

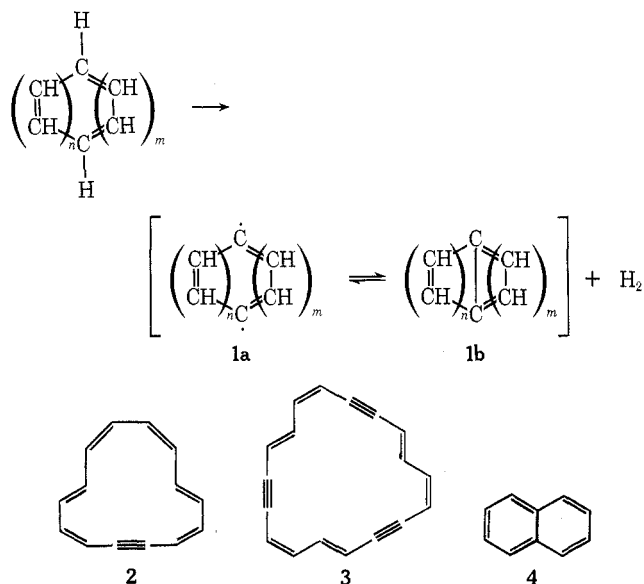
Reactive 1,4-Dehydroaromatics¹

Robert G. Bergman

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91109

Received August 1, 1972

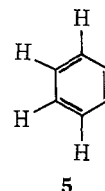
Dehydroaromatic molecules (general structure 1) are formally derived from their aromatic counterparts by removal of two hydrogen atoms.² These atoms may be removed from adjacent carbons, to give 1,2-dehydroaromatics (examples are the large class of dehydroannulenes,³ such as dehydro[14]annulene (2) and tridehydro[18]annulene (3), or from carbons separated by a number of intervening atoms (an example is naphthalene (4), which may be thought of as a 1,6-dehydro[10]annulene).



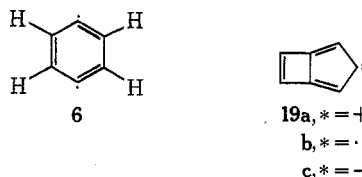
Dehydroaromatics span a wide range of stability and reactivity. The level of stability is often strongly influenced by the extent of interaction between the two electrons left behind by hydrogen removal. Naphthalene is very stable; part of this stability is undoubtedly due to the strength of the 1,6 σ bond. As the aromatic ring grows smaller, however, strong bonding between the "dehydro" electrons is harder to achieve, and such systems become very reactive.

Few reactive small-ring dehydroaromatics have been isolated or even generated in transient form. One of the few exceptions to this generalization is 1,2-dehydro[6]annulene (5), more often referred to as benzyne or *o*-benzyne.⁴ For this reason (and because it is seldom, if ever, possible to carry out the formal

dehydrogenation reaction in the laboratory), such molecules provide a synthetic challenge as well as a source of information to use in the improvement and evaluation of current theoretical bonding concepts.

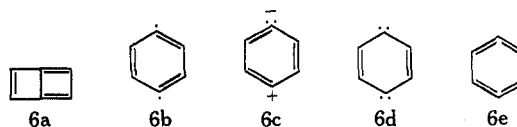


The purpose of this article is to discuss the synthesis and chemistry of the 1,4-dehydrobenzene system (6), which has a diradical structure and therefore no bond between the dehydrogenated carbons, and the 1,4-dehydrocycloheptatrienyl system (19), in which the new central bond appears to be fully intact. Thermal rearrangements of 1,5-diacetylenes have played a central role in the synthesis of molecules in both classes, and so attention will also be paid here to the mechanism of these isomerizations.



1,4-Dehydrobenzene

One of the simplest—and perhaps the most fundamental—1,4-dehydroaromatic molecules is 1,4-dehydrobenzene (6). A number of possible structures for this species⁵ are illustrated below (6a–e). Despite the



central position of this molecule in the field of reactive intermediates and aromaticity, and despite the large amount of experimental work devoted to the study of its 1,2-dehydrobenzene isomer,⁴ only a few isolated reports of attempted synthesis and characterization of this molecule have appeared in the literature.

(1) Contribution No. 4600 from the Gates and Crellin Laboratories of Chemistry.

(2) In its most general sense, formula 1 represents all monocyclic dehydroconjugated molecules. For brevity, discussion is limited here to dehydroaromatics.

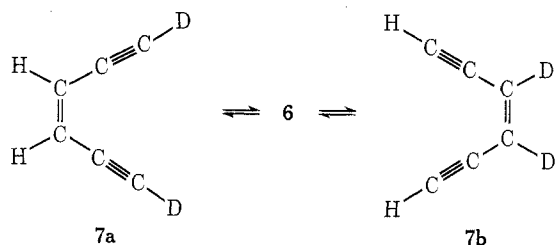
(3) For a review, see F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

(4) For a review, see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

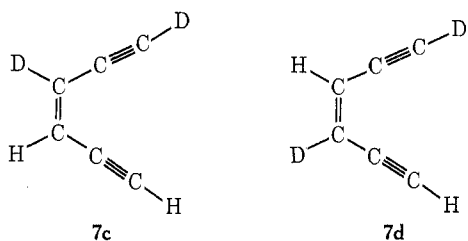
(5) The drawings 6a–e represent limiting structures for 1,4-dehydrobenzene. It is possible that the true ground state of 6 has contributions from one or more of the limiting forms illustrated.

