

8/15/80

LBL-10828
Preprint c.2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED

LAWRENCE BERKELEY LABORATORY

AUG 21 1980

LIBRARY DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to the Journal of the American Chemical Society

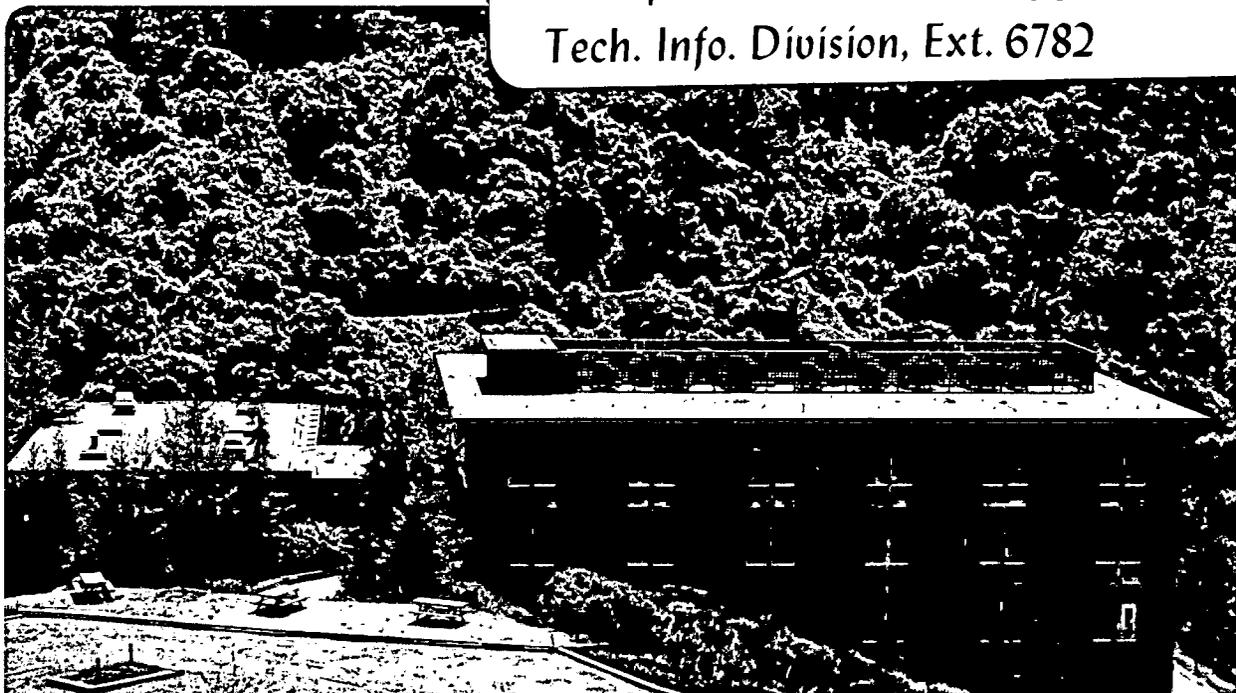
2,3-DI-n-PROPYL-1,4-DEHYDROBENZENE

Thomas P. Lockhart, Charles B. Mallon, and Robert G. Bergman

June 1980

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-10828
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

2,3-di-n-propyl-1,4-dehydrobenzene

by Thomas P. Lockhart, Charles B. Mallon, and Robert G. Bergman

Abstract

2,3-Di-n-propyl-1,4-dehydrobenzene (5) has been generated by the thermal rearrangement of Z-4,5-diethynyl-4-octene (4). Solution pyrolysis of the starting diacetylene in inert aromatic solvents produces three unimolecular products (Z-dodeca-4,8-diyne-6-ene (8), o-allyl-n-propylbenzene (9) and benzocyclooctene (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 are obtained. Kinetic and trapping studies indicate that the 1,4-dehydrobenzene has a finite lifetime and undergoes reactions consistent with a biradical structure. Our results also indicate that two subsequent biradical intermediates are formed from the 1,4-dehydrobenzene by sequential intramolecular [1,5] hydrogen transfer. CIDNP has been observed in one of the unimolecular reaction products and provides further evidence for the presence of one of the biradical intermediates.

