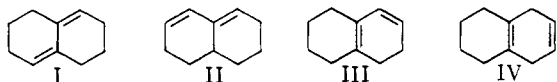


We have equilibrated the hexahydronaphthalenes with 1,3- and 1,4-diene systems and the dihydrobenzenes, and found that some new factors must be employed to explain the results.

Four hexahydronaphthalenes were detected<sup>2</sup> in the equilibrium mixture, prepared by heating  $\Delta^{1,8}$ -hexahydronaphthalene<sup>3</sup> (II) or  $\Delta^{2,9}$ -hexahydronaphthalene<sup>4</sup> (IV) with potassium *t*-amyloxide in *t*-amyl alcohol at 184° for 24 hr.:  $\Delta^{1(9),5(10)}$ -hexahydronaphthalene (I), 53.7%; II, 25.5%;  $\Delta^{1,9}$ -hexahydronaphthalene (III), 14.1%; IV, 6.4%. Taking statistical factors into account (*i.e.*, II and III are favored in isomerizations by factors of two over I and IV), these percentages indicate the other hexahydronaphthalenes to be less stable than I by 1.31 (II); 1.85 (III); 1.93 (IV); and at least 3.6 kcal./mole (other isomers, assuming that as much as 1% of another isomer would have been detected). At 95.0°, the equilibrium mixture of dihydrobenzenes (prepared from either isomer) contained 68.9% of 1,2-dihydrobenzene (V) and 31.1% of 1,4-dihydrobenzene (VI); with the statistical factor considered, V is only 0.07 kcal./mole more stable than VI at this temperature.



A well recognized factor affecting alkene stability is the degree of substitution by alkyl groups; although there is considerable disagreement as to the cause of the effect, its magnitude is known to be about 2–4 kcal./mole.<sup>5</sup> This factor undoubtedly contributes to making I–IV the four most stable hexahydronaphthalenes.

It was surprising to find in the two systems that 1,4-cyclohexadienes (IV and VI) are of essentially the same stability as the corresponding 1,3-cyclohexadienes (III and V).<sup>6</sup> This appears to be a special feature of cyclohexadienes, since in acyclic systems<sup>7,8</sup> and cyclooctadienes,<sup>10</sup> the conjugated isomer is more stable than the unconjugated isomer by several kcal./mole, due to delocalization and/or hybridization.<sup>7,8</sup> That some special destabilizing effect in 1,3-cyclohexadienes is not responsible is suggested by the heats of hydrogenation of cyclohexene and 1,3-cyclohexadiene<sup>7</sup>; there must, then, be a stabilizing feature of about 2 kcal./mole in 1,4-cyclohexadienes which is absent in other 1,4-dienes. This probably involves interaction between the double bonds; in what has been suggested as the most stable conformation,<sup>9</sup> the  $\pi$ -electrons of

the two double bonds are quite close on one side of the ring.<sup>10</sup>

Another factor which is readily noticeable in the hexahydronaphthalene series is that *transoid dienes are more stable than cisoid dienes with the same degree of alkyl substitution by about 2–4 kcal./mole*.<sup>11</sup> Thus, I is more stable than III by 1.84 kcal./mole and  $\Delta^{1(9),4}$ -hexahydronaphthalene (VII) by at least 3.6 kcal./mole; II, the other *transoid* hexahydronaphthalene, is more stable than  $\Delta^{1(9),2}$ -hexahydronaphthalene by at least 2.9 kcal./mole.<sup>12</sup> This effect had been previously observed<sup>13</sup> and given some theoretical basis<sup>14</sup> for butadiene, but with butadiene the question of the contribution of the steric interaction between the "inside" protons on carbons 1 and 4 in *cisoid* butadiene always remained.<sup>8a</sup> From the current results, it appears likely that this steric interaction is not the major factor causing the observed preference of butadiene for the *transoid* conformation.

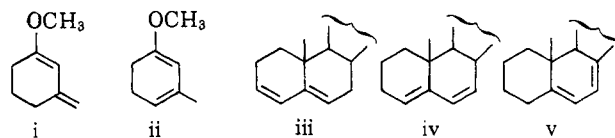
Isomerization studies on other dienes are in progress.<sup>15</sup>

(9) F. H. Herbststein, *J. Chem. Soc.*, 2292 (1959).

(10) For a suggestion of a similar effect in cycloheptatrienes, see R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, 839 (1962).

(11) Doering and co-workers (ref. 6) have noted this "destabilizing *cis* effect" in other systems.

(12) There are cases in which *transoid* dienes have been shown to be more stable (qualitatively) than *cisoid* dienes with more alkyl substituents, *e.g.*, i is more stable than ii (A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 5376 (1961)) and iii (J. C. Eck and E. W. Hollingsworth, *J. Am. Chem. Soc.*, **63**, 107 (1941)) and iv (K. Dimroth and G. Trautmann, *Ber.*, **69**, 669 (1936); H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 575 (1937)) are more stable than v.



(13) (a) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); (b) W. B. Smith and J. L. Massingill, *J. Am. Chem. Soc.*, **83**, 4301 (1961).

