

more than that of the starting **5**. First, for an examination of the role of a π bond existing between the two cyclopropane rings of **5**, the reduction of 3,3,8,8-tetrachlorotricyclo[5.1.0.0^{2,4}]octane (**17**) with sodium was carried out in a mixed solvent of ammonia and THF at -95°C ($17/\text{Na}/\text{EtOH} = 1/8/8$) or in HMPA at -35°C . Only the parent hydrocarbon **20** was obtained besides unreacted **17** (in ammonia, 92% and 8%, respectively). Thus, the π bond is not a requisite, and the effect should be exerted only in the bicyclopropane system.

In addition, a framework examination on **17**¹² reveals that the cyclopropane ring orbitals at positions C-1 and C-2 meet at approximately right angles, and therefore the conjugative effect through p orbitals, which might have explained the difference in reactivity between **5** and **9**, could not have been exerted. Consequently, it seems most rational that the initially formed α -halocyclopropyl anion **18** (or radical) weakens the C-X bond of the other ring by orbital interaction through bonds of this rigid tricyclic system in a fashion similar to an 1,4-elimination mechanism (Scheme II).¹³ Depiction of **18** illustrates this idea in which the elimination of halide and the electron transfer at C-8 of **18** are occurring almost simultaneously.

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Supplementary Material Available: Additional data on the reduction of **5** and **17** (7 pages). Ordering information is given on any current masthead page.

(12) The stereochemistry of the two cyclopropane rings of **5** is determined as anti by X-ray crystallography.

(13) The partial cleavage of the C₁-C₂ bond of **18** may be involved in the transition state in which the dicyclopropenyl structure emerges to some extent. However, all processes including electron transfer will take place almost simultaneously.

Photoinduced Electron-Transfer Reactions. Radical Cations of Norbornadiene and Quadricyclene

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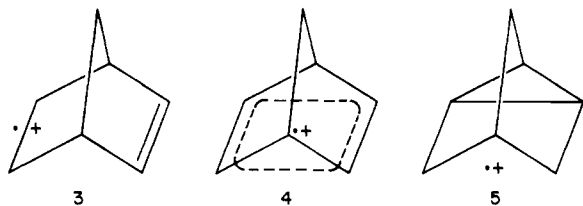
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We have observed different nuclear spin polarization patterns during the photoreaction of electron acceptors with norbornadiene (**1**) and with quadricyclene (**2**). These results are incompatible with the concept of a single intermediate, **4**, for both reactions. Instead, they indicate that two discrete radical cations, **3** and **5**, respectively, with lifetimes greater than several nanoseconds are derived from the two hydrocarbons.¹



(1) The structures **3** and **5** are meant to conveniently designate the valence isomeric radical cations of **1** and **2**, respectively. They are not meant to represent the actual geometry of these intermediates.

Although the interconversion of norbornadiene and quadricyclene is well characterized in the excited singlet and triplet states,² the energy surface of the radical cations derived from the pair of valence isomers is not fully understood. The photoelectron spectra of **1** and **2** reveal the existence of two discrete radical cation states,³ an assignment which is supported by MINDO/3 calculations.^{3c} On the other hand, γ irradiation of frozen solutions containing either **1** or **2** gives rise to the same species to which the structure of a norbornadiene radical cation has been assigned.^{3c} Similarly, the observation that the mass spectra of **1** and **2** have nearly identical fragmentation patterns led to the conclusion that their molecular ions are identical with regard to energy and structure.⁴ We have applied the CIDNP technique in an attempt to elucidate this energy surface.

