

Figure 1.

like transition state or the twofold rotation axis in the chair-like form. The scheme shown is for the former case, and the diagram for the latter is qualitatively similar. The correlation of reactant bonding levels with product bonding levels, characteristic of a symmetry-allowed thermal reaction, should be noted. At the half-way mark in the reaction the level ordering is recognizable as that of two interacting allyl radicals. The actual behavior of the levels along the reaction coordinate is abstracted from extended Hückel calculations.<sup>4</sup>

If the correlation diagrams are qualitatively similar for four- and six-center reactions, where does the observed preference come from? An explanation requires the construction of a further correlation diagram (Figure 2) for the hypothetical process of two allyl radicals

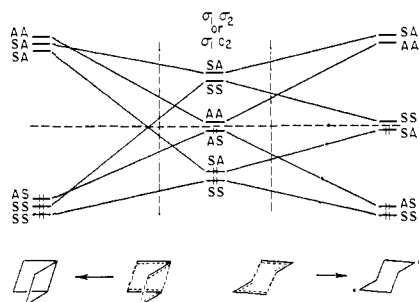


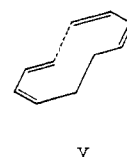
Figure 2.

approaching each other from infinity, in parallel planes, so as to pass through the symmetrical half-way points in the reaction surface for the actual Cope rearrangement. In these motions there are two symmetry elements: (1)  $\sigma_1$ , the plane passing through carbons 2 and 5, and (2) in the boat form a plane,  $\sigma_2$ , parallel to and half-way between the planes of the approaching radicals, in the chair form a twofold axis  $C_2$  perpendicular to  $\sigma_1$ . To complete the correlation one must specify the end products of this hypothetical motion; these are a bicyclohexane in the boat approach, a cyclohexyl biradical in the chair pathway. Among the occupied levels the essential difference in the two pathways is in the behavior of the occupied SA level, which in the boat approach correlates to an antibonding  $\sigma$  orbital while in the chair form it goes over to a nonbonding radical level. The crucial point of the argument now is that reactions proceeding as in Figure 1 must pass at the half-way point through some point

(4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

in the correlation diagrams of Figure 2, and that this point is approximately the same horizontal distance along in the two alternate pathways of Figure 2 (marked by vertical dashed lines). Further, at any such point the chair-like transition state is at lower energy as a result of the difference in correlation properties of the SA orbital. Or to rephrase the situation in terms of Figure 1, the occupied A level, which is 1-6 and 3-4 antibonding and consequently decreases in energy on approaching the transition state, decreases less in the boat form than in the chair. In this sense, the argument represents a further development of the simple orbital repulsion effect suggested by Doering and Berry.<sup>2</sup>

For the 5,5 sigmatropic shift, a variety of transition state conformations is available. Considerations similar to those given for the Cope rearrangement lead to the conclusion that of all these arrangements a chair-like transition state derived from a *cis,cis*-decatetraene (V) is clearly preferred.<sup>5</sup>



It should be emphasized that the effects discussed here are, not unexpectedly, small ones, and that in systems possessing special geometrical restraints which necessitate a boat-like transition state 3,3 sigmatropic changes take place with no special difficulty.<sup>6</sup>

(5) D. H. Gibson and R. Pettit, *J. Am. Chem. Soc.*, **87**, 2620 (1965), find evidence for homolytic cleavage and radical recombination in the pyrolysis of a *trans,trans*-decatetraene. The desired geometry (V) could not be attained in this case.

(6) J. M. Brown, *Proc. Chem. Soc.*, 226 (1965); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); R. Merényi, J. F. M. Oth, and G. Schröder, *Ber.*, **97**, 3150 (1964); H. A. Staab and F. Vöglte, *Tetrahedron Letters*, 54 (1965).

(7) Junior Fellow, Society of Fellows, Harvard University.