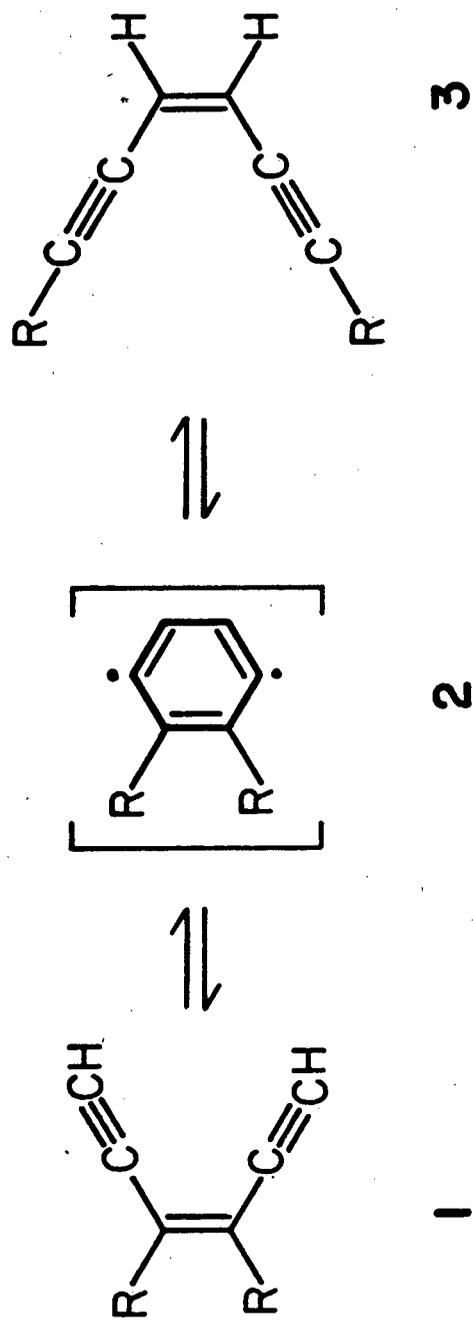
2,3-di-n-propyl-1,4-dehydrobenzene

Sir:

Rearrangement and trapping studies¹ have implicated an "open" or biradical form (2) of 1,4-dehydrobenzene as an intermediate in the thermal reaction of Z-hexa-1,5-diyne-3-ene (1, R = H; Scheme 1). Attempts to obtain kinetic evidence for the existence of a true intermediate in this reaction, however, have been frustrated by the low yield of aromatic products obtained in solution pyrolyses of several compounds of type 1. In this paper we wish to report a detailed study of the thermolysis of Z-4,5-diethynyl-4-octene (4).² This reaction gives high yields of products formed by rearrangement, intramolecular and intermolecular trapping of the intermediate 1,4-dehydrobenzene 5. The kinetics of the solution pyrolysis of 4 in the presence and absence of trapping agent establish that the 1,4-dehydrobenzene is a discrete intermediate on the pathway leading to products. By following this reaction in the probe of an NMR spectrometer at high temperature we have, for the first time, observed CIDNP in a 1,4-dehydrobenzene reaction. This observation, along with kinetic and chemical trapping evidence, indicates the subsequent formation of two additional intermediates on the pathway to products. The observation of CIDNP, coupled with the reactivity exhibited by 5 and the other two intermediates, implicate a biradical description of these molecules.

Reaction of 4 in the gas phase (N₂ flow, 320°C)

