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Radical Cations of Tetraalkylcyclopropanes. The Cyclopropane Moiety as an Electron Donor

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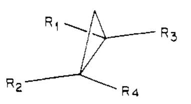
Abstract: The radical cations of simple tri- and tetraalkylcyclopropanes have been generated by light-induced electron transfer to chloranil and fluoranil. Nuclear spin polarization effects observed during these reactions are compatible with radical cations in which the most highly substituted cyclopropane bond is broken or weakened. In all these reactions the intermediate radical ion pairs recombine to regenerate the reactant hydrocarbons. In the case of tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (**1f**) and of 1,6-dimethylbicyclo[4.1.0]hept-3-ene (**1g**), the photoreaction also results in the dehydrogenation of the reactants to yield 1,6-dimethylcycloheptatriene (**6**) and bicyclo[4.4.1]undeca-1,3,5,8-tetraene, respectively. The polarization of the dehydrogenation products identifies the radical cations, **3f,g**, as primary intermediates in the dehydrogenation reaction.

Organic radical ions are of interest as synthetically useful intermediates in many reactions, but they also command attention as a class of species that are interesting in their own right. Radical ions can be generated by a variety of methods and studied by many techniques. The choice of an appropriate technique to study a radical ion is dictated by its lifetime and by the phase in which it is generated. Gas-phase techniques, such as ion cyclotron resonance, mass spectrometry, or photoelectron spectroscopy, allow the convenient study of radical ions that may be quite unstable in condensed phases.

In condensed phases, fast, time-resolved optical spectroscopy is a useful tool for studying the kinetics of formation and decay of chemical intermediates, but this method does not provide much structural information. Other laser spectroscopic techniques may reveal detailed structural information about relatively simple or highly symmetrical molecules. Electron spin resonance (ESR) allows an insight into the structures of radical ions by probing the distribution of unpaired spin density in these species. This technique has been applied to a large number of radical ions, but its application is generally limited to species with lifetimes well above the millisecond range.

We have applied chemically induced nuclear spin polarization (CIDNP), an indirect method complementary to the ESR technique, to the study of radical ions.[1-5] This method allows the assignment of relative spin densities on the basis of transient enhanced nuclear magnetic resonance (NMR) signals, in absorption (A) or emission (E), shown by some products of radical reactions. We have generated the radical cations of appropriate hydrocarbons by reaction with photoexcited electron acceptors, and among these, the perhalogenated *p*-benzoquinones, chloranil and fluoranil, are especially useful. Because of their strong oxidizing power, which is enhanced further by photoexcitation, their triplet-state reactions are exothermic even with poor electron donors.

The CIDNP method has given us insight into radical cations derived from a number of small-ring compounds. In most of these substrates the donor character of the cyclobutane or cyclopropane moiety is enhanced by conjugation with phenyl groups or other elements of unsaturation. Hydrocarbons such as benzonortricyclene,[5] benzonorcaradiene,[6] or diphenylcyclopropane[3] are substrates whose radical cations are stabilized because of the conjugation of the cyclopropane ring with phenyl and olefinic groups. In the case of quadricyclane an array of several strained rings is present that make this hydrocarbon a good donor.[4] In order to evaluate the intrinsic donor properties of the cyclopropane moiety we have investigated the photoreactions of chloranil with several cyclopropane derivatives that do not contain an element of unsaturation or in which the unsaturated group is not conjugated with the strained ring. These substrates include 1,1,2,2-tetramethylcyclopropane (**1a**), 1,1,2-trimethylcyclopropane (**1b**), three isomeric dimethylcyclopropanes (**1c–c**), and three compounds in which the cyclopropane ring is bridged with an unsaturated four-carbon unit (**1f–h**).



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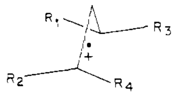

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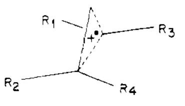

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a, $R_1, R_2, R_3, R_4 = CH_3$
b, $R_1, R_2, R_3 = CH_3; R_4 = H$
c, $R_1, R_2 = CH_3; R_3, R_4 = H$
d, $R_4 = CH_3; R_2, R_3 = H$
e, $R_1, R_3 = CH_3; R_2, R_4 = H$
f, $R_1R_2, R_3R_4 = CH_2CH{=}CHCH_2$
g, $R_1R_2 = CH_2CH{=}CHCH; R_3, R_4 = CH_3$
h, $R_1R_2 = CH_2CH{=}CHCH_2; R_3, R_4 = H$

Experimental Section

Typical samples used in this study were acetone-d_6 (Aldrich, Gold label, 99.5%) or acetonitrile-d_3 solutions (Merck, Sharp and Dohme, 99%) containing 0.02 M each of an electron acceptor (chloranil, Eastman Organics; fluoranil, Aldrich) and an electron donor hydrocarbon. These samples were purged with argon for 3 min and irradiated with the collimated beam of an Osram 200-W high-pressure mercury lamp in the probe of a Bruker WH90 Fourier transform NMR spectrometer. A pulse angle of 90° was employed to minimize the total acquisition time for the spectra (typically 100 s for 25 pulses).

