

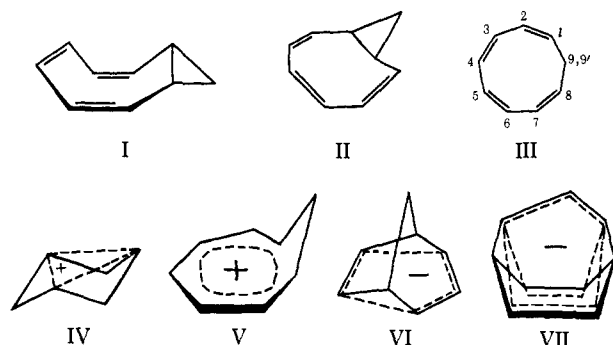
# Monohomocyclooctatetraene or Cyclononatetraene Anion Radical<sup>1</sup>

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**Abstract:** The anion radicals of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (I), *trans*-bicyclo[6.1.0]nona-2,4,6-triene (II), and *cis*<sup>4</sup>-cyclononatetraene (III) have been prepared and their esr spectra measured. Comparison of the esr spectral data shows that I and III yield a species which is a nonclassical nine  $\pi$ -electron, monohomocyclooctatetraene, while II produces an anion radical which is a classical seven  $\pi$ -electron hexatrienyl system.

Various homoaromatic species such as the tris-homocyclopropyl cation (IV),<sup>3,4</sup> the monohomocyclopropyl cations (V),<sup>3,5</sup> 1,3-bishomocyclopentadienide anion (VI),<sup>3,6</sup> and bicyclo[3.2.2]nonatrienyl anion (VII)<sup>3,7</sup> with delocalized two, six, and eight  $\pi$ -electron systems have been reported and discussed.



Generally, in the field of electron spin resonance of organic paramagnetic species, attention has been focused on investigations of anionic, cationic, and neutral radicals of classical  $\pi$  and  $\sigma$  systems. Prior to this work,<sup>1</sup> the use of electron spin resonance spectroscopy as a tool in observation and investigation of the phenomenon of homoconjugation in odd electron systems had not been reported. The electron spin resonance investigation of the radical anions of certain seven and

(1) Portions of this work have been published as communications: R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4729 (1966); G. Moshuk, G. Petrowski, and S. Winstein, *ibid.*, **90**, 2179 (1968).

(2) (a) Deceased Nov 23, 1969; (b) deceased Jan 1972; (c) University of North Carolina; (d) to whom inquiries should be sent at the Virginia Polytechnic Institute and State University.

(3) S. Winstein, *Chem. Soc. Spec. Publ.*, No. 21, 5 (1967); Nonclassical Ions and Homoaromaticity (British Chemical Society 1967 Centenary Lecture), *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(4) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, **81**, 6523, 6524 (1959); **83**, 3235, 3244 (1961).

(5) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. Friedrich, *ibid.*, **87**, 3267 (1965); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966); (c) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962).

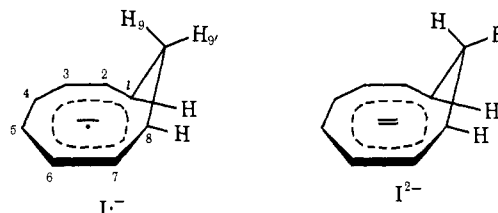
(6) (a) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967); (b) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); *J. Chem. Soc. B*, 411 (1968); (c) J. M. Brown, *Chem. Commun.*, 638 (1967); (d) J. W. Rosenthal and S. Winstein, *Tetrahedron Lett.*, 2683 (1970); (e) J. M. Brown and E. N. Cain, *J. Amer. Chem. Soc.*, **92**, 3821 (1970); (f) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971); (g) P. K. Freeman and T. A. Hardy, *ibid.*, 3939 (1971); (h) J. M. Brown, E. N. Cain, and M. C. McIvor, *J. Chem. Soc. B*, 730 (1971).

(7) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968).

nine  $\pi$ -electron species, namely those derived from I, II, and III, provides strong evidence that nonclassical electron delocalization occurs in such odd electron systems.

## Results

Previously,<sup>1,8</sup> it was reported that upon reduction of *cis*-fused I with potassium metal in 1,2-dimethoxyethane (DME) at low temperature, monohomocyclooctatetraene (MHCOT) anion radical,  $I^{\cdot-}$ , was formed as an intermediate to the dianionic ten  $\pi$ -electron system, the monohomocyclooctatetraene dianion,  $I^{2-}$ . Simultaneously, Katz and Talcott<sup>9</sup> reported the results



of similar investigations on  $I^{\cdot-}$  employing a liquid  $NH_3$  electrolysis technique to generate the anion radical. The large disparity between the sets of observed  $a_H$  values (Table I) reported for  $I^{\cdot-}$  using the different

**Table I.** Comparison of Observed  $a_H$  Values of the Anion Radical Generated from III and Those of the MHCOT Anion Radical ( $I^{\cdot-}$ )

Species	Method	$a_H$ (G) at position					
		1	2	3	4	9	9'
III <sup>-</sup>	Reduction with K	5.87	0.85	5.28	2.08	4.71	12.15
$I^{\cdot-}$	Reduction with K	6.70	0.90	4.50	1.10	2.00	16.80
$I^{\cdot-}$	Electrolysis	5.24	1.02	5.24	2.04	4.80	12.00
$I^{\cdot-}$	Electrolysis	5.87	0.84	5.26	2.11	4.90	12.15
$I^{\cdot-}$	Reduction with K	5.72	0.87	5.12	1.99	4.54	12.18

<sup>a</sup> As reported by Katz and Talcott.<sup>9</sup> <sup>b</sup> As reported by F. J. Smentowski.<sup>11</sup> <sup>c</sup> Refined  $a_H$  values, this work.

reduction methods was the cause of further investigation on the system.

Reduction of I with a potassium mirror in DME at low temperatures ( $-84^\circ$ ) for brief times, produced a much sharper spectrum. Analysis of this spectrum afforded essentially the same coupling constants as

(8) M. Ogliaruso, R. Rieke, and S. Winstein, *ibid.*, **88**, 4731 (1966).