Robert Bergman took his Ph.D. at the University of Wisconsin in 1966 under Jerome A. Berson, after receiving a B.A. in Chemistry at Carleton College. He then received one of the few North Atlantic Treaty Organization postdoctoral fellowships awarded to an American for study in his own country and spent 1966–1967 in Ronald Breslow's laboratories at Columbia University. Following that, he came to Caltech as a Noyes Research Instructor; he now holds the rank of associate professor. In 1970 he received an Alfred P. Sloan Foundation Fellowship and a Camille and Henry Dreyfus Foundation Teacher-Scholar Award. Besides the synthesis and study of nonbenzenoid aromatics, his research involves investigation of the mechanisms of organic reactions, primarily those involving orbital symmetry controlled pathways and diradical and carbonium ion intermediates.

It occurred to us some time ago that a particularly clean synthesis of 1,4-dehydrobenzene might be obtained if the molecule could be generated in a unimolecular isomerization reaction. The most important requirement for a substrate would be that it have a relatively high heat content, making the dehydrobenzene energetically accessible, and also that it be just kinetically unreactive enough to enable us to synthesize and manipulate it. The molecule *cis*-3-hexene-1,5-diyne (7) seemed an ideal candidate. Although air sensitive, this material had been prepared⁶ and isolated. In addition, its structure provided an intriguing means of determining the energetic accessibility of 1,4-dehydrobenzene—because of the expected symmetry of the dehydrobenzene, any reversible conversion of 7 into 6 would render the vinyl and acetylenic hydrogens chemically equivalent.



We therefore prepared both 7 and its trans isomer 8, but modified Sondheimer's synthesis⁶ to allow deuterium labeling of the acetylenic positions.⁷ We were pleased to find⁷ that 7a underwent a rapid deuterium scrambling reaction at 200°. After 5 min at this temperature in the gas phase, nmr analysis showed deuterium evenly distributed between the acetylenic and vinyl positions. The trans isomer, similarly labeled, was completely inert under these conditions. After washing out exchangeable deuterium in basic medium, mass spectral analysis showed 50:50 d_0 and d_2 species, and no d_1 material. This experiment demonstrated that the mixture contained only 7a and 7b, without contamination from 7c and 7d; pyrolysis of a mixture of labeled and unlabeled 7 and mass spectral examination of the product demonstrated that the scrambling reaction was indeed unimolecular.^{7,8}



(6) (a) F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 270 (1961); (b) W. H. Okamura and F. Sondheimer, *ibid.*, **89**, 5991 (1967).

(7) R. R. Jones and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 660 (1972).

(8) (a) Hopf has reported^{8b} that 6-deuteriohexa-1,2-dien-5-yne undergoes a degenerate rearrangement which interconverts it with the 2-deuterio isomer and converts it ultimately to labeled 2-ethynylbutadiene. Because this reaction is essentially a Cope rearrangement, its mechanism may be quite different from that of the 7a = 7b interconversion; however, Hopf considers the possibility that bicyclo[2.2.0]hexa-1,4-diene (a dihydro derivative of "butalene," 6a) may be an intermediate in the production of the butadiene. (b) H. Hopf, *Ber.*, **104**, 1499 (1971).

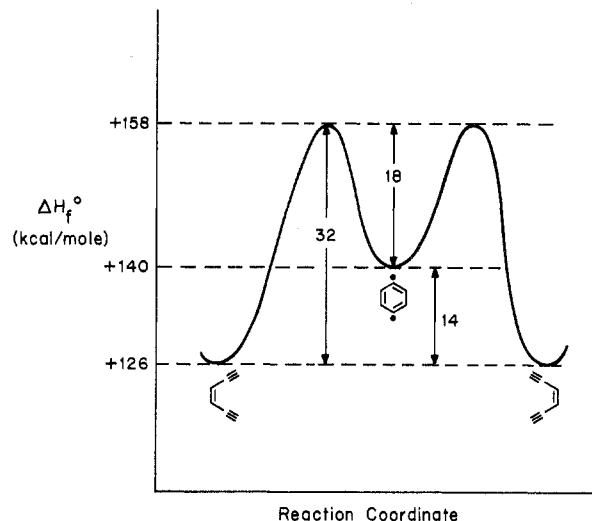
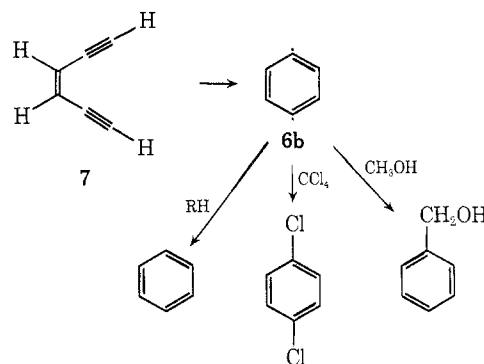


Figure 1. Reaction coordinate diagram for the degenerate rearrangement of 3-hexene-1,5-diyne (7).

