temperature-independent hydrogen isotope effects, k^H/k^D, similar to those reported for $C_6H_5C^iHBrCF_2Br$ (II) and $C_6H_5C^iHClCF_2Cl$ (III).[12a] However, the parameters chosen to mimic the k^H/k^D behavior will not allow calculation of the observed temperature dependence of k^D/k^T. Thus the experimental results appear not to agree with either an E2 mechanism or a simple E1cb pathway that features internal return.

In an attempt to understand this behavior better, we used both III-*h* and III-*d* for chlorine isotope effect studies. Experimental results are summarized in Table I. Alkoxide-promoted dehydrochlorination of III resulted in k^{35}/k^{37} values of 1.01255 (III-*h*) and 1.01025 (III-*d*) in methanol and 1.01229 (III-*h*) and 1.01003 (III-*d*) in ethanol. These values are much larger than those measured for I-Cl, and the k^{35}/k^{37} values for III-*h* appear to be the largest chlorine isotope effects reported to date. Although the reaction occurs 17 times faster in ethanol than in methanol and k^H/k^D differs in the two alcohols (2.3 in MeOH vs. 2.9 in EtOH), the observed chlorine isotope effects for III-*h* are within experimental uncertainty of each other when measured in each solvent. The same is true for III-*d*. On the other hand, differences between III-*h* and III-*d* are well outside the limits of experimental uncertainty. On the basis of values obtained for III-*h*, we anticipated that k^{35}/k^{37} should be between 1.00300 and 1.00600 for III-*d*. Thus the observed differences between III-*h* and III-*d* are too large for an E2 mechanism and much smaller than predicted by a simple E1cb with internal return.

Of special interest was $C_6H_5C^iHClCH_2Cl$ (IV) which features the activating β chlorine but has the eliminated chloride leaving from $-CH_2Cl$ (similar to I-Cl) rather than from $-CF_2Cl$ (similar to III). Primary hydrogen isotope effects for IV are $k^H/k^D = 3.2$ (MeOH) and 4.5 (EtOH) at 50 °C.[12b] The magnitudes of the chlorine isotope effects are smaller than those for III but larger than those for I-Cl (see Table I). The differences between k^{35}/k^{37} for IV-*h* and IV-*d* are similar to the observed differences for III-*h* and III-*d*.

Replacement of the benzylic chloride of IV with hydrogen, $C_6H_5CH_2CH_2Cl$ (V), causes both hydrogen and chlorine isotope effects to revert back to values quite similar in magnitude to those observed for I-Cl. Values of k^H/k^D are 5.59 (V) and 5.37 (I-Cl) at 75 °C,[8] and the observed k^{35}/k^{37} of 1.00580 is virtually the same as that reported for I-Cl-*h*. Reaction of V with ethanolic sodium ethoxide results in 4-5% substitution competing with the elimination reaction. Therefore, chlorine isotope effects were not measured by using $C_6H_5CD_2CH_2Cl$, since substitution now accounts for ~25% of the reaction product.[14]

This unique method of measuring a hydrogen isotope effect on the heavy-atom isotope effect and using it to assign mechanisms to elimination reactions need not be limited to leaving groups. Carbon atoms directly involved in the elimination could be used in a similar manner. Results for dehydroiodination of $C_6H_5C^iH(CH_3){}^*CH_2I$ (I-I) give k^{12}/k^{14} values of 1.034 ± 0.007 (I-I-*h*) and 1.028 ± 0.004 (I-I-*d*) when reaction is carried out in methanolic sodium methoxide at 50 °C, and these values also support an E2 mechanism for this reaction. The magnitude of either α or β carbon isotope effects is difficult to predict for an elimination reaction since the atoms are not only involved in more than one bond making and breaking but are also undergoing hybridization changes. The advantage of making use of both protio and deuterio compounds is that one could determine a mechanism prior to attempting to interpret the magnitude of the heavy-atom isotope effect.

