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THE ELECTRON TRANSFER INDUCED INTERCONVERSION OF CYCLOBUTANES AND DIOLEFINS

Heinz D. Roth and Marcia L. M. Schilling
Bell Laboratories
Murray Hill, NJ 07974, USA

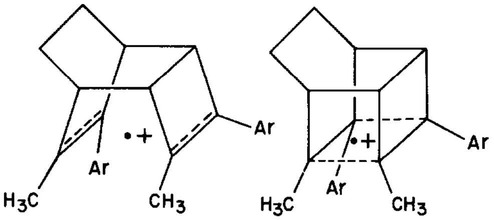
Toshio Mukai and Tsutomu Miyashi
Tohoku University
Sendai 980, Japan

The photoreactions of quinones with diolefins (**1**) or cage compounds (**2**) give rise to nuclear spin polarization predominantly for the diolefins. These findings indicate that the cage cations (**4**) have shallow energy minima and suffer fast ring opening to the diolefin cations (**3**).

The photoinduced dimerization of olefins and the photocleavage of cyclobutane derivatives can be achieved either by direct irradiation or by photosensitization. A variety of key intermediates have been invoked for these reactions, including excited singlet or triplet states, exciplexes, and radical cations. For the corresponding radical cations there does not appear to be a clear-cut preference for either the cyclobutane or the diolefin structure. For example, it has been demonstrated that some olefins form dimers (cyclobutanes) in the presence of oxidants or electron acceptors,[1] but in other cases cyclobutanes undergo facile fragmentation in the presence of electron acceptors.[2] Additional insight into the addition/fragmentation behavior of olefin/cyclobutane radical cations should be available in systems in which two olefinic moieties are held in close proximity to each other.

Several systems of this type have been studied. For the pair norbornadiene-quadricyclane, CIDNP evidence showed conclusively that two different radical cations exist and that the quadricyclane cation rearranges readily to the more stable norbornadiene cation.[3] The analogous system, hexamethyl(Dewarbenzene)-hexamethylprismane, provided evidence for a hexamethylprismane radical cation with a shallow minimum.[4] This species rearranges readily to the cations of hexamethyl(Dewarbenzene) and hexamethylbenzene. Finally, the pentacyclic cage compounds[5] **2** have been shown to undergo ring opening to tricyclo-[4.2.2.0^{2,5}]deca-3,7-diene derivatives (**1**) in the presence of quinones. This reaction can be induced by charge transfer in the dark or by electron transfer upon irradiation of the quinone.[6]

In this paper we describe the application of the CIDNP technique[7] to the photoreaction of quinones with several derivatives of **1** and **2** in an attempt to gain an insight into the structure of the radical cations, **3** and **4**, of the diolefins and the cage compounds, respectively. In view of the facile ring opening of **2**, it was of special interest whether the cage cation **4** has a discrete minimum or whether it is completely dissociative.



3 4

a) Ar = C_6H_5 b) Ar = p-$CH_3C_6H_4$ c) Ar = p-$OCH_3C_6H_4$

The irradiation of acetone-d_6 solutions of appropriate quinones containing either the cage compounds or the diolefins gave rise to strong nuclear spin polarization effects for the methyl signals of the diolefins regardless of the type of reactant. Apparently, the ring opening of the cage cations is quite facile. The parameters governing the observed polarization can be assigned readily:[8] quinones have short-lived excited singlet states and react as triplets ($\mu > 0$); the g factors of the cations ($g_{3,4} \sim 2.0027$) should be considerably lower than those of the semiquinone anions ($g \sim 2.0050$; $\Delta g < 0$); the polarized methyl groups are attached to the carbon atoms involved in the reorganization - these protons should have positive hyperfine coupling constants in the radical cations ($a > 0$). Given these parameters, the observed polarization (emission) requires *geminate recombination* of the radical ion pairs. Since polarization is observed principally for the diolefins, the cycloreversion of the cage cations **4** must be faster than the recombination, a facile reaction indeed. Nevertheless, the radical cations **4** cannot be totally dissociative. The fact that weak emission was observed for one signal of **2a** (Figure 1a) suggests that **4a** has a discrete minimum, however shallow.