(9) T. J. Katz and C. Talcott, *ibid.*, **88**, 4733 (1966).

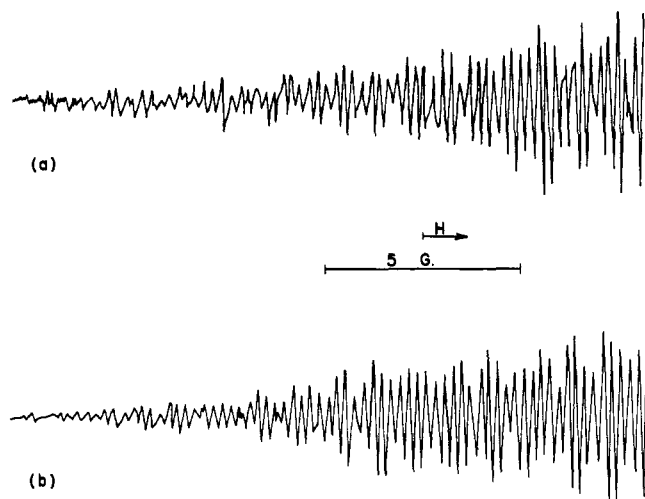


Figure 1. ESR spectra (one-half spectra shown) of 9,9'-D<sub>2</sub>-MHCOT·<sup>-</sup>: (a) observed, -84°; (b) calculated, 0.13-G peak width.

those reported by Katz and Talcott<sup>9</sup> and are recorded in Table I. Exchange broadening similar to that observed for cyclooctatetraene (COT) radical anion<sup>10</sup> was the probable cause for excessive line broadening in the original spectra reported and thus, the difference in the  $a_H$  values reported.

Partial confirmation of the  $a_H$  analysis was obtained by reducing the corresponding 9,9'-D<sub>2</sub>-I to its anion radical (Figure 1a). Taking  $a_{D_1}$  and  $a_{D_2}$  as 2/13 of the corresponding  $a_H$  values, along with  $a_{H_1}$  to  $a_{H_8}$  values similar to those in I·<sup>-</sup>, a spectrum (Figure 1b) was constructed which compared very favorably with the observed spectrum of the 9,9'-D<sub>2</sub>-MHCOT anion radical.

At the same time that these reinvestigations were being conducted in our laboratories, we learned that similar investigations were being conducted elsewhere. It was reported<sup>11</sup> that upon variation of the reducing metal (Li, Na, and K), solvent (DME and THF), and temperature (-90 to -30°), no significant change in  $a_H$  values for the MHCOT anion radical occurs.

The more refined  $a_H$  values determined for the species obtained upon reduction of I, do not in any way affect the original arguments proposed for the structure of the resulting species, the monohomocyclooctatetraene anion radical.

**trans-Bicyclo[6.1.0]nona-2,4,6-triene.** The remarkable effect of the cis-fused cyclopropyl on the electronic distribution and structure of the odd electron species formed upon reduction of I, immediately suggested a course for subsequent research. Since it was conceivable that the observed effect may be the consequence of the peculiar cyclopropyl "banana-shaped" bonds, which are intermediate between  $sp^3$  and  $sp^2$  in character, and not the result of  $C_1-C_3$   $\sigma$ -bond ring opening and  $C_1-C_8$  p-orbital homointeraction, it was clear that the generation of the corresponding anion radical from trans-fused II would be interesting and informative in this respect. A synthetic method for the preparation of II was communicated to us by Vogel and Grimme<sup>12</sup>

(10) H. L. Strauss, T. J. Katz, and G. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 2360 (1963).

(11) F. J. Smentowski, R. M. Owens, and B. D. Faubion, *ibid.*, **90**, 1537 (1968).

(12) E. Vogel and W. Grimme, University of Koln, personal communications, 1967.

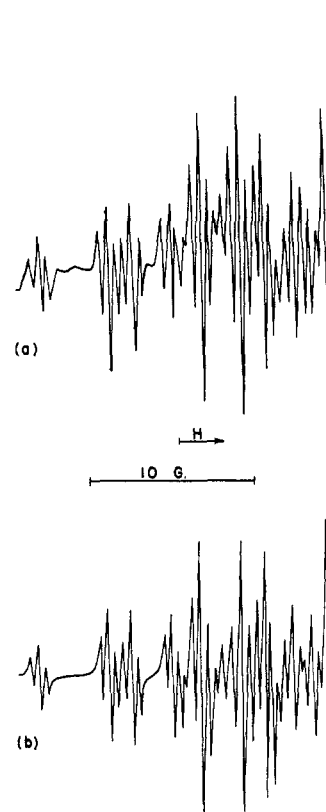
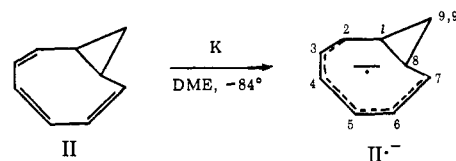


Figure 2. ESR spectra (one-half spectra shown) of trans-fused MHCOT·<sup>-</sup> (II·<sup>-</sup>): (a) observed, -90°; (b) calculated, 0.16-G peak width.

and we can now claim the successful generation and observation of the anion radical derived from trans-fused II.

The trans-fused compound (II) was prepared by irradiation of cis-fused I with a low-pressure Hg lamp. Depending upon the photolysis conditions employed, various yields of II were obtained.<sup>13</sup> Using appro-



appropriate light filters and a low irradiation temperature, up to 11% photoisomerization of *cis*-I to *trans*-II occurred. The corresponding 9,9'-D<sub>2</sub>-II, with its deuterium unscrambled, was obtained from 9,9'-D<sub>2</sub>-I using similar methods.

Treatment of II in DME with a potassium mirror at -90° produced an anion radical whose esr spectrum (Figure 2a) is well resolved and relatively simple. The spectrum can be readily analyzed and is simulated excellently (Figure 2b) with the  $a_H$  values summarized in Table II. These  $a_H$  values are very different from those observed for the anion radical generated from the cis-fused compound, but are quite similar to those reported (Table II) for the anion radical generated from cycloheptatriene.<sup>14</sup> Evidently, the hyperfine splittings (hfs) of the bridgehead monolefinic protons must be essentially zero. An upper limit of |0.10| G was

(13) G. Petrowski, Ph.D. Dissertation, University of California, Los Angeles, 1969.