Because the optical absorption of chloranil (λ_{max} 285 nm (ϵ 2.8 × 10^4) λ_{max} 365 nm (ϵ 2.6 × 10^2)) and fluoranil (λ_{max} 250 nm (ϵ 2.3 × 10^4) λ_{max} 333 nm (ϵ 2 × 10^2)) far exceeds that of the hydrocarbons (only end absorption) and since no charge-transfer bands are observed, essentially all the light (>99%) is absorbed by the electron acceptors.

Of the donor hydrocarbons employed, the dimethylcyclopropanes (**1c–e**) as well as tri- (**1b**) and tetramethylcyclopropane (**1a**) were obtained from Wiley Organics and used without further purification. Tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (**1f**) was synthesized from 1,4,5,8-tetrahydronaphthalene according to published procedures[7,8] and bicyclo[4.1.0]hept-3-ene (**1h**) as well as its 1,6-dimethyl derivative (**1g**) were prepared by analogous procedures from cyclohexa-1,4-diene and 2,5-dihydro-*o*-xylene.

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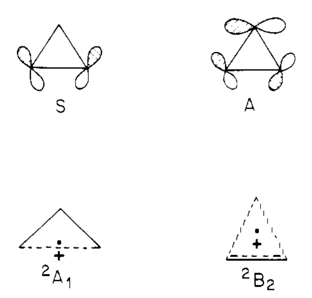
Chart I



Potential Structures of Cyclopropane Radical Cations

An insight into the structure of the radical cations discussed here is provided by the CIDNP patterns observed for the parent cyclopropane compounds. However, before an assignment is discussed it is useful to consider the nature of the highest occupied molecular orbitals (HOMOs) of cyclopropane.[9-14] One of its degenerate HOMOs is symmetrical and bonding between two carbon atoms. Removal of an electron from this orbital would place spin and charge on two carbon atoms and would weaken the bond between them. The resulting radical cation could be described as a trimethylene species with a one-electron bond between the terminal methylene groups (structure type $^2A_1$). The second HOMO has C_s symmetry; it is antibonding between two carbons and bonding between either of these and the third one. Removal of an electron from this orbital would generate a species which may be described as a π complex between ethylene and a methylene cation (structure type $^2B_2$). This radical cation would have considerable spin density on the third carbon atom. Two of its carbon–carbon bonds would be weakened whereas the third one would be strengthened. A recent ab initio calculation of the cyclopropane radical cation[15] suggests that the lowest energy surface has low-lying saddle points corresponding to the general structure types $^2A_1$ and $^2B_2$. The minima are of lower symmetry and have geometries intermediate between $^2A_1$ and $^2B_2$. The two degenerate HOMO's and schematic representations of the radical cations derived from them are shown in Chart I.

Although the lowest transition in the photoelectron spectrum of cyclopropane has been assigned to the ionization from the antisymmetrical orbital,[11-14] this conclusion does not necessarily have any bearing on the structure of the radical cations in solution. The relative energies of states in solution may be changed significantly by solvation. The generation of nuclear spin polarization effects requires radical (ion) pairs with lifetimes in the nanosecond range.[1-6] This time scale is sufficient to allow the intermediates to dissipate excess energy. Accordingly, the CIDNP results can be expected to reflect the equilibrium geometry of the intermediates.

The general structure type that may be formed in cases of favorable interaction between aromatic/olefinic group and cyclopropane moiety is best illustrated for the isomers of 1,2-diphenylcyclopropane.[3] The CIDNP results observed for these compounds suggest positive spin densities not only in the aromatic group but also on the benzylic carbons. These features are best accommodated in a structure in which the 3°–3° cyclopropane bond is broken or weakened, i.e., a structure of type $^2A_1$. On the other hand, the spin polarization effects observed for benzonorcaradiene[6] suggest the involvement of the alternative structure ($^2B_2$) in which two cyclopropane bonds are weakened.

