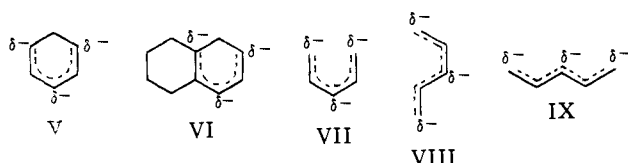


have recently been the subject of molecular orbital calculations.<sup>5</sup>

The factors affecting pentadienyl carbanion stability will strongly influence the rates of reactions in which the rate-determining transition state resembles the pentadienyl carbanion (*e.g.*, base-catalyzed diene isomerizations; from the generalization stated later regarding carbanion stabilities and the relative stabilities of the dienes involved, it would have been possible to predict that  $\Delta^{2,9}$ -hexahydronaphthalene (I) can be isomerized to  $\Delta^{1,9}$ -hexahydronaphthalene (II) in 66% yield, as we have observed experimentally). Another reason for evaluating these factors is that it is possible to generate these carbanions in high concentration relative to their conjugate acids,<sup>1a,2c,4</sup> and in systems in which there are several pentadienyl carbanions, it will probably prove possible to equilibrate between them.



Birch and co-workers have obtained qualitative evidence that alkyl groups destabilize pentadienyl carbanions, and they attribute this more to steric hindrance to solvation than to the inductive effect of the alkyl group.<sup>2c</sup> In a quantitative study, we have shown the rate constant for the isomerization of 1,4-dihydrobenzene (III) to 1,3-dihydrobenzene (IV) (*via* V) with potassium *t*-amyloxide at 95° to be larger than that for the isomerization of I to II (*via* VI) by a factor of 22.1. Correcting for a statistical factor of 2, this corresponds to a difference in  $\Delta F^\ddagger$  for the two reactions of 1.75 kcal./mole. It is difficult to say how much of this difference is due to alkyl stabilization of starting material (two substituents involved), and how much to alkyl destabilization of transition state (primarily due to the substituent on carbon 1 of the pentadienyl system), but the total should be of some utility.

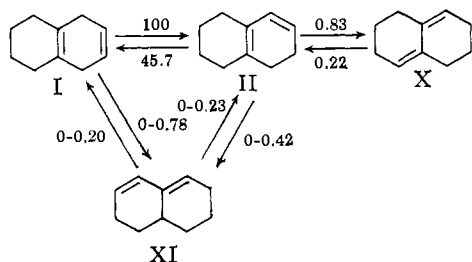


Fig. 1.—Relative rate constants ( $k_{I \rightarrow II} = 100$ ) for isomerizations with potassium *t*-butoxide in *t*-butyl alcohol at 101°;  $k_{XI \rightarrow I} = 0.39k_{I \rightarrow XI}$ ;  $k_{XI \rightarrow II} = 0.55k_{II \rightarrow XI}$ ; a reasonable fit was obtained provided that  $k_{I \rightarrow IX} + 1.85k_{II \rightarrow IX} = 0.78$ ; from other results dealing with the rate of formation of VI from I and II, approximate values for  $k_{I \rightarrow IX}$ ,  $k_{II \rightarrow IX}$ ,  $k_{IX \rightarrow I}$ , and  $k_{IX \rightarrow II}$  are 0.63, 0.08, 0.25, and 0.04, respectively.

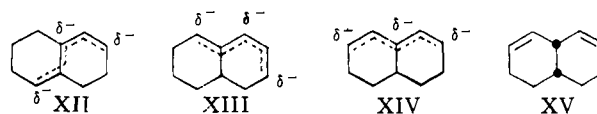
A hitherto undiscussed problem is the effect of the shape of pentadienyl carbanions on their stabilities. There are three planar shapes, "U" (VII), "sickle" (VIII), and "W" (IX); representatives of each type are found among the six pentadienyl carbanions derivable by the removal of a proton from a hexahydronaphthalene. With the aid of an analog computer,<sup>6</sup> we have determined rate constants for several hexahydronaphthalene interconversions (Fig. 1), and these

(5) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 44, 51, 56, 58.

