

Kinetic Evidence for the Formation of Discrete 1,4-Dehydrobenzene Intermediates. Trapping by Inter- and Intramolecular Hydrogen Atom Transfer and Observation of High-Temperature CIDNP

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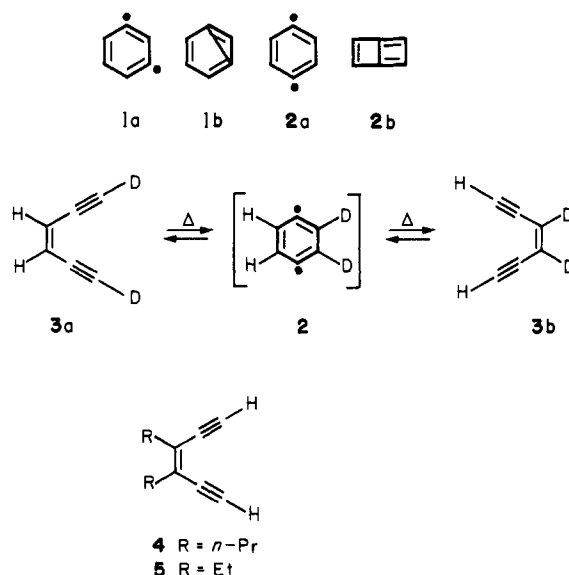
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Abstract: Upon being heated, alkyl-substituted *cis*-1,2-diethynyl olefins undergo cyclization to yield reactive 1,4-dehydrobenzenes; the products isolated may be derived from either unimolecular or bimolecular reactions of the intermediate. (*Z*)-4,5-Diethynyl-4-octene (**4**) undergoes rearrangement to yield 2,3-di-*n*-propyl-1,4-dehydrobenzene (**17**). Solution pyrolysis of **4** in inert aromatic solvents produces three unimolecular products, (*Z*)-dodeca-4,8-diyn-6-ene (**7**), benzocyclooctene (**9**), and *o*-allyl-*n*-propylbenzene (**10**), in high yield. When 1,4-cyclohexadiene is added to the pyrolysis solution as a trapping agent, high yields of the reduced product *o*-di-*n*-propylbenzene (**12**) are obtained. The kinetics of solution pyrolysis of **4** in the presence and absence of trapping agent establish that 2,3-di-*n*-propyl-1,4-dehydrobenzene is a discrete intermediate on the pathway leading to products. When the reaction was run in the heated probe of an NMR spectrometer, CIDNP was observed in **10**. This observation, along with kinetic and chemical trapping evidence, indicates the presence of two additional intermediates, formed from **17** by sequential intramolecular [1,5] hydrogen transfer, on the pathway to products. The observation of CIDNP, coupled with the reactivity exhibited by **17** and the other two intermediates, implicates a biradical description of these molecules. Biradical **17** has been estimated to have a lifetime of about 10^{-9} s at 200 °C and to lie in a well of about 5 kcal per mole with respect to the lowest energy unimolecular pathway ([1,5] hydrogen transfer). Ring opening (expected to be the lowest energy process for 1,4-dehydrobenzenes in which intramolecular hydrogen transfer is unlikely) to the isomeric diethynyl olefin **7** appears to have an activation enthalpy of about 10 kcal/mol. Upon thermal reaction in the gas phase (400 °C) or in solution in inert solvents (*Z*)-2,3-diethylhexa-1,5-diyn-3-ene (**5**) rearranges in good yield to the isomeric diethynyl olefin (*Z*)-deca-3,7-diyn-5-ene (**8**) again presumably via 2,3-diethyl-1,4-dehydrobenzene **20** (addition of 1,4-cyclohexadiene to the reaction solution leads to a good yield of *o*-diethylbenzene, the expected trapping product of biradical **20**). The absence of products due to intramolecular [1,4] hydrogen transfer indicates that this process is at least 1 or 2 orders of magnitude slower than [1,5] hydrogen transfer in **17**. At 500 °C in the gas phase products due to [1,4] hydrogen transfer begin to appear.

The highly reactive group of isomeric dehydrobenzenes, or benzynes, has provided challenging synthetic, mechanistic, and theoretical targets for a number of years.¹ Of particular interest in these molecules is the extent of interaction between the dehydro centers. The *o*-benzene isomer has been well characterized experimentally; it has been studied spectroscopically² in a matrix at 8 K and its reactivity toward a variety of substrates examined.^{1a,b} These studies indicate that substantial π bonding exists between the dehydro centers.

The 1,3-³ and 1,4-dehydrobenzenes⁴⁻¹³ have yielded less easily to experimental investigation. For these isomers both bicyclic and biradical structures (**1a,b** and **2a,b**) must be considered. Offsetting the energetic gain of forming a bond between the dehydro centers is the substantial strain energy associated with the bicyclic structures. In addition, the bicyclic 1,4-dehydrobenzene (butalene) may be further destabilized due to antiaromatic cyclobutadiene resonance. The 1,3- and 1,4-dehydrobenzenes are molecules, then, in which the gain in energy due to bonding of the unpaired electrons may be more than offset by the increase in strain energy. Thus they may belong to a small, unusual class of organic molecules containing a negative bond dissociation energy.¹⁴ An additional consideration regarding the biradical structures is whether the lowest energy open-shell electronic state is a singlet or a triplet. The relative energies of these spin states will depend on the extent of interaction between the dehydro centers.¹⁵ The possibility that **1** and **2** may possess several energetically similar structures has made them challenging subjects for study.

Early attempts to generate 1,4-dehydrobenzene have been surveyed previously.^{6b} We have reported the gas phase thermal



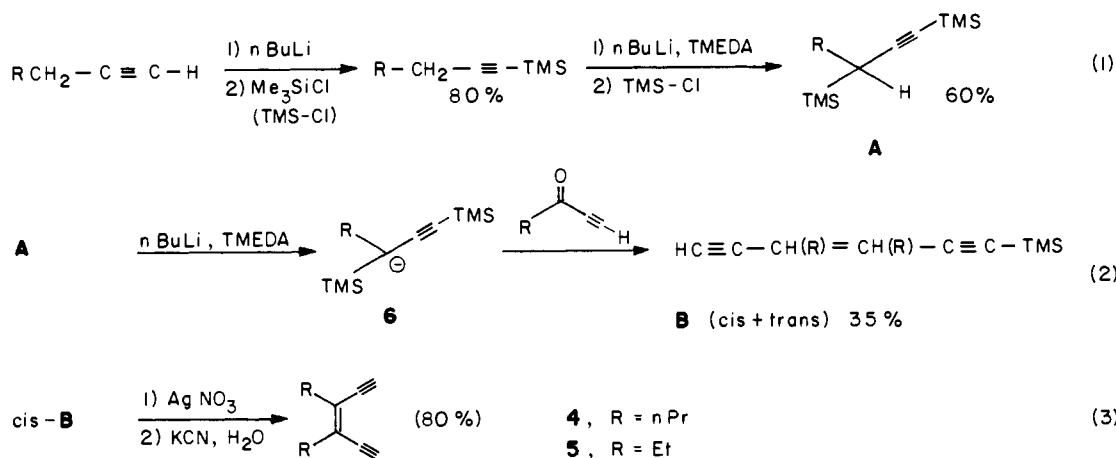
equilibration of hexa-1,5-diyn-3-ene **3a** and **3b**; when these molecules were heated in solution, aromatic products consistent

(1) For reviews, see: (a) Hoffman, R. W. "Dehydrobenzenes and Cycloalkynes"; Academic Press: New York, 1967. (b) Fields, E. K. In "Organic Reactive Intermediates"; McManus, S. P., Ed.; Academic Press: New York, 1973; pp 449-508. Levin, R. H. "Reactive Intermediates"; Jones, M.; Moss, R. A., Eds.; Wiley: New York, 1978; vol I.

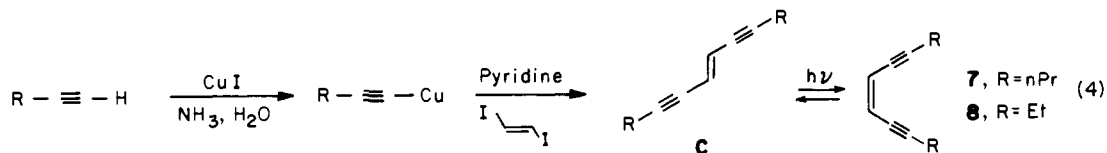
(2) (a) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. J. *Am. Chem. Soc.* **1973**, *95*, 6134. (b) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *Ibid.* **1975**, *97*, 6586.

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Scheme I



Scheme II



with the trapping of the 1,4-dehydrobenzene biradical were obtained.⁶ In a recent study performed in our laboratory,⁷ evidence for the conversion of a substituted 1,4-dehydrobenzene to the 1,3 isomer was observed in high-temperature gas-phase experiments. Both isomers appeared to demonstrate biradical reactivity. Observations by Chapman,⁸ Masamune,⁹ and Sondheimer¹⁰ and their co-workers on the reactions of polycyclic 1,4-dehydroaromatics also indicated biradical reactivity.

In contrast to the studies cited above, which implicate an "open" or biradical electronic structure of 1,4-dehydroaromatics, Breslow and co-workers^{11,12} have reported experiments which suggest that the bicyclic structure **2b** may exist at subambient temperatures. They performed a base-induced elimination of HCl from 1-chlorobicyclo[2.2.0]hexa-2,5-diene and obtained modest yields of a product apparently derived from Diels-Alder trapping of the intermediate butalene. A subsequent study¹³ indicated that the reaction was complex and that formation of products via the butalene intermediate may represent only one of several competing reaction pathways.