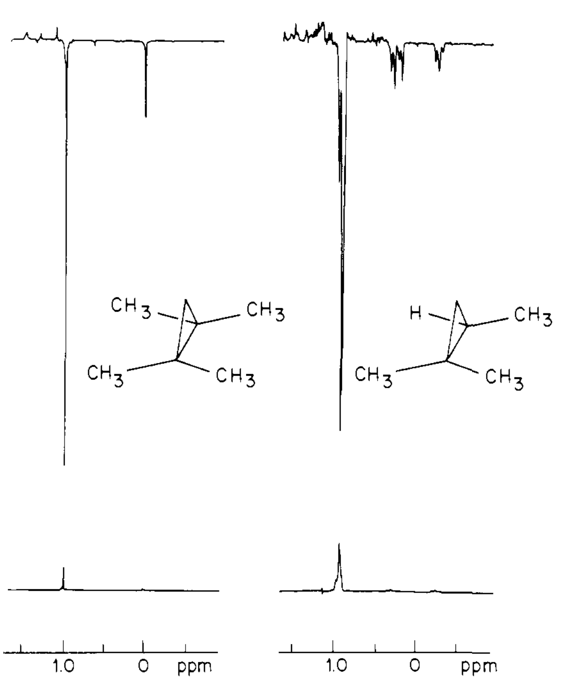


Figure 1. ^1H NMR spectra (90 MHz) of 0.02 M chloranil solutions in acetone-d_6 containing 0.02 M 1,1,2,2-tetramethylcyclopropane (**1a**; left) or 1,1,2-trimethylcyclopropane (**1b**; right) in the dark (bottom) and during UV irradiation. The gain for the spectra of **1b** was 32 times as high as for the spectra of **1a**.

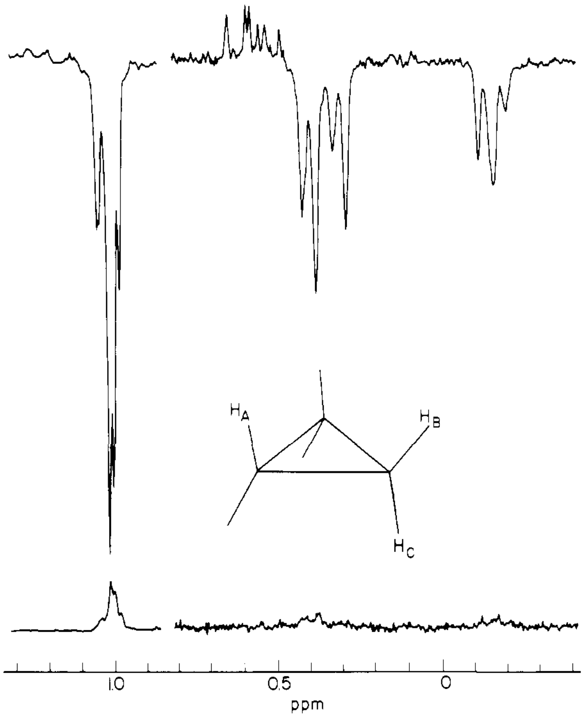


Figure 2. ^1H NMR spectra (90 MHz) of a 0.02 M chloranil solution in acetone-d_6 containing 0.02 M 1,1,2-trimethylcyclopropane in the dark (bottom) and during UV irradiation.

Results and Discussion

The irradiation of chloranil in acetone solutions containing 1,1,2,2-tetramethylcyclopropane (**1a**) resulted in strong emissive polarization for both the methyl groups and the geminal secondary protons (Figure 1). Analogous but weaker effects were observed for 1,1,2-trimethylcyclopropane (**1b**) as substrate (Figure 1). In a similar experiment with the tricyclic hydrocarbon, **1f**, emission was observed for the allylic (2.2 ppm) and for the geminal cyclopropane protons (0.55 ppm). Finally, with the bicyclic hydrocarbon, **1g**, as substrate, the methyl protons (1.1 ppm), the allylic protons (2.1 ppm), and the two doublets representing the

