

central iron atom stabilized in an unusually high (+4) oxidation state.

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### CIDNP in Dispiro[2.2.2]deca-4,9-diene in Its Thermolysis. CIDNP Derived from a Short-Chain Singlet Biradical

Sir:

The phenomenon of CIDNP has been successfully accounted for by the radical pair theory proposed by Closs<sup>1</sup> and by Kaptein and Oosterhoff.<sup>2-5</sup> According to this theory, to observe CIDNP it is necessary that a radical pair separates after its birth to a distance where the S-T<sub>0</sub> splitting in the pair is sufficiently small and spends a sufficiently long time at that distance to allow substantial S-T<sub>0</sub> mixing by hyperfine interactions and g shift. In normal radical pairs, the above condition is easily fulfilled by diffusive displacements of the components.<sup>6</sup> In biradicals, however, radical centers cannot be separated beyond the distance the molecular structure allows. Therefore, such a requirement can be a severe limitation to the observation of (S-T<sub>0</sub>) CIDNP in the reactions of short-chain biradicals and, to our knowledge, (S-T<sub>0</sub>) CIDNP has not been observed in the products derived from these species. We report here the observation of CIDNP effect in a product which seems certain to be derived from a short-chain singlet biradical.

The nmr spectrum of dispiro[2.2.2]deca-4,9-diene (**1**) consists of two sharp singlets at  $\delta$  0.6 and 4.8.<sup>7</sup> An nmr tube containing the solution of **1** in triglyme was placed in the probe of a JEOL PS-100 spectrometer preheated at 193° and the spectrum was recorded repeatedly. After an initial period of time for the sample to warm up, the intensity of the singlet at  $\delta$  0.6 began to increase rapidly and reached a maximum<sup>8</sup> after ca. 150 sec, while that of the singlet at  $\delta$  4.8 decreased and the signal turned to emission after ca. 70 sec (Figure 1). During the decomposition of **1**, CIDNP signals which would be due to the reaction products<sup>9</sup> were also observed.<sup>10,11</sup> The polarization in **1** was observed in *p*-di-

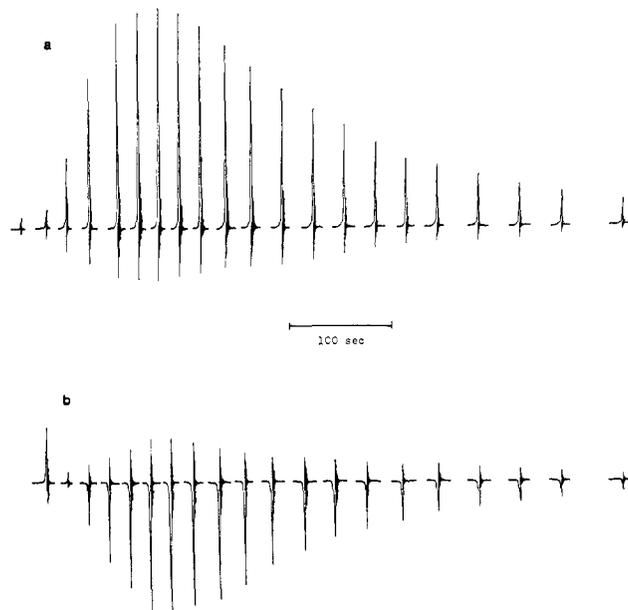
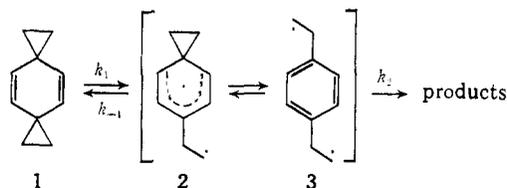


Figure 1. Time development of the polarization during decomposition of dispiro[2.2.2]deca-4,9-diene in triglyme at 193°, obtained by repeated sweeping through regions of  $\delta$  0.6 (a) and 4.8 (b). The spectrum amplitude of (b) is ten times that of (a).

bromobenzene and diphenyl ether as well as in triglyme.