Chemically induced nuclear spin polarization (CIDNP) effects are exceedingly useful for studying reactions proceeding via radical ion pairs and, particularly, involving the recombination of these pairs in the triplet state.⁵ Successful applications of the CIDNP technique include the identification of aminium radical ions and aminoalkyl radicals in the photoreduction of keto compounds by tertiary amines,⁶ the elucidation of several mechanisms underlying the electron-transfer induced isomerization of several classes of the electron-transfer induced isomerization of several classes of olefins,⁷ and the elucidation of the structure of the diphenylcyclopropane radical cation.⁸

The study reported here was undertaken to elucidate the structure(s) of the radical cation(s) of **1** and **2** and, particularly, to ascertain whether they are two discrete species or whether they are best represented by a single, homoallylic structure (**4**). Ultraviolet irradiation of electron acceptors, such as chloranil (**6**) or cyanonaphthalene (**7**), in the presence of **1** or **2** gives rise to characteristic CIDNP effects which allow an insight into the structure of the intermediates and into the energy surface connecting them.

The irradiation of **6** in acetonitrile-*d*₃ solutions containing **1** (1 kW high-pressure Hg lamp) gives rise to strongly enhanced absorption (A) for the olefinic protons (6.6 ppm) of the reactant and weak emission (E) for its bridge protons (2.0 ppm) but does not produce any polarization for the rearranged hydrocarbon (Figure 1, top). The observed signal direction is compatible with a mechanism involving electron-transfer quenching of triplet **6** by **1** and regeneration of the reactants by reverse electron transfer after intersystem crossing. In analogy to other olefin radical cations^{5,7} the "olefinic" protons of the norbornadiene radical cation (**3**) are assumed to have a negative hyperfine coupling constant (hfc) and the *g* factor of **3**, like that of other hydrocarbon radical ions very likely close to the free electron value,⁹ should be much smaller than that of the chloranil radical anion (**8**, *g* = 2.0057).⁹ Radical ion pairs not reacting by reverse electron transfer diffuse apart, allowing their polarization to decay by spin-lattice relaxation.

In contrast to the reaction of **6** the irradiation of **7** in solutions containing **1** gives rise to polarization for the rearranged product, **2** (cyclobutane protons, A; bridge protons, E) as well as for the reactant (olefinic protons, E; bridge protons, A; Figure 1, center). This polarization pattern is once again indicative of the radical cation **3**, this time paired with the cyanonaphthalene radical anion (**9**) generated by electron transfer from **1** to the excited singlet

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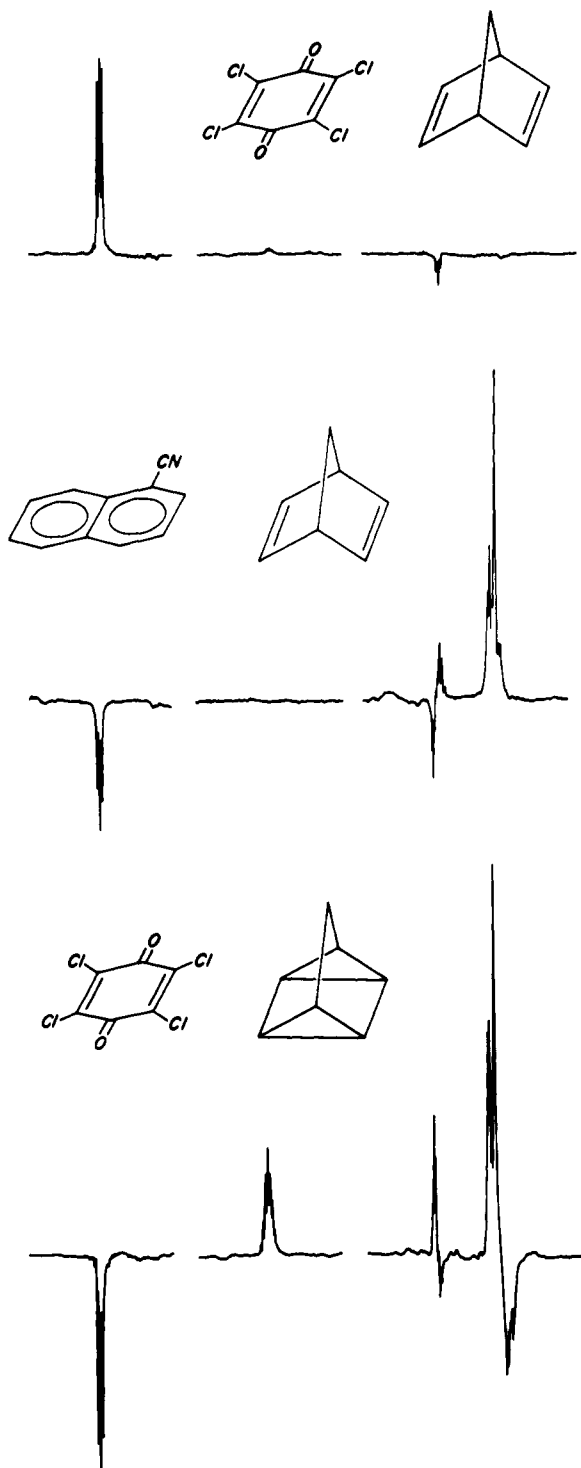