(14) D. H. Levy and R. J. Meyers, *J. Chem. Phys.*, **43**, 3063 (1965).

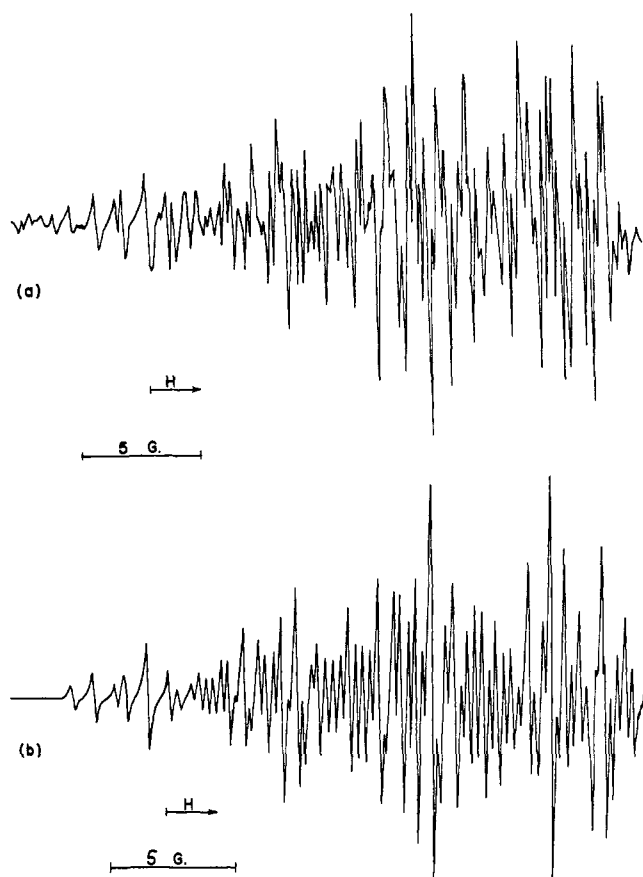


Figure 3. (a) Observed esr spectrum of the anion radical generated from *cis*<sup>4</sup>-CNT,  $-94^\circ$ ; (b) calculated esr spectrum of *cis*<sup>4</sup>-CNT anion radical, 0.13-G peak width.

**Table II.** Observed  $a_H$  Values for the *trans*-Bicyclo[6.1.0]nona-2,4,6-triene Anion Radical as Compared with Those of Cycloheptatriene<sup>a</sup>

Species	$a_H$ at position				
	1	2	3	4	5
Trans-fused II $\cdot^-$	5.61 or 4.22	8.11	0.00 ( $< 0.10 $ )	4.22 or 5.61	0.49
Cycloheptatriene $\cdot^-$	2.16	7.64	0.59	4.90	

<sup>a</sup> D. H. Levy and R. J. Meyers, *J. Chem. Phys.*, **43**, 3063 (1965).

established for this constant by including it in spectrum reconstruction and observing the effect of its inclusion on the appearance of the calculated spectrum. Generation of the 9,9'-dideuterio-*trans*-fused anion radical produced a spectrum composed of fewer lines because of the absence of the 0.46 G splitting. Consequently, this splitting must arise from the 9,9' protons. The remaining  $a_H$  values were assigned upon the basis of spin density calculations, the method employed is discussed in greater detail in the calculations section.

The anion radical of II showed no tendency to rearrange to any other paramagnetic species upon long observation (6 hr) at  $-90^\circ$ , as the esr spectrum remained the same. An increase of the temperature at which the anion radical was observed caused the species to decay, and thus a decrease of the esr line intensity occurred. At temperatures above  $-60^\circ$ , a paramagnetic species could no longer be detected.

***cis*<sup>4</sup>-Cyclononatetraene (CNT).** The completely different behavior exhibited by I upon reduction as com-

pared to II aroused our interest in the completely opened monocyclic all *cis*-CNT.

The thermally unstable *cis*<sup>4</sup>-CNT (half-life at  $23^\circ$ , ca. 50 min)<sup>13</sup> and its 9-D analog were prepared by quenching lithium cyclononatetraenide<sup>15</sup> with cooled ( $0^\circ$ ) water and D<sub>2</sub>O.<sup>16</sup> The quench, work-up, and purification steps were conducted in a cold room ( $-20$  to  $0^\circ$ ) to prevent excess thermal rearrangement of CNT.<sup>17</sup> Preparative gas chromatographic purification of III was carried out using a short column, composed of 3% bis( $\beta$ -cyanoethoxy)ethane, while maintaining the column at  $0^\circ$  with ice cooling. Utilizing such conditions, III could be separated from *cis*- and *trans*-8,9-dihydroindene<sup>17</sup> as well as *cis*-fused I if it were present, without thermally rearranging substantial quantities of III. Immediately prior to reduction, analytical gas chromatography purified III showed the sample to contain 4.0% *cis*- and 4.8% *trans*-8,9-dihydroindene. A similar analysis of 9-D<sub>1</sub>-III showed approximately the same amounts of 8,9-dihydroindene-*d*<sub>1</sub> (4.2% *cis*- and 5.0% *trans*). Because of the thermal instability of III, a purer product could not be obtained chromatographically employing the above conditions. However, when these impurities were treated separately with potassium in DME, no reaction occurred; *i.e.*, no solution color change or esr signal was observed, indicating that their presence should not hinder the esr investigation on III.

A DME solution of III was reduced with potassium taking special precautions to keep the solution at low temperature. The anion radical which was formed and observed at  $-94^\circ$  produced the esr spectrum shown in Figure 3a, and the solution was not extremely stable under these conditions, as a fairly rapid decay of signal intensity was observed. The signal intensity as measured by the peak heights, diminished to one-half the initial intensity in approximately 10 min. As the temperature was increased from  $-94^\circ$ , the esr signal became weaker and at temperatures above  $-50^\circ$ , a paramagnetic species could no longer be detected. After 10–15 anion radical generations and observations, the DME solution became dark greenish brown and contained precipitated particles. The instability of the anion radical could possibly be due to the lack of 100% purity of III and/or to the rapid conversion of the anion radical to a diamagnetic form, *i.e.*, a dianion.

