

The transition state to the formation of free radical may be pyramidal. Further conversion to more stable planar form then takes place if this is not structurally inhibited. Spectroscopic evidence supports the idea that free radicals are most stable in the planar ( $sp^2$ ) form.<sup>8</sup> In addition, Bartlett reported elegant experiments detecting an  $sp^3$  radical of short life and the possible sequence less stable  $sp^3 \rightleftharpoons$  (strained)  $sp^2 \rightleftharpoons$  more stable  $sp^3$  was postulated.<sup>9,10</sup>

In the adamantane reaction, the adamantyl-1 radical is formed more easily from adamantane than the adamantyl-2, presumably because of the usual effects which stabilize tertiary radicals more than secondary. In addition, the 1 position, which has only equatorial character, may be more sterically accessible than the 2 position, which is axial. Thus the transition state for attack at the 1 position is more favorable than for that at the 2 position. However, the adamantyl-1 radical has to stay in a pyramidal ( $sp^3$ ) state and gains no more stabilization, but adamantyl-2 is capable of further stabilization by means of rehybridization to the planar ( $sp^2$ ) state.<sup>11</sup> This explanation should be applicable to radicals at weakly strained bridgehead positions such as in bicyclo[2.2.2]octane.

**Acknowledgment.** The authors wish to thank Professor P. von R. Schleyer for helpful discussions.

(8) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961). Karplus also claimed planar or very nearly planar structure from esr: M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959); M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

(9) P. D. Bartlett, R. E. Pincok, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965).

(10) Similar stereochemical studies of free radicals have been reported by F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875, 882 (1967).

(11) Professor Schleyer kindly pointed out that the observed selectivity can also be explained by the difference of the second barrier (from adamantyl radical to products) without crossover of energy diagram. However, this explanation also concedes that the 1 radical is destabilized (relative to its transition state) to a greater extent than is the 2 radical. We feel this is the most important point. The extent to which the 1 radical is destabilized may bring its energy either below or above that of the 2 radical. More work is needed to decide this point.

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## Radical-Anion Reactions in Hexamethylphosphoramide

Sir:

Solvent exerts a large effect upon the equilibria and kinetics of reactions involving radical ions by modifying their state of aggregation.<sup>1</sup> For example, the equilibrium between the free ions and ion pairs, or the structure of ion pairs, is greatly modified by the solvent.<sup>2</sup> We wish to report now the dramatic effects observed in radical-anion reactions performed in hexamethylphosphoramide (HMPA).

Conductance studies<sup>3</sup> demonstrated that  $10^{-3}$  M solu-

(1) (a) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961); (b) P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962); (c) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964); (d) N. Hirota and R. Kreilick, *ibid.*, **88**, 614 (1966); (e) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967); (f) M. C. R. Symons, *ibid.*, **71**, 172 (1967); R. V. Slates and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 6043 (1967).

(2) (a) J. F. Garst and R. S. Cole, *ibid.*, **84**, 4352 (1962); (b) T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307 (1966); (c) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).

(3) S. N. Bhadani, J. Jagur-Grodzinski, and M. Szwarc, submitted for publication.

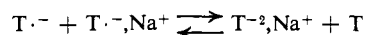
tions of lithium, sodium, or potassium salts of anthracene radical anions are virtually completely dissociated in HMPA at 25°. Similar results were obtained with various alkali and quaternary alkylammonium salts of tetraphenyl boride.<sup>3</sup> Therefore, it is plausible to assume that alkali salts of most radical ions are completely dissociated in this solvent. Conversion of ion pairs into free ions enormously affects the equilibria and rates of some radical-ion reactions. Three examples are singled out to illustrate these phenomena: disproportionation of radical ions of tetraphenylethylene, dimerization of radical ions of diphenylacetylene, and dimerization of radical ions of quinoline.

(1) Disproportionation of radical ions of tetraphenylethylene ( $T\cdot^-$ ) into the salts of dianion ( $T^{2-}$ ) and the parent hydrocarbon (T) is shifted far to the right in most ethereal solvents. At room temperature a large excess (about 1000-fold) of the hydrocarbon (T) has to be present to maintain an appreciable concentration of radical anions ( $T\cdot^-$ ) in the THF solution.<sup>4</sup> In HMPA virtually all  $T\cdot^-$  remain as radical ions, even in the absence of the parent hydrocarbon. This is evident from the following observations.