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[14] A substitution reaction competing with the elimination process is also observed for I-Cl-*d* (3-4%). Reactions of IV are also subject to wrong way elimination, $PhCHClCH_2Cl \rightarrow PhCCl{=}CH_2$, which occurs with IV-*h* (1-2%) and IV-*d* (3-8%) depending on temperature and alcohol used as solvent. These minor amounts of side products will not alter k^{35}/k^{37} significantly and k^H/k^D is readily corrected for the competing reaction.

Photoinduced Electron-Transfer Reactions. Radical Cations of the 1,2-Diphenylcyclopropanes

Sir:

The photosensitized geometric isomerization of diarylcyclopropanes may involve either a triplet state, generated by triplet energy transfer, a radical ion, generated by electron transfer, or a cyclopropyl radical, generated by hydrogen abstraction, as a key intermediate.[1] While the structure of the cyclopropyl radical appears to be understood,[2] those of the triplet state and the radical ion are open to question. They could be "closed", having the charge and/or the unpaired spin(s) localized in one aryl group, or they could attain an "open" form where the tertiary-tertiary cyclopropane bond is broken or weakened so that charge and/or spin(s) are delocalized over both aryl groups.

We have studied the reaction of *cis*- and *trans*-1,2-diphenylcyclopropane (**1**) with photoexcited acceptors, such as tetrachlorobenzoquinone (chloranil, **2**), and have applied the CIDNP technique[3] in an attempt to identify the nature of the intermediates. This technique is a sensitive tool for radical pair[3] and radical ion pair reactions[4] and has been useful, inter alia, in establishing the intermediacy of aminium radical ions in the photoreaction of ketones with tertiary amines[5] and in studying the mechanism involved in the electron-transfer-induced isomerization of olefins.[6] CIDNP effects reflect the signs and magnitudes of the hyperfine coupling constants (hfc) of the intermediate in which the polarization is generated and, therefore, can be used to differentiate between potential intermediates provided that their hfc patterns are sufficiently different.

The irradiation of chloranil in acetonitrile or acetone solutions containing either *cis*- or *trans*-**1** resulted in strong CIDNP effects for the reactant. The aromatic and the benzylic protons showed enhanced absorption (A) whereas the secondary protons appeared in emission (E; Figure 1). However, neither experiment showed any evidence for a polarized rearrangement product.

The nature of the reactants and key experimental observations allow us to eliminate some intermediates from consideration. Since chloranil has a lower triplet energy[7] than other sensitizers, whose reactions with **1** have been studied, and since it fails to cause any

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(1) For a recent review see: Hixson, S. S. *Org. Photochem.* **1979**, *4*, 191.

(2) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(3) (a) Lepley, A. R.; Closs, G. L., Eds. "Chemically Induced Magnetic Polarization"; Wiley: New York, 1973. (b) Roth, H. D. *Mol. Photochem.* **1973**, *5*, 91. (c) Kaptein, R. *Adv. Free Rad. Chem.* **1975**, *5*, 319.

(4) Roth, H. D. In "Chemically Induced Magnetic Polarization"; Muus, L. T., et al., Eds.; Reidel: Dordrecht, The Netherlands, 1977; p 39.

(5) (a) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1974**, *96*, 6270. (b) Roth, H. D.; Manion, M. L. *Ibid.* **1975**, *97*, 6886.

(6) (a) Taylor, G. N. Unpublished results, cited in ref 4. (b) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1979**, *101*, 1898. (c) *Ibid.* **1980**, *102*, 4303.

(7) Kasha, M. *Chem. Rev.* **1947**, *41*, 401.