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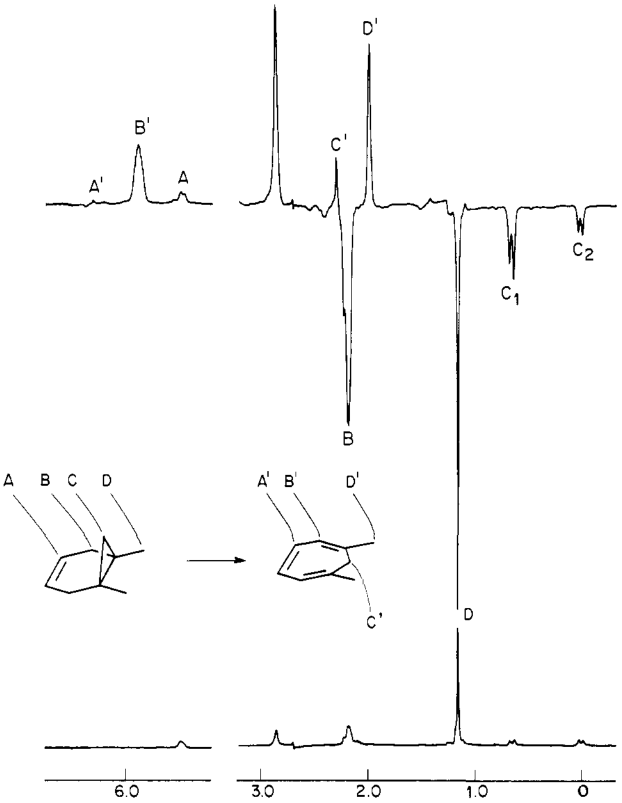


Figure 3. ^{1}H NMR spectra (90 MHz) of 0.02 M chloranil solutions in acetone-d_6 containing 0.02 M 1,6-dimethylbicyclo[4.1.0]hept-3-ene (**1h**) in the dark (bottom) and during UV irradiation (top).

cyclopropane protons (−0.1 ppm, 0.7 ppm) appeared in emission (Figure 3). In contrast, the disubstituted cyclopropanes studied, **1c–e,h**, failed to give rise to any spin polarization effects.

The polarization observed for the cyclopropane derivatives **1a,b,f,g** suggests the involvement of short-lived radical pairs. The results are compatible with a mechanism involving electron-transfer quenching of triplet chloranil by the cyclopropane derivatives. The resulting radical ion pairs undergo hyperfine-induced intersystem crossing and then reverse electron transfer to regenerate the reactants.

The CIDNP results indicate that essentially all polarized nuclei occupy similar positions relative to the carbon atom(s) bearing spin density. This suggests a structure type in which the unpaired spin is located on the more highly substituted carbon atom. However, the data available for three of the substrates do not allow the subtle distinction between a trimethylene structure, **2**, in which the most highly substituted bond is broken, and a π complex structure, **3**, with a dialkyl carbon unit as the apex. Information pertinent to this question is available only for the radical cation of **1b**.

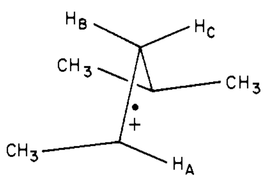
Of the cyclopropane derivatives discussed here only 1,1,2-trimethylcyclopropane has a different degree of substitution at every carbon atom. Consequently, the hyperfine coupling patterns of the potential intermediates are unique so that the observed polarization pattern allows an unambiguous identification of the radical ion structure.

In principle, three structures of each type can be derived from **1b**. However, we will limit the discussion to the one representative of each structure type which appears to be most stable. As a representative of the trimethylene structure type we discuss the cation **2b**, which is most highly substituted in the positions where charge and spin are located. Similarly, we choose the structure with the most highly substituted apex (**3b**) to represent the potential cation resembling a π complex.

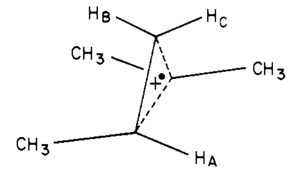
Both structures have in common that the geminal methyl groups are attached to a carbon atom bearing positive spin density and that the methylene group is also attached to such a center. Accordingly, the protons of these groups should have positive hfc's in either structure. The principal difference between the two structures lies in the fact that the tertiary carbon bears spin density in the case of **2b** but is adjacent to a carbon with spin density in the case of **3b**. Accordingly, the single methyl group would have a sizeable positive hfc in **2b** but a negligible one in **3b**, whereas the single proton would have a negative hfc in **2b** but a positive one in **3b**. These hyperfine coupling patterns are summarized in Table I.