Two geometry-optimized theoretical treatments of the biradical/butalene energy surface have been made.^{16,17} In both cases

the biradical structure was predicted to be substantially lower in energy than the butalene isomer although butalene may lie in a shallow local energy minimum.

One of our goals has been to obtain kinetic evidence for the existence of a discrete 1,4-dehydrobenzene intermediate in the thermal reaction of diethynyl olefins. We were also interested in further characterizing the reactivity of the 1,4-dehydrobenzene intermediate produced in these reactions. There are several drawbacks, however, to the use of diethynyl olefin **3** as a thermal precursor of 1,4-dehydrobenzene. The yield of aromatic products in solution pyrolyses of **3** is generally quite low (<50%).⁶ In addition, the sensitivity of **3** toward air oxidation and rapid thermal polymerization (even at subambient temperatures) makes it rather inconvenient to work with. It was hoped that substitution of the diethynyl olefin framework would lead to improved stability at ambient temperature and to kinetic stabilization against adventitious side reactions during thermal reaction in solution. Ideally, the substituents should be ones that have an insignificant effect on the electronic structure of 1,4-dehydrobenzene.

In this paper we describe mechanistic investigations of the thermal reaction of two 3,4-dialkyl-substituted hexa-1,5-diyne-3-enes, **4**¹⁸ and **5**. These studies provide compelling evidence for the occurrence of true 1,4-dehydrobenzene intermediates on the pathways leading to products. Furthermore, the reactivity exhibited in unimolecular and bimolecular reactions, coupled with the observation of CIDNP in one of the reaction products, strongly indicates the biradical nature of the 1,4-dehydrobenzene intermediates at the temperatures involved in these reactions. Our efforts to obtain evidence pertaining to the spin state of the 1,4-dehydrobenzenes present in the solution reaction of hexa-1,5-diyne-3-enes is described elsewhere.¹⁹

Results and Discussion

Synthesis. Four diethynyl olefins were prepared in the course of the mechanistic investigations reported in this paper. Two contained alkyl substituents at both vinyl positions (**4**, **5**). The synthetic route to these compounds followed a general method previously employed in this laboratory (Scheme I).⁷ The key step

(3) (a) For experimental evidence for bicyclic 1,3-dehydrobenzene **1b** see: Washburn, W. N.; Zahler, R. *J. Am. Chem. Soc.* **1978**, *100*, 5873 and references therein. (b) Evidence for the biradical isomer **1a** is presented in Billups, W. E.; Buynak, J. D.; Butler, D. *J. Org. Chem.* **1979**, *44*, 4218.

(4) Fischer, I. P.; Lossing, F. P. *J. Am. Chem. Soc.* **1963**, *85*, 1018.

(5) Berry, R. S.; Clardy, J.; Schaefer, M. E. *Tetrahedron Lett.* **1965**, 1003.

(6) (a) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(b) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.

(7) Johnson, G. C.; Stofko, J. J.; Lockhart, T. P.; Brown, D. W.; Bergman, R. G. *J. Org. Chem.* **1979**, *44*, 4215.

(8) Chapman, O. L.; Chang, C. C.; Kolc, J. *J. Am. Chem. Soc.* **1976**, *98*, 5703.

(9) Darby, N.; Kim, C. U.; Salaun, J. A.; Shelton, K. W.; Takada, S.; Masamune, S. *J. Chem. Soc. D* **1971**, 1516.

(10) Wong, H. N. C.; Sondheimer, F. *Tetrahedron Lett.* **1980**, 217.

(11) Breslow, R.; Napierski, J.; Schmidt, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5906.

(12) Breslow, R.; Napierski, J.; Clarke, T. C. *J. Am. Chem. Soc.* **1975**, *97*, 6275.

(13) Breslow, R.; Khanna, P. L. *Tetrahedron Lett.* **1977**, 3429.

(14) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091. The [1.1.1] and [2.1.1] propellanes may also belong to this unhappy club; for a discussion see: Greenberg, A.; Liebman, J. F. "Organic Chemistry"; Academic Press: New York, 1978, Vol. 38, pp 344-351.

(15) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(16) Dewar, J. J. S.; Li, W.-K. *J. Am. Chem. Soc.* **1974**, *96*, 5569.

(17) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

(18) A preliminary description of the thermal chemistry (Z)-4,5-diethynyl-4-octene (**4**) has been published: Lockhart, T. P.; Mallon, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5976.

(19) Lockhart, T. P.; Bergman, R. G., *J. Am. Chem. Soc.*, following article in this issue.

Table I. Product Yields and Rate Constants in the Solution Pyrolysis of 4^a

run	T, °C	k _{obsd} , s ⁻¹	1,4-cyclohexadiene, M	absolute yield, ^b %				
				8	10	9	12	total (8-12)
1	196		0.0	20.3	36.9	20.8		78
2	196		0.4	10.1	8.9	5.4	48	71
3	196		10.6	~1.0	<1	<1	76	<79
4	166	1.3 × 10 ⁻³	0.0	13.5	38.5	20.0		72
5	156	6.9 × 10 ⁻⁴	0.0	11.8	35.8	17.2		65
6	145	2.9 × 10 ⁻⁴	0.0	9.8	37.3	17.6		65
7	132	9.3 × 10 ⁻⁵	0.0	7.9	38.5	16.4		63
8	156	7.1 × 10 ⁻⁴	0.19	8.7	13.5	8.7	27.6	58
9	156	6.4 × 10 ⁻⁴	0.38	5.2	6.7	3.1	47.4	62

^a [4] = 0.01 M. ^b Yields determined by digital integration of FID VPC trace and reference to an internal standard.

(eq 2) is an olefination reaction by the method of Pederson.²⁰ Anion 6 undergoes both addition to the carbonyl and acetylenic H abstraction; this led to only modest yields of the desired diethynyl olefins, which were produced in roughly a 40:60 ratio of cis and trans isomers. Separation of the isomers was conveniently effected by column chromatography on silica gel. Photolysis of the trans olefin in alkane solvents led to cis-trans isomerization. By this method the trans product of the olefination reaction was converted to a mixture (ca. 1:1) of the cis and trans isomers. Finally, removal of the acetylenic trimethylsilyl (Me₃Si) group was accomplished in high yield by the method of Arens and Schmidt (eq 3).²¹

We also required two compounds, 7 and 8, substituted at the acetylenic positions. Compounds of this type are most conveniently prepared by the coupling of copper acetylides²² with *trans*-1,2-diiodoethylene²³ (Scheme II). Photoisomerization of the trans isomer followed by column chromatography gave the desired cis isomer.

Although the diethynyl olefins obtained after chromatography on silica gel were >95% pure, before pyrolysis they were usually further purified by preparative gas chromatography. This method provided the diacetylenes in >99% purity. The neat diacetylenes could be handled briefly at room temperature in the air but yellow coloration appeared after several minutes under these conditions. When stored in solution (ca. 1-5% v/v), their lifetime was greatly improved, although temperatures of -60 °C were required to effectively eliminate discoloration due, presumably, to polymerization.

Thermal Reactions. Gas-phase experiments were performed by passing the diacetylenes through a heated quartz tube either under a stream of N₂ (1-atm pressure) or at reduced pressure. The products were collected on a cold finger at -196 °C. Solution reactions were carried out in sealed glass tubes. The concentration of the diacetylenes was usually 10⁻² M or less, and the samples were subjected to four freeze-pump-thaw cycles to remove oxygen.

Compound 4 was pyrolyzed in the gas phase and in a number of solvents. The thermal reaction of 4 in the gas phase (N₂ flow, 320 °C) produced a quantitative yield of three products: isomeric diyne 7, benzocyclooctene (9), and *o*-allyl-*n*-propylbenzene (10, Scheme III). The three products were isolated by preparative VPC and characterized by their NMR, IR, and high-resolution mass spectra.²⁴ The structure of 7 was confirmed by independent synthesis. When 7 was heated in the gas phase at 400 °C (N₂ flow, contact time ca. 1.5 min), greater than 95% conversion to 9 and 10 was observed.