The labeling results require that the thermal isomerization proceed through a species having a new C_2 axis of symmetry, *i.e.*, a 1,4-dehydrobenzene. However, they provide no information concerning the structure of this molecule, nor do they tell us whether the symmetrical species is an intermediate or transition state. Fortunately, such information was obtained on pyrolysis of 7 in solution. Heating 7, 0.01 *M* in 2,6,10,14-tetramethylpentadecane, caused the disappearance of the starting material and the quantitative production of benzene. Because free radicals are virtually the only intermediates capable of removing hydrogens from a hydrocarbon,⁹ this immediately suggested that the structure of 1,4-dehydrobenzene was that of 1,4-benzenediyl (6b). Confirmation of this inference was obtained by pyrolysis in carbon tetrachloride, where *p*-dichlorobenzene was the only volatile product observed. Even when presented with methanol, a molecule capable of reacting in either a dipolar or radical fashion, the latter mode was selected—benzyl alcohol, rather than anisole—was the product.⁷

Formulation of the structure of 1,4-dehydrobenzene as 1,4-benzenediyl (6b) allows an interesting thermochemical analysis to be made of the 6 = 7 reaction system. The heat of formation of 7 can be



reliably estimated from group equivalent techniques¹⁰ to be +126 kcal/mol. Assuming that the

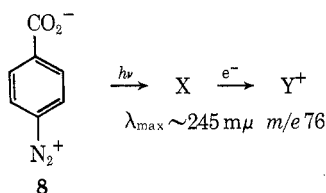
(9) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(10) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

para C-H bond energy in phenyl radical is equivalent to that of the benzene C-H bond energy, the heat of formation of **6b** can also be estimated; it is simply the heat of formation of benzene, plus two benzene C-H bond energies, minus the bond energy in molecular hydrogen.¹¹ This gives a value of +140 kcal/mol as the heat of formation of **6b**. The conclusion arising from these estimates is that **6b** lies only 14 kcal/mol above the starting material **7** (cf. Figure 1).

Were this the only barrier to be crossed on the pathway to **6**, however, the deuterium scrambling reaction would occur at room temperature. On the contrary, it occurs considerably more slowly. The extreme sensitivity of compound **7** has so far precluded careful kinetic studies, but from the half-life of the rearrangement at 200°, one can estimate that (in the absence of unprecedented entropy effects) the activation energy for the rearrangement must be around 32 kcal/mol. As is illustrated in the reaction coordinate diagram (Figure 1), this indicates that 1,4-benzenediyl lies in a very substantial (18 kcal/mol) energy well. In agreement with this picture, solution experiments on deuterated **7a** show that, although the rate of disappearance of **7a** is not significantly increased, the intermediate is largely trapped and very little **7b** is formed.¹²

These studies are of some interest when compared with Berry, Clardy, and Schaefer's results¹³ on the flash photolytic decomposition of 1,4-benzenediazoniumcarboxylate (**8**). Using flash-absorption optical

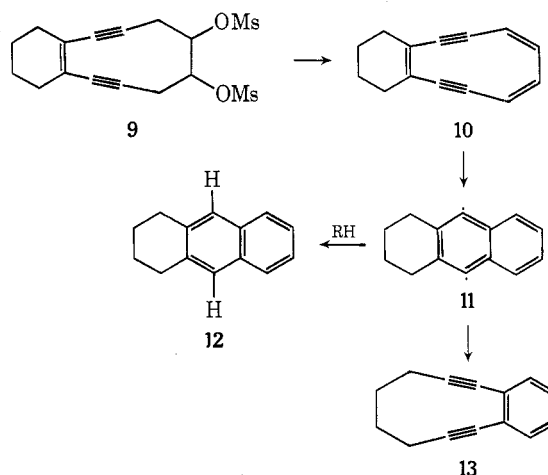


spectroscopy and time resolved mass spectrometry, these authors found that irradiation of **8** gave rise to a mixture of products which showed broad absorption with a possible flat maximum at 244–247 mμ. The absorbing material is present at times 50 μsec to at least 0.5 sec after flashing. Most interestingly, the mass spectrum has a strong peak at m/e 76 which arose from a species having a lifetime of at least 2 min. Berry and coworkers assigned the structure of the material giving rise to this peak as 1,4-dehydrobenzene.¹³ It is important that, despite a careful search, no 3-hexene-1,5-diyne (**7** or **8**) was detected in the product mixture. Certainly if Berry's species were identical with the intermediate generated in our experiments, there would have been ample time for it to relax to compound **7**. We can only conclude that some difference exists in either the structure or electronic states of the molecules investigated in the two experiments.

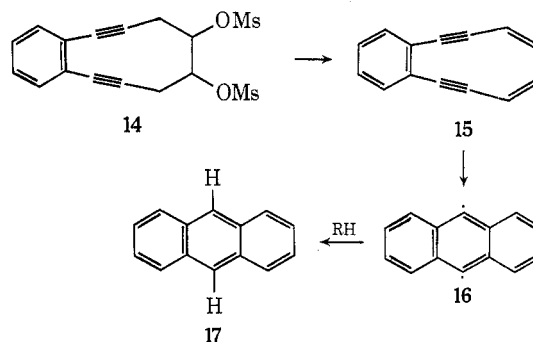
Fisher and Lossing have examined the high-temperature pyrolysis of *p*-diiodobenzene in a reactor

coupled to a mass spectrometer.¹⁴ They identified a product which gives a mass peak at m/e 76 and has an apparent ionization potential of 9.46 eV. On the basis of this value, they assigned the structure of the ionizing species as 3-hexene-1,5-diyne, which they estimated should have an ionization potential close to that observed. Amusingly, 1,3-diiodobenzene gave rise to an m/e 76 species with an identical ionization potential. Finally, Bertorello, Rossi, and de Rossi have examined the thermal decomposition of 1,4-benzenediazoniumcarboxylate (**8**) and its 2-nitro analog in solution, but no strong evidence for the production of 1,4-dehydrobenzenes was obtained.¹⁵