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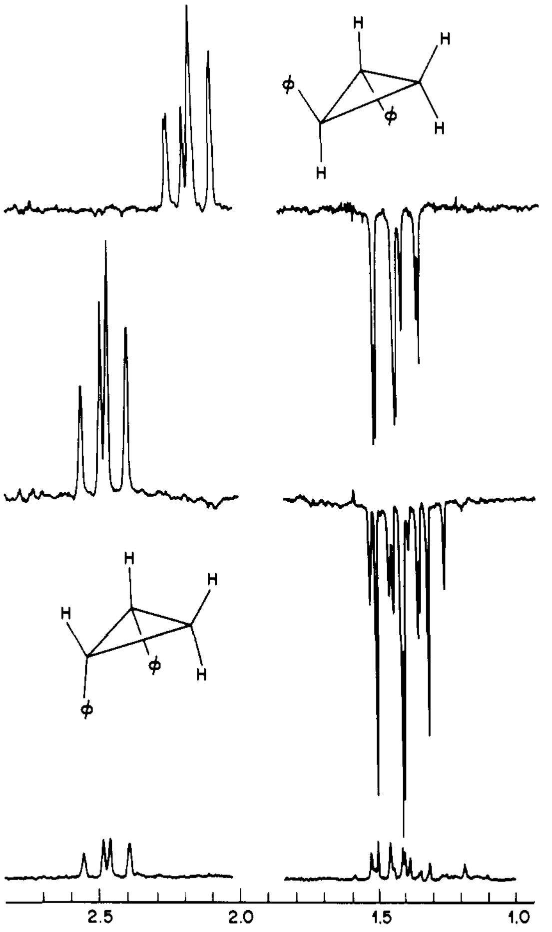
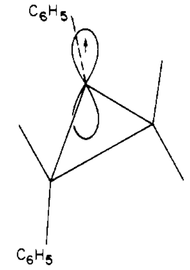


Figure 1. ^{1}H NMR spectra (90 MHz) observed during the irradiation of chloranil (0.02 M) in acetonitrile-d_3 solutions containing 0.02 M *trans*- (top) and *cis*-diphenylcyclopropane (bottom), respectively.

isomerization of **1**, triplet energy transfer is unlikely to be involved to any significant degree. A cyclopropyl radical (**3**), potentially



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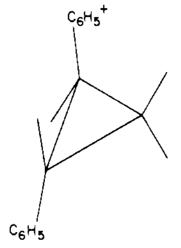
generated by hydrogen abstraction, can also be eliminated as an intermediate. EPR studies have shown that the cyclopropyl radical is either a π radical or a rapidly equilibrating σ radical.[2] Accordingly, its involvement should lead to isomerization. Moreover, in this intermediate the remaining benzylic proton and the secondary protons occupy equivalent positions relative to the unpaired spin. Accordingly they should have hyperfine couplings and show polarization of identical sign. Neither feature is compatible with the experimental observations.

An electron-transfer pathway, on the other hand, is compatible with the nature of the reactants as well as with the experimental observations. Chloranil has an exceedingly low reduction potential,[8] rendering an electron-transfer reaction strongly exothermic.[9] The elegant studies of Weller and his colleagues have shown that electron transfer in such a system can be very fast. Accordingly, the observed polarization is attributed to the intermediacy of diphenylcyclopropane radical cation paired with the chloranil radical anion (**7**) and generated by electron transfer from **1** to photoexcited **2**. The observed signal directions are compatible with the following parameters. In view of the short singlet lifetime of chloranil we assume that its triplet state is involved ($\mu > 0$)[12] and, further, that the reactants are regenerated by geminate electron return ($\epsilon > 0$).[12] We also note that the intermediate pair has a large g factor difference ($g_5 = 2.0027$;[13] $g_7 = 2.00568$;[14] $\Delta g < 0$).[12] Given these parameters, we can use the observed polarization pattern to identify the structure of the diphenylcyclopropane radical cation. For this intermediate one can envision a closed structure (**4**) in which spin and charge are localized in one aryl group or one of two open forms in which spin and charge are fully delocalized. In one of the open forms (**5**), each pair of substituents lies in a plane perpendicular to that of the cyclopropane ring, and the π orbitals overlap in the plane of that ring. In the other open form (**6**), the entire π system is coplanar.

Table I. Hyperfine Coupling Patterns of Cyclopropane-Derived Radicals and Radical Ions

protons	3	4	5	6
aromatic	–[a]	–	–[a]	–[a]
benzylic	+	+	–	–
secondary	+		+	+

[a] Weak positive hfc's for the aromatic meta protons are neglected in the presence of the strong, negative hfc's of the ortho and para protons.