The reduction of III was repeated on different samples of the compound having approximately the same composition as reported above. The spectrum illustrated in Figure 3a was the most intense and well resolved of all of the esr spectra measured. Generally, the observed spectra were composed of broad, unresolved lines.

A more detailed inspection of the esr spectrum revealed that it was quite similar to that observed for I $\cdot^-$  obtained from I. In fact, this spectrum is almost identical with that observed for I $\cdot^-$ , produced by

(15) E. LaLancette and R. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).

(16) P. Radlick and G. Alford, *ibid.*, **91**, 6529 (1969).

(17) Work by G. Petrowski at the University of California, Los Angeles, showed that *cis*<sup>4</sup>-CNT thermally rearranges solely to *cis*-8,9-dihydroindene: Ph.D. Dissertation, 1969; G. Boche, H. Bohme and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **8**, 594 (1969); S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969); A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969).

prolonged contact of the DME solution of I with potassium metal.

The observed  $a_H$  values for the anion radical generated from III are summarized in Table I, where they are compared with those of  $I\cdot^-$ , and were assigned on a similar basis.

The spectrum shown in Figure 3b, constructed with the  $a_H$  values reported in Table I, compares favorably with the observed spectrum. Line positions correspond perfectly, but due to the fact that certain groups of lines are clustered and not completely resolved in the observed spectrum, line intensities do not match perfectly.

Along with the gas chromatographic purification and analysis showing that III was free of I, additional evidence that the esr spectrum was not arising from an impurity of I was obtained by reducing 9-D<sub>1</sub>-III. The nmr spectrum of the material produced upon quenching the lithium cyclononatetraenide showed singlet resonance peaks at  $\tau$  4.3 (8 olefinic protons) and 7.0 (1 methylene proton), indicating that deuterium scrambling had not occurred.

The anion radical of the monodeuterated compound produced a spectrum (Figure 4a) which was composed of fewer and broader lines, spread over a narrower total line width (40 G), than the undeuterated III spectrum. At first glance, reduction of 9-D<sub>1</sub>-III to its anion radical would be expected to produce a species similar to the species formed when undeuterated III is reduced. However, the C<sub>9</sub> methylene position of the CNT anion radical was observed to have two magnetically nonequivalent hydrogens. Consequently, when 9-D<sub>1</sub>-III is reduced, a mixture of anion radicals, with deuterium equally in each of the unequivalent 9 positions, would be expected. A mixture composed of 50% 9-D<sub>1</sub>-III and 50% 9'-D<sub>1</sub>-III should result from the reduction of 9-D<sub>1</sub>-III. Thus, using similar  $a_H$  values as observed for the undeuterated species, and applying the  $^{2/13}$  factor to the 9 and 9'  $a_H$  values, a spectrum (0.16-G peak width, Figure 4b) was calculated for the 50-50% mixture of radicals. The spectrum, calculated in this manner, compares quite favorably with the observed spectrum. From the efforts which went into simulating the experimental spectrum, it is evident that the deuterium in the molecule is the major cause of the extensive line broadening. The observed spectrum of the 9-D<sub>1</sub>-III anion radical is merely a superimposition of the spectrum of the two radicals.

Variations of temperature did not affect the spectrum of CNT anion radical significantly. The lines of the observed spectrum were broadened upon increasing the temperature.

### Calculations

It is clear that the methylene hydrogens of the MH-COT anion radical are  $\beta$  to a center bearing unpaired spin density since the observed  $a_{CH_2}$  values are very large. The fact that the two methylene proton  $a_H$  values are largely different at all temperatures indicates that the molecule is not flat. The net result of a twisting of the methylene group out of the plane is to force considerable overlap of the 2p orbitals at C<sub>1</sub> and C<sub>8</sub>. The overlap of these orbitals produces by definition a monohomocyclooctatetraene system. In contrast, the small and equal  $a_{CH_2}$  values of the trans-fused II anion

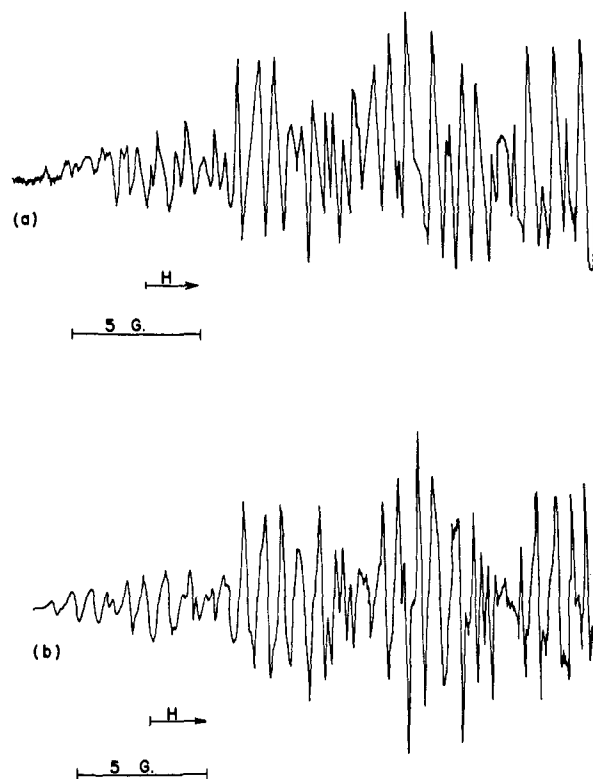


Figure 4. ESR spectra (one-half spectra shown) of 9-D<sub>1</sub>-cis<sup>4</sup>-CNT anion radical: (a) observed, -94°; (b) calculated (using a mixture of 50% 9- and 50% 9'-D<sub>1</sub>-cis<sup>4</sup>-CNT anion radicals), using Lorentzian lines of 0.16-G peak width.

radical indicates that the methylene hydrogens are  $\gamma$  to the nearest center bearing spin density, and that the C<sub>1</sub>-C<sub>8</sub> cyclopropyl bond is not involved in odd electron delocalization. Thus, the  $a_H$  value assigned to the C<sub>1</sub>-C<sub>8</sub> ring hydrogens of  $I\cdot^-$ , generated from both I and III, along with the  $a_H$  assignment to the hydrogens of the C<sub>2</sub>-C<sub>7</sub> hexatriene system of  $II\cdot^-$ , was based on spin density calculations for such systems. Unpaired spin densities were calculated by simple HMO and more sophisticated McLachlan<sup>18</sup> methods. The  $a_H$  values were calculated by applying the McConnell<sup>19</sup> relation ( $a_H = Q\rho$ ), with the observed hfs being assigned to the respective hydrogens by comparison with these values.