We studied the thermal chemistry of 4 in solution so that we could obtain accurate kinetic data for its cyclization. Aromatic solvents were expected to be unreactive toward free radical hydrogen atom abstraction and, indeed, proved to be almost com-

Scheme III

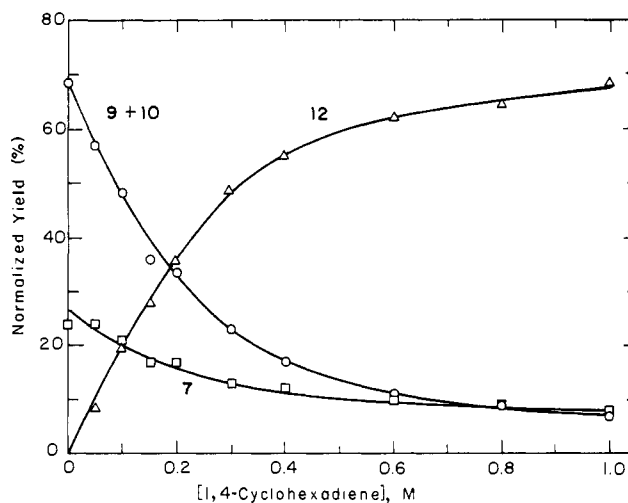
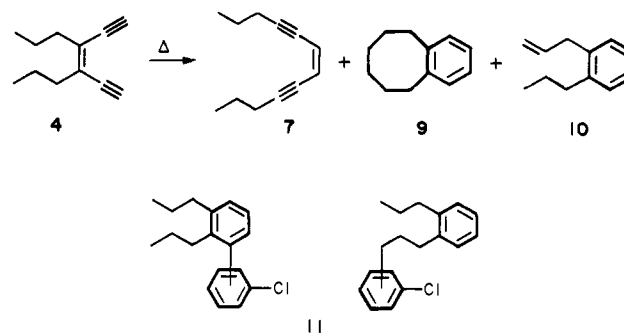


Figure 1. Plot of normalized product yields as a function of the amount of 1,4-cyclohexadiene in the reaction solution.

pletely inert toward the intermediates produced during the reaction of 4. Heating 4 at 196 °C for 15 min in diphenyl ether, chlorobenzene, or benzene led to complete conversion of the starting material to 7, 9, and 10 in high yield (Table I). At this temperature diacetylene 7 was quite stable and did not react detectably. In addition to unimolecular products, in chlorobenzene several isomeric compounds (total yield <5%) of empirical formula C₁₈H₂₁Cl were observed by VPC-mass spectroscopy (11). These compounds appear to be formed by addition of reactive intermediates to the solvent.

We also wanted to find a suitable trapping agent for the intermediate(s) produced in the reaction of 4. First we investigated the reaction of 4 with simple alkanes and alkylsubstituted aromatic solvents which, we reasoned, would effectively transfer hydrogen to biradical and radical intermediates. Unfortunately, the yield of tractable products was quite low (<40%) when these solvents were employed. The reacted solutions were badly discolored, suggesting the occurrence of competitive polymerization reactions. Subsequently, we found that the addition of a small amount (<15% by volume) of a better hydrogen atom donor to solutions

(20) Pederson, D. J. *J. Org. Chem.* **1968**, *33*, 780.

(21) Schmidt, H. M.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1141.

(22) Castro, C. E.; Gaughan, E. J.; Owsley, D. C. *J. Org. Chem.* **1966**, *31*, 4071.

(23) Ellis, C. P. *J. Chem. Soc.* **1934**, 726.

(24) Waugh, J. S.; Fessender, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846.

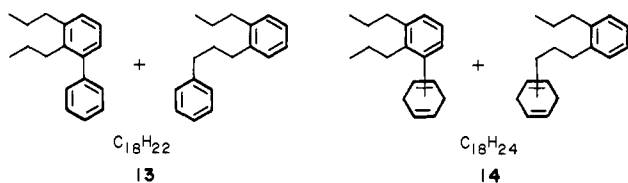
Table II. Product Yields in the Reaction of 5

run	phase	T, °C	absolute yield, ^a %					
			8 cis + trans	styrene	benzo-cyclobutene	<i>o</i> -ethylstyrene	tetralin	<i>o</i> -diethylbenzene
1	gas ^b	400	100	0	0	0	0	0
2	gas ^b	500	76.8	1.3	7.8	8.8	1.6	0
3	benzene solution ^c	195	51	0	0	0	0	5
4	benzene + 1,4-cyclohexadiene (1.1 M) ^c	195	6	0	0	0	0	75

^a Yields determined by digital integration of FID VPC trace and reference to internal standard. ^b N₂ flow. ^c [5] = 0.01 M.

of 4 in one of the inert solvents produced a high yield of products. Both 1,4-cyclohexadiene and 9,10-dihydroanthracene were effective as hydrogen donors; 1,4-cyclohexadiene was most convenient to use because of its solubility properties. In the presence of these trapping agents a new product, *o*-di-*n*-propylbenzene (12), was obtained in high yield. The yield of 12 increased with added trapping agent at the expense of the three unimolecular products (see Table I, runs 1–3, and Figure 1). Several higher molecular weight products (total yield roughly one fourth that of 12) were also observed in these pyrolyses. By VPC–mass spectroscopy these compounds were found to be isomers of molecular formula C₁₈H₂₂ (13) and C₁₈H₂₄ (14) and are believed to be aryl/cyclohexadienyl radical combination products (see discussion later). In addition, several products with the molecular formula C₁₂H₁₄ and C₁₂H₁₂ were formed in modest yield. These are believed to be dimers formed by the combination of cyclohexadienyl radicals.

When 2,2,5,5-tetradeuterio-1,4-cyclohexadiene was employed as the trapping agent, the 12 formed contained two deuteria per molecule. The yield of tractable products in this reaction, however, was substantially lower than when undeuterated cyclohexadiene was used. This is believed to reflect reduced reactivity of the deuterated trap toward the intermediate biradicals.²⁵ When cyclohexadiene-*d*₄ was employed as trapping agent the high molecular weight products formed, 13 and 14, contained two and



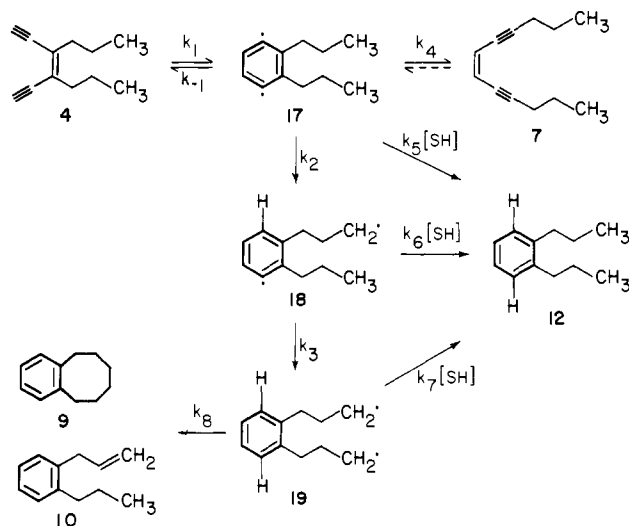
four deuteria per molecule, respectively, as determined by mass spectroscopy. As expected, the unimolecular products formed showed no incorporation of deuterium. The location of deuterium in 12 was determined in the following way: with use of the method of Werstiuk and Kadai²⁶ the aromatic deuteria were selectively exchanged for protons through acid catalysis. After the exchange was completed, 12 was examined by mass spectroscopy and the molecular ions (corresponding to zero, one, and two residual deuteria per molecule) were measured. The results indicate that, when 4 was heated in chlorobenzene with 1,4-cyclohexadiene-*d*₄ (0.8 M), 66% of the product 12 formed contained two aromatic deuteria, 33% contained one aromatic and one aliphatic deuteria, and about 1% of product 12 contained two aliphatic deuteria. The ramifications of this result are considered in the discussion section.

The kinetics of disappearance of 4 in chlorobenzene solution (10⁻² M) were measured both in the presence and absence of added cyclohexadiene (Table I). In chlorobenzene, linear first-order plots for three reaction half-lives were obtained at four temperatures spanning a range of 34 °C. Clean first-order kinetics were also observed for the reaction of 4 in 0.19 and 0.38 M solution of 1,4-cyclohexadiene with chlorobenzene solvent. In the presence of added trapping agent, the reaction rate was unchanged within experimental error (Table I, runs 5, 8, and 9).

(25) k_H/k_D may be determined by comparing the ratio of D:H found in 12 with the amount of residual hydrogen in the trapping agent (2.3%). This analysis gives an effective k_H/k_D of 4.3.

(26) Werstiuk, N. H.; Kadai, T. *Can. J. Chem.* 1973, 51, 1485.

Scheme IV



The thermal reactions of 5 and 8 in the gas phase were also investigated. At temperatures below 425 °C quantitative conversion of 5 to 8 was the only process observed. At higher temperatures additional unimolecular products appeared. The predominant products were *o*-ethylstyrene, tetralin, benzocyclobutene, and styrene (Table II). These products were also observed when 8 was allowed to react under similar conditions.

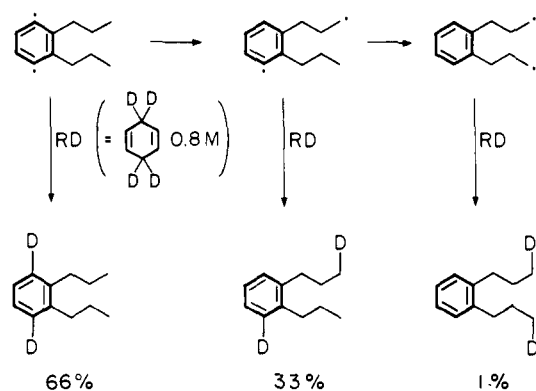
Thermal reaction of 5 in benzene solution (10⁻² M, see Table II) gave diacetylene isomer 8 plus a small amount of *o*-diethylbenzene, bibenzyl, and a product (15) of molecular formula C₁₆H₁₈ (VPC–mass spectroscopy). When 5 was heated at 190 °C in a solution of benzene-*d*₆, *o*-diethylbenzene containing deuterium in the ratio $d_0:d_1:d_2 = 3:3.4:1$ was formed, demonstrating that significant abstraction of deuterium from benzene took place. The bibenzyl produced was found to be fully deuterated and is believed to have been formed as a result of this reaction channel. The source of hydrogen is assumed to have been diacetylenes 5 and 8 and the protio reaction products.