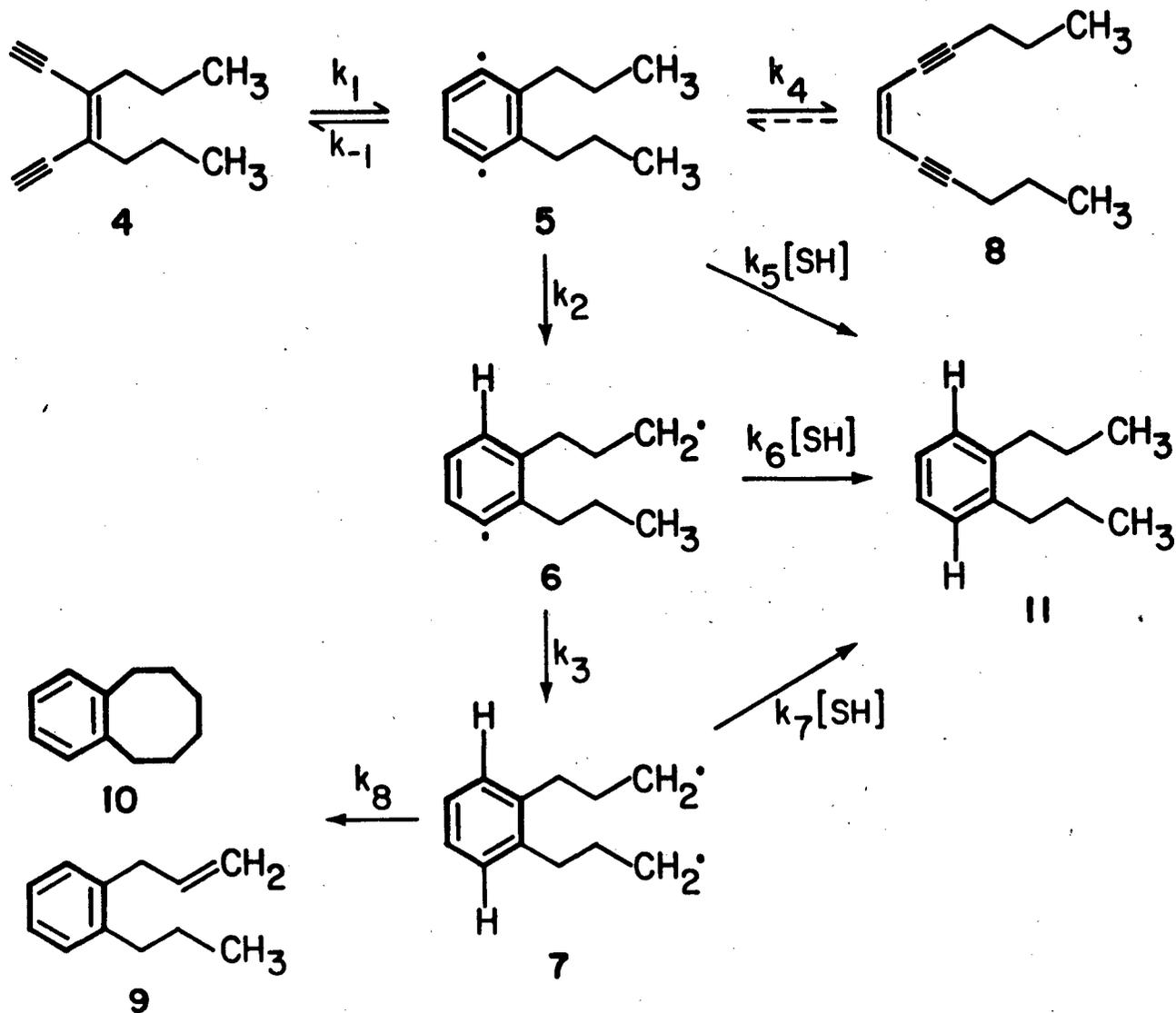
Scheme I



quantitatively produces three products: isomeric diyne 8, o-allyl-n-propyl-benzene (9), and benzocyclooctene (10).³ The yield of 8 is dependent on the reaction temperature; at 400°C 8, prepared by independent synthesis, is converted to 9 and 10 in high yield. Products 8, 9 and 10 are obtained in high mass balance when compound 4 is heated to 196°C in a solvent inert toward free radical hydrogen atom abstraction such as diphenyl ether, chlorobenzene or benzene.^{4,5} At this temperature the more stable isomer 8 does not react appreciably during the course of the reaction. Pyrolysis of 4 in an inert solvent to which a good hydrogen atom donor (1,4-cyclohexadiene or 9,10-dihydroanthracene) has been added gives reduced product 11 in addition to 8, 9 and 10.⁶ Increasing the percent of trapping agent in solution increases the yield of 11 at the expense of the three unimolecular products (see Table, runs (1)-(3)).

The mechanism outlined in Scheme 2 accounts for the observed products. We postulate that 1,4-dehydrobenzene 5 is the initial intermediate. Intramolecular hydrogen transfer from the ends of the alkyl chains sequentially converts 5 into 6 and then 7. Performing the thermal reaction in the presence of 2,2,5,5-tetradeuterio-1,4-cyclohexadiene⁷ provides information about the amount of reduced product 11 arising from each of these intermediates, since 5 gives rise to 11 containing only aromatic deuterium, 7 leads to 11 containing only aliphatic deuterium, and 6 gives 11 containing one aliphatic and one aromatic deuterium.⁸ Assay for these three differently labeled products was performed by selectively⁹ washing out aromatic deuterium using acid-

Scheme 2



catalyzed exchange, and then analyzing the resulting *o*-dipropylbenzene for d_0 , d_1 , and d_2 isomers by mass spectroscopy. These experiments demonstrated that when a solution of **4**, 0.8 M in cyclohexadiene- d_4 , is subjected to thermal reaction, 66% of product **11** is formed directly from the 1,4-dehydrobenzene, 33% is formed from the singly-rearranged biradical **6**, and only 1% arises from **7**. As might be expected, therefore, biradical **7** undergoes intramolecular ring-closure and hydrogen transfer considerably faster than intermolecular reaction with deuterated cyclohexadiene.