Figure 1. ^1H NMR spectra (90 MHz) observed during the photoreaction of chloranil (0.02 M) with norbornadiene (0.02 M) (top), 1-cyanonaphthalene (0.02 M) with norbornadiene (0.02 M) (center), and chloranil (0.02 M) with quadricyclane (0.02 M) (bottom). The resonances of norbornadiene and quadricyclane are denoted N and Q, respectively. Lower case indices identify the bridgehead (bh), bridge (b), and the olefinic/cyclobutane positions (o).

state of **7**. The different precursor spin multiplicities account for the opposite signal directions observed for **1** in the two reactions. The remaining factors affecting the signal direction are similar in both reactions; Δg and hfc are negative, and the mechanism regenerating the reactants involves electron return in pairs of single spin multiplicity.

The observation of polarized **2** in the reaction of **7** with **1** suggests that the triplet pairs arising by intersystem crossing from the initially generated singlet pairs undergo a specific reaction

not occurring in the system, **6-1**. The principal difference between the two reactions lies in the free energy of the intermediate pairs.¹⁰ The reduction potential of **7**¹¹ is considerably higher than that of **6**,¹² raising the energy of the pair **3-9** above the triplet energies of **1** and **7**.¹³ Accordingly, this pair can recombine in the single manifold, regenerating the ground state of the reactants, and the triplet manifold, populating one reactant triplet state. The decay of triplet **1** to **2** accounts for the polarization of the valence isomer. However, this pathway is quite inefficient.¹⁶ The CIDNP result provides evidence for a new mechanism of norbornadiene rearrangement and adds a new facet to the phenomenon of triplet recombination which is commanding ever increasing attention.¹⁷

The two experiments discussed above allow two conclusions about the radical cation **3**: that it has significant spin density only in the olefinic position, and, in contrast to triplet **1**, the doublet **3** does not allow ready conversion to the quadricyclic structure. Additional insight into the energy surface connecting the radical ions of **1** and **2** is provided by the photoreaction of chloranil with quadricyclane.¹⁸ This reaction leads to the polarization of all three types of protons for both reactant and isomerization product. The cyclobutane protons and the bridge protons of **2** appear in absorption, whereas the bridgehead protons show emission. In contrast, the olefinic and bridge protons of **1** show emission, whereas the bridgehead protons appear in absorption (Figure 1, bottom).

These results are compatible with electron transfer from **2** to triplet **6** and regeneration of the reactants by reverse electron transfer after intersystem crossing. The observation of a polarized rearrangement product requires an intermediate which allows ring opening, and the fact that the polarization of **1** is opposite to that of **2** requires an alternative mechanism of product formation. These observations are compatible with a mechanism involving triplet recombination and rearrangement in the triplet state or a pathway involving the separation of radical ions by diffusion, rearrangement, and electron exchange with a neutral electron donor.