Reaction of 5 in a benzene solution containing 1,4-cyclohexadiene gave greatly reduced yields of unimolecular products; *o*-diethylbenzene was obtained in good yield (Table II). Several high molecular weight products formed were detected by VPC–mass spectroscopy and have the molecular formula C₁₆H₂₀ (16).

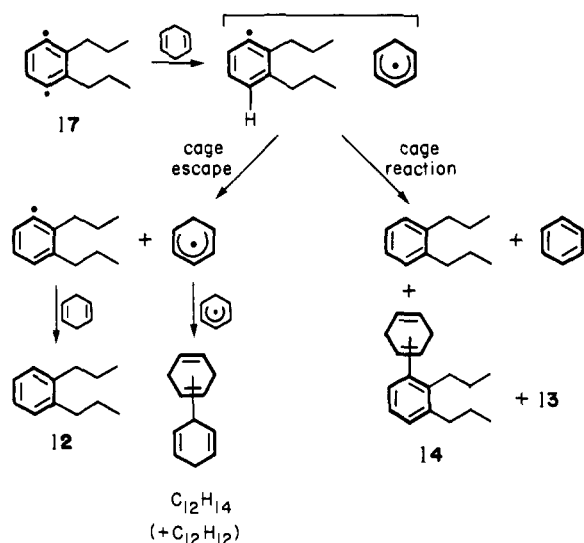
Proposed Mechanisms. To account for the results obtained in the thermolysis of 4, we propose the mechanism outlined in Scheme IV which involves initial ring closure of 4 to produce the 2,3-di-*n*-propyl-1,4-dehydrobenzene biradical 17. In the absence of trapping agent two unimolecular pathways are available to 17. Ring opening to form rearranged diacetylene 7 (or return to the starting compound) may take place in analogy with the results observed for the deuterium-labeled diacetylene 3a.⁶ Additionally, biradical 17 may transfer hydrogen from the terminus of a propyl group to the nearest aromatic radical site to produce biradical 18. This is expected to be a facile process since a kinetically favorable six-membered transition state is involved.²⁷ Further-

(27) Wilt, J. W. in "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 384.

Scheme V



Scheme VI

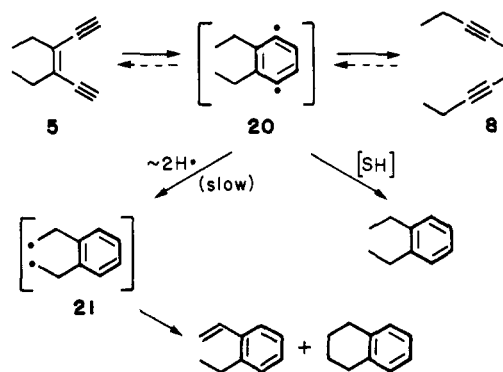


more, the heat of formation of biradical **18** is estimated to be about 12 kcal/mol less than that of **17**, the difference in strength of primary alkyl and aryl C-H bonds.²⁸ Ring closure in **18** to give a [3]metacyclophane is expected to be unfavorable as the smallest known [*n*]metacyclophane has a pentamethylene bridge (*n* = 5) and rearranges to indane at 150 °C.²⁹ Instead, a second intramolecular hydrogen transfer to produce biradical **19** may take place. Unimolecular products **9** and **10** argue very forcefully for the presence of **19** on the reaction pathway and strongly suggest the location of the radical sites at the termini of the *n*-propyl substituents. In fact, the failure to observe smaller ring benzocycles or *o*-propyl- β -methylstyrene argues against the occurrence of other intramolecular hydrogen-transfer modes (i.e., [1,4]) in **17** or **18**.

The presence of 1,4-cyclohexadiene in the reaction solution leads to the formation of **12** which may in principle come from trapping of any of the three biradical intermediates. The results of the deuterium-labeling study mentioned previously indicate that trapping occurs predominantly from biradicals **17** and **18** (Scheme V). Only 1% of **12** formed was found to contain two deuteria in the alkyl side chains when the pyrolysis solution was 0.8 M in cyclohexadiene-*d*₄.

The formation of high molecular weight products in the solution reaction of **4** is readily understood in terms of the proposed mechanism. Product **11** appears to have been formed from attack on the chlorobenzene solvent by intermediate biradicals **17** and **18**. By our mechanism (Scheme VI), transfer of hydrogen from

Scheme VII



cyclohexadiene to one of the biradical intermediates generates a radical pair; transfer of a second hydrogen within the solvent cage led to the **12** formed. Cage escape may also have led to the formation of cage-escaped cyclohexadienyl radicals appears to have been responsible for the formation of products with the molecular formula C₁₂H₁₄ and C₁₂H₁₂ (in the reaction with cyclohexadiene-*d*₄ these products have new molecular weights corresponding to C₁₂D₁₂ and C₁₂D₁₄). Cage combination of the radical pair may be responsible for the several isomers with the formula C₁₈H₂₄ (**14**) found. Hydrogen loss from some of these combination products (either under the reaction conditions or in the mass spectrometer) accounts for the formation of products of formula C₁₈H₂₂ (**13**) observed. Supporting the identification of **13** and **14** are the observations that (1) these compounds only appeared in reaction solutions containing cyclohexadiene, (2) the yields of **13** and **14** were directly related to the yield of trapping product **12**, (3) mass spectral fragmentation gives large peaks due to the phenyl cation, cyclohexadienyl radical cation, and dipropylbenzene cation (C₁₂H₁₈), and (4) when cyclohexadiene-*d*₄ was used, **13** was formed containing two deuteria per molecule, **14** with four deuteria per molecule.

It is informative to consider here the results of the thermal reactions of diacetylenes **5** and **8** (Table II). The products obtained in the gas phase and in solution pyrolyses in benzene suggest the mechanism presented in Scheme VII. Intermediate **20** appears to undergo intramolecular [1,4] hydrogen transfer slowly relative to ring opening to diacetylene **5** or **8**. Thus, **5** may be converted quantitatively to **8** in the gas phase (400 °C) without appreciable intramolecular trapping of the 1,4-dehydrobenzene intermediate. Only at much higher temperatures (ca. 500 °C), where **8** is repeatedly converted to **20**, were products of intramolecular hydrogen transfer found.³⁰

In intramolecular solution **5** was similarly converted to **8**. No intramolecular hydrogen transfer was observed, though in the presence of added cyclohexadiene the 1,4-dehydrobenzene intermediate was efficiently trapped to give *o*-diethylbenzene. At the temperatures employed in the solution studies, the rearrangement of **20** to **8** is essentially irreversible. Each molecule of **5**, therefore, can generate **20** only a single time in the course of this reaction. Our failure to detect even trace amounts of tetralin or *o*-ethylstyrene indicates that the rate of [1,4] hydrogen transfer must be several orders of magnitude slower than ring opening to **8**.

We may reasonably assume that the rate of rearrangement of **20** to **8** is comparable to that of **17** rearranging to **7**. This provides a reasonable explanation for the failure to detect [1,4] hydrogen transfer in **17**, where [1,5] transfer is faster than ring opening to **7**.

Kinetic Studies. In accord with the mechanism presented in Scheme IV, the disappearance of **4** shows first-order kinetics. From the rate data measured over a 34 °C range, activation parameters can be determined from an Arrhenius plot (Figure

(28) Benson, W. S. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; Table A.22, p 309.

(29) van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* 1977, 4667. See also: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: San Francisco, 1978; p 160.

(30) The mechanism of formation of benzoecyclobutene and styrene are uncertain. Pathways from biradicals **20** and **21** (possibly via 1,3-dehydrobenzenes) may be imagined.

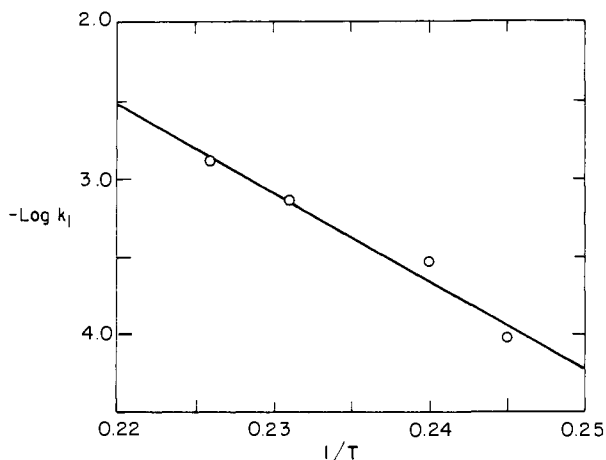


Figure 2. Arrhenius plot of unimolecular rate constants observed in the reaction of **4** (0.01 M) in chlorobenzene.

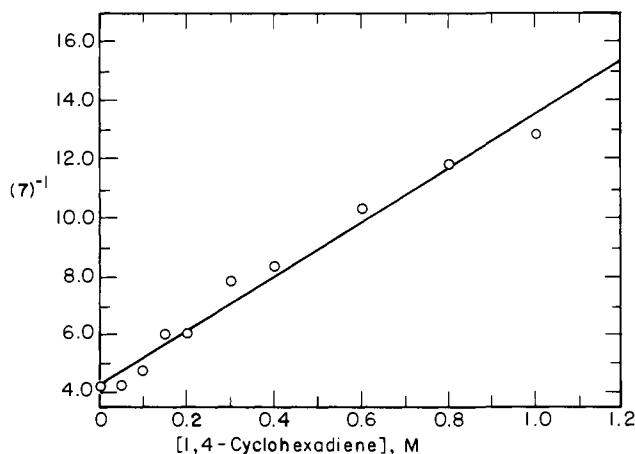


Figure 3. Plot of (normalized yield of **7**)⁻¹ vs. concentration of 1,4-cyclohexadiene: concentration of **4** = 0.01 M; *T* = 190 °C.