Table I. Hyperfine Coupling Pattern of Trimethylcyclopropane Radical Cations and CIDNP Results

	gem CH_3	CH_3	H_A	H_B	H_C
trimethylene cation	+	+	−	+	+
π complex	+		+	+	+
CIDNP	E	E	A	E	E



2b



3b

The experimental results (Figure 2) leave little doubt about the identity of the intermediate. The complex multiplet representing the single proton (H_A) shows enhanced absorption whereas the doublet of the adjacent methyl group appears in emission as do the remaining signals of **1b**. Every detail of these results is compatible with an intermediate of structure **2b**. At the same time, the polarization observed for H_A and the adjacent methyl group is incompatible with a radical cation of structure **3b** (cf. Table I). Similarly, none of the alternative, intuitively less stable structures of either the "trimethylene" or the "π-complex" type can explain the overall polarization of **1b** nor can they account for the important individual features. Although small contributions from any of these structures cannot be ruled out, there is no doubt that **2b** is the principal structure of the radical cation derived from **1b**.

Additional significant information about the intermediate radical cations is provided by the complete absence of any olefinic polarization for the bicyclic cyclopropane derivative **1f** and for the tricyclic derivative **1g**. This observation eliminates any participation of the olefinic groups and identifies the cyclopropane moiety as the effective electron donor in these bifunctional substrates.

The fact that CIDNP effects are observed in these systems allows us to estimate an upper limit for the oxidation potential, E_{D/D^+}, of the cyclopropane derivatives. The electron-transfer process can only be expected to proceed at a reasonably fast rate, if the free energy of the raction,[16]

$$\Delta G = E_{D/D^+} - E_{A^-/A} - E_T - e^2/\epsilon a$$

is sufficiently exothermic. In this equation, $E_{A^-/A}$ is the reduction potential of the acceptor (−0.02 V for chloranil), E_T is the triplet excitation energy (2.7 eV for chloranil), and $e^2/\epsilon a$ is a Coulomb term that accounts for ion pairing. This term is close to 0.2 eV for an ion pair in a polar solvent (ϵ = 38) at a distance of 7 Å. Accordingly, the oxidation potentials of the cyclopropane derivatives **1a,b,f,g**, for which CIDNP effects were observed, should fall within the range 2–2.5 V, probably closer to the lower end of this range. Oxidation potentials in this range are compatible with the observation that neither UV nor NMR spectra show any indication for charge-transfer interactions in the ground state. Accordingly, the cyclopropane moiety cannot be considered to be more than a marginal donor.

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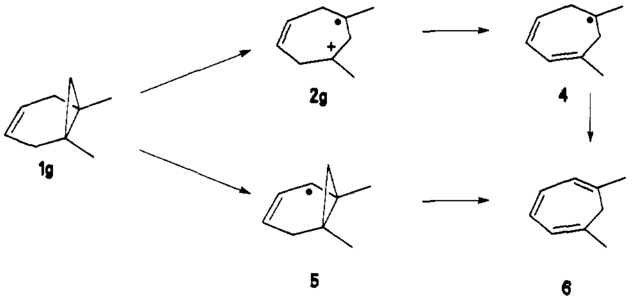
During the photoreactions of the simple cyclopropane derivatives **1a** and **1b**, substantial polarization is observed only for the reactants. In contrast, the reactions of the unsaturated substrates, **1f** and **1g**, give rise in addition to strong spin polarization effects for the dehydrogenation products 1,6-dimethylcycloheptatriene[17] (**6**) and bicyclo[4.4.1]undeca-1,3,5,8-tetraene,[18,19] respectively. The polarization pattern observed for these products is virtually the same as in the reactants: protons originating in positions adjacent to the quaternary carbons are polarized whereas the protons originating in the olefinic positions fail to show any polarization (Figure 3). This finding suggests the involvement of identical or similar intermediates. However, the signal direction of the dehydrogenation products is opposite to that of the reactants, suggesting that the products are formed by a different reaction mechanism. The observed signal direction is compatible with formation of the dehydrogenation product after its paramagnetic precursor has separated by diffusion from its geminate counter radical.

These results shed light on the detailed mechanism of the photosensitized dehydrogenation of the hydrocarbons **1f** and **1g**. This reaction could be initiated either by electron transfer, which would generate a pair of radical ions, or by hydrogen abstraction generating a pair of neutral radicals. An alternative pathway to the neutral radical involves a two-step sequence, electron transfer followed by loss of a proton either to the radical anion or to a propitious base. These pathways have been discussed in detail for the photoreactions of ketones with amines.[1,22]

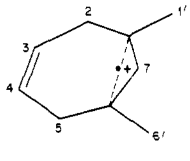
The bicyclic substrate **1g** and the tricyclic substrate **1f** chosen here have the advantage that two different neutral radicals are expected to result from the two competing pathways. Deprotonation of the radical ions **2** would produce radicals of structure **4** with localized spin density and with a hyperfine coupling pattern similar to that of **2**. Abstraction of an allylic hydrogen atom, on the other hand, would generate delocalized radicals of structure **5**.