Although the polarization pattern as such may be misleading due to cross relaxation,¹⁹ the observation of different polarization patterns in the reactions of norbornadiene (Figure 1a,b) and quadricyclane (Figure 1c) allow the unambiguous conclusion that two discrete radical cations are generated by electron transfer from the two valence isomers. Each of these species must have a lifetime of at least several nanoseconds to explain the generation of nuclear spin polarization. It is further significant that under identical reaction conditions the cation **5** gives rise to a polarized rearrangement product (**1**) while the cation **3** does not lead to polarized **2**. We explain this observation by assuming an energy surface with two intermediates of different energies. The higher energy intermediate (**5**) lies sufficiently close to the transition state to allow the isomerization, whereas the intermediate of lower energy lies too low for an efficient conversion. The available thermo-

(10) Pair energies are calculated according to $\Delta G = E_{(D/D^+)} - E_{(A-/A)} - e^2/\epsilon a$ from the reduction potential of the acceptor and the oxidation potential of the donor and from a Coulomb term (~ 0.2 eV) accounting for ion pairing: Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257.

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(13) The reduction potential of **7** (-1.8V vs. SCE)¹¹ and the oxidation potential of **1** ($+1.54\text{V}$ vs. SCE)¹⁴ place the pair energy (3.2 eV, ~ 74 kcal/mol) well above the triplet energy of **7** (~ 60 kcal/mol)¹⁰ and close to the triplet energy of **1** ($68-70$ kcal/mol).¹⁵

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(16) Although the cyanonaphthalene fluorescence is quenched efficiently ($\phi = 0.71$ at $[I] = 0.02$ M), the conversion is quite inefficient ($\phi_{1\rightarrow 2} = 0.01$): Jones, G., II; Becker, W. G.; Schwarz, W., unpublished results.

(17) See ref 7c and publications cited therein.

(18) The chloranil photosensitized isomerization of **2** is efficient ($\phi = 0.64$): Jones, G., II; Becker, W. G.; Schwarz, W., unpublished results.

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chemical and photoelectron spectroscopic data support this assignment.²⁰

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(20) The oxidation potential of **2** (0.91V vs. SCE)¹⁴ is 0.63 V lower than that of **1**¹⁴ but its ground state lies at least 22 kcal/mol²¹ and possibly as much as 27 kcal/mol²² above that of **1**.¹⁴ Accordingly, the energy of **5** lies ~ 14 kcal/mol above that of **3**.

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Useful Impurities for Optical Resolutions. 1. On the Crystallization of Photopolymerizing Dienes in the Presence of Their Chiral Topochemical Products

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We report in this series a novel systematic approach to preferential crystallization of enantiomers, in the presence of tailor-made impurities, which provides a general method for resolution of conglomerates and an empirical method for the assignment of absolute configuration and which may provide a way to selectively control some physicochemical properties of crystals. Understanding of the mechanism of the impurity action came from our studies concerned with generation and amplification of optical activity in closed symmetrical systems.

A number of "absolute" asymmetric syntheses via topochemical reactions in chiral crystals have been reported from this laboratory. In one of these,¹ quantitative enantiomeric yields of dimers, trimers, and oligomers were obtained starting from achiral dienes (Scheme I). In these reactions the absolute configuration of the parent crystal determines the chirality of the product. In the absence of an outside chiral agent, the chances of crystallization of the achiral starting material in either of the two enantiomorphic phases *d* or *l* are equal, and thus, in a large number of experiments, no net chirality of product is expected. In order to preserve the chirality generated in the first successful experiment, a highly efficient mechanism of amplification is therefore needed.

In this context, Green and Heller² performed an elegant experiment which showed that introduction of the chiral bromination product of 4,4'-dimethylchalcone into the crystallizing melt of this chalcone caused preferential crystallization of the unwanted *d* crystal if the bromide originated from an *l* crystal and vice versa.