Hückel molecular orbital calculations neglecting overlap ( $S = 0$ ) were performed on various models of  $I\cdot^-$ . The models included (Table III): (1) a

Table III. Models Employed in  $a_H$  Calculations for  $I\cdot^-$

$\beta_{C-C}$ (in $\beta_0$ )	Model					
	1	2 <sup>a</sup>		3 <sup>b</sup>		
		a	b	a	b	c
$\beta_{1,2}$	1.0	0.89	0.81	1.0	1.0	0.89
$\beta_{2,3}$	1.0	0.93	0.89	1.0	1.0	0.93
$\beta_{3,4}$	1.0	0.81	0.81	1.0	1.0	0.81
$\beta_{4,5}$	1.0	1.0	1.0	1.0	1.0	1.0
$\beta_{1,8}$	Varied	Varied	Varied	0.50	0.60	0.60

<sup>a</sup> Similar parameters as used by R. Rieke, unpublished work at University of California, Los Angeles. <sup>b</sup> Similar hyperconjugation parameters included for the methylene group as suggested by C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(18) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

(19) H. M. McConnell, *J. Chem. Phys.*, 24, 632, 764 (1956).

planar C<sub>1</sub>-C<sub>8</sub> system in which all resonance integrals were equal to unity except  $\beta_{1,8}$  which was varied from 0 to 1; (2) a system in which the carbon p orbitals were tilted slightly inward or outward to minimize ring strain, while varying  $\beta_{1,8}$  from 0 to 1; (3) a model which included hyperconjugation parameters for the methylene group. Using a  $Q = 27.40$  and  $28.16$  for the anion radicals generated from I and III, respectively, and the Hückel and McLachlan spin densities obtained from the HMO calculations, the  $a_H$  values as summarized in Table IV were calculated.

Table IV. Calculated  $a_H$  Values for I<sup>-</sup>

Model	$\beta_{1,8}$	Position							
		1		2		3		4	
		(i) <sup>a</sup>	(ii) <sup>b</sup>	(i) <sup>a</sup>	(ii) <sup>b</sup>	(i) <sup>a</sup>	(ii) <sup>b</sup>	(i) <sup>a</sup>	(ii) <sup>b</sup>
1 <sup>c</sup>	0.50 $\beta_0$	4.80	6.29	2.03	0.88	3.91	4.22	2.96	2.31
	0.75 $\beta_0$	4.10	4.78	2.75	2.22	3.65	3.81	3.20	2.89
2(a) <sup>c</sup>	0.50 $\beta_0$	4.92	6.83	1.78	0.35	4.35	4.90	2.64	1.16
	0.60 $\beta_0$	4.59	6.11	2.11	0.97	4.24	4.71	2.77	2.32
2(b) <sup>c</sup>	0.75 $\beta_0$	4.09	4.09	2.55	1.92	4.11	4.73	2.95	2.99
	0.50 $\beta_0$	5.06	7.15	2.04	0.53	4.06	4.45	2.59	1.60
3(a) <sup>d</sup>	0.75 $\beta_0$	4.07	4.11	2.88	2.47	3.86	4.22	2.91	2.91
	0.50 $\beta_0$	4.68	6.19	1.64	0.43	3.73	4.07	2.67	2.00
3(b) <sup>d</sup>	0.60 $\beta_0$	4.47	5.75	1.89	0.88	3.64	3.95	2.76	2.19
3(c) <sup>e</sup>	0.60 $\beta_0$	4.52	6.19	1.52	0.21	3.93	4.46	2.34	1.42
Observed									
$a_H$ 's from I <sup>-</sup>		5.72		0.87		5.12		1.99	
Observed									
$a_H$ 's from III <sup>-</sup>		5.87		0.85		5.28		2.08	

<sup>a</sup> These  $a_H$  values calculated from Hückel spin densities. <sup>b</sup> These  $a_H$  values calculated from McLachlan spin densities ( $\lambda = 1.00$ ). <sup>c</sup> Calculated with  $Q = 27.40$  (i.e., I<sup>-</sup> from I). <sup>d</sup> Calculated with  $Q = 28.16$  (i.e., I<sup>-</sup> from III).

The actual agreement between the calculated and the observed  $a_H$  values for I<sup>-</sup> is best when McLachlan spin densities and a  $\beta_{1,8}$  of  $0.60\beta_0$  are employed in the calculations. However, for all models with  $\beta_{1,8} = 0.75\beta_0$  or less, the calculated hfs sequence  $a_{1,8} > a_{3,6} > a_{4,5} > a_{2,7}$  is predicted by both Hückel and McLachlan spin densities. The agreement is not improved when hyperconjugation parameters are included for the methylene group when a nonplanar C<sub>1</sub>-C<sub>8</sub> model (model 3c) is considered (using McLachlan spin densities). When these parameters are included in calculations for a model which exhibits C<sub>1</sub>-C<sub>8</sub> planarity, the fit between calculated and observed  $a_H$ 's is improved slightly. The calculated  $a_H$  values of I<sup>-</sup> from I and III are essentially the same, differing only by a small  $Q$  value factor.