The kinetics of disappearance of **4** in chlorobenzene solution ($[4] = 0.01$ M) are well behaved. First order plots are linear for two to three half-lives over a range of 34°C (Table). These data give $E_a = 27.4 \pm 0.5$ kcal/mol and $\log_{10} A = 10.8 \pm 0.3$ sec⁻¹.

If 2,3-di-*n*-propyl-1,4-dehydrobenzene is a true intermediate in the reaction of **4**, and the reaction rates leading to **6**, **8** and **11** are fast with respect to k_{-1} , then the rate of disappearance of **4** should be independent of added 1,4-cyclohexadiene trapping agent. The yield of unimolecular products, however, should be strongly dependent on the presence of trapping agent in the reaction solution. The rate data obtained at 0.19 M and 0.38 M added 1,4-cyclohexadiene at 156°C are identical, within experimental error, to the data obtained in the absence of trapping agent (Table; runs (5), (8) and (9)). Thus, while the rate of reaction of **4** is unchanged, the increase in cyclohexadiene concentration increases the yield of **11** from 0 to 47%, in accord with the prediction.

A specific relationship of the yield of diyne **8** to the 1,4-

cyclohexadiene concentration is predicted by Scheme 2. Application of the steady state approximation to the concentration of 5 (Scheme 2) leads to the prediction that the reciprocal of the yield of 8 should be proportional to the concentration of 1,4-cyclohexadiene in solution (eq. (1)). As shown in Fig. 1, this relationship is observed experimentally.

The absolute yields of products 8, 9 and 10 show pronounced, but different, dependences on the concentration of trapping agent. The yields of both 9 and 10 fall off rapidly as the 1,4-cyclohexadiene concentration increases; the dependence of 8 is much smaller. From the d_4 -cyclohexadiene trapping experiments, we know that a negligible amount of 11 arises from 7; thus $d[9 + 10]/dt \approx k_3[6]$ (Scheme 2), and we obtain the relationship in eq. (2) which relates the ratio of 8 to 9 + 10 as a function of added trapping agent. The experimental data are plotted in Fig. 2. The straight line obtained confirms that a second intermediate exists and is being trapped by added cyclohexadiene. From the y-intercept, $k_4/k_2 = 0.36 \pm 0.01$. The ratio k_6/k_3 , given by the slope/y-intercept, = 2.0 M^{-1} . In the absence of trapping agent the ratio of unimolecular products, $8/[9 + 10]$, gives k_4/k_2 directly. The value obtained experimentally, 0.35, falls almost exactly on the line in Fig. 2. This indicates that cyclohexadiene does not produce a significant solvent effect on the reaction rates at the concentrations studied.

It is informative to estimate the absolute rate constants and activation energies for the processes shown in Scheme 2. A reasonable model for k_6 is the rate constant for reaction of

Equation 1.

$$\frac{1}{8} = 1 + \frac{k_2}{k_4} + \frac{k_5}{k_4} \quad [\text{SH}]$$

Equation 2.

$$\frac{8}{9 + 10} = \frac{k_4}{k_2} + \frac{k_4 k_6}{k_2 k_3} \quad [\text{SH}]$$

phenyl radical with diphenylmethane ($7.7 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 60°C)¹⁰ which gives $k_6 = 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ at 60°C . The unimolecular rate constants k_2 , k_3 and k_4 are thus expected to lie between 10^6 and 10^7 sec^{-1} ; k_8 must be at least one or two orders of magnitude slower (vide supra). The ratio of products 8/[9 + 10] shows a marked dependence on the reaction temperature (Table). This is convincing evidence that at least one of the intramolecular processes leading from 5 is activated. A good linear plot of $\ln(8/[9 + 10])$ versus $1/T$ is obtained over a range of 64°C ; from the slope of the line $\Delta E_a(E_a(k_4) - E_a(k_2))$ is found to be $5.2 \pm 0.4 \text{ kcal/mole}$. The E_a for [1,5] hydrogen transfer in 5 should be similar to that for exothermic [1,5] hydrogen transfer in the 2,2-dimethylpentoxyl radical ($E_a \cong 5.0 \text{ kcal/mole}$).¹⁰ The conversion of 5 to 6 should therefore have an E_a of about 10 kcal/mole .