Our results suggest that 1,4-dehydrobenzene-type intermediates were probably involved in a study recently reported by Masamune's group.¹⁶ Treatment of dimesylate **9** with sodium methoxide gave both tetrahydroanthracene **12** and substituted diethynylbenzene **13**. This experiment is the direct analog of



our own, and we suggest that the likely intermediate responsible for the formation of both products is substituted dehydronaphthalene **11**, which is formed by 3,8 bond formation in the proposed initial elimination product **10**. Masamune and coworkers also report¹⁶ that dimesylate **14** "invariably provided anthracene under various elimination conditions" and furthermore that the two new hydrogen atoms had been added (as shown by the deuterium labeling studies) at the **9** and **10** positions. Once again, it seems likely that 9,10-dehydroanthracene (**16**) is an intermediate in this reaction.



(11) This technique has been applied to a number of more conventional diradicals; cf. (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970); (c) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963).

(12) R. R. Jones and R. G. Bergman, unpublished results.

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

(14) I. P. Fisher and F. P. Lossing, *J. Amer. Chem. Soc.*, **85**, 1018 (1963).

(15) R. Hoyos de Rossi, H. E. Bertorello, and R. A. Rossi, *J. Org. Chem.*, **35**, 3328 (1970).

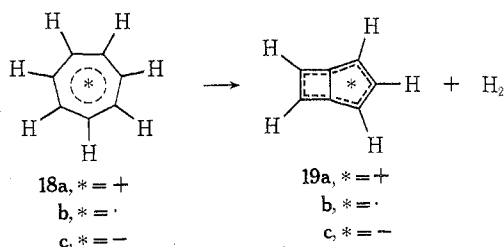
(16) N. Darby, C. U. Kim, J. A. Salaün, K. W. Shelton, S. Takada, and S. Masamune, *Chem. Commun.*, 1516 (1972).

We have as yet obtained no information concerning the electronic states or spin multiplicity of 1,4-dehydrobenzene. Hoffmann, Imamura, and Hehre have applied the extended Hückel molecular orbital method to this and other dehydroaromatic systems; their calculations predict relatively strong coupling between the two radical lobes through the σ bond system, and the interaction is such that it places the energy of the symmetric combination of these lobes 1.4 eV higher than that of the antisymmetric combination.^{17a} Also predicted is a slight C-1,C-4 repulsion, agreeing with our inference that there is no bond between these positions (*i.e.*, "butalene" structure **6a** is of higher energy than **6b**). The selection of the antisymmetric combination of the radical lobes as the highest occupied molecular orbital classifies the $7 \rightleftharpoons 6$ transformation as a formally "allowed" reaction in the orbital symmetry sense.

Gheorghiu and Hoffmann have carried out more sophisticated (although still semiempirical) calculations on the benzynes using a CNDO/2 method which includes configuration interaction.^{17b} In such a calculation the highest occupied and lowest unoccupied orbitals mix strongly, thereby losing much of their cleanly "symmetric" and antisymmetric" character and rendering allowedness predictions correspondingly ambiguous. The more sophisticated method predicts the ground state of 1,4-dehydrobenzene to be a triplet state; confirmation of this prediction awaits the test of further experiments.

1,4-Dehydrocycloheptatrienyl Systems

The seven-carbon analog of 1,4-dehydrobenzene is the 1,4-dehydrocycloheptatrienyl (or dehydrotropyl) molecule (**19**). As with the 6-carbon system, this molecule can be formally derived by removing two hydrogen atoms from cycloheptatrienyl (**18**); in this



case, the presence of an extra carbon atom makes 1,4 bond formation energetically more feasible than it is in the lower homolog. Construction of a simple correlation diagram which pictures the π -system electronic changes that take place during the formal dehydrogenation and bond-formation reaction is instructive, even when only simple Hückel molecular orbitals are used.¹⁸ As can be seen from the diagram (Figure 2), each set of degenerate levels in the seven-fold symmetric system is split by joining C-1 and C-4. Furthermore, one of the lowest antibonding molecular orbitals in cycloheptatrienyl becomes a non-bonding level in the final dehydroaromatic system.

(17) (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) M. D. Georghiu and R. Hoffmann, *Rev. Roum. Chim.*, **14**, 947 (1969).

(18) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, 1965.