Assuming coplanarity of the methylene C<sub>9</sub> with the remaining  $\pi$  system, and in particular with C<sub>1</sub> and C<sub>8</sub>, large and equal hfs of 20-30 G were calculated for the methylene hydrogens of I<sup>-</sup>, using various models which both included and disregarded C<sub>1</sub>-C<sub>8</sub> homo-interaction. The method of Levy and Meyers<sup>20</sup> was employed in these calculations of  $\beta$  hydrogen splitting which arises mainly through hyperconjugative interaction. Applying an orientation dependence<sup>21</sup> (1)

(20) D. H. Levy and R. J. Meyers, *J. Chem. Phys.*, **43**, 3063 (1965); D. H. Levy, Ph.D. Dissertation, University of California, Berkeley, 1965.

(21) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962); C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960); M. C. R. Symons, *J. Chem. Soc.*, **48**, 277 (1959).

on the methylene hydrogen splitting, we can estimate  $\theta$ ,

$$a_\beta = (B_0 + B_2 \cos^2 \theta)\rho \quad (1)$$

the dihedral angle between  $p_z$  on C<sub>1</sub> or C<sub>8</sub> and each C-H bond on C<sub>9</sub>. In this relationship (1),  $B_0$  and  $B_2$  are constants ( $B_2 \gg B_0$ ) and  $\rho$  represents the spin density at the trigonal carbon of the attachment. To account for the vast difference in the observed methylene hfs, angles of approximately 52 and 67° are required for the orientation of each C<sub>9</sub> hydrogen bond with the C<sub>1</sub> or C<sub>8</sub>  $p_z$  orbital.

The  $a_H$  values calculated for various planar and nonplanar (helical) hexatriene models of II<sup>-</sup>, including hyperconjugation parameters for the methine hydrogen, were in very good agreement (Table V) with the ob-

Table V. Calculated  $a_H$  Values for II<sup>-</sup> (in Gauss)

Model	$a_H$ at position					
	2		3		4	
	(i) <sup>a</sup>	(ii) <sup>b</sup>	(i) <sup>a</sup>	(ii) <sup>b</sup>	(i) <sup>a</sup>	(ii) <sup>b</sup>
Using Hückel $\rho$ 's						
Planar <sup>c</sup>	6.70	7.45	1.33	1.48	4.31	4.79
Nonplanar <sup>c,e</sup>	5.90	6.57	1.65	1.84	4.78	4.45
Planar <sup>d</sup>	6.22	6.92	1.21	1.35	4.00	4.71
Nonplanar <sup>d,e</sup>	5.52	6.14	1.56	1.73	4.46	5.61
Using McLachlan $\rho$ 's ( $\lambda = 1.00$ )						
Planar <sup>c</sup>	8.96	9.97	-0.69	-0.76	4.05	4.51
Nonplanar <sup>c,e</sup>	7.77	8.64	-0.13	-0.15	4.70	5.22
Planar <sup>d</sup>	8.12	9.07	0.48	0.53	3.89	4.33
Nonplanar <sup>d,e</sup>	7.11	7.91	0.06	0.07	4.48	4.99
Observed	8.11	8.11	0.00	0.00	4.22	5.61

<sup>a</sup> The  $a_H$ 's in columns (i) are calculated with  $Q = 24.66$ . <sup>b</sup> The  $a_H$ 's in columns (ii) are calculated with  $Q = 27.44$ . <sup>c</sup> Hyperconjugation parameters not included for methine hydrogen. <sup>d</sup> Hyperconjugation parameters included for methine hydrogen. <sup>e</sup>  $\beta_{3,4} = \beta_{4,5} = 0.80\beta_0$ .

served  $a_H$  values. The  $Q$  value used in the calculations was taken as 24.66 or 27.44. An ambiguity remains as to the proper assignment of an  $a_H$  to C<sub>2</sub> and C<sub>7</sub> (4.22 or 5.16 G) as both  $Q$  values are reasonable. The  $Q$  value of 35.88, obtained by summing  $a_{H_1}$  to  $a_{H_8}$ , however, is well out of the range of known  $Q$  values and provides further evidence that the C<sub>1</sub>-C<sub>8</sub> cyclopropyl electrons are not involved in electron delocalization. The calculation which included hyperconjugation parameters for the methine hydrogens, along with a spin polarization correction term for the calculated  $a_H$  values, produced an  $a_{H_{1,8}}$  value of approximately 7.5 G, which favors a  $Q$  value of 24.66 and  $a_{H_{1,8}} = 5.16$  G. Hückel  $\rho$ 's do not give as good a fit of calculated with observed  $a_H$ 's as McLachlan  $\rho$ 's, but do predict the correct sequence  $a_{H_2} > a_{H_4} > a_{H_3}$ .

## Discussion

The behavior of cis-fused I upon addition of an electron parallels that previously observed for cyclooctatetraene.<sup>22</sup> Instead of entering an antibonding olefinic molecular orbital, an additional electron supplied to tub COT prefers to enter a nonbonding orbital of planar COT. The most probable conformation of I has been suggested to be VIII.<sup>23</sup> Addition of an

(22) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

(23) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).



VIII

extra electron will tend to flatten the hexatriene portion of the molecule. The opening of the cyclopropane ring may occur upon the addition of the extra electron or it may involve a finite activation energy. In any event, it is clear that the C<sub>1</sub>-C<sub>8</sub> bond has been broken from the large coupling constants of the methylene protons. If the resulting radical anion were planar, little or no overlap would occur between the p orbital on C<sub>1</sub> and the p orbital on C<sub>8</sub>. However, the non-equivalency of the methylene protons indicates that C<sub>9</sub> is tilted out of the plane of the molecule. The tilting of the p orbitals result in a 1,8 interaction of a  $\sigma$  2p-2p type as well as the usual  $\pi$  2p-2p type. Simple calculations<sup>24</sup> using Slater orbitals indicate substantial overlap integrals for even small degrees of tilting. Accordingly 1,8 interaction is likely to be substantial and hence the description of this radical anion as the monohomocyclooctatetraene radical anion. The exact driving force for this type of rearrangement to this particular geometry is not clear. It may arise from a lowering of  $\pi$ -electron energies or a relief of strain. However, the substantial 1,8 interaction necessitates the description of this species as a homoconjugated cyclooctatetraene.