When 4 is pyrolyzed in diphenyl ether or o-dibromobenzene at 160°C in the probe of an NMR spectrometer, several emissive signals are observed (Fig. 3). We assign these CIDNP signals to the vinyl protons and, tentatively, to the alkyl protons (terminal methyl and methylene) in 10. The assignment of the polarized protons and the peculiar observation that all enhancements are emissive suggest strongly that the polarization arises from biradical 7.¹¹

The observations reported here constitute strong support for the mechanism outlined in Scheme 2, and provide information about the relative rates of several of the fast reactions of intermediates 5, 6, and 7. Experiments now in progress are aimed

at determining the reactive spin state of 5.

Acknowledgements. We gratefully acknowledge the joint research support of the Divisions of Basic Energy (Chemical Sciences) and Fossil Energy (Advanced Research), U.S. Department of Energy, both under contract No. W-7405-Eng-48.

Thomas P. Lockhart, Charles B. Mallon,
Robert G. Bergman.*

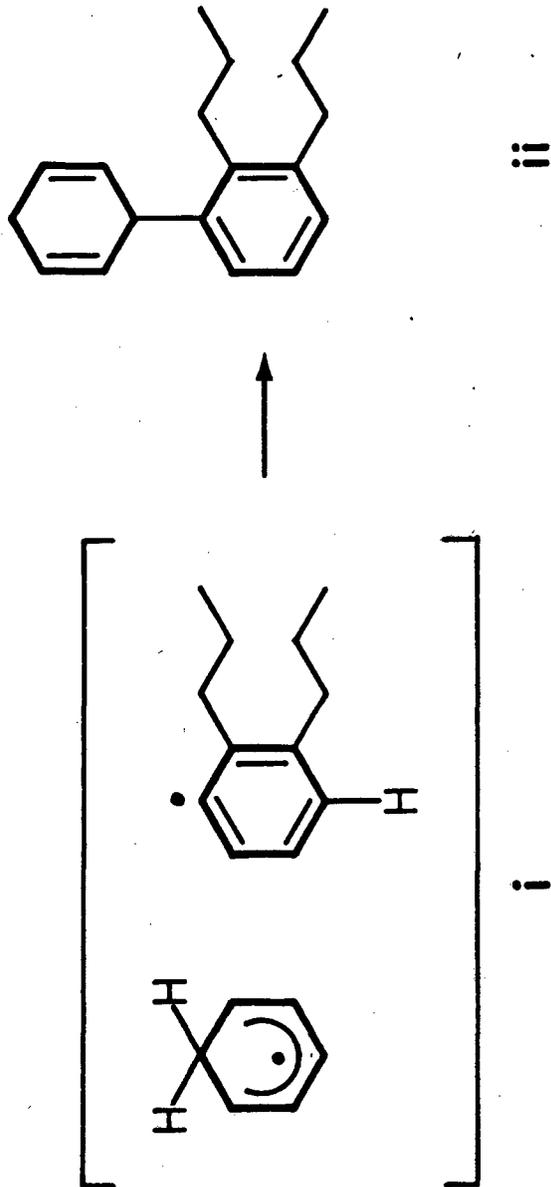
Contribution from the Division of
Chemistry and Chemical Engineering,
California Institute of Technology,
Pasadena, California 91125, the
Department of Chemistry, University of
California, Berkeley, California 94720,
and the Materials and Molecular
Research Division, Lawrence Berkeley
Laboratory.

References

1. (a) Jones, R.R., Bergman, R.G., J. Am. Chem. Soc. 1972, 94, 660; (b) Bergman, R.G., Acc. Chem. Res. 1973, 6, 25; (c) Johnson, G.C., Stofko, J.J., Lockhart, T.P., Brown, D.W., Bergman, R.G., J. Org. Chem., 1979, 44, 4215. See also, however, (d) Breslow, R., Napierski, J., Clarke, T.C., J. Am. Chem. Soc. 1976, 98, 5703; (e) Breslow, R., Khanna, P.L., Tetrahedron Lett., 1977, 3429.
2. Details of the synthesis of compound 4 will be presented in a

full paper.

