then cooled to −30° while a stream of O_3 (1 mmol min^{-1} O_3 in 1 l min^{-1} O_2) was blown over the surface for 60 s. Me_2S (0.2 ml, 3.8 mmol) was added with swirling, the mixture warmed to 0°, then immediately cooled to −78°, and finally subjected to GC–MS analysis.

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