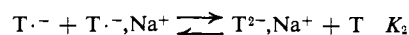
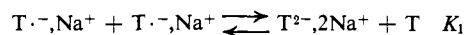
(a) A slight excess of T added to a solution of  $T^{2-}$  changes the spectrum into that attributed to  $T\cdot^-$  (see ref 4 for the pertinent spectral data). Further addition of a large excess of T does not change the spectrum any more. The intensity of the esr signal demonstrates that the concentration of free spins is nearly equivalent to the initial concentration of alkali, even if only a slight excess of T was added to a solution of  $T^{2-}$ .

(b) Similar results were obtained by adding a slight excess of T to a solution of sodium naphthalene.

The enormous change in the position of equilibrium is caused by the virtually complete dissociation of  $T\cdot^-, Na^+$  into free ions. The dianion is only half dissociated; *i.e.*, its bulk is present in the form of  $T^{2-}, Na^+$ . The equilibrium



is shifted, therefore, to the left because the concentration of  $T\cdot^-, Na^+$  is vanishingly small. The equilibrium constants of reactions



were determined previously in tetrahydrofuran<sup>4b</sup> at a temperature range of  $-20$  to  $+20^\circ$ .

It is obvious that quantitative studies of  $T\cdot^-$  radical ions now become feasible. For example, the electron affinity of T in HMPA has been determined,<sup>5</sup> whereas such studies were impossible in tetrahydrofuran.<sup>6</sup> Also, electron-transfer reactions,  $T\cdot^- + T \rightleftharpoons T + T\cdot^-$  and  $T\cdot^- + T^{2-} \rightleftharpoons T^{2-} + T\cdot^-$ , have been successfully studied.<sup>6</sup>

(2) Diphenylacetylene reacts with alkali metals, or other electron donors, yielding the respective radical

(4) (a) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 495 (1965); (b) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

(5) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, submitted for publication.

(6) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

anions.<sup>7</sup> These rapidly combine in THF solution;<sup>8</sup> e.g., at 20° their concentration decreases from  $\sim 10^{-3}$  to  $\sim 10^{-4}$  in a few seconds,<sup>9</sup> and eventually equilibrium is established between dimers and the radical ions in which the former species is greatly favored. In HMPA the radical anions do not dimerize; neither their optical spectra nor the esr signal show any detectable change after 3 hr. Changes are observed after 24 hr; however, the products are then different from dimers.

(3) Electron transfer from biphenylsodium to quinoline in THF solution produces probably dimeric dianions, the concentration of free spins being only a few per cent of their initial value. Different behavior is observed in HMPA where a quantitative conversion of  $B\cdot^-, Na^+$  into quinoline radical ions takes place. The resulting radical anions remain stable; their uv and esr spectra were recorded. In contradistinction, the reaction with pyridine leads to radical ions which apparently dimerize and eventually are converted to dipyridyl through dehydrogenation in which sodium hydride is formed.

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(7) (a) C. S. Johnson, Jr., and R. Chang, *J. Chem. Phys.*, **43**, 3183 (1965); (b) J. G. Broadhurst and E. Warhurst, *J. Chem. Soc., Sect. A*, 351 (1966); (c) R. E. Sioda, D. O. Cowan, and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 230 (1967).

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(9) E. Franta, unpublished results from this laboratory.

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## Stereospecific Conrotatory Valence Isomerization of Octatetraenes to Cycloocta-1,3,5-trienes

Sir:

*cis,cis*-Octa-1,3,5,7-tetraene cyclizes quickly at room temperature to give cycloocta-1,3,5-triene.<sup>1</sup> *all-cis*-1,8-Dimethoxycyclooctatetraene yields at 120° 7,8-dimethoxybicyclo[4.2.0]octadiene, for which the methoxy groups were suggested to be in *trans* position;<sup>2</sup> certainly the cyclooctatriene derivative is the intermediate.<sup>3</sup> A recent report<sup>4</sup> on the formation of *cis*- and *trans*-7,8-dimethylbicyclo[4.2.0]octadienes (VII and IV) provided indirect evidence that *trans,cis,cis,trans*- and *cis,cis,cis,trans*-deca-2,4,6,8-tetraene occurred as intermediates. The assumption of a conrotatory ring closure was based on nmr data of the bicyclo[4.2.0]octadienes and on the pyrolysis (200°) of dimethyl acetylenedicarboxylate adducts which were not isolated from a multicomponent mixture. We now wish to report on the highly stereospecific cyclization of the three geometrically isomeric decatetraenes I, II, and