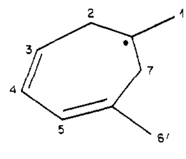
However, the dehydrogenation pathway in this system is plagued by a different mechanistic ambiguity: the neutral radical, **5**, generated by hydrogen abstraction is a cyclopropylcarbinyl system whose rearrangement[23] might generate the same cycloheptadienyl radical accessible via deprotonation of **4g**. In order to evaluate the potential effect of a conversion, **5** → **4**, on the CIDNP effects of the dehydrogenation product, **6**, we consider results observed by Kaptein during the thermal decomposition of cyclopropyl acetyl peroxide.[24] This reaction gives rise to polarized 4-chlorobut-1-ene. The strongest polarization in this compound, a complex multiplet for the olefinic methylene group, reflects the strongest hyperfine coupling of the cyclopropylcarbinyl radical and not that of the ring-opened butenyl radical. In the light of these results, one would expect any dimethylcycloheptatriene generated by the route **5** → **4** → **6** to reflect the hyperfine coupling pattern of the bicyclic radical, **5**.

Table II. Hyperfine Coupling Patterns of a Radical Cation and Two Radicals Derived from 1,6-Dimethylbicyclo[4.1.0]hept-3-ene and CIDNP Results

position	2g	4	5	CIDNP	
				1g	6
1′	+	+	negl	E	A
6′	+	negl	negl		
2	+	+	−	E	A
5	+	negl	+		
3	negl	negl	+	negl	negl
4	negl	negl	−		
7	+	+	negl	E	A



2g



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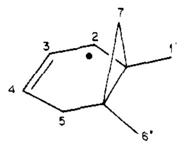

5

An examination of the hyperfine coupling pattern expected for **4** and **5** (Table II) and a comparison with the nuclear spin polarization patterns observed for the products unambiguously support the two-step pathway initiated by electron transfer and eliminates the mechanistic alternative involving **5**. This species would have sizeable spin density and hyperfine couplings in one olefinic position, for which no polarization is observed, and negligible hyperfine couplings for the methyl groups and the bridging methylene group, for which strong polarization is observed.

Additional evidence in support of the proposed mechanism can be based on the failure to observe substantial polarization during the photoreaction of chloranil with **1f** or **1g** in nonpolar solvents such as benzene or cyclohexane. In solvents of this type, the electron-transfer reactions should be substantially depressed whereas the hydrogen abstraction reaction should be essentially unaffected. For example, the photoreaction of fluoranil with indan in polar solvents gives rise to CIDNP effects that can be ascribed to two competing reactions: electron transfer and hydrogen abstraction. In nonpolar solvents, the polarization ascribed to electron transfer is suppressed whereas that ascribed to hydrogen abstraction persists. In view of these results, the failure to observe more than insignificant polarization in the reaction of chloranil with **1g** in nonpolar solvents is a strong argument against the hydrogen abstraction mechanism.

Conclusion

The finding that simple cyclopropane derivatives are electron donors and that they surpass disubstituted monoolefins is somewhat surprising. However, the donor character is displayed only toward the excited state of a very strong electron acceptor, and it falls off with decreasing substitution.

Registry No. 1a, 4127-47-3; **1b**, 4127-45-1; **1c**, 930-18-7; **1d**, 2402-06-4; **1e**, 1630-94-0; **1f**, 27714-83-6; **1g**, 38749-44-9; **1h**, 16554-83-9; chloranil, 118-75-2; fluoranil, 527-21-9.

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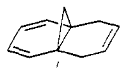
(18) Roth, H. D. Dissertation, University of Cologne, 1965.

(19) In a recent ACS meeting abstract[20] it was suggested that the radical anion of 1,6-methano[10]annulene reacts with water to yield tricyclo[4.4.1.0^{1,6}]undeca-2,4,8-triene, i. However, the NMR spectroscopic data,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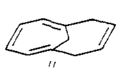
ii

specifically the chemical shift of the bridge protons, 0.6 and 2.7 ppm, and their geminal coupling constant, 8.5 Hz, leave little doubt that this hydrocarbon exists in the bicyclic form, ii, rather than as the tricyclic valence isomer.[21]

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