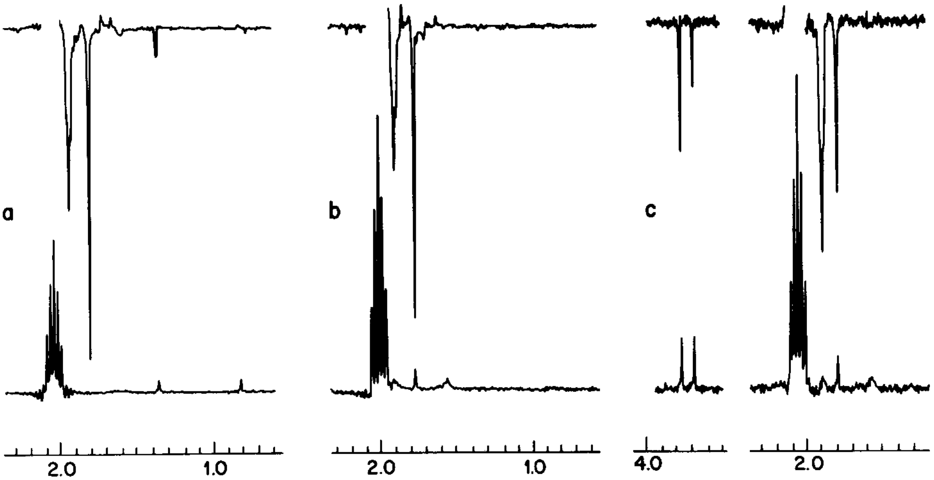


Figure 1: PMR spectra (90 MHz) of acetone-d_6 solutions containing a) 0.02M chloranil and 0.002M cage compound **2a**; b) 0.02M chloranil and 0.002M diolefin **1a**; and c) 0.02M naphthoquinone and 0.002M diolefin **1c**. The bottom traces were recorded in the dark whereas the top traces were accumulated during UV irradiation of the samples.

Several additional features of the polarization also deserve comment. First, we note that the radical cations **3** and **4** have no element of symmetry; accordingly, the spin density need not be distributed evenly over the four pivotal carbon atoms. The preferential polarization of one methoxy signal of **1c** (Figure 1c) may indicate an unsymmetrical spin density distribution. Another interesting observation concerns the polarization intensity as a function of the acceptor. For **1a** (E = 1.4V vs. S.C.E.) substantial polarization is found with chloranil as acceptor (E = −0.02V vs. S.C.E.), whereas the reaction with naphthoquinone (E = −0.6V vs. S.C.E.) or anthraquinone (E = −0.9V vs. S.C.E.) results in only weak polarization. For **1c**, on the other hand, which has a lower oxidation potential (E = 1.1 vs. S.C.E), appreciable polarization is observed only with naphthoquinone, whereas considerably weaker effects are generated with partners of higher or lower reduction potentials. The reasons for this interesting difference are under investigation.

Finally, we comment on the observation that the CIDNP effects are much stronger at relatively low donor concentrations (~0.002M) than at higher ones. The weakening of CIDNP effects with increasing reactant concentrations is observed frequently in electron transfer reactions and has been ascribed to fast, degenerate electron exchange.[7,9,10] In the system discussed here, exchange reactions such as

$$\mathbf{2} + \mathbf{3} \rightarrow \mathbf{4} + \mathbf{1}$$

$$\text{or} \quad \mathbf{1} + \mathbf{3} \rightarrow \mathbf{3} + \mathbf{1}$$

can be invoked. Accordingly, the suppression of CIDNP at higher donor concentrations is compatible with the free radical cation chain reaction previously postulated[6] for the cycloreversion **2** → **1** and also invoked for the ring opening of hexamethyl(Dewarbenzene).[11,12]

In conclusion, the CIDNP results reported here support the view that the cage radical cations (**4**) have shallow energy minima and undergo rapid cycloreversion; conversely, no evidence was found for a cyclization of the diolefin cations.

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