Roald Hoffmann,<sup>7</sup> R. B. Woodward

Department of Chemistry, Harvard University  
Cambridge, Massachusetts 02138

Received August 16, 1965

## The Cycloheptatrienide Dianion Radical

Sir:

We wish to report the preparation of the first aromatic dianion radical.

The Hückel energy levels for the cycloheptatrienyl system are shown in Figure 1. The low-energy antibonding molecular orbitals ( $E = \alpha - 0.44\beta$ ) are only half-filled in the cycloheptatrienide anion, the preparation of which was recently reported.<sup>1</sup> The possibility of addition of further electrons to the system is obvious. Reaction of tropylium methyl ether with a sodium mirror in purified tetrahydrofuran on a vacuum line<sup>2</sup> quickly gives the deep blue diamagnetic anion reported by Dauben and Rifi. Further reaction (20-40

(1) H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963).

(2) The reaction vessel was of the usual type<sup>3</sup> except that it had five capillary side arms into which samples could be decanted at intervals for e.s.r. analysis. Pure alkali metal mirrors were distilled from a side arm and pure solvents were distilled from storage over potassium benzophenone. Reactions were run at room temperature.

(3) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

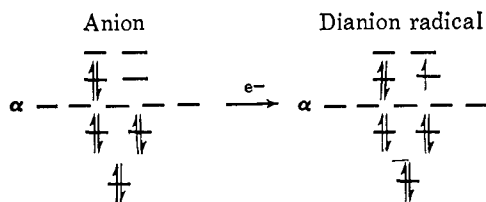
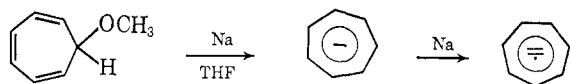


Figure 1.

min.), while periodically removing samples for e.s.r., gives a deep green radical. The e.s.r. spectrum (Figures 2 and 3), recorded at  $-100^\circ$ , is an octet (splitting



by seven equivalent protons with hyperfine splitting constant  $a_H = 3.48$  gauss). Each member of the octet is further split into a septet ( $a_{2Na^+} = 1.74$  gauss) which is best seen by magnifying the wings of the spectrum.

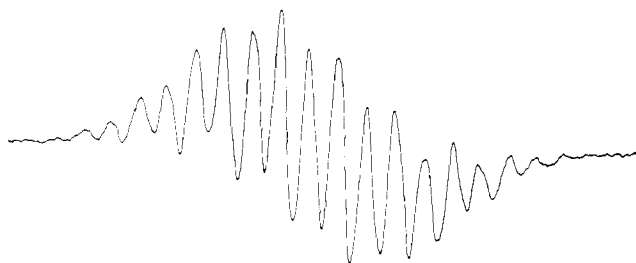


Figure 2. E.s.r. spectrum of disodium tropenide in THF at  $-100^\circ$ .

$^{23}\text{Na}$  has nuclear spin  $I = 3/2$ . Two sodium nuclei thus have an aggregate nuclear spin of  $I = 3$  and lead to  $2I + 1 = 7$  lines. No previous instance of splitting by two alkali metal ions has ever been noted for hydrocarbon radicals.<sup>4</sup> This is seen as compelling evidence that the observed radical is a dianion. The major splitting by seven equivalent protons excludes all possibilities other than the cycloheptatrienide (tropenide) dianion radical.<sup>5</sup>

The value of  $a_H$  calculated from the simple McConnell equation<sup>7</sup> is  $a = -3.86$  gauss. Employing the

(4) Splitting by one metal nucleus is common among anion radicals. See, e.g., the  $a_{Na^+} = 1.05$  gauss shown by sodium naphthalene in THF: N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961). We also have noted splitting by two metal ions in other dianion radical e.s.r. spectra.