2): $E_a = 27.4 \pm 0.5$ kcal/mol; $\log A = 10.8 \pm 0.3$ s⁻¹.

If the return of 1,4-dehydrobenzene **17** to **4** (k_{-1}) is slow with respect to the other reaction rates (k_4 , k_2 , $k_5[\text{SH}]$), these Arrhenius parameters are associated with the simple first cyclization step (k_1) in Scheme IV. If this is the case, the disappearance of **4** will be independent of the presence of cyclohexadiene in the reaction solution, but the product distribution will be dependent on the cyclohexadiene concentration when $k_5[\text{SH}]$ is of comparable magnitude to the unimolecular reaction rates. In agreement with this hypothesis, the rate constants for disappearance of **4** obtained when 0.19 and 0.38 M added 1,4-cyclohexadiene was heated with **4** at 156 °C are, within experimental error, identical with that obtained in the absence of trapping agent (Table I, runs 5, 8, and 9). As predicted by our mechanism, while the rate of reaction of **4** was unchanged, the increase in cyclohexadiene concentration changed the yield of **12** from 0 to 47%.

The mechanism in Scheme IV makes several other specific predictions about the dependence of product yields on the concentration of trapping agent in the reaction solution. Application of the steady-state approximation to the concentration of **17** gives eq 5, which predicts that the yield of **7** will be inversely proportional to the concentration of 1,4-cyclohexadiene. The experi-

$$(\text{normalized yield of } \mathbf{7})^{-1} = 1 + \frac{k_2}{k_4} + \frac{k_5[\text{SH}]}{k_4} \quad (5)$$

mental data are plotted in Figure 3 and show good agreement with the mechanism proposed.

The absolute yields of the unimolecular products **7**, **9**, and **10** are strongly dependent on the concentration of trapping agent (Figure 1). The yields of **9** and **10** show a more pronounced decrease upon the addition of cyclohexadiene than does the yield

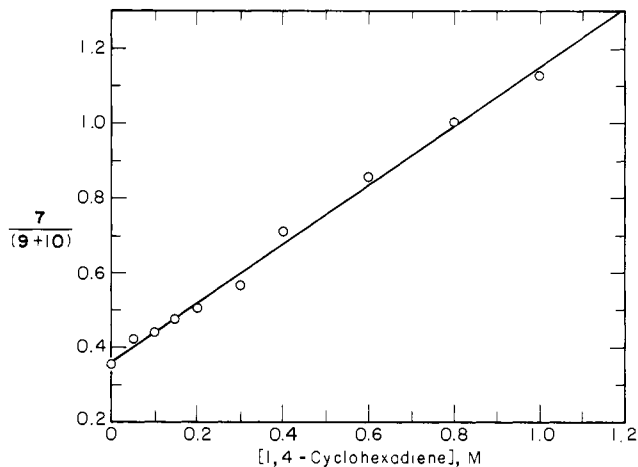


Figure 4. Plot of the ratio of the observed yields of **7**/(**9** + **10**) as a function of 1,4-cyclohexadiene concentration: concentration of **4** = 0.01 M; *T* = 190 °C.

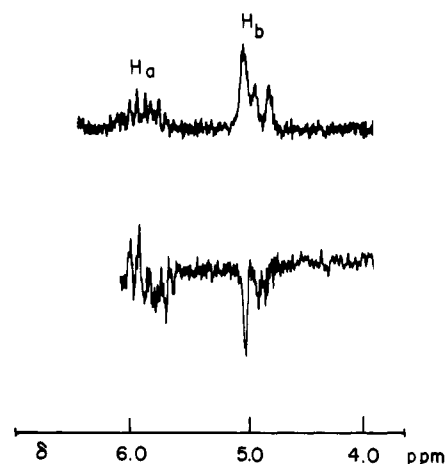


Figure 5. The upper spectrum (90 MHz, ¹H) shows the vinyl region of a purified sample of *o*-allyl-*n*-propylbenzene recorded at 30 °C. The lower spectrum shows the emissive signals observed during reaction of **4** at 160 °C in a 90-MHz NMR probe. The signals appearing in absorption on the left side of the lower spectrum are spinning side bands of the solvent (*o*-dibromobenzene).

of **7** (the ratio **9**/**10**, however, remains constant). We may explain the nature of this dependence with the proposed mechanism if we make use of the following simplifying assumption: from experiments with cyclohexadiene-*d*₄ we know that a negligible amount of **12** arises from trapping of biradical **19**. Therefore, $d[\mathbf{9} + \mathbf{10}]/dt \approx k_3[\mathbf{18}]$. Equation 7 follows from eq 6 by application of the steady-state approximation to intermediates **17** and **18**.

$$\frac{\text{yield of } \mathbf{7}}{\text{yield of } \mathbf{9} + \mathbf{10}} = \frac{k_4}{k_3} \quad (6)$$

$$\frac{\text{yield of } \mathbf{7}}{\text{yield of } \mathbf{9} + \mathbf{10}} = \frac{k_4}{k_2} + \frac{k_4 k_6 [\text{SH}]}{k_2 k_3} \quad (7)$$

Equation 7 relates the ratio of **7** to **9** and **10** as a function of added cyclohexadiene. The linear plot obtained by applying this function to the experimental data (Figure 4) confirms the existence of a second intermediate which undergoes trapping with cyclohexadiene (in agreement with the cyclohexadiene-*d*₄ experiments). The intercept of that plot gives the value of k_4/k_2 as 2.0 M⁻¹. Since the intercept of the line agrees with the ratio of unimolecular products observed in the absence of trapping agent (0.35), the presence of cyclohexadiene does not significantly affect the reaction rates at the concentrations studied.

CIDNP. When a solution of **4** in *o*-dibromobenzene or diphenyl ether was heated at 160 °C in the probe of an NMR spectrometer,

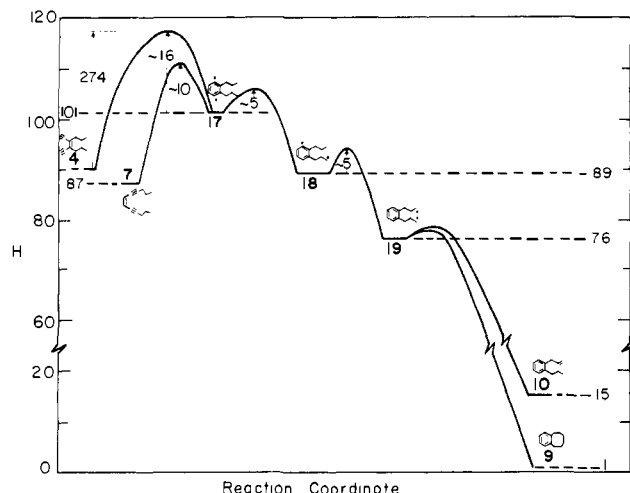


Figure 6. Enthalpy diagram for the reaction of **4** (all units in kilocalories per mole).

several emissive signals were observed (Figure 5). These signals are assigned to the vinyl protons and, tentatively, to the alkyl protons (terminal methyl and methylene) in polarized **10**. The observation that only polarization of the hydrogens at the two end carbons of the propyl and propenyl chains occurred and that all enhancements were emissive strongly implicate biradical **19** as the polarizing species. Thus, although 1,4-cyclohexadiene is not sufficiently reactive to trap biradical **19** to an appreciable extent, CIDNP provides evidence for the presence of that intermediate.³¹

Estimated Absolute Rate Constants and Reaction Energetics. It is possible to estimate the absolute rate constants and activation energies for the reaction steps in Scheme IV. A reasonable model for cyclohexadiene trapping of **17** is the rate constant for abstraction of hydrogen from diphenylmethane by phenyl radicals (estimated to be $7.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 60°C).³² The unimolecular rate constants k_2 , k_3 , and k_4 also are expected to be of this order of magnitude at 60°C ; k_8 must be at least 1 or 2 orders of magnitude faster (vide supra).

A marked dependence of the ratio $7/(9 + 10)$ on the reaction temperature is observed (Table I, runs 1, 4, 5, 6, and 7). This is convincing evidence that at least one of the intramolecular processes leading from **17** is activated. The difference in activation energies and A factors of the steps involving k_4 and k_2 can be obtained by a plot of $\ln [7/(9 + 10)]$ vs. $1/T$ (eq 8). A linear

$$\ln \frac{[7]}{[9] + [10]} = \ln \frac{A_2}{A_4} + \frac{E_4 - E_2}{RT} \quad (8)$$

relationship is observed over a range of 64°C (Figure 6); from the slope of the line the difference in activation energies $E_4(k_4) - E_2(k_2)$ was found to be $5.2 \pm 0.4 \text{ kcal/mol}$. The ratio $A_4(k_4)/A_2(k_2)$ was determined from the intercept to be 10^2 . The E_a for [1,5] hydrogen transfer in **17** should be similar to that for the exothermic [1,5] hydrogen transfer observed in the 2,2-dimethylpentoxyl radical ($E_a \approx 5.0 \text{ kcal/mol}$).³³ The conversion of **17** to **7** therefore has an E_a of about 10 kcal/mol . The absolute magnitude of the A factor for the rearrangement of **17** to **18** may be of similar magnitude to that of the rearrangement of the 2,2-dimethylpentoxyl radical ($10^{11.5} \text{ s}^{-1}$). This seems reasonable since $A(k_4)$ is consequently predicted to be $10^{13.5} \text{ s}^{-1}$, an appropriate magnitude for the ring opening reaction. Thus at 200°C **17** is a discrete intermediate, but it has a lifetime of only ca. 10^{-9} s .³⁴

(31) Kaptein, R. *Adv. Free-Radical Chem.* **1975**, *5*, 338.