3. Satisfactory analytical data were obtained on all new compounds. In addition, 8 was synthesized independently to confirm its identification.
4. Samples were prepared for pyrolysis by placing a 0.01 M solution of 4 into hexamethyldisilazane-treated pyrex tubes and freeze-pump-thawing 4 times to 0.02 torr. The tubes were then sealed under vacuum.
5. In addition, several isomeric products were observed which appear to be derived from the addition of radical intermediates to the aromatic solvent (< 5% total yield, identified by vpc-ms).
6. Several new isomeric products of molecular formula $C_{18}H_{24}$ and $C_{18}H_{22}$ were observed by vpc-ms (total yield ca. one-fourth that of compound 11). These compounds presumably arise from combination of the radical pairs (e.g., i ii) produced upon transfer of hydrogen from the trapping agent to the intermediate biradicals.
7. 1,4-cyclohexadiene- d_4 was prepared by base-catalyzed exchange of the allylic protons for deuterium by treatment with d_5 -dimethylsilyl anion in DMSO- d_6 . Deuterium incorporation = 98%; >98% pure.
8. Deuterium substitution in 1,4-cyclohexadiene substantially reduces its efficiency as a radical trap. In the pyrolysis of 4, $k_H/k_D = 4.3$. The overall yield of tractable products suffers as a result; 8, 9, 10 and 11 were obtained in a total yield of about 40%.
9. Pyrolysis solutions were concentrated and then heated with 4% HCl in H_2O at $260^\circ C$ for 42 hours (cf. Werstiuk, N.H., Kadai, T.



Can. J. Chem., 1973, 51, 1485. The exchange was repeated, at which time all aromatic deuterium had been exchanged for protons. This method is very effective for exchanging aromatic protons without exchanging the protons in pendant alkyl groups. We confirmed this by exchanging the deuterium in toluene-d₈ for protons under identical conditions to those employed in the dipropylbenzene experiment. The exchange stopped at toluene-d₃ (by mass spectral analysis) and NMR showed no proton incorporation into the methyl group.

10. Ingold, K.U. in "Free Radicals," Vol. I, Kochi, J.K., Ed., J. Wiley and Sons, New York, 1973, Chapter 2.

11. For reviews of CIDNP observed in the products of biradical reactions see (a) Kaptein, R., in "Advances in Free Radical Chemistry," Vol. 5, 1975, p. 319; (b) Closs, G.L., in "Chemically Induced Magnetic Polarization," Lepley, A.R. and Closs, G.L., Eds., J. Wiley and Sons, 1973, p. 130.

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

Run	T (°C)	k _{obs} (sec ⁻¹)	1,4-cyclohexadiene (M)	Absolute Yield (%) ^b				
				8	9	10	11	Total (8-11)
(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 x 10 ⁻³	0.0	13.5	38.5	20.0	--	72
(5)	156	6.9 x 10 ⁻⁴	0.0	11.8	35.8	17.2	--	65
(6)	145	2.9 x 10 ⁻⁴	0.0	9.8	37.3	17.6	--	65
(7)	132	9.3 x 10 ⁻⁵	0.0	7.9	38.5	16.4	--	63
(8)	156	7.1 x 10 ⁻⁴	0.19	8.7	13.5	8.7	27.6	58
(9)	156	6.4 x 10 ⁻⁴	0.38	5.2	6.7	3.1	47.4	62

^a[4] = 0.01 M

^bYields determined by digital integration of FID vpc trace and reference to an internal standard.

Figure Captions

Figure 1. Plot of $(\delta_{\text{normalized}})^{-1}$ versus concentration of 1,4-cyclohexadiene.

Figure 2. Dependence of the ratio $\delta/[\delta_9 + \delta_{10}]$ on 1,4-cyclohexadiene concentration.

Figure 3. The upper spectrum (90MHz, ^1H) shows the vinyl region of a purified sample of o-allyl-n-propylbenzene recorded at 30°C. The lower spectrum shows the emissive ^1H signals observed during pyrolysis of 4 at 160°C in a 90MHz NMR probe. The signals appearing in absorption on the left side of the lower spectrum are spinning side bands of the solvent (o-dibromobenzene).