On the other hand, addition of an electron to monocyclic *cis*<sup>4</sup>-CNT promotes partial C<sub>1</sub>-C<sub>8</sub> ring closure to the same delocalized nine  $\pi$ -electron system which was formed upon reduction of I. The *cis*<sup>4</sup>-CNT needs only to undergo a slight geometrical rearrangement upon the addition of an electron to attain the proper geometry to become identical with a MHCOT anion radical.

The behavior exhibited by *trans*-fused II upon addition of an electron is in direct contrast to that of the corresponding *cis*-fused compound. The arrangement of the hexatriene portion of the *trans*-fused compound is nearly planar about the *trans*-cyclopropyl and cyclooctatriene ring fusion. Actual models of the hydrocarbon show the hexatriene portion of the *trans*-fused compound to be in a helical arrangement about the *trans*-ring fusion. The uv absorption of the *trans* compound confirms its increased planarity as a  $\lambda_{\text{max}}$  of 311  $\mu$  is observed for the *trans* compound as compared to a  $\lambda_{\text{max}}$  of 247  $\mu$  for the *cis*-fused compound. Since the situation would be more favorable for conjugation in such a planar triene form, valence tautomerism does not occur and the additional electron remains delocalized in a  $\pi$ -hexatriene system.

The inclusion of the C<sub>1</sub>-C<sub>8</sub> cyclopropane electrons in the delocalized electronic system of the MHCOT anion radical and their exclusion in the *trans*-fused anion radical is very meaningful. With the aid of an orbital symmetry argument of the type employed by Woodward and Hoffmann<sup>25</sup> for electrocyclic reactions,

the difference between the two cases may be understood. The symmetry of the highest occupied MO of an octatetraene system with an additional electron is such that the conversion of an opened CNT anion radical to a bicyclic hexatriene anion radical and the reverse reaction are predicted to be disrotatory. The opening of the anion radical from the *cis*-fused I leads to the anion radical of *cis*<sup>4</sup>-CNT, and its geometry favorable for a compromised delocalized electronic system intermediate in character between the bicyclic hexatriene and monocyclic CNT anion radical. The reverse process, disrotatory C<sub>1</sub>-C<sub>8</sub> ring closure leading to the same MHCOT anion radical, occurs when monocyclic *cis*<sup>4</sup>-CNT is reduced. A disrotatory opening of the *trans*-fused anion radical is toward a very uncomfortable *trans,cis*<sup>3</sup>-CNT, and a geometry which is unfavorable for olefinic conjugation and C<sub>1</sub>-C<sub>8</sub> interaction. Clearly, it is more advantageous for the *trans*-fused anion radical to remain a relatively favorable hexatriene type anion radical than to open.

The ring-opening process, rationalized on the basis of MO symmetries, is not as clear if the symmetries of all occupied orbitals in starting material and product(s) are considered. The orbital correlation diagrams<sup>26</sup> for disrotatory and conrotatory modes of cyclopropyl ring opening in *cis*-fused bicyclononatriene anion radical to MHCOT anion radical show that both processes are formally disallowed as the symmetries of starting material and product are different.<sup>27</sup> However, if one assumes  $\beta_{1,8} = 1.0\beta_0$  for the ring-opened product a disrotatory mode of ring opening is allowed for the dianion. Thus it is possible that it is the dianion which undergoes the ring opening. The ring opened dianion would, of course, establish an equilibrium between the radical anion and the dianion.

### Experimental Section

Anion radicals were prepared by reduction of the compounds with potassium metal in DME at low temperatures (-78 to -94°), using conventional vacuum line techniques.

The esr spectra were recorded using a Varian Model V-4502 X-band spectrometer with 12-in. magnets. Temperature was controlled within  $\pm 1^\circ$  by a Varian V-4557 variable-temperature control.

Spin density calculations were performed with IBM 7094 and 360 computers, while calculated spectra were obtained with a Cal Comp adaptation to the 7094 computer.

*cis*-Bicyclo[6.1.0]nona-2,4,6-triene (I). This compound was prepared by treating potassium cyclooctatetraenide in THF with methylene chloride, according to the procedure of Katz and Garratt.<sup>28</sup> The product was purified by preparative gas chromatography on a 15% SE-30 on Chromosorb W column (60°). Analysis of the chromatographed material with a PE-800 analytical gas chromatograph showed the compound to be greater than 99.9% pure.

9,9-Dideuterio-*cis*-bicyclo[5.1.0]nona-2,4,6-triene. The 9,9-dideuterated compound was prepared by reacting potassium cyclooctatetraenide (0.1 mol) with an equimolar amount of dideuteriomethylene chloride using a similar procedure as for the parent hydrocarbon: yield 6.9 g (50%); nmr (neat)  $\tau$  4.10-4.16 (d, 6, vinyl H), 8.97 (s, 2, allylic H); mass spectrum showed 1.9 D per molecule.

*trans*-Bicyclo[6.1.0]nona-2,4,6-triene<sup>12,13</sup> (II). The *cis*-fused I (1.5 g) was dissolved in 220 ml of methanol and then placed in the Pyrex well of a photolysis apparatus. A Nester-Faust low-pressure Hg lamp was immersed in the methanol solution which was purged with nitrogen for a few hours prior to irradiation.

The apparatus was placed in a water bath (23°) while the irradiation

(24) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 15.

(25) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (c) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(26) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(27) As pointed out by J. I. Brauman, Stanford University, private communication.

(28) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

tion was in progress. After approximately 24 hr of irradiation, the solvent was removed and the reaction products were separated and collected by glc. A 20% bis( $\beta$ -cyanoethoxy)ethane on Chromosorb W column (85°) was utilized for the separation. In addition to *trans*-8,9-dihydroindene (6%), tricyclo[3.3.1.0<sup>8,9</sup>]nonadiene (30%) and *cis*-fused I (18%) were obtained. *Trans*-fused compound (164 mg) was collected (11%): uv (EtOH)  $\lambda_{\max}$  311 nm ( $\epsilon$  4500); nmr (neat)  $\tau$  4.1 (s, 6, vinyl H) and 9.0 (m, 4, allylic and cyclopropyl H). Analysis of the compound on an analytical glc instrument prior to reduction with potassium showed it to be >99.9% pure.