(32) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 2.

(33) Reference 32, p 94.

(34) The short lifetime predicted by this analysis stands in contrast to the lifetime of the species (assigned as 1,4-dehydrobenzene) produced by Berry, Clardy, and Schaefer on photodecomposition of 1,4-benzenediazonium carboxylate.⁵ Their failure to detect 1,5-hexadiene-3-ene as a decomposition product further suggests that 1,4-dehydrobenzene was not, in fact, generated in their system.

Surprisingly, perhaps, a small temperature dependence was also observed on the relative yields of **9** and **10**. Treatment of the yield of **9** vs. **10** as in eq 8 gives a linear plot from which the difference in the activation energies leading to **9** and **10** is found to be 1.6 kcal/mol , favoring rearrangement to **10**. The ratio of the frequency factors favors rearrangement to **9** by a factor of 3. The absolute magnitudes of the activation energies for ring closure and disproportionation of biradical **19** are expected to be very close to zero and certainly less than 5 kcal/mol . We may combine the activation energies estimated above with group additivity estimates of the heats of formation²⁸ of the discrete molecular species in Scheme IV to produce the energy surface for the reaction of **4** shown in Figure 6.³⁵

Conclusions

We have presented observations that constitute strong support for the intermediacy of 1,4-dehydrobenzene biradicals in the thermal reactions of diethynyl olefins. We have also elucidated several unimolecular and bimolecular reaction pathways of 2,3-dialkyl-1,4-dehydrobenzenes and have obtained information about the relative rates of these fast reactions.

In relating the data obtained for **17** to the parent 1,4-dehydrobenzene (**2**), it seems reasonable to postulate that 1,4-dehydrobenzene lies in an energy minimum as does **17**. The absence of an intramolecular hydrogen-transfer pathway such as that available to **17** should make the fastest reaction channel available to 1,4-dehydrobenzene the ring opening back to diacetylene **3**. The barrier to ring opening is likely to be within the range observed for opening of **17** to **4** and **7** (ca. 10 and 16 kcal/mol , respectively) and $\log A$ is probably on the order of 13.

A final question that needs to be addressed is whether or not the data presented here rule out the possibility that the lowest energy state of 1,4-dehydrobenzene may correspond to the bicyclic butalene structure.¹¹⁻¹³ While the reactivity demonstrated by the 1,4-dehydrobenzene intermediate **17** is clearly that of a biradical and several theoretical treatments predict the bicyclic structure to be substantially higher in energy than the "open" or biradical form, the possibility that a bicyclic ground state may be in equilibrium with the biradical or that the reactivity of butalene may be identical with the reactivity expected of the 1,4-biradical cannot be rigorously ruled out.

Experimental Section

General Data. Pyridine was distilled from CaH_2 after being heated at reflux for several hours. Dry diethyl ether was obtained from a commercial source (Mallinckrodt, anhydrous) and was used fresh from the container without further purification or drying. Absolute ethanol was also commercially available and was used without further purification. Reagent grade petroleum ether (bp $35\text{--}60^\circ \text{C}$) was purified by passing it through a column of activity I alumina. Pyrolysis solvents were purified by repeated fractional distillation through a glass helices packed column until only trace amounts of impurities ($<0.1\%$) were detected by analytical VPC. IR spectra were obtained on a Perkin-Elmer Model 237 or Model 257 grating spectrophotometer. ^1H NMR spectra were recorded by an EM-390 spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. High-resolution mass spectra (HRMS) were obtained on an AEI-MS12 spectrometer. VPC-mass spectral (VPC-MS) analyses were carried out by using a Finnigan 4000 GC-mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry, University of California, Berkeley, CA. Melting and boiling points are reported uncorrected. Preparative VPC was performed on a Varian 90P instrument. Analytical VPC was conducted on either a Perkin-Elmer 3920 or a Perkin-Elmer Sigma 3 chromatograph. Both were equipped with flame ionization detectors (FID) and were interfaced with a Spectra Physics Autolab System 1 computing integrator. The VPC columns used in the work reported here were the following: for preparative VPC Column A, $10 \text{ ft} \times 1/4 \text{ in.}$ glass 10% SF-96 on 60/80 Chrom W; Column B, $12 \text{ ft} \times 1/4 \text{ in.}$ glass 10% SE-30 on 60/80 Chrom W-AW/DMCS; for analytical VPC, Column C, $9 \text{ ft} \times 1/8 \text{ in.}$ stainless steel 10% SF-96 on 100/120 Chrom W-AW/DMCS; for VPC-MS analyses, 30-m glass capillary SP2100 wall-coated open tubular (WCOT) column.

(35) The heat of formation of the 1,4-dehydroaromatic was taken to be that of *o*-*d*-*n*-propylbenzene less the bond energy in a molecule of H_2 .

Gas-phase pyrolyses were performed with a Hoskins Manufacturing Co. Type FD 303A Electric Furnace. The pyrolysis tube was made of quartz tubing 35 cm in length \times 12 mm in diameter and was fitted with 14/20 outer joints on the end. Flow pyrolyses were performed by passing a stream of N_2 gas over a magnetically stirred sample of the material to be heated; after going through the heated quartz tube the gas flow passed through a liquid N_2 cooled trap and finally through a meter with which the flow rate was determined. Vacuum pyrolyses were performed with the same apparatus except that a vacuum (regulated by a manostat) was applied after the cold trap. Because of low volatility, the compounds studied were usually heated gently in order to increase their vapor pressure.

Solution pyrolyses were performed in the following way: the diethynyl olefins were isolated >99% pure by preparative VPC and promptly dissolved in the pyrolysis solvent in order to prevent discoloration due to polymerization. The solutions were syringed into hexamethyldisilazane treated glass tubes fitted with 14/20 female joints. After four freeze-pump-thaw cycles (to 0.02 torr) the tubes were sealed under vacuum. Samples for the CIDNP experiment were prepared in the same way except that NMR tubes fitted with 14/20 female joints were used, and the hexamethyldisilazane treatment was eliminated. Solutions were allowed to react by submersing them in an oil bath heated to the desired temperature. The concentration of the diacetylenes was determined by comparing the integrated peak area observed by FID-equipped VPC with the area of a known amount of an internal standard which had been added to the solution. The internal standards were *n*-alkanes of carbon number similar to the starting diacetylene. The error in the diacetylene concentration estimated by this method is expected to be small. The yield of unimolecular products was determined by using the assumption that the response factors of compounds of the same molecular formula are equal.³⁶ The yield of higher molecular weight products was estimated by assuming that the response factors of these hydrocarbons, relative to those of the unimolecular products, was proportional to the number of carbon atoms in each.³⁶

Samples for kinetic experiments were prepared in the same manner. The reaction temperature was controlled by submersing the reaction tubes in a vigorously refluxing solvent (e.g., bromobenzene, bp 156 °C). Care was taken to minimize the contact of the sample tube with the walls of the solvent flask since this could have introduced an error into the reaction temperature. Data points were derived from the mean value of three VPC analyses of each sample.

Syntheses. The synthetic schemes employed in the preparation of the pairs of diacetylenes **4** and **5**, and **7** and **8**, were identical. Procedures are described in detail for the syntheses leading to **4** and **7**. Only the properties of the corresponding intermediates leading to **5** and **8** are given.

Propyl Ethynyl Ketone and Ethyl Ethynyl Ketone. These compounds were prepared by the method of Jones et al.³⁷ Propyl ethynyl ketone: bp 52–53 °C (45 torr) (lit.³⁷ bp 65–66 °C (100 torr); ¹H NMR (CDCl₃) δ 0.95 (t, 3 H, *J* = 7 Hz), 1.67 (sextet, 2 H, *J* = 7 Hz), 2.52 (t, 2 H, *J* = 7 Hz), 3.20 (s, 1 H). Ethyl ethynyl ketone (a strong lachrymator and sternutator) was isolated in 58% yield: bp 108–110 °C (1 atm); ¹H NMR (CDCl₃) δ 1.12 (t, 3 H, *J* = 8 Hz), 2.56 (q, 2 H, *J* = 8), 3.15 (s, 1 H); IR (thin film) 3260 (acetylenic C–H stretch), 2790–2990 (alkyl C–H stretch), 2090 (C–C triple bond stretch), 1690 cm⁻¹ (carbonyl). This compound was too easily air oxidized to allow satisfactory elemental analysis; the HRMS, however, was obtained: molecular weight calcd for C₅H₆O, 82.0419; found, 82.0422.