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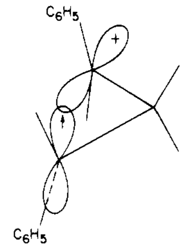

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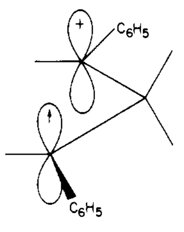

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Both the closed (**4**) and the open forms (**5** or **6**) should have predominantly negative hfc's for the aromatic protons, but the protons of the strained rings are expected to have characteristically different hfc's. The benzylic (α) protons should have positive hfc's in the closed form but negative hfc's in the open form, whereas the β protons are expected to have small or negligible hfc's in the closed form but large positive hfc's in the open form (see Table I).

The observation of the same signal direction for aromatic and benzylic protons and of equally strong but opposite effects for the β protons is compatible with the substantial spin density in the benzylic position ($a < 0$).[12] Therefore, any significant involvement of a closed radical cation (**4**) is eliminated, and the intermediate is identified as a radical cation with an open structure. However, the CIDNP pattern does not differentiate between structures **5** and **6** (see Table I).

A more detailed consideration of the CIDNP effects allows us to differentiate between the two open structures. We note that

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(8) Peover, M. E. *Nature (London)* **1961**, *191*, 702.

(9) Calculated according to $\Delta G = E_{(D/D^+)} - E_{(A^-/A)} - E_T - e^2/\epsilon a$[10] from the reduction potential of chloranil, $E_{(A^-/A)} = -0.02$ V vs. SCE,[8] an estimated oxidation potential of diphenylcyclopropane, $E_{(D/D^+)} \sim 1.5$ V vs. SCE,[11] and the triplet energy of chloranil, $E_T = 62$ kcal/mol.[7]

(10) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257.

(11) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101.

(12) (a) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732. (b) *J. Am. Chem. Soc.* **1972**, *94*, 6251.

(13) Assumed in analogy to typical hydrogen radical ions, cf. ref 14.

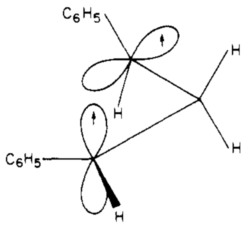
(14) Blois, M. S., Jr.; Brown, H. W.; Maling, J. E. Proceedings, Neuvième Colloque Ampère, Geneva, Librarie Payot, 1960, p 243.

the planar intermediate (**6**) should provide a ready pathway for isomerization since it could collapse to regenerate either the *cis*- or the *trans*-cyclopropane. Accordingly, the involvement of structure **6** can be expected to result in polarized isomerization products. The alternative structure (**5**), on the other hand, cannot be expected to permit ready isomerization but should preserve the steric integrity of the reactant. In view of these considerations, the failure to observe polarized rearrangement products identifies the nonplanar radical cation (**5**) as the intermediate in which the polarization is generated.

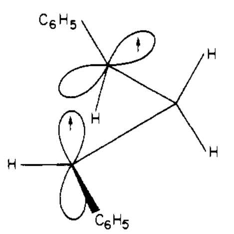
The lack of isomerization during the photoreaction of **1** and **2** stands in marked constrast to the reaction of **1** with acceptors such as 1,4-dicyanonaphthalene (**8**), suggesting a principally different reaction mechanism. Wong and Arnold applied the CIDNP technique to study the reaction of *trans*-**1** with **8**.[11] They observed a single, apparently weak A/E multiplet which they assigned to the benzylic resonance of *cis*-**1**. On the basis of this result, they postulated a mechanism involving electron transfer from **1** to **8** and triplet recombination[15] of the resulting radical ion pair. The energetics of the system are not inconsistent with the proposed mechanism.[16] However, the observation of only one signal fails to identify the structure of the postulated radical cation and leaves questions concerning the polarization mechanism unanswered.

In view of the recent interest in the recombination of triplet pairs,[15] it appeared desirable to have the benefit of additional experimental evidence. Accordingly, we extended our study to include the reactions of 1,4-dicyanonaphthalene (**8**) and 9-cyanophenanthrene (**9**) with **1**.[16] The irradiation of **8** in the presence of *trans*-**1** resulted in CIDNP effects for all signals of reactant as well as rearranged cyclopropanes. A/E multiplet polarization was observed for the benzylic protons of the cis isomer and E/A polarization was observed for the benzylic protons of *trans*-**1**. The signals of the geminal protons of *cis*- and *trans*-**1** overlap, but a detailed analysis reveals A/E polarization for the cis isomer and E/A polarization for the trans isomer (Figure 2, top). The reaction of **9** with *trans*-**1** resulted in the exclusive polarization of the cis isomer (Figure 2, bottom).

