

Of perhaps greatest interest is the fact that the distribution of products varies significantly when different counterions are present (see Table I). It can be seen

**Table I.** Relative Yields of Major Products from the Reaction of 0.08 M 5-Methyl-5-phenyl-1,3-cyclohexadiene (**1**) with 0.8 M Alkali Metal Amide in Liquid Ammonia at 25° for 49 Hr

Products <sup>b</sup>	Relative yield, % <sup>a</sup>			
	LiNH <sub>2</sub> <sup>c</sup>	NaNH <sub>2</sub>	KNH <sub>2</sub>	CsNH <sub>2</sub>
Toluene <sup>d</sup>	53	62	60	60
Biphenyl	18	26	20	7
<b>3</b>	24	6	6	3
<b>6 + 7</b>	5 <sup>e</sup>	6	14	30

<sup>a</sup> Average of at least two runs; generally reproducible to  $\pm 10\%$  of the listed value. All values are corrected for gpc molar response factors. <sup>b</sup> All products are stable under the reaction conditions. <sup>c</sup> Largely heterogeneous but not affected by a 40-fold dilution. <sup>d</sup> There was normally 5–35% less benzene than toluene. <sup>e</sup> Approximate value.

that the relative yields of **3**, biphenyl, and **6 + 7** are greatest with lithium, sodium, and cesium amides, respectively. These results cannot be correlated by a straightforward application of the principle of hard and soft acids and bases<sup>17</sup> (HSAB) since the "hardest" cation (lithium)<sup>18</sup> appears to be paired with the "softest" activated complex (elimination of hydride).<sup>17,19</sup> However, a correlation can be made if one considers the solvation of the counterions in the activated complexes. By this analysis elimination of "hard" methide and the somewhat "softer" cyclopropyl ring cleavage proceed (relatively) fastest when present as contact ion pairs (or higher aggregates) involving sodium and cesium, respectively, whereas elimination of "soft" hydride is fastest with "soft" solvated lithium.<sup>20</sup>

This interpretation was tested and given strong support by the observation that when 0.08 M **1** is caused to react with 0.8 M potassium amide in the presence of 0.8 M dicyclohexyl-18-crown-6, a cyclic polyether capable of complexing with potassium ions,<sup>21,22</sup> the relative yield of **3** increases to 22%, similar to that for lithium amide.<sup>23</sup> Although the reasons for HSAB correlations are not entirely clear,<sup>15,16a</sup> this analysis nevertheless does provide evidence for the nature of the ion pairing in the various activated complexes.<sup>24</sup>

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(22) We thank Drs. H. E. Simmons and D. J. Sam of E. I. du Pont de Nemours and Co. for providing a sample of this compound.

(23) The other relative yields were 59% toluene, 9% biphenyl, and 10% **6 + 7**; in this case the yield of benzene exceeded that of toluene.

(24) Each of these processes can, in principle, occur *via* both contact and solvent-separated ion-pair activated complexes; this is perhaps most probable in the formation of benzene and toluene and the cyclohexadienes.

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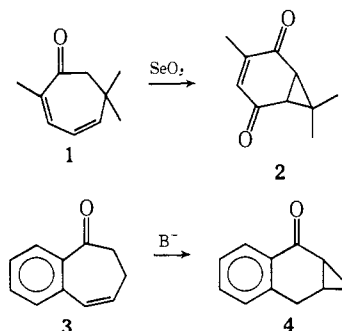
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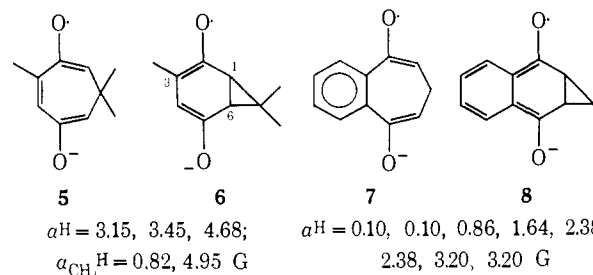
## Application of Electron Spin Resonance Spectroscopy to Studies of Valence Isomerization. II. Bicyclo[4.1.0]heptene-2,5-semidiones<sup>1</sup>