1-(Trimethylsilyl)hexyne. To an oven-dried 1-L three-neck flask fitted with two addition funnels, a condenser cooled to 5 °C, and an N_2 inlet was added 500 mL of anhydrous ethyl ether and 1-hexyne (30 g, 0.37 mol). The solution was cooled to –20 °C under an atmosphere of N_2 and stirred rapidly with a magnetic stirring bar. A 165-mL sample of a 2.42 M (0.40 mol) hexane solution of *n*-BuLi was added over 1 h. After addition the solution was allowed to warm to room temperature over 1 h. A white precipitate (the alkynyl lithium salt) rapidly formed. The solution was cooled to –20 °C, and trimethylsilyl chloride (45.7 g, 0.42 mol) was added over 20 min. Reaction was complete after the solution was stirred at room temperature for 4 h. The reaction was worked up by pouring 400 mL of H₂O into the flask and then separating the mixture. The aqueous phase was washed with 250 mL of ethyl ether. The combined organic phases were washed with 150 mL of H₂O and then dried over Na₂SO₄. The ethyl ether solution was concentrated on a rotary evaporator, and the product was isolated by fractional distillation through a Ta wire column. The product was obtained as a colorless

liquid, bp 70–71 °C (35 torr): isolated yield, 44.1 g, 77% (99% pure by VPC analysis). The NMR and boiling point agreed with those reported in the literature.³⁸

1-(Trimethylsilyl)pentyne. The isolated yield (see preceding preparation) was 38 g, 74% (96% pure by VPC): bp 55–57 °C (35 torr). The physical properties agreed with those reported in the literature.³⁹

1,3-Bis(trimethylsilyl)hexyne. An oven-dried 500-mL three-neck flask was fitted with two addition funnels and an N_2 inlet. A 200-mL sample of anhydrous ethyl ether and 15.4 g (0.10 mol) of 1-(trimethylsilyl)hexyne were added, and the solution was stirred magnetically at –20 °C under an N_2 atmosphere. *n*-BuLi (45 mL of a 2.42 M hexane solution, 0.11 mol) was added over 15 min followed by TMEDA (11.6 g, 0.10 mol). The solution was stirred for 2 h at –20 °C and then for 1 h at 10 °C. After the solution was cooled to –20 °C again, trimethylsilyl chloride (12.0 g, 0.11 mol) was added over 15 min. A white precipitate (LiCl) formed immediately. The reaction solution was stirred for 1 h at –20 °C and then warmed to room temperature for 1 h. To work up the reaction, 100 mL of H₂O was added and the mixture separated. The aqueous phase was washed with 100 mL of ethyl ether. The combined organic phases were washed with 100 mL of H₂O and then dried over Na₂SO₄. After the product solution was concentrated on a rotary evaporator, the products were distilled through a Ta wire column (isolated yield, 57% (>95% pure)). The product was a colorless liquid but developed a pink color on short exposure to air at room temperature; bp 92–97 °C (20 torr); ¹H NMR (CDCl₃) δ 0.09 (s, 9 H), 0.14 (s, 9 H), 0.88 (t, 3 H, *J* = 7 Hz), 1.82–1.18 (m, 5 H); IR (thin film) 2950, 2150, 1460, 1400, 1250, 1055, 960, 835, 760 cm⁻¹; HRMS calcd for C₁₂H₂₆Si₂ 226.1573, found 226.1578.

1,3-Bis(trimethylsilyl)pentyne was prepared by the method described above for the hexynyl isomer. The product was a colorless liquid (bp 86–90 °C (30 torr)) which rapidly turned pink on exposure to air at room temperature: isolated yield, 18 g, 62% (>95% pure by VPC analysis). Preparative VPC gave samples of high purity for the following analyses: ¹H NMR (CDCl₃) δ 0.10 (s, 9 H), 0.16 (s, 9 H), 1.05 (t, 3 H, *J* = 6 Hz), 1.23–1.68 (m, 3 H); IR (thin film) 2980, 2943, 2920, 2168, 1258, 1075, 1034, 990, 904, 850, 763, 702, 640, 618 cm⁻¹; HRMS calcd for C₁₁H₂₄Si₂ 212.1416, found 212.1419.

(E)- and (Z)-4-Ethynyl-5-((trimethylsilyl)ethynyl)-4-octene. To an oven-dried 100-mL round-bottom flask capped with a rubber septum and flushed with N_2 was added 25 mL of anhydrous ethyl ether and 1,3-bis(trimethylsilyl)hexyne (3.0 g, 13 mmol). With rapid magnetic stirring at –20 °C, *n*-BuLi (5.2 mL of a 2.4 M hexane solution, 13 mmol) was added over 10 min followed by TMEDA (1.5 g, 13 mmol). After stirring for 2 h, the solution was cooled to –70 °C and propyl ethynyl ketone (1.25 g, 13 mmol) was added in less than 3 s (in order to minimize abstraction of the acetylenic hydrogen). The solution was slowly warmed to room temperature over 2 h and then stirred for an additional 1 h. The reaction solution was poured into 40 mL of an aqueous solution of NH₄Cl, and then the organics were separated and washed two times with 40 mL of H₂O. The organics were dried over Na₂SO₄ and then passed through 5 g of silica gel to remove polymeric materials. Concentration on a rotary evaporator gave a light brown oil. Chromatography on 80 g of silica gel using petroleum ether eluant gave satisfactory separation of the reaction products. **(Z)-4-Ethynyl-5-((trimethylsilyl)ethynyl)-4-octene:** isolated yield, 0.61 g, 22% (>98% pure determined by VPC analysis); ¹H NMR (DCCl₃) δ 0.16 (s, 9 H), 0.87 (t, 6 H, *J* = 7 Hz), 1.43 (quintet, 4 H, *J* = 7 Hz), 2.12 (t, 4 H, *J* = 7 Hz), 3.13 (s, 1 H); IR (thin film) 3315, 3283, 2960, 2932, 2875, 2140, 1460, 1248, 870, 840, 756 cm⁻¹. Anal. Calcd for C₁₅H₂₄Si: C, 77.54; H, 10.41. Found: C, 77.72; H, 10.34. **(E)-4-Ethynyl-5-((trimethylsilyl)ethynyl)-4-octene:** isolated yield, 0.50 g, 15%; ¹H NMR (CDCl₃) δ 0.16 (s, 9 H), 0.85 (t, 6 H, *J* = 7 Hz), 1.46 (quintet, 4 H, *J* = 7 Hz), 2.30 (t, 4 H, *J* = 7), 3.30 (s, 1 H); IR (thin film) 3315, 2962, 2932, 2876, 2138, 1460, 1250, 1167, 964, 872, 840, 756 cm⁻¹. Attempts to obtain an elemental analysis of this compound were unsatisfactory due to decomposition of the sample during handling. HRMS: calcd for C₁₅H₂₄Si, 232.1647; found, 232.1648.

(E)- and (Z)-1-(Trimethylsilyl)-2,3-diethylhexa-1,5-diyne-3-ene. These compounds were prepared by the procedure described immediately above. **(Z)-1-(Trimethylsilyl)hexa-2,3-diethyl-1,5-diyne-3-ene:** isolated yield, 1.23 g 17%; ¹H NMR (CDCl₃) δ 0.21 (s, 9 H), 1.07 (t, 6 H, *J* = 7), 2.19 (quartet, 4 H, *J* = 7 Hz), 3.12 (s, 1 H); IR (thin film) 3320, 3295, 2980, 2944, 2880, 2140, 1468, 1546, 1251, 1161, 1048, 984, 958, 905, 842, 759 cm⁻¹; HRMS calcd for C₁₃H₂₀Si 204.1334, found, 204.1335. **(E)-1-(Trimethylsilyl)-2,3-diethylhexa-1,5-diyne-3-ene:** isolated yield, 0.6 g, 9%; ¹H NMR (CDCl₃) δ 0.21 (s, 9 H), 1.07 (t, 6 H, *J* = 6 Hz), 2.36 (quartet, 4 H, *J* = 6 Hz), 3.32 (s, 4 H); IR (thin film) 3320, 2980, 2942, 2880,

(36) Walker, J. Q.; Jackson, M. T.; Maynard, J. B. "Chromatographic Systems;" Academic Press: New York, 1972; p 161.

(37) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* 1946, 39.

(38) Skinner, D. L.; Peterson, D. J.; Logan, T. J. *J. Org. Chem.* 1967, 32, 1033.

(39) Boekman, R. K.; Blum, D. M. *J. Org. Chem.* 1974, 39, 3307.

2135, 1466, 1255, 987, 894, 850, 759 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{Si}$ 204.1334, found 204.1335.

(*Z*)-4,5-Diethynyl-4-octene (**4**). This compound was prepared from (*Z*)-4-ethynyl-5-(trimethylsilyl)ethynyl-4-octene in 81% yield by the method of Arens and Schmidt.²¹ The reaction products were passed through a short column of silica gel after workup, and 0.41 g of **4** was obtained >98% pure (determined by VPC analysis). **4** was a clear liquid which discolored rapidly upon standing at room temperature: ^1H NMR (CDCl_3) δ 0.80 (t, 6 H, $J = 7$ Hz), 1.42 (sextet, 4 H, $J = 7$ Hz), 2.06 (t, 4 H, $J = 7$ Hz), 3.05 (s, 2 H); IR (thin film) 3316, 3292, 2964, 2938, 2878, 2097, 1460, 1380, 1250, 1110, 1090, 842, 792, 736 cm^{-1} . The sensitivity of **4** to air and thermal decomposition resulted in an unsatisfactory elemental analysis. HRMS: calcd for $\text{C}_{12}\text{H}_{16}$, 160.1252; found, 160.1253.