(5) J. Dos Santos-Veiga, *Mol. Phys.*, **5**, 639 (1962), has observed an eight-line spectrum, not further resolved, upon reaction of ditropyl with potassium-sodium alloy in DME. This was attributed to the tropyl radical adsorbed on the metallic surface since decantation or filtration through glass wool greatly weakened the signal. This interpretation is invalidated by the following observations: (i) the initially formed blue species (tropenide anion) is diamagnetic and only later is the green radical formed; (ii) the radical is stable after decantation from the metal even after several hours; (iii) the tropyl radical has  $a = -3.87$  gauss or greater at  $-100^\circ$ ; (iv) filtration, *in vacuo*, through a fritted glass filter does not reduce the intensity or resolution of our signal; and (v) the signal is split by two alkali metal ions.

(6) G. Vincow, *Chem. Eng. News*, **43**, No. 26, 43 (1965).

(7)  $a_{Hi} = Q\rho_i$  where  $Q = -27$  gauss and  $\rho_i$  is the spin density at carbon  $i$  (here  $1/7$ ): H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

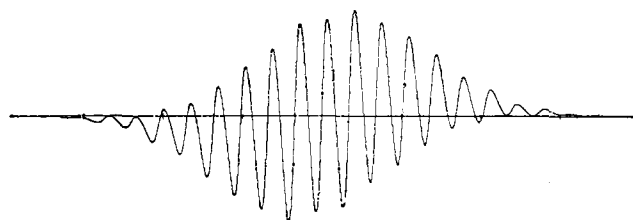


Figure 3. Calculated spectrum of disodium tropenide.

Colpa-Bolton equation<sup>8</sup>  $a_H = -3.34$  gauss is predicted. The experimental value is in much better accord with the latter equation, which predicts lower h.f.s. for more negatively charged radicals. No doubt part of the small disagreement stems from the temperature dependence of the h.f.s.<sup>6</sup>

The cycloheptatrienide dianion radical should be subject to Jahn-Teller stabilization, but no evidence is available on this point.

**Acknowledgments.** We thank the National Institutes of Health for support of this research and Messrs. Larry Wheeler and Tom Atkinson for e.s.r. measurements.

(8)  $a_{Hi} = Q_1\rho_i + Q_2q_i\rho_i$ , where  $q_i$  is the charge density at carbon  $i$  ( $-2/7$  here).  $Q_1$  and  $Q_2$  are taken as  $-27.0$  and  $-12.8$  gauss<sup>9</sup>: J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(9) L. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).

N. L. Bauld, M. S. Brown

Department of Chemistry, University of Texas  
Austin, Texas 78712

Received May 17, 1965

## Catalysis of Phosphoryl Group Transfer by Alkali Ions

Sir:

Specific catalysis by alkali ions is not a common occurrence in chemistry and therefore may be of considerable interest, particularly to investigators concerned with the transport of sodium and potassium ions through biological membranes. Verheyden and co-workers<sup>1</sup> reported that in the absence of pyridine nucleoside polyphosphates do not dismutate in dimethyl sulfoxide solutions of their tri-*n*-butylamine salts. We found likewise that there was no appreciable phosphoryl group transfer between adenosine 5'-diphosphate (ADP) molecules in a dimethyl sulfoxide solution of their tetra-*n*-butylammonium salt at 25 and 60 $^\circ$ , respectively. However, partial or complete replacement of the tetra-*n*-butylammonium ion by  $\text{Na}^+$  or  $\text{K}^+$  causes the phosphoryl group transfer to take place readily at these temperatures.  $\text{Rb}^+$  and  $\text{Cs}^+$  also catalyze this reaction, but  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Zn}^{2+}$  do not.

In the present work the ADP was used in the form of the tri- or bis(tetra-*n*-butylammonium) salt, prepared by stirring stoichiometric amounts of the barium salt of ADP (Sigma Chemical Co.) and tetra-*n*-butylammonium sulfate, centrifuging out the precipitated  $\text{BaSO}_4$ , and freeze-drying the supernatant. The early phase of the dismutation reaction of ADP in dimethyl sulfoxide (DMSO, Matheson, Spectral Quality) solution was followed by measuring the rate of increase of ATP

(1) D. L. M. Verheyden, W. E. Wehrli, and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 2257 (1965).