The rate of disappearance of **1** ( $4.53 \times 10^{-3} \text{ sec}^{-1}$  at 193° in triglyme) was in good agreement with that of the decay of the polarized signals, and maximum intensity of the enhanced absorption at  $\delta$  0.6 was found to depend linearly on the concentration of **1** ranging from 0.01 to 0.1 *M*. These results clearly showed that the responsible species for the polarization in **1** was formed in a first-order reaction from **1**. The first step of the reaction would no doubt be homolytic cleavage of the cyclopropane ring. The resulting biradical, **2**,



would further rearrange to **3** because **2** was structurally equivalent to the intermediate postulated in 1,2-aryl migration.<sup>12-16</sup> In the presence of radical scavenger

(12) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(13) The possibility that **3** underwent further rearrangement to **4** will



be slight, though it cannot be ruled out rigorously. Although the allyl-carbinyl-cyclopropylcarbinyl radical rearrangement, to which **2**  $\rightleftharpoons$  **3** corresponds, is the well-documented process,<sup>14-16</sup> few, if any, instances of the allylcarbinyl-cyclobutyl radical rearrangement have been known. We have obtained no experimental results which indicated the intermediacy of **4**.

(14) C. Walling, "Molecular Rearrangements," Vol. 1, P. DeMayo, Ed., Interscience, New York, N. Y., 1963.

(15) L. K. Montgomery, J. W. Watt, and J. R. Wefster, *J. Amer. Chem. Soc.*, **89**, 923 (1967); L. K. Montgomery and J. W. Watt, *ibid.*, **89**, 934, 3050 (1967).

(16) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 3051 (1967).

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(5) R. G. Lawler, *Accounts Chem. Res.*, **5**, 25 (1972).

(6) F. J. Adrian, *J. Chem. Phys.*, **54**, 3912 (1971).

(7) T. Tsuji, S. Nishida, and H. Tsubomura, *J. Chem. Soc., Chem. Commun.*, 284 (1972).

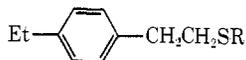
(8) The maximum enhancement factor  $I_{\text{max}} - I_0/I_0$ , where  $I_{\text{max}}$  was the maximum intensity and  $I_0$ , the thermal equilibrium intensity, was ca. 20.

(9) The thermolysis of **1** in diglyme afforded *p*-diethylbenzene in 73% yield.

(10) An enhanced triplet absorption at  $\delta$  1.2, an enhanced quartet absorption at  $\delta$  2.5, and a sharp singlet emission at  $\delta$  7.0.

(11) Samples were deoxygenated by argon bubbling. One of the samples was degassed through four freeze-thaw cycles on a vacuum line ( $1 \times 10^{-3}$  mm).

such as *p*-thiocresol and benzylmercaptan, the rate of disappearance of **1** was accelerated more than 10 times, indicating that  $k_{-1}/k_2 \geq 10$  in the absence of the radical scavenger. Because the polarization in **1** was not observable under the above conditions, the radical responsible for the polarization in **1** or one equilibrating with it must have been efficiently trapped. *p*-Diethylbenzene and the addition product **5** were the major



**5**, R = *p*-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> for *p*-thiocresol  
= C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> for benzyl mercaptan

products. Thus, only **2** and **3** seem conceivable as the species in which the polarization arose.<sup>17</sup> Indeed the thermal reactions of **1** investigated so far were all accountable in terms of the intermediacy of **2** and **3**.<sup>7,18</sup> The possibility that the polarization was brought about through the dynamic behavior of the rather long-chain biradical **3**, however, is ruled out on the ground that spin-selection in a pair of equivalent radicals ( $\Delta g = 0$ ) cannot give net polarization.<sup>1,2,19</sup> Therefore the polarization would certainly be brought about through the dynamic processes of the singlet (thermally generated from ground state) biradical **2**.<sup>20</sup>

According to the current theory, radical centers in a biradical must be separated to the distance where S-T<sub>0</sub> splitting  $2J$  becomes the order of hyperfine interactions to give rise to (S-T<sub>0</sub>) CIDNP. Therefore, unless the biradical is large enough to fulfill the above condition, no CIDNP effect is expected in its reaction. Recently Closs and Doubleday<sup>21</sup> reported that the average S-T<sub>0</sub> splitting in the 1,7-biradical resulting from the photo- $\alpha$ -cleavage of cycloheptanone amounted to 1.87 cm<sup>-1</sup> (20 kG), which was *ca.* 10<sup>3</sup> times the magnitude of a typical hyperfine interaction. Present results imply that even in **2**, the exchange interaction is sufficiently small to give rise to (S-T<sub>0</sub>) CIDNP.