(*Z*)-2,3-Diethylhexa-1,5-diyne-3-ene (**5**) was prepared by the method used for **4** above: ^1H NMR (CDCl_3) δ 1.11 (t, 6 H, $J = 8$ Hz), 2.22 (quartet, 4 H, $J = 8$ Hz), 3.17 (s, 2 H); IR (thin film) 3292, 2980, 2943, 2882, 2097, 1466, 1380, 1250, 1055, 952, 887, 630 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{12}$ 132.0939, found, 132.0939.

(*E*)-Dodeca-4,8-diyne-6-ene and (*E*)-Deca-3,7-diyne-5-ene. The procedure reported by Ukhin and co-workers for the preparation of (*E*)-1,6-diphenylhexa-1,5-diyne-3-ene, except for the workup, was employed.⁴⁰ The workup was changed as follows: the reaction solution was cooled to room temperature and filtered to remove the copper salts. The solids were washed with petroleum ether, and the combined organic solutions were washed twice with aqueous 10% HCl and once with H_2O . After being dried over Na_2SO_4 , the solution was concentrated on a rotary evaporator to produce a brown oil. The oil was chromatographed on silica gel by using petroleum ether as eluant, and the desired product was obtained in >95% purity. Both diacetylenes crystallized from petroleum ether solution at -20°C and could be further purified by drawing off the supernatant liquid with a pipet. (*E*)-Dodeca-4,8-diyne-6-ene: isolated yield, 75%; ^1H NMR (CDCl_3) δ 0.98 (t, 6 H, $J = 7$ Hz), 1.54 (sextet, 4 H, $J = 7$ Hz), 2.31 (t, 4 H, $J = 7$ Hz), 5.87 (s, 2 H); IR (thin film) 3035, 2962, 2936, 2875, 2817, 2220, 1753, 1460, 1428, 1380, 1338, 1327, 1278, 935 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{12}$: C, 89.93; H, 10.07. Found: C, 89.84; H, 9.99. (*E*)-Deca-3,7-diyne-5-ene: isolated yield, 71%; ^1H NMR (CCl_4) δ 1.13 (t, 6 H, $J = 8$ Hz), 2.28 (quartet, 4 H, $J = 8$ Hz), 5.70 (s, 2 H); IR (thin film) 3030, 2980, 2940, 2910, 2878, 2842, 2220, 1455, 1435, 1320, 1185, 1060, 938 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{12}$ 132.0939, found 132.0938.

2,2,5,5-Tetradeuterio-1,4-cyclohexadiene. 1,4-Cyclohexadiene- d_4 was prepared by base-catalyzed exchange of the allylic protons for deuterium by treatment with the dimsyl- d_5 anion in $\text{Me}_2\text{SO}-d_6$: to oil-free⁴¹ NaH (24 mmol) was added dry $\text{Me}_2\text{SO}-d_6$ (Merck and Co., 99.5% D, 0.29 mol) in a flask fitted with a condenser (5°C) and flushed with N_2 . The mixture was heated to 75°C for 45 min to generate the dimsyl anion.⁴¹ The solution was cooled to 23°C , and, with rapid stirring, 1,4-cyclohexadiene (43 mmol) was added as fast as possible. A red color rapidly developed, and the reaction was quenched by addition of D_2O (50 mmol, 99.7% D) after 1 min. Hexadecane (15 mL) and ice water (30 mL) were added and, after being stirred for several minutes, the mixture was forced through a coarse-frit filter to remove solids. The organic phase was removed and washed twice with cold H_2O . The aqueous phase was washed twice with hexadecane, and the organic phases were combined and dried over Na_2SO_4 . The volatiles were isolated by bulb to bulb distillation at 0.05 torr. Preparative VPC (column A, 30°C) gave 21% isolated yield of 1,4-cyclohexadiene with 92% deuterium incorporation in the allylic positions. After additional drying over Na_2SO_4 the exchange was repeated a second time; the isolated yield after two exchanges was 9% and by ^1H -NMR and MS the product was observed to have 97.7% deuterium incorporation in the allylic positions. The primary complication encountered with this procedure was the presence of competing reactions which generated benzene and cyclohexene. Exchange was the (slightly) faster process; short reaction times minimized side-

product formation. Perhaps the best way to improve this reaction would be to use an additional solvent such as diglyme which may be cooled to temperatures lower than those obtainable with neat Me_2SO .

Thermal Reactions. Pyrolysis of (*Z*)-4,5-Diethynyl-4-octene (4**).** The gas-phase pyrolysis was performed under a flow of N_2 with a contact time of ca. 2 min and an oven temperature of 320°C . The pyrolysate, composed of **7**, **9**, and **10**, was a yellow liquid at room temperature. The isolated yield of products was 76%. Preparative VPC (column B, 70°C) afforded the pure products. Thermal reactions of **4** in solution were analyzed on column C by using the following temperature program: initial temperature 150°C for 15 min; increase at $5^\circ\text{C}/\text{min}$; hold at 220°C for 20 min. The injector temperature was kept $<235^\circ\text{C}$ to prevent significant injector port reaction of **4**. Compound **12** was obtained pure for analysis from the thermal reaction of 5 mL of a 3×10^{-2} M solution of **4** in chlorobenzene plus 1,4-cyclohexadiene (10% v/v), followed by preparative VPC on column A (at 125°C).

Benzocyclooctene (9**):**²⁴ ^1H NMR (CCl_4) δ 1.34 (br m, 4 H), 1.66 (br m, 4 H), 2.67 (d of d, 4 H, $J = 5$ Hz), 6.93 (s); IR (thin film) 3000, 2910, 2836, 1486, 1463, 1445, 1353, 1110, 748, 704 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{16}$ 160.1252, found 160.1258.

o-Allyl-*n*-propylbenzene (**10**): ^1H NMR (CCl_4) δ 0.97 (t, 3 H, $J = 7$ Hz), 1.60 (sextet, 2 H, $J = 7$ Hz), 2.54 (t, 2 H, $J = 7$ Hz), 3.32 (d, 2 H, $J = 7$ Hz), 4.74–5.12 (m, 2 H), 5.65–6.18 (m, 1 H), 7.00 (s, 4 H); IR (CCl_4) 2940, 2915, 2855, 1635, 1435, 990, 915 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{16}$ 160.1252, found 160.1250.

o-Dipropylbenzene (**12**): ^1H NMR (CCl_4) δ 0.97 (t, 6 H, $J = 7$ Hz), 1.60 (sextet, 4 H, $J = 7$ Hz), 2.56 (t, 4 H, $J = 7$ Hz), 6.98 (s, 4 H); IR (thin film) 3062, 3018, 2962, 2936, 2874, 1488, 1466, 1452, 1376, 746 cm^{-1} . HRMS calcd for $\text{C}_{12}\text{H}_{18}$ 162.1408, found 162.1414.

Acid-Catalyzed Exchange of Aromatic Hydrogen in **12.**²⁶ A solution of **4** in chlorobenzene plus cyclohexadiene- d_4 (8.3% v/v) was heated at 190°C for 15 min in a sealed glass tube. The solution was then concentrated to 0.3-mL total volume by static transfer (0.05 torr) of solvent. The solution was divided into two samples which were each treated in the following way: the chlorobenzene solution was placed in a glass tube with 0.5 mL of an aqueous solution of HCl (4% v/v). After a freeze-pump-thaw of the tubes to remove oxygen, they were sealed and heated at 260°C for 42 h. The tubes were opened, and the organic phases were removed by pipet. After VPC-MS analysis of **12** for deuterium content, the solution was sealed in a tube as before with fresh aqueous HCl. After a second period of heating, VPC-MS analysis of **12** indicated no further change in the deuterium content (Scheme 1).

Pyrolysis of (*Z*)-2,3-diethylhexa-1,5-diyne-3-ene (5**):** Gas-phase and solution thermal reaction of **5** gave the products shown in Table I. The solution and gas-phase reaction mixtures were analyzed by VPC-MS. *o*-Ethylstyrene and tetralin were isolated from the gas-phase reaction mixture by preparative VPC (column A, 90°C) and identified by comparison of their NMR spectra with authentic samples.⁴² Benzocyclobutene and *o*-diethylbenzene were identified by VPC retention time (column C, initial temperature = 105°C for 15 min, temperature program = $6^\circ/\text{min}$, final temperature = 200°C) and by comparison with the mass spectra obtained from authentic samples under identical conditions of analysis.

CIDNP Experiment Using (*Z*)-4,5-Diethynyl-4-octene (4**).** Solutions of **4** (0.1–0.5 M) in diphenyl ether and *o*-dibromobenzene gave identical CIDNP signals upon reaction in the heated probe of a Varian EM-390 ^1H NMR spectrometer (155–170 $^\circ\text{C}$). At the concentrations employed, reduction to yield *o*-dipropylbenzene occurred to the extent of ca. 5% of the yield of the unimolecular products; otherwise, the product distributions were the same as that observed in more dilute solution pyrolyses.

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(40) Ukhin, L. Yu.; Sladkov, A. M.; Gorskov, V. I. *Z. Org. Khim.* **1968**, *4*, 25.

(41) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

(42) *o*-Ethylstyrene was identified by comparison with the NMR spectrum reported in the literature: de Meijere, A. *Chem. Ber.* **1974**, *107*, 1684.