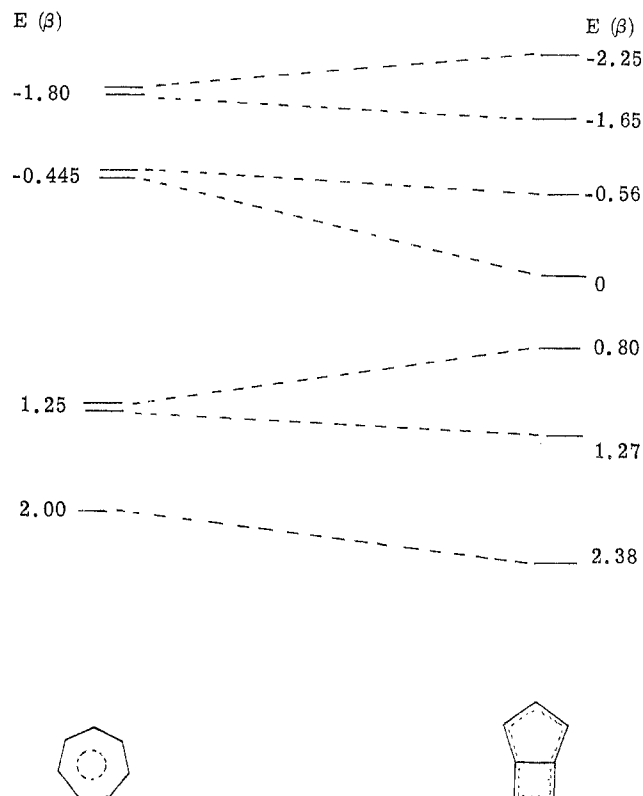
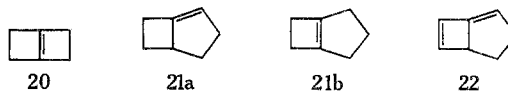


Figure 2. Changes in the simple π molecular orbital framework of the cyclic seven-orbital system induced by 1,4 interaction.

The most important consequence of this change is that the system can now accommodate eight, rather than six, electrons without introducing antibonding character. This suggests that not only the cation but also the radical and anion of 1,4 dehydrocycloheptatrienyl might be accessible.¹⁹

Synthesis and Reactions of 2,5-Dehydrotropylidene. In our synthetic approach to the dehydrocycloheptatrienyl system, we selected bicyclo[3.2.0]hepta-1,4,6-triene ("2,5-dehydrotropylidene," **25**) as our first goal and as a possible precursor to the dehydroaromatics **19**. However, it was clear at the beginning of our study that a bicyclo[3.2.0]heptyl system containing three double bonds would be very highly strained. No such molecule had yet been isolated, although compounds **20**, **21a**, **21b**, and **22** have now been prepared.²¹⁻²⁴



We therefore decided that an ideal reaction would be one that could generate both the bicyclic ring system and the proper unsaturation in one step. A reac-

(19) Although this approach indicates that anion **19c** should be more stable than cycloheptatrienide (**18c**), perturbation theory²⁰ arguments can be used to show that **19c** is still destabilized relative to an acyclic reference ion.

(20) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, 1969, New York, N. Y., Chapter 6.

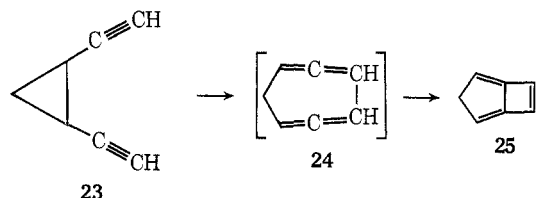
(21) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Amer. Chem. Soc.*, **93**, 246 (1971).

(22) R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969).

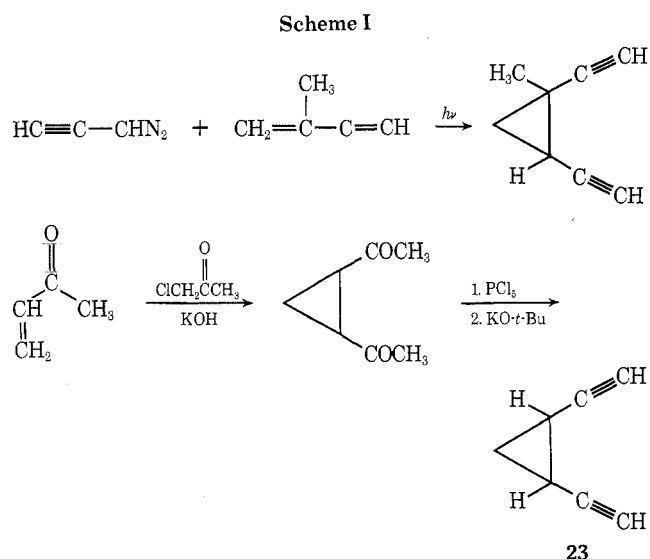
(23) W. Kirmse and K. H. Pook *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966).

(24) R. A. Moss, U.-H. Dolling, and J. R. Whittle, *Tetrahedron Lett.*, 931 (1971).

tion with this characteristic was suggested by the earlier discovery of Huntsman and Wristers that 1,5-hexadiyne rearranged cleanly to 3,4-bismethylenecyclobutene, presumably through the intermediacy of 1,1 bisallene.²⁵ An analogous rearrangement of 1,2-diethynylcyclopropane (**23**) should lead to bicyclo[3.2.0]hepta-1,4,6-triene (**25**), provided the rather highly strained cyclic bisallene **24** were energetically



accessible. We therefore set out to prepare the cyclopropane starting materials. This was accomplished by two different routes: 1-methyl-1,2-diethynylcyclopropane was synthesized by the addition of propargylene²⁶ to 2-methylvinylacetylene, and the parent cis- and trans-1,2-diethynylcyclopropanes were prepared by chemical modification of 1,2-diacetylcyclopropane (Scheme I).



Pyrolysis in either a static reactor at 200–240° or in a gas-phase flow reactor at 480° gave rise cleanly to the corresponding trienes.^{27,28} Both triene **25** and its 2-methyl analog were surprisingly unreactive; although they underwent polymerization in neat form and were air sensitive, they could be stored for long periods of time at nmr-observable concentrations in solution at room temperature.