(14) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

(15) 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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RECEIVED JULY 22, 1963

## Diene Studies. II. Relative Stabilities of Some Pentadienyl Carbanions

Sir:

Pentadienyl carbanions have long been proposed as intermediates in nucleophilic aromatic substitution,<sup>1</sup> and more recently in Birch reductions of aromatic compounds and in base-catalyzed isomerizations of 1,3- and 1,4-dienes.<sup>2</sup> Possibly the best evidence that they are intermediates in the latter case is that double bonds in 1,3- and 1,4-dienes migrate far more rapidly in base than isolated double bonds<sup>3</sup> and when a particularly stable carbanion is involved or a particularly strong base is used, their metal salts have been obtained in high concentration.<sup>1a,2c,4</sup> Pentadienyl carbanions

(1) (a) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); (b) J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963).

(2) (a) A. J. Birch, *Quart. Rev.*, **4**, 69 (1950); (b) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); (c) A. J. Birch, E. M. A. Shoukry and F. Stansfield, *J. Chem. Soc.*, 5376 (1961); (d) W. von E. Doering, G. Schroeder, K. Trautner, and S. Staley, 144th National Meeting of the American Chemical Society, 1963, p. 14M.

(3) We have found that the isomerization of *cis*- $\Delta^1$ -octahydronaphthalene to  $\Delta^{9,10}$ -octahydronaphthalene is slower than the isomerization of I to II by a factor of at least 10<sup>5</sup>.

(4) R. Paul and S. Tchelitcheff, *Compt. Rend.*, **239**, 1222 (1954); G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

Brown, *J. Am. Oil Chemists' Soc.*, **33**, 521 (1956); (h) H. B. White, Jr., and F. W. Quackenbush, *ibid.*, **36**, 653 (1959).

(2) All of the dienes described were characterized using their n.m.r., ultraviolet, and infrared spectra, and elemental analyses. III (which shows one sharp peak in the vinyl region of its n.m.r. spectrum) was distinguished from VII by the presence of vinyl proton absorption in the n.m.r. spectrum of its adduct with tetracyanoethylene.

(3) Prepared by dehydrating  $\Delta^{1(9),2}$ -octalol (H. Böhme and G. Peters, *Z. Naturforsch.*, **12b**, 5 (1957)) with 3,5-dinitrobenzoyl chloride in pyridine and removing *cisoid* conjugated dienes by adduct formation with tetracyanoethylene.

(4) C. B. Wooster, U. S. Patent 2,182,242 (1939) (*Chem. Abstr.*, **34**, 1993 (1940)); A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(5) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 247. It is important to note that this generalization holds well for the octahydronaphthalenes (A. S. Hussey, J.-F. Sauvage, and R. H. Baker, *J. Org. Chem.*, **26**, 256 (1961)).

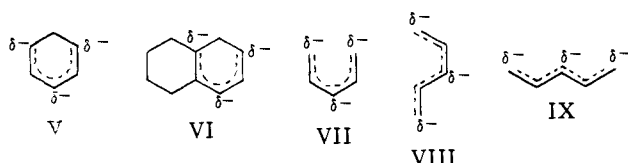
(6) W. von E. Doering, G. Schroeder, K. Trautner, and S. Staley, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, California, 1963, p. 14M. These authors have also isomerized the dihydrobenzenes, finding a similar small difference in stability when the statistical factor of 0.6 kcal./mole is taken into account.

(7) See, for example, G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 80.

(8) (a) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959); (b) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **5**, 166 (1959); (c) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

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.

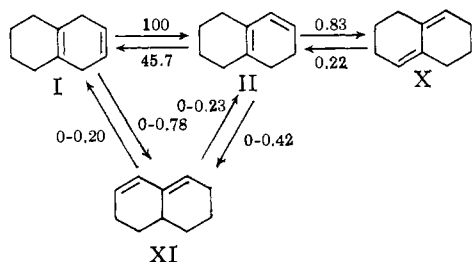


Fig. 1.—Relative rate constants ( $k_{I \rightarrow II} = 100$ ) for isomerizations with potassium *t*-butoxide in *t*-butyl alcohol at 101°;  $k_{XI \rightarrow I} = 0.39k_{I \rightarrow XI}$ ;  $k_{XI \rightarrow II} = 0.55k_{II \rightarrow XI}$ ; a reasonable fit was obtained provided that  $k_{I \rightarrow IX} + 1.85k_{II \rightarrow IX} = 0.78$ ; 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.

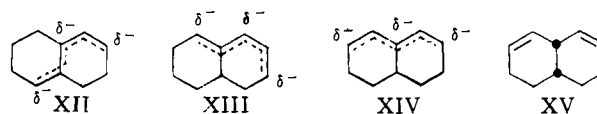
A hitherto undiscussed problem is the effect of the shape of pentadienyl carbanions on their stabilities. There are three planar shapes, "U" (VII), "sickle" (VIII), and "W" (IX); representatives of each type are found among the six pentadienyl carbanions derivable by the removal of a proton from a hexahydronaphthalene. 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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RECEIVED JULY 22, 1963

### 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).