**9,9-Dideuterio-*trans*-bicyclo[6.1.0]nona-2,4,6-triene.** Using similar conditions as described in the previous experiment, 0.7 g of 9,9-D<sub>2</sub>-I in methanol was irradiated with a low-pressure Hg lamp for 18 hr. After concentrating the reaction mixture, the following compounds were separated and collected by gas chromatography on the column used above: 5,5-dideuterio-*trans*-dihydroindene (22%); 5,5-dideuterio-*cis*-dihydroindene (3%); 2,2-dideuterio-tricyclo[3.3.1.0<sup>8,9</sup>]nonadiene (52%); 5,5-dideuterioindene (8%); and 9,9-D<sub>2</sub>-II, 105 mg (15%), nmr (neat)  $\tau$  4.1 (s, 6, vinyl H) and 9.0 (s, 2, allylic H).

***cis*<sup>4</sup>-Cyclononatetraene<sup>16</sup> (III).** *anti*-9-Chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-triene<sup>28</sup> (7.5 g, 0.01 mol) and 4 ml of THF, previously distilled from lithium aluminum hydride, were placed in a 25-ml round-bottomed Schlenk flask equipped with a mechanical stirring bar and a micro condenser, while maintaining a nitrogen atmosphere in the flask. Lithium metal (180 mg), cut in small pieces, was then added to the solution. The reaction was allowed to proceed at room temperature under a nitrogen atmosphere for 24 hr, after which time it turned dark brown in color. The mixture was then cooled to 0° and 10–15 ml of water (0°) was quickly added with stirring. The quench of the lithium cyclononatetraenide and the

work-up were conducted in a cold room at –20 to 0°. The CNT produced from the quench was quickly extracted with three 3-ml portions of chilled pentane (0°), and the combined pentane extracts were dried over MgSO<sub>4</sub>. After filtration and concentration of the pentane solution, it was chromatographed by glc on a 3% bis( $\beta$ -cyanoethoxy)ethane on 60–80 Chromosorb W column (3/8 in.  $\times$  1.3 ft) at 0°. The preparative gas chromatographic instrument was placed in the cold room in order to maintain low-temperature conditions for the collection. When a sufficient amount (100 mg) of III was collected, the chromatography was stopped and the collected material was analyzed on an analytical PE-800 gas chromatograph (employing the same column as above) and it showed the following composition: 4.0% *cis*-8,9-dihydroindene; 4.8% *trans*-8,9-dihydroindene; and 91.2% III, nmr (D<sub>8</sub>-THF)  $\tau$  4.3 (s, 8, vinyl H), 7.1 (t, 2, allylic H).

**9-Deuterio-*cis*<sup>4</sup>-cyclononatetraene.** Lithium cyclononatetraenide<sup>15</sup> (0.01 mol) in THF solution was quenched with D<sub>2</sub>O (15 ml) at 0°. The product was worked up in the same manner as described above. Analytical glc showed the following composition for the material which was purified by preparative gas chromatography: 4.2% *cis*- and 5.0% *trans*-8,9-dihydroindene; 90.8% 9-D<sub>1</sub>-III, nmr (D<sub>8</sub>-THF)  $\tau$  4.3 (s, 8, vinyl H) and 7.1 (broad s, 1, allylic H).

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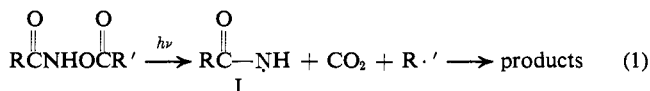
## Diacylamino and Diacyl Nitroxide Radicals from Triacylhydroxylamine Photolyses<sup>1</sup>

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Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521. Received August 12, 1972

**Abstract:** Irradiation of *N,N,O*-tripropionylhydroxylamine, *N,N,O*-triacetylhydroxylamine, and *N*-acetoxysuccinimide causes photolysis to produce mainly CO<sub>2</sub>, the corresponding imide, and the *N*-alkylimide. A mechanism is proposed which involves formation of a diacylamino radical which undergoes hydrogen abstraction, coupling, and in one case disproportionation. Thus, photolysis of triacylhydroxylamines will provide a simple method for producing both cyclic and acyclic diacylamino radicals. A strong epr signal was observable during photolysis of the triacylhydroxylamines, but this signal proved identical with that obtained during Pb(OAc)<sub>4</sub> oxidation of the corresponding *N*-hydroxy compounds or the triacylhydroxylamines themselves and was thus assigned to the diacyl nitroxide rather than the diacylamino radical. A minor photolytic pathway yielding CO and the diacyl nitroxide was proposed to account for the epr signal which occurred during photolysis.

Some time ago, the photolysis of *N,O*-diacylhydroxylamines was found<sup>2,3</sup> to produce products shown to arise from the acylamino radical I. It was suggested<sup>3</sup>

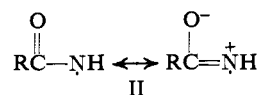


that the chemical evidence was in favor of I existing as a  $\sigma$  radical II (with the unpaired electron in a  $\sigma$

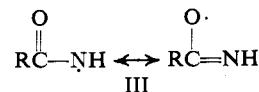
(1) This work was supported in part by Grant GM-15425 from the National Institute of General Medical Sciences and by a BSSG grant from NIH to Colorado State University.

(2) B. Danieli, P. Manitto, and G. Russo, *Chem. Ind. (London)*, 329 (1969).

(3) B. Danieli, P. Manitto, and G. Russo, *ibid.*, 203 (1971).



orbital), rather than as a  $\pi$  radical III (with the unpaired



electron in a  $\pi$  orbital). Epr spectra were not reported as supporting evidence. More recently, results<sup>4</sup> of a diacyldimethyltetrazene photolysis to yield IV were

(4) P. Tordo, E. Flesia, and J. M. Surzur, *Tetrahedron Lett.*, 183 (1972).