(6) We thank the Electrical Engineering Department of the University of Illinois for the use of their Pace 16-31R instrument.

rates reflect indirectly the stabilities of the various pentadienyl carbanion intermediates.

Taking into account the relative stabilities of the dienes involved,<sup>7</sup> the rate-determining transition state for the reactions *via* VI (I  $\rightleftharpoons$  II) is more stable than that for the reactions *via* XII (II  $\rightleftharpoons$  X) by 2.3 kcal./mole, and for the reactions *via* XIII (I  $\rightleftharpoons$  XI and II  $\rightleftharpoons$  XI) by at least 3.4 kcal./mole. In another experiment, the rate of isomerization of *cis*- $\Delta^{1,7}$ -hexahydronaphthalene (XV)<sup>8</sup> to XI was found to be greater than the I  $\rightarrow$  II rate by a factor of 3.6; employing a statistical correction, the rate-determining transition state for the reaction *via* XIV (XV  $\rightarrow$  XI) is less stable than that for the reactions *via* VI (I  $\rightleftharpoons$  II) by at least 2.6 kcal./mole. Thus, it appears that in this system<sup>9</sup> *U-shaped pentadienyl carbanions are more stable than other planar types with similar substitution by about 2-5 kcal./mole.* This might be due to the ease of solvation of U-shaped carbanions by metal cations (in this case, potassium); a similar rationale has been used by Bauld in a four-carbon system.<sup>10</sup> Alternatively, there may be some 1,5  $\pi$  orbital overlap (at least on one side) in cyclohexadienyl anions, which are homocyclopentadienyl anions; structural evidence indicating the possibility of overlap on one side of the ring in a cycloheptatriene derivative has been presented.<sup>11</sup>



We are currently gaining further evidence regarding the stabilities of these and other pentadienyl carbanions.<sup>12</sup>

(7) Part I: R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3030 (1963).

(8) This compound was prepared in 46% yield by the pyrolysis of 1,7-diacetoxydecalin with predominantly *cis* ring juncture and was characterized by n.m.r., microanalysis, and lack of ultraviolet absorption. It was determined by a careful v.p.c. study that there was less than 0.1% of XV present in the equilibrium mixture of hexahydronaphthalenes, and thus it is less stable than X by at least 5.6 kcal./mole.

(9) It should be noted that all of the carbanions derivable from hexahydronaphthalenes except for XIII have two secondary and one tertiary carbon bearing negative charge. In acyclic systems, nonbonded steric interactions between "inside" substituents on the 1 and 5 carbons of U-shaped pentadienyl carbanions will probably be sufficiently serious to make this shape energetically less favorable than the other two shapes, but this remains to be demonstrated experimentally.

(10) N. L. Bauld, *J. Am. Chem. Soc.*, **84**, 4347 (1962).

(11) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, 839 (1962).

(12) We gratefully acknowledge financial support from the National Science Foundation (Fellowship to R. H. C.) and the Public Health Service (GM-07689, R. B. B. and C. E. S.).

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### Diene Studies. III. Position of Protonation of Some Pentadienyl Carbanions

*Sir:*

Previous papers in this series described diene isomerizations in which pentadienyl carbanions are intermediates, with emphasis on the stabilities of various dienes<sup>1</sup> and pentadienyl carbanions<sup>2</sup>; these species correspond to the minima on energy diagrams for the isomerization reactions. It would be useful to know the heights of the maxima on these energy diagrams, since an understanding of them would allow the prediction of the course of rate-controlled protonations of

(1) Part I: R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3030 (1963).