Sir:

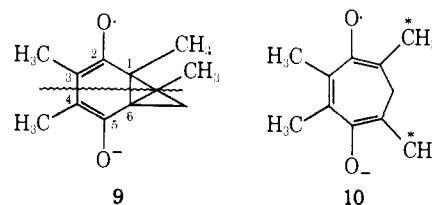
Valence isomerizations of the enolate anions derived from eucarvone (**1**) or 2,3-benzocyclohepta-2,4-dienone (**3**) are known.<sup>2,3</sup> Treatment of **1** with base followed



by a trace of oxygen yields a semidione that is also produced by treatment of **2** with potassium *t*-butoxide in DMSO solution. The semidione could have structure **5** or **6**. In a similar fashion treatment of **3** or **4** with base followed by a trace of oxygen yields a semidione that can have either structures **7** or **8**.



Structures **6** and **8** for the semidiones are instinctively preferred because the parent diones must have these bi- and tricyclic structures. The magnetic nonequivalence of the methylene hydrogen atoms in **7** and **8**, or of the *gem*-dimethyl groups in **5** and **6**, is more consistent with structures **6** and **8** than **5** and **7**. Final proof of structure is furnished by semidione **9** prepared by treatment of the bicyclic dione<sup>4</sup> with base in DMSO.



$\alpha^H = 1.95, 0.87 \text{ G}$   
 $\alpha_{CH_3}^H = 5.20, 5.20, 0.25, 0.25 \text{ G}$   
 $\sim\sim =$  nodal plane in  $\psi_4$

(1) This work was supported by grants from the National Science Foundation and the Army Research Office (Durham); part I: G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **91**, 2813 (1969).

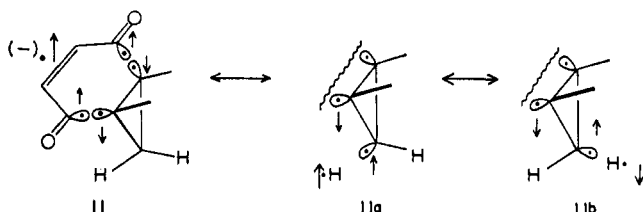
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(3) S. Julia and Y. Bonnet, *Bull. Soc. Chim. France*, 1340 (1957); E. E. van Tamelen, J. McNary and F. A. Lornitzo, *J. Amer. Chem. Soc.*, **79**, 1231 (1957).

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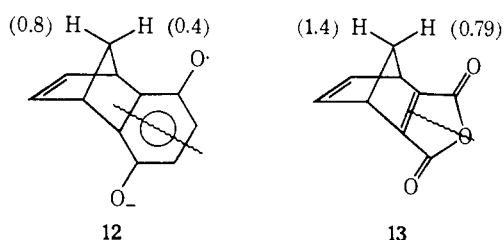
Structure **10** would require that the values of  $a_{\text{CH}_2^{\text{H}}}$  and  $a^*_{\text{CH}_3^{\text{H}}}$  be roughly equivalent since hyperconjugation of the methylene and starred methyl hydrogen atoms would be nearly equal. Such is obviously not the case and structure **9** is demanded. By analogy, **6** and **8** are preferred to **5** and **7**. The large methyl splittings in **6** and **9** must be associated with the methyl groups at C-3.<sup>5</sup>

Semidiones **6**, **8**, and **9** possess the interesting property that the nodal plane in the HOMO bisects the cyclopropane ring. The opposite signs of the coefficients at C-2 and C-5 in  $\psi_4$  prevents the delocalization of the unpaired spin into the cyclopropyl methylene position since such an interaction takes the form<sup>8</sup>  $a^{\text{H}} = Q(c_2 + c_5)^2$ . A spin polarization mechanism is required to introduce the spin from the  $\pi$  system into the  $\sigma$  framework. Such a mechanism, as pictured in structure **11**, would allow  $a^{\text{H}} = Q(c_2^2 + c_5^2)$ .