Some rather short-chain biradicals generated in the triplet state have been reported to exhibit CIDNP due to S-T<sub>-</sub> mixing.<sup>21-23</sup> CIDNP in **1**, however, is apparently not due to S-T<sub>-</sub> mixing because all the polarization should occur in emission or absorption in the (S-T<sub>-</sub>) CIDNP spectrum.

CIDNP is a highly useful tool for the mechanistic investigations on the radical reactions. The results reported here show that CIDNP may be expected in the products derived from short-chain singlet biradicals in

(17) The biradical species formed reversibly by the reaction of **2** or **3**



with solvent may be rejected because the CIDNP effect was observed in solvents widely different in chemical properties: triglyme, *p*-dibromobenzene, and diphenyl ether.

(18) T. Tsuji and S. Nishida, *J. Amer. Chem. Soc.*, **95**, 7519 (1973).

(19) Even if  $\Delta g \neq 0$ , the polarization of olefinic protons whose hyperfine couplings in **3** should be small is difficult to explain; *cf.* J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

(20) The distribution of odd electron density in the cyclohexadienyl radical has been reported to be 0.349 on C<sub>1</sub> and C<sub>5</sub>, -0.103 on C<sub>2</sub> and C<sub>4</sub>, and 0.506 on C<sub>3</sub>: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963); **39**, 2147 (1963).

(21) G. L. Closs and C. E. Doubleday, *J. Amer. Chem. Soc.*, **95**, 2735 (1973).

(22) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971).

(23) G. L. Closs, *J. Amer. Chem. Soc.*, **93**, 1546 (1971); G. E. Closs and C. E. Doubleday, *ibid.*, **94**, 9248 (1972).

certain cases.<sup>24-26</sup> We make this preliminary report because the present results promise to be of considerable importance, in view of current interests in the CIDNP phenomenon and the chemistry of short-chain biradicals.

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(24) Since S-T<sub>0</sub> mixing by the hyperfine interactions does not involve any change in the *z* components of nuclear spins, to observe CIDNP *via* spin selection, spin-independent competitive process is required. In the normal radical pair reactions, diffusive separation of the components generally provides such a process. In the biradical reactions, diffusive separation is absent. Closs and Trifunac<sup>1</sup> predicted that (S-T<sub>0</sub>) CIDNP would not be observed in the biradical reactions because of the absence of diffusive process. However, (S-T<sub>0</sub>) CIDNP is apparently observed as shown in this reaction and others.<sup>26,26</sup> Rearrangement of **2** to **3** and subsequent solvent transfer reaction would provide the spin-independent process for **2** in this reaction.

(25) R. Kaptein, M. Frater-Schroeder, and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1971).

(26) T. Tsuji and S. Nishida, *Chem. Lett.*, 1335 (1973).

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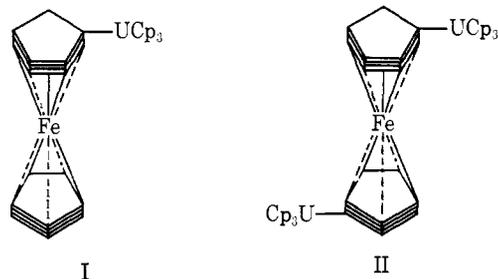
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### Synthesis of a New Type of $\sigma$ -Bonded Organouranium Compound. Mono- and Bis[tris( $\eta^5$ -cyclopentadienyl)uranium]ferrocene<sup>1</sup>

Sir:

In recent years, there has been a growing interest in organoactinide chemistry, with particular emphasis on seeking evidence for covalency and possible 5f orbital participation in the bonding.<sup>2</sup> Two important types of compounds have been prepared and studied: the  $\pi$ -bonded "uranocenes"<sup>3</sup> and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>UR (R is a  $\sigma$ -bonded alkyl or aryl group).<sup>4</sup> In our further studies of this latter class of compounds, we wish to report the preparation and some properties of two new novel derivatives, [tris( $\eta^5$ -cyclopentadienyl)uranium]ferrocene (I) and 1,1'-bis[tris( $\eta^5$ -cyclopentadienyl)uranium]ferro-



cene (II). These are the first compounds of the type  $\eta^5$ -Cp<sub>3</sub>UR (Cp = cyclopentadienyl) where R is an

(1) Organolanthanides and Organoactinides. VIII.

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