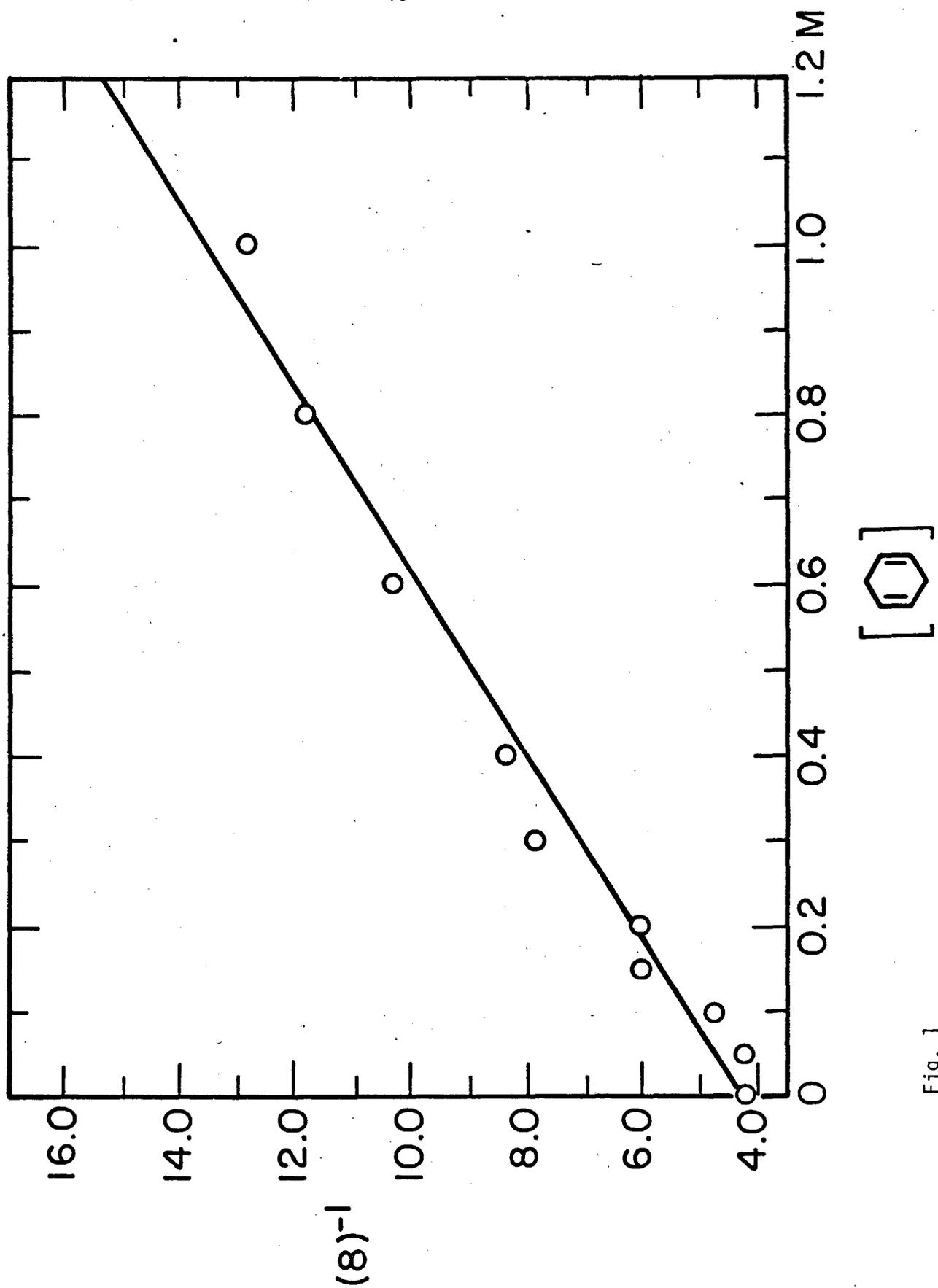


Fig. 1

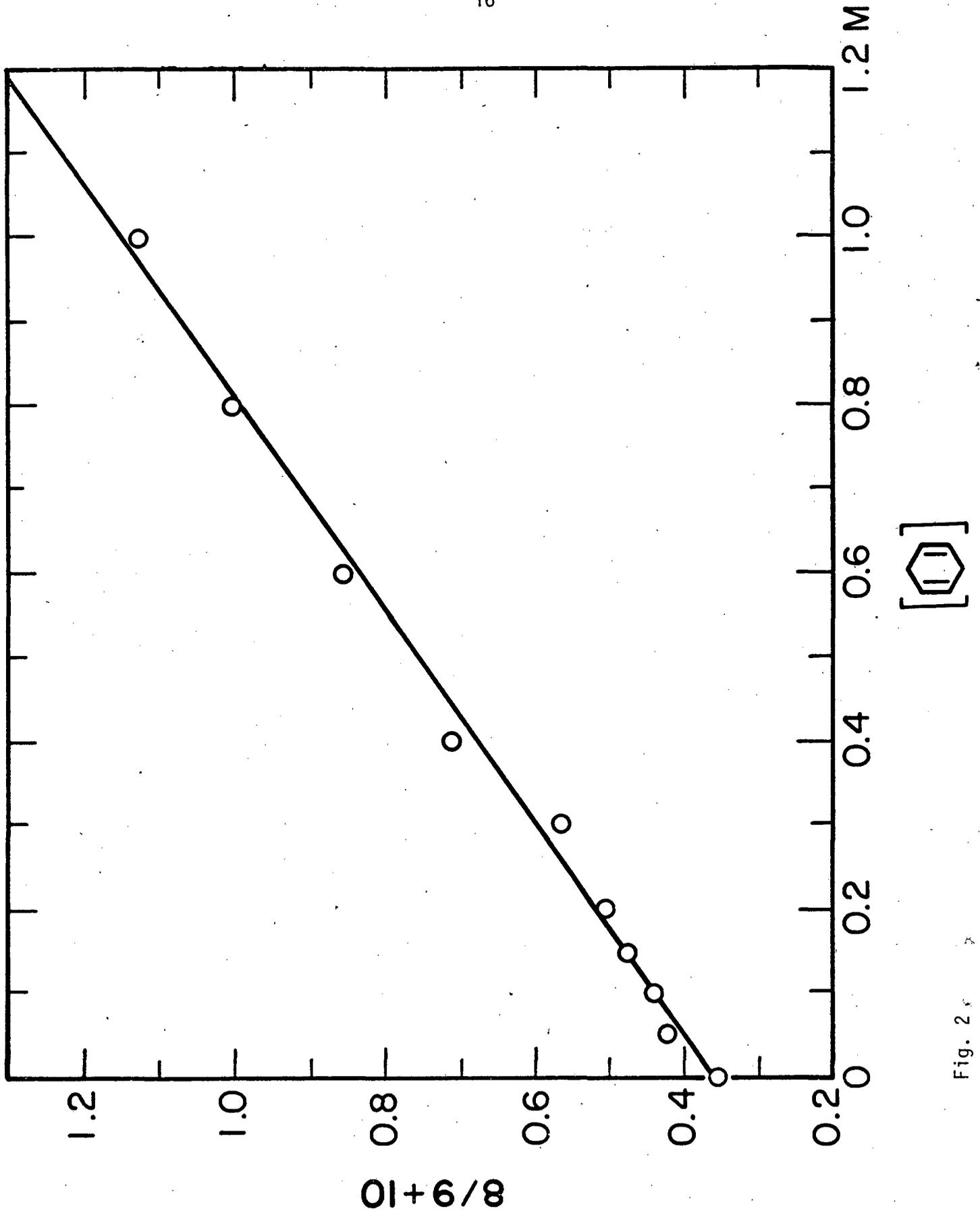


Fig. 2