Such a process of asymmetric crystallization induced by topochemical products on their parent phases is investigated here systematically, using systems where a strict relationship links the stereochemistry of the former with the structure of the substrate. The aim was to reach a general understanding of the effect and thence to design a system appropriate for amplification. The crystallization of monomers 1-6 was studied (Table I) in the presence of their resolved chiral products (Scheme I). These systems are suited to our purpose, since a given product molecule (say *P_R*) can conceivably, with only a slight deformation, take the place of a corresponding number of monomer units in the parent

Scheme I

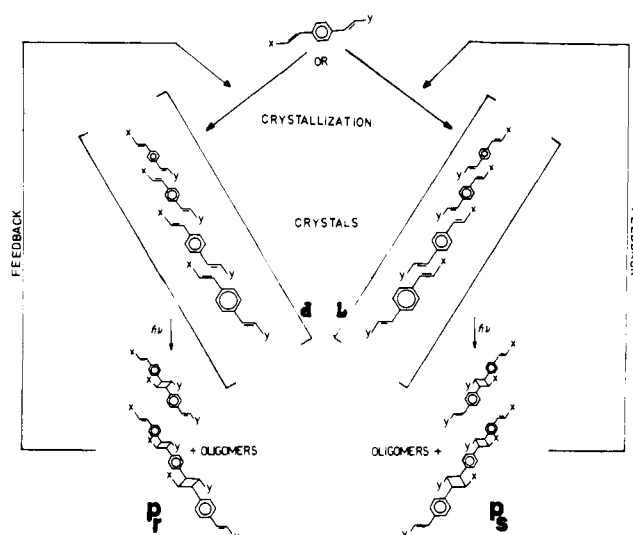
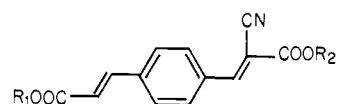


Table I. Results on Asymmetric Crystallization of Monomers 1-6 Induced by Impurity,^a Given as Specific Rotation of Dimers^b Obtained After Irradiation



- 1, R₁ = 3-pentyl; R₂ = methyl
- 2, R₁ = 3-pentyl; R₂ = ethyl
- 3, R₁ = 3-pentyl; R₂ = *n*-propyl
- 4, R₁ = isopropyl, 3-pentyl; R₂ = ethyl
- 5, R₁ = (*R,S*)-*sec*-butyl; R₂ = ethyl
- 6, R₁ = (*R,S*)-*sec*-butyl; R₂ = *n*-propyl

mono- mer ^b	chirality	[α] _D , deg					
		dimer				trimer oligomer	
		15% ^c	15% ^d	8% ^d	3% ^d	15% ^c	8% ^c
1 (P ₂)	+	-70	-62	-74	-75	-92	-11
	-		+61	+89	+83	+75	+52
2 (P ₁ or P ₁ ⁻)	+	-47	0 ^e	0	0	-30	
	-	+73	0	0	0		
3 (P ₁)	+	-67	-61	-40	-59	-31	-21
	-	+38	+65	+54	+58	+45	+36
4 (P ₁)	+	-42 ^f	-47	-51	-40	-41	-9
	-	+46	+47	+56	+36	+30	+15
5 (P ₁)	+	-21	-12	-3	-30		
	-	+33	+8		+17		
6	+	+31	-36	-27	-54		
	-	45	42	40	+30		

^a Reference 4. ^b [α]^o_D of 100% optically pure dimers ranges from 100 to 110° depending on the side chains. In the whole family of [α]^o_D compounds, (+)-dimers have absolute configuration *RRRR* around the cyclobutane ring. ^c Fast crystallization (~4 h). ^d Slow crystallization (~2 weeks). ^e Upon slow crystallization the stable polymorph of this monomer is obtained which has a centrosymmetric space group (*P*₁⁻) and thus no induction is expected or obtained. ^f The reported rotation refers to the homodimer with isopropyl-isopropyl side chains.

(*d*) crystal, while this is not true in the enantiomorphic crystal (*l*).

Monomers 1-8³ were melted together with variable amounts (3-15%) of resolved dimer, trimer, and oligomer of **5** (the "impurity") of either chirality,⁴ in closed nitrogen-flushed vials, allowed to crystallize, either rapidly (4 h) or slowly (~2 weeks), and then crushed and subjected to irradiation (UV light, four

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(3) Full crystallographic information on these systems will be reported in a following publication.

(4) The reaction products of resolved **5** were used, since these are easily obtained in high optical purity from the monomer.