Diacetylene **23** led only to triene **25** at atmospheric pressure, but at low pressures (≤ 1 Torr) other compounds began to appear as kinetic products of the reaction.²⁸ These materials are fulvenallene (**26**), a mixture of ethynylcyclopentadienes (**27**), and a trace

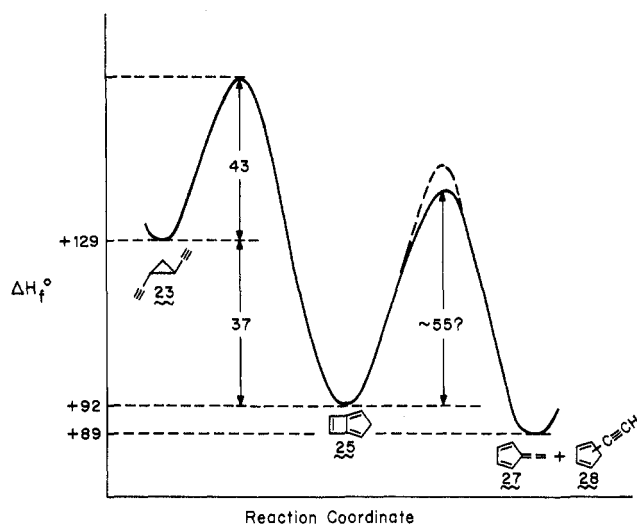
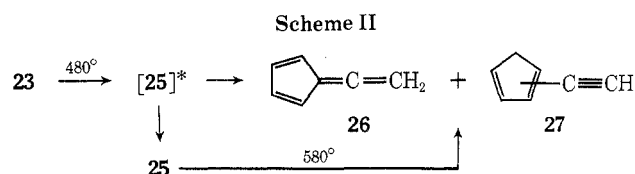


Figure 3. Reaction coordinate-energy diagram for the thermal rearrangements of *trans*-1,2-diethynylcyclopropane and bicyclo[3.2.0]hepta-1,4,6-triene.



of heptafulvalene (**28**). Interestingly, **26** and **27** were also formed on pyrolysis of triene **25**, but only at temperatures ($\sim 580^\circ$, flow system) much higher than those needed for the conversion of cyclopropane **23**.

These observations suggest that, in the low-pressure reaction, triene **25** is produced initially in a highly vibrationally excited state (cf. Scheme II and Figure 3). Group equivalent techniques¹⁰ allow us to estimate the heat of formation of diethynylcyclopropane, and a minimum heat of formation of **25** can also be estimated from the knowledge that the $25 \rightarrow 26 + 27$ reaction must be exothermic.²⁹ Such considerations indicate that the $23 \rightarrow 25$ reaction is about 37 kcal/mol exothermic. We have also determined the activation energy for the isomerization,²⁸ which is 43 kcal/mol starting from *trans*-**23**. As is shown on the reaction coordinate diagram (Figure 3), these numbers indicate that, at the instant of its birth, triene **25** contains energy about 80 kcal/mol in excess of its ground vibrational state. This is apparently sufficient to carry it across the next (and higher) energy barrier, if the pressure is low enough to prevent complete deactivation by collisions with cooler molecules in the surrounding gas.³⁰

Further evidence for this point of view, as well as information about the mechanism of rearrangement of triene **25**, has been obtained from deuterium labeling studies.³¹ *trans*-**23**, labeled in the acetylenic

(25) W. D. Huntsman and H. J. Wristers, *J. Amer. Chem. Soc.*, **89**, 342 (1967). For a complementary study, see B. A. W. Coller, M. L. Heffernan, and A. J. Jones, *Aust. J. Chem.*, **21**, 1807 (1968).

(26) (a) P. S. Skell and J. Klebe, *J. Amer. Chem. Soc.*, **82**, 247 (1960); (b) R. A. Bernheim, R. J. Kenpf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965).

(27) R. G. Bergman and M. B. D'Amore, *J. Amer. Chem. Soc.*, **91**, 5694 (1969).

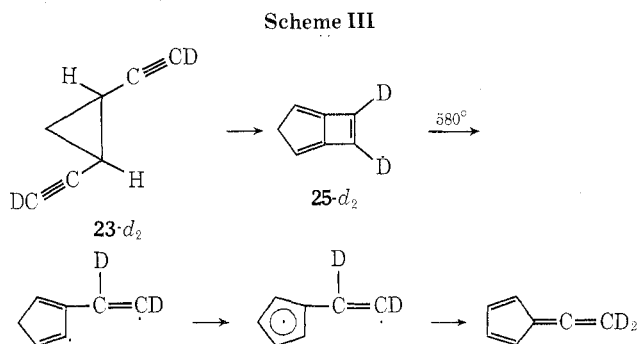
(28) M. B. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.*, **49** (1972). The cis isomer of **23** rearranges at temperatures as low as 100°; *trans*-**23** rearranges at $\sim 250^\circ$.

(29) Because **25** is converted completely to **26** and **27** on pyrolysis, the free energy of this reaction must be negative. Assuming there are no unusual entropic effects associated with this process, the reaction also must be exothermic. Group equivalent calculations¹⁰ give ΔH_f° for **27** as 89 kcal/mol; thus ΔH_f° for **25** can be no lower than about 92 kcal/mol. This leads to a strain energy for **25** of at least 51 kcal/mol.