These results are compatible with the mechanism suggested by Wong and Arnold but they also elucidate the structure of the intermediate radical ion and they reveal the presence of singlet recombination. Electron-transfer quenching of the excited-singlet acceptors ($\mu < 0$) generates the open cyclopropane radical cation (**5**) paired with acceptor anions of similar g factors ($\Delta g \sim 0$). The reactant is regenerated by geminate electron return in singlet pairs ($\epsilon > 0$), whereas the rearranged cyclopropane is formed via triplet recombination yielding a triplet state (^{3}**1**-Z or ^{3}**1**-E) with orthogonal p orbitals. This intermediate can decay to the ground state of either geometric isomer. Accordingly, the polarization due to triplet recombination is partitioned between reactant and rearranged cyclopropane, thus weakening the singlet return polarization of the reactant.



^{3}1-Z



^{3}1-E

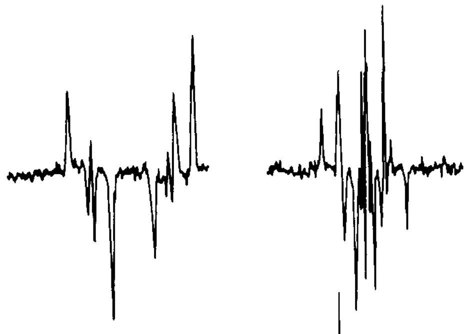


Figure 2. ^{1}H NMR spectra (90 MHz) observed during the irradiation of 9-cyanophenanthrene (0.02 M; center) or of 1,4-dicyanonaphthalene (0.02 M; top) in acetonitrile-d_3 solutions containing 0.02 M *trans*-diphenylcyclopropane. A dark spectrum of the cyclopropane is shown as the bottom trace.

The finding that in the reaction of **9** the polarization of the rearranged cyclopropane is stronger than that of the reactant is interpreted as evidence that triplet recombination can be more efficient than singlet recombination, a trend which has been invoked repeatedly in recent years.[15] Photoreactions of arylcyclopropanes with fixed geometries and of related diphenylcyclobutane compounds are presently under investigation to further delineate the mechanisms and structures discussed in this paper.

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[15] (a) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153. (b) Orbach, N.; Ottolenghi, M. *Chem. Phys. Lett.* **1975**, *35*, 175. (c) In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 25. (d) Michel-Beyerle, M. E.; Haberkorn, R.; Bube, W.; Steffens, E.; Schröder, H.; Neusser, N. J.; Schlag, E. W.; Seidlitz, H. *Chem. Phys.* **1976**, *17*, 139. (e) Schulten, C. K.; Staerk, H.; Weller, A.; Werner, H. J.; Nickel, B. *Z. Phys. Chem.* (*Wiesbaden*) **1976**, *101*, 371. (f) Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6127. (g) Bargon, J. *Ibid.* **1977**, *99*, 8351.

[16] The reduction potentials of **8**, $E_{(A^-/A)} \sim -1.3$ V,[17] and **9**, $E_{(A^-/A)} = -1.92$ V vs. SCE,[18] would place the pair energy above the triplet energy of **1** ($E_T \sim$ 50–60 kcal/mol).[19]

[17] Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

[18] Park, S. M.; Caldwell, R. A. *J. Electrochem. Soc.* **1977**, *124*, 1859.

[19] Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G. *J. Am. Chem. Soc.* **1972**, *94*, 6584.

Why Is Tetra-*tert*-butylcyclobutadiene Almost Square?

Sir:

The X-ray structures of three derivatives of cyclobutadiene (CBD) have been published, and the bond lengths found in the four-membered ring of each are reproduced in Figure 1. As shown, the near equality of the ring bond lengths in the tetra-

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