(2) Part II: *ibid.*, **85**, 3031 (1963).

pentadienyl carbanions and, with less accuracy, similar carbanion reactions such as carboxylations and reactions with ethylene oxide.<sup>3</sup>

The studies which most clearly involve the protonation of pentadienyl carbanions were qualitative and complicated by the presence of methoxyl substituents.<sup>4</sup> In Birch reductions of aromatic compounds, protonation of a pentadienyl carbanion (often free from oxygen-containing substituents) has been postulated to be the last step.<sup>4a,5</sup> In these reactions, it appears that protonations of U-shaped<sup>2</sup> pentadienyl carbanions take place faster at the central carbon atom than at the end carbons; it has been suggested that this is due to greater electron density on the central carbon.<sup>4a</sup> There is some evidence that these anions react with other reagents faster at the central carbon.<sup>3</sup> We wish to report quantitative experiments showing how rapidly cyclohexadienyl carbanion (I) protonates at a as compared to b under certain diene isomerization conditions (see Fig. 1).

In separate reactions, 1,2-dihydrobenzene (II) and 1,4-dihydrobenzene (III) were partially isomerized with potassium *t*-amyloxide in *t*-amyl alcohol-*O-d*<sup>6</sup> for 45 min. at 95°, and the yields of II and III in various states of deuteration were measured (after separation of total II from total III by v.p.c.) by mass spectrometry.<sup>7</sup> This early in the isomerizations, there was less than 0.3% of di- and polydeuterated II or III. In the isomerization starting from II, the yields of monodeuterated II and monodeuterated III were 5.10 and 1.28%, respectively, indicating, if deuteration of I is indeed the reaction which gives these species, that I deuterates 8 times as fast at a as at each b.<sup>8</sup> Starting from III, the yields of monodeuterated II and III were 1.49 and 0.37, respectively, again giving a factor of 8 for the rate difference. There is an acute lack of information regarding the nature of the solvation of I, but it is noteworthy that the two experiments give virtually the same rate ratio, a result consistent with the idea that a common intermediate is reacting with deuterated alcohol.

Since the isotope effects for reaction at a and at b in I should be very similar, under these conditions *I is protonated by solvent 8 times as fast at a as at each b.*<sup>9</sup> This corresponds to an energy difference of 1.52 kcal./mole for the transition states for protonation of I at a ( $\ddagger_a$ ) and at each b ( $\ddagger_b$ ), and, with previous data,<sup>1,2,10</sup>

(3) I. L. Mador and T. S. Soddy, U. S. Patent 2,960,544 (1960) (*Chem. Abstr.*, **55**, 9308 (1961)); D. R. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962). The second carbon dioxide, ethylene oxide, and trimethylchlorosilane are almost certainly reacting with pentadienyl carbanions.

(4) (a) A. J. Birch, *Quart. Rev.*, **4**, 69 (1950); (b) A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 5376 (1961).

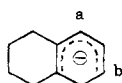
(5) (a) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 425.

(6) D. J. Cram and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 2178 (1961). The alcohol used in the current study was 95% deuterated.

(7) We thank Messrs. H. Bondarovich and S. K. Freeman of International Flavors and Fragrances, Inc., for the mass spectral results, and the National Science Foundation (fellowship to R. H. C.) and the Public Health Service (GM-07689, R. B. B. and C. E. S.) for financial support.

(8) Considerable undeuterated II was formed from III and considerable undeuterated III from II, suggesting that the same sort of intramolecular transfer that was found by D. J. Cram and R. T. Uyeda (*J. Am. Chem. Soc.*, **84**, 4358 (1962)) is occurring here.

(9) Experiments in the hexahydronaphthalene series have shown that the rate of protonation of



at a as compared to b is at least 2.5; an upper limit was not established in this case.