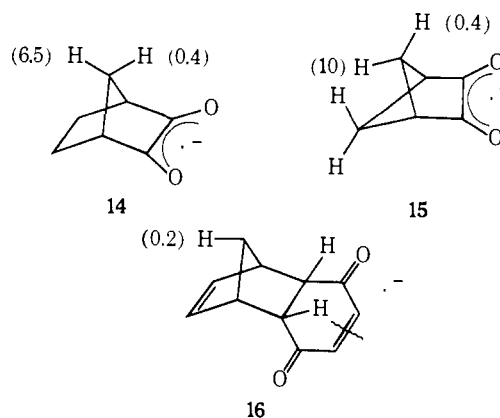


The low stereoselectivity observed for the methylene hydrogen splitting in **8** and **9** is consistent with further delocalization of the unpaired electron *via* hyperconjugation structures **11a** and **11b**. Extended Hückel calculations indicate that the magnitude of interaction **11b** should be about twice of that of structure **11a**.<sup>9</sup>

The present results define the magnitude of long-range interactions involving spin polarization as well as the low stereoselectivity of  $2V$  spin transmittal by this mechanism. This spin polarization mechanism, also involved in the splittings shown for **12** and **13**,<sup>10,11</sup> does not appear to contribute significantly to long-range splittings of the magnitude and stereoselectivity

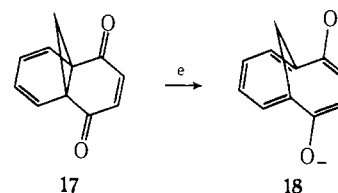


observed for **13** and **15**.<sup>12,13</sup> However, not all long-



range interactions initiated by spin polarization between  $\pi$  and  $\sigma$  electrons have a low stereoselectivity. The  $2.5V$  interactions observed for the *anti*-methyl group of **6**, or the *anti* hydrogen of **16**,<sup>14</sup> appear to be as highly stereospecific as the  $2V$  splittings observed for **14** or **15**.

The present results also exclude a homoaromatic, ring-opened structure for the semidione derived from bicyclo[4.1.0]heptene-2,5-dione. The homoaromatic structure is also excluded for cycloheptatriene radical anion.<sup>15</sup> In the latter case, the orbital symmetry of  $\psi_4$  prevents bonding between the terminal carbon atoms of the  $\pi$  system.<sup>16</sup> However, such a restriction does not apply to the semidione, *e.g.*,  $\psi_5$  for **10**. It might be argued that in **10** the carbonyl groups are cross-conjugated with the  $\pi$  system, thereby favoring the bicyclic structure. That such ring opening with delocalization can occur in a bicyclo[4.1.0]heptene-2,5-semidione is demonstrated in the conversion of **17** to **18**. Treatment of the tricyclic diketone<sup>17</sup> with a



mild reducing agent, such as the enolate anion of propiophenone, yields the bicyclic semiquinone **18** wherein the unpaired electron has been extensively delocalized into the entire  $\pi$  system:  $a_{\text{CH}^{\text{H}}} = 2.85, 2.85, 0.78, 0.78, 0.25, \text{ and } 0.25 \text{ G}$ ;  $a_{\text{CH}_2^{\text{H}}} = 0.78 \text{ and } 0.25 \text{ G}$ .

(5) The unsubstituted and *anti*-7-methyl semidiones have also been prepared and exist in the bicyclic structure (unpublished results of Dr. J. R. Dodd). The 1,4-di-*t*-butylbicyclo[4.1.0]heptane-2,5-dione<sup>8</sup> gives a semidione with  $a^{\text{H}} = 4.1$  (C-3), 2.2 (C-6 or *anti* C-7), 1.4 (*anti* C-7 or C-6), and 0.9 (*syn* C-7) G and  $a_{\text{CH}_3^{\text{H}}} = 0.2 \text{ G}$  for two methyl groups. Conformational preference and hindered rotation of the 4-*t*-butyl group<sup>7</sup> are thus seen.

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(17) A sample of the diketone was generously supplied by Professor E. Vogel (Diplomarbeit, E. Lohmar, University of Cologne, 1965).

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