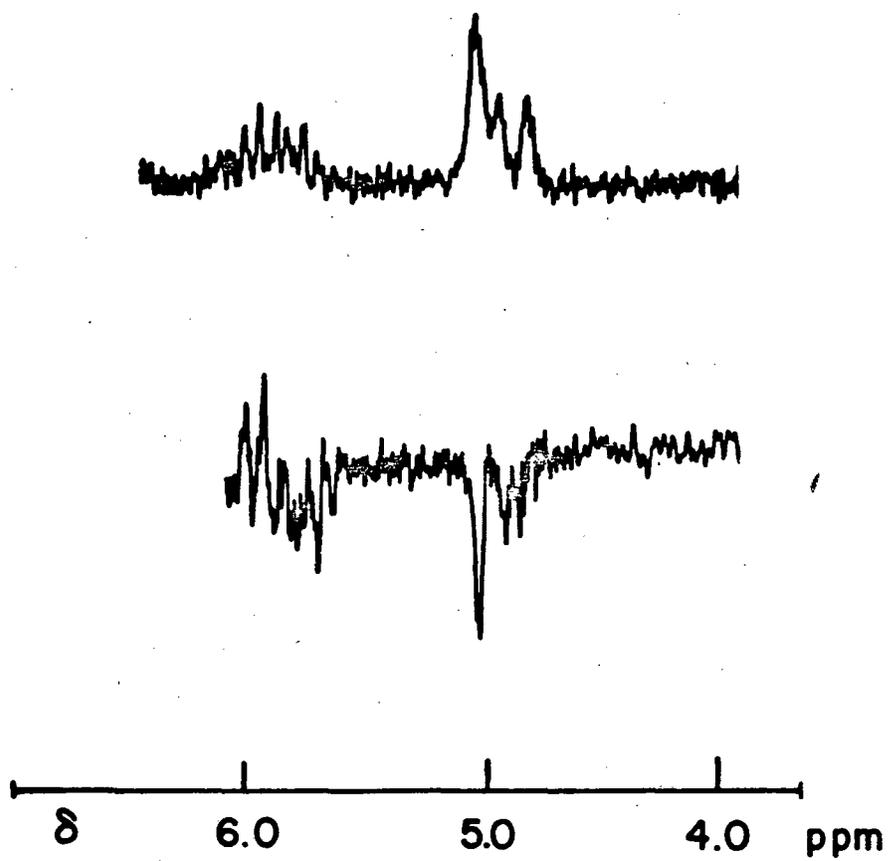


Fig. 3

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720