(10) The rate constant for the conversion of II to III used in this diagram was  $2.19 \times 10^{-4}$  sec.<sup>-1</sup>, taken from a reaction in which 21 mg. of potassium

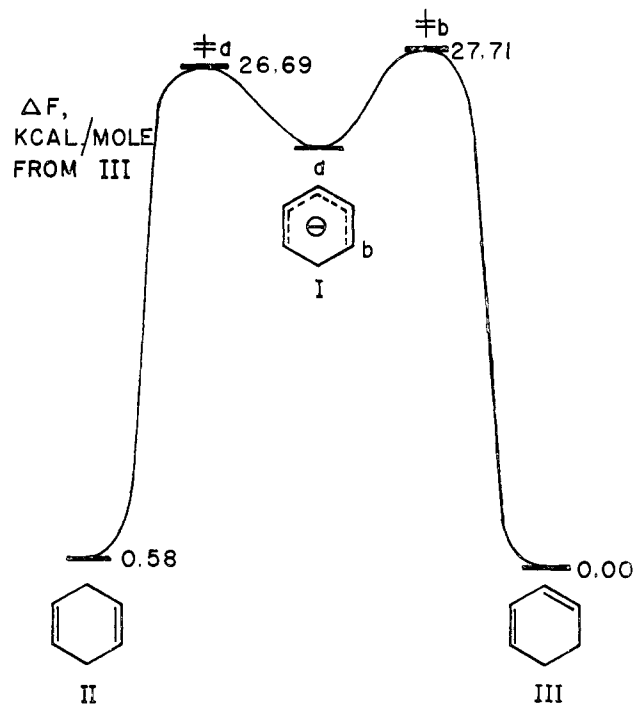


Fig. 1.—Energy diagram for the interconversion of II and III at 95.0°, without statistical corrections.

allows the assignment of numerical values to four of the five extremes in the energy diagram for the isomerization of II to III (see Fig. 1).

It is interesting that under certain conditions<sup>5a,11</sup> the ratio of protonation of I at a as compared to b appears to be larger than what we have found, and under other conditions, transfer of a hydride ion to a hydroxylic species occurs faster than abstraction of a proton.<sup>12</sup>

was treated with 257 mg. of *t*-amyl alcohol, 906 mg. of II was added, and the ampoule was sealed and immersed in a 95° bath.

(11) W. von E. Doering, G. Schroeder, K. Trautner, and S. Staley, 144th National Meeting of the American Chemical Society, Los Angeles, California, April, 1963, p. 14M.

(12) R. Paul and S. Tchelitcheff, *Compt. Rend.*, **239**, 1222 (1954); G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957). This competing hydride transfer may be a serious problem with cyclohexadienyl carbanions, but will not be with most other types of pentadienyl carbanions.

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## On the Photochemical Cyclization of Saturated Ketones and Aldehydes to Cyclobutanols<sup>1</sup>

Sir:

The photochemical formation of cyclobutanols from saturated ketones possessing  $\gamma$ -hydrogen atoms has provided a convenient synthetic tool in numerous cases.<sup>2-4</sup> A stepwise mechanism<sup>2a</sup> has been proposed for this reaction postulating  $\gamma$ -hydrogen abstraction and subsequent cyclization of the intermediate diradical (eq. 1). Available experimental data, how-

(1) Photochemical Reactions, Part 23; Part 22: *Helv. Chim. Acta*, **46**, 1599 (1963).

(2) (a) N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958); (b) *Tetrahedron Letters*, **4**, 10 (1960).

(3) (a) P. Buchschacher, M. Cereghetti, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **42**, 2122 (1959); (b) M. Cereghetti, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, **43**, 354, 367 (1960); (c) H. Wehrli, M. Cereghetti, K. Schaffner, J. Urech, and E. Vischer, *ibid.*, **44**, 1927 (1961); (d) H. Wehrli, M. S. Heller, K. Schaffner, and O. Jeger, *ibid.*, **44**, 2162 (1961); **45**, 1261 (1962); (e) J. Iriarte, K. Schaffner, and O. Jeger, *ibid.*, in press.