(30) For other examples of "chemical activation," see B. S. Rabinovitch and M. C. Flowers, *Quart. Rev., Chem. Soc.*, **18**, 122 (1964).

(31) T. J. Henry and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 5103 (1972).

positions, rearranges (as expected) to cyclobutene-labeled **25** (Scheme III). Pyrolysis of **25** at 580° in a flow system leads to fulvenallene with most (87%) of the deuterium in the methylene position. A mechanism which accounts for this labeling pattern is outlined in Scheme III; it is interesting that rearrangement appears to be initiated by cleavage of a cyclobutene vinyl-vinyl bond. However, some other (as yet unknown³²) mechanism places about 13% of the isotope label in the five-membered ring. When diethynylcyclopropane **23** is pyrolyzed at low pressure, the fulvenallene is similarly deuterated, except that now 23% of the deuterium is found in the ring, *despite the fact that this reaction is carried out at lower temperature*. The vibrational excitation hypothesis accounts nicely for this result—triene arising from **23**, 80 kcal/mol above its ground vibrational state, should be considerably less selective than triene generated near its threshold for rearrangement by direct pyrolysis.



The Dehydrocycloheptatrienyl Anion. Our first experiments with triene **25** were directed toward its conversion to dehydrotropyl anion **19c**. Although the anion has not been isolated, Breslow's group and our own have obtained evidence for its existence both in solution and in the gas phase.^{33a, 34, 35}

Breslow's group has carried out a series of experiments on reactive species derived from the bicyclic chloro diene **29**. Treatment of this material with potassium *tert*-butoxide in Me₂SO yields two compounds, formulated as dimers of triene **30**; in deuterated solvent these materials are found to have incorporated two deuterium atoms.^{33a} Treatment of **29** with lithium cyclohexylamide and tetraethylenediamine in tetrahydrofuran gives a solution which can be quenched with deuterated acids to yield the deuterated dimers. Thus the solution apparently contains anion **19c**. Quenching with acids of varying pK_a and examination of the deuteration level in the dimers allowed Breslow and Washburn to estimate the solution pK_a of **19c** as similar to that of xanthene,³⁴ *i.e.*, approximately **29**.

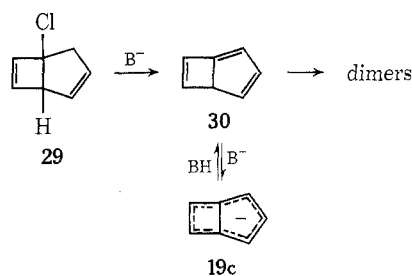
Our discovery²⁸ that triene **25** was considerably less reactive than **30** made it seem curious that **25**

(32) The small amount of heptafulvalene isolated suggests that some part of this reaction finds its way into the phenylcarbene-cycloheptatrienyliene manifold (*cf.* J. A. Myers, R. C. Joines, and W. M. Jones, *J. Amer. Chem. Soc.*, **92**, 4740 (1970), and references cited there), which may account for the minor amount of label scrambling seen here.

(33) (a) R. Breslow, W. Washburn, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 196 (1969); see also (b) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *ibid.*, **91**, 2787 (1969).

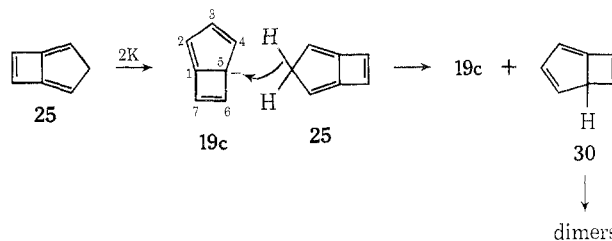
(34) R. Breslow and W. Washburn, *J. Amer. Chem. Soc.*, **92**, 427 (1970).

(35) M. B. D'Amore and R. G. Bergman, unpublished results.

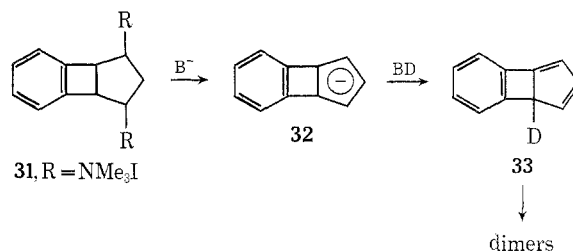


was not discovered in the deuterium exchange reaction of **29**—*i.e.*, that anion **19c** appeared to protonate only at C-1 and not at C-3. Generating the anion from **25** provided a means of testing this point. Treatment of triene **25** with successive amounts of a solution of KO-*t*-Bu/Me₂SO-*d*₆ and observation of the reaction by nmr showed no exchange in **25**; as the triene disappeared, only the dideuterated dimers were generated in moderate yield.³⁵ It therefore appears that anion **19c** does in fact protonate predominantly, if not exclusively, at C-1. This indicates that the charge density at C-1 is higher than that at C-3, a situation presently unrationalized by either simple Hückel calculations¹⁹ or the more sophisticated Pariser-Parr-Pople technique.³⁶

Attempts to generate anion **19c** in either isolable or nmr-observable form in solution have not yet met with success. Even under conditions where the supply of protons should be minimal (potassium mirror in tetrahydrofuran, vacuum line conditions), good yields of dimers are obtained.³⁵ It may be that starting triene **25** itself is the proton source; if small amounts of anion can abstract protons from **25**, this protonation will occur primarily at C-1 or C-5, followed by rapid dimerization of the triene **30** produced.