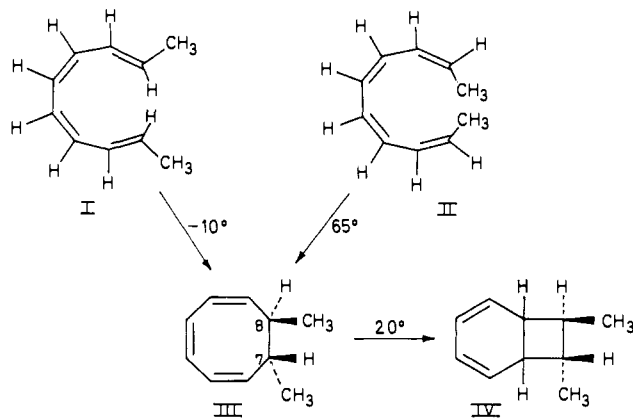
(1) W. Ziegenbein, *Chem. Ber.*, **98**, 1427 (1965).

(2) H. Meister, *ibid.*, **96**, 1688 (1963).

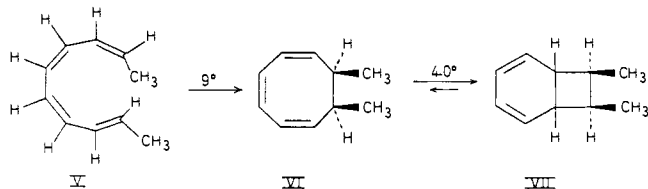
(3) In contrast to M. Kröner's opinion (*ibid.*, **100**, 3172 (1967)) all our experimental evidence speaks against the assumed direct cyclization of octatetraenes to give bicyclo[4.2.0]octadienes which violates the Woodward-Hoffmann rules.

(4) E. N. Marvell and J. Seubert, *J. Am. Chem. Soc.*, **89**, 3377 (1967).

V which were obtained crystalline. The structures of the pure products III and VI were based on conclusive evidence.



The valence isomerization of *trans,cis,cis,trans*-deca-2,4,6,8-tetraene (I) in chloroform was nearly complete at  $-10^\circ$  after 30 hr.<sup>5</sup> The pure *trans*-7,8-dimethylcycloocta-1,3,5-triene (III) underwent at  $20^\circ$  in 8 hr a second tautomerization to give *trans*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (IV).<sup>6</sup> The *all-cis* isomer II cyclized, likewise quantitatively, at  $65^\circ$ ; here, of course, the bicyclic compound IV was the only isolable product.



The rate of cyclization of *cis,cis,cis,trans*-decatetraene (V) is between that of I and II. At  $9^\circ$ , 90% of the *cis*-7,8-dimethylcyclooctatriene (VI) and 10% of its bicyclic tautomer VII were obtained. After reaching thermodynamic equilibrium at  $40^\circ$ , an approximate ratio of 15:85 was established for VI and VII.

Thus, the electrocyclic conversions of the three decatetraenes are *conrotatory* as predicted by the Woodward-Hoffmann rules;<sup>7</sup> detection limits: nmr,  $\leq 3\%$  IV in the presence of VII and *vice versa*; glpc,  $\leq 0.05\%$  and  $\leq 0.5\%$  VII in the product IV from I and II, respectively, and  $\leq 0.5\%$  IV after the cyclization of V.

The *all-cis*-octatetraene system constitutes somewhat more than one turn of a helix and offers ideal conditions for a *conrotatory* cyclization. The model shows the increasing hindrance by one or two *cis*-methyl groups in V and II, respectively. Kinetic measurements have so far been completed for the slow cyclization  $II \rightarrow III$ :  $\Delta H^\ddagger = 21.7 \pm 1.0$  kcal/mole and  $\Delta S^\ddagger = -12 \pm 3$  eu.<sup>8</sup> For comparison, the *disrotatory* cyclization of *trans,cis,trans*-octa-2,4,6-triene to give *cis*-5,6-dimethyl-

(5) Polymerization was best inhibited by using traces of dicyclohexylammonium picrate.

(6) Valence tautomeric equilibria of substituted cycloocta-1,3,5-trienes were investigated by R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, Special Publication No. 19, The Chemical Society, London, 1965, p 3.

(7) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(8) Based on rate data at seven temperatures from 57.8 to 79.0° in CDCl<sub>3</sub>.