Cava and coworkers³⁷ have examined a related benzo-fused system and found that, although the triene **33** appears to be as reactive toward dimerization as its parent **30**, the benzene ring may confer some extra stability on the "norbiphenylene" anion (**32**). Treatment of bis(tetramethylammonio) iodide **31** with dimsyl anion in Me₂SO produces a stable



(36) We are grateful to Dr. Howard Simmons for carrying out these calculations for us.

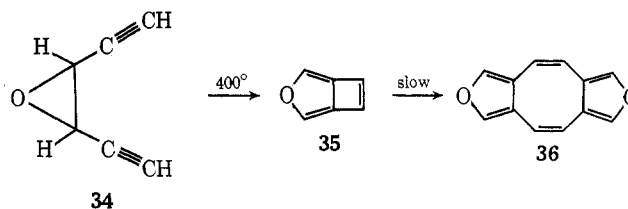
(37) M. P. Cava, K. Narasimhan, W. Zieger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, **91**, 2378 (1969).

deep brown solution, presumably of the anion, exhibiting a uv band at λ_{\max} 590 m μ . Addition of D₂O to this solution produces two dimers, each containing two deuterium atoms. Once again, the anion appears to prefer to protonate at the bridgehead carbon. Unfortunately, no nmr spectral data have been reported for the brown solution.

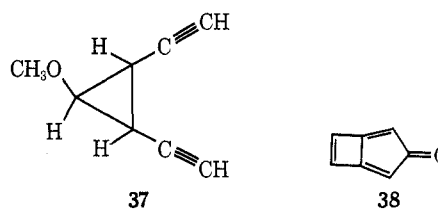
Triene **25** reacts with methoxide ion cleanly in the gas phase in the cell of an ion cyclotron resonance spectrometer.³⁸ This reaction gives a stable anion with mass 89, which we presume to be **19c**. Other anions, such as cycloheptatrienide, 1,4-pentadienide, and cyclopentadienide, can be generated under similar conditions. Proton transfer between these hydrocarbon anions occurs very slowly, hindering the establishment of equilibrium and the precise determination of gas-phase basicities. However, we have been able to determine that the proton affinities of **19c**, cycloheptatrienide, and 1,4-pentadienide all lie in the range 362–377 kcal/mol, whereas cyclopentadienide's proton affinity is probably about 354 kcal/mol. The gas-phase basicity difference between cyclopentadienide and **19c**, therefore, could well be very similar to the 10-kcal/mol gap determined by Breslow and Washburn in solution.³⁴

3,6-Dehydrooxepin. Very recently we have succeeded in preparing³⁹ *cis*- and *trans*-1,2-diethynylloxiranes (**34**). Pyrolysis of either of these compounds in a flow system at 400° (contact time ~20 sec) gives as the sole product 3,6-dehydrooxepin (**35**; ~10% yield). This compound, a white, crystalline solid at -78°, is the first unsubstituted cyclic planar eight- π -electron system to be prepared and isolated. It is extremely sensitive; it polymerizes instantaneously on exposure to oxygen and must be handled entirely on a vacuum line. Compound **35** is a furan analog of benzocyclobutadiene but, unlike the latter compound, undergoes dimerization only slowly ($t_{1/2} \cong 4$ days at room temperature at ~0.2 M concentration). The eventual product of the dimerization reaction is the known⁴⁰ bisfuranocyclooctatetraene **36**. The nmr

spectrum of **35** in CCl₄ shows resonances at δ 6.11 and 6.33 ppm, indicating that the diamagnetic ring current characteristic of furan (α hydrogens at δ 7.40 ppm) has been completely suppressed in **35**.



Work in Progress. The diethynylcyclopropane rearrangement can in principle be used to generate a wide variety of 1,4-dehydrotropyll systems, and a number of studies using this technique are now in progress. Treatment of triene **25** with triphenylmethyl fluoroborate fails to give a stable cation at nmr concentrations, but triphenylmethane is produced in the reaction and a careful search for the cation is being conducted.⁴¹ Functionalized derivatives of diethynylcyclopropane may lead to derivatives of triene **25** which will generate the anion and cation under milder conditions. For example, the methoxy derivative **37** has been prepared and its thermal reactions are being investigated;⁴¹ experiments are also under way aimed at preparing and studying 3,6-dehydrotropone (**38**).



The work described in this paper owes its existence to the skillful experimental ability, dedication, intellectual acumen, and good humor of a number of my coworkers, notably Michael B. D'Amore, Richard R. Jones, Timothy J. Henry, and K. Peter C. Vollhardt. I am grateful for the opportunity to collaborate with Dr. E. Hedaya and his research group at the Union Carbide Corporation, and for financial support from the National Science Foundation, the Petroleum Research Fund administered by the American Chemical Society, and the Research Corporation.

(38) M. B. D'Amore, J. L. Beauchamp, and R. G. Bergman, unpublished results.

(39) K. P. C. Vollhardt and R. G. Bergman, *J. Amer. Chem. Soc.*, in press.

(40) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, 89, 5080 (1967); 92, 973 (1970).

(41) R. R. Jones and R. G. Bergman, unpublished results.