Magnetic resonance methods in the mechanistic photochemistry of ketones, olefins, and oximes

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Abstract - Magnetic resonance techniques have been applied in some photo-reactions originally investigated by Ciamician and Silber, and in related systems inspired by their studies. Some photoreactions of ketones, oximes, and olefins are discussed. These studies have conveyed insight into mechanistic details and revealed the existence of unique intermediates.

Modern molecular photochemistry offers a seemingly limitless variety of reactions. Nevertheless, the number of primary reaction types is strictly limited. In the broadest sense, we divide primary photochemical reactions into four general reaction types, two each of unimolecular and bimolecular nature. The unimolecular reactions include rearrangements and fragmentation or cleavage reactions, whereas the bimolecular category is comprised of cyclo-additions and abstraction or transfer reactions. Many abstractions and fragmentations have been shown to proceed via radical pair, biradical, or carbene intermediates. In contrast, the intermediates involved in rearrangements and cycloadditions have been more elusive, leading to speculation that these reactions may be concerted.

The pioneering work of Giacomo Ciamician and his associate Paul Silber in Bologna between 1900 and 1915 provided an early indication of the rich variety of photochemical reactions. Interestingly, their substrates were chosen so that their work covered the full range of the general reaction types mentioned above. Indeed, many of the specific reactions investigated by the Bologna group have remained at the focus of much attention, although the emphasis of the investigations has changed. Current interest is centered on mechanistic questions, particularly on the nature of the potential intermediates, whereas Ciamician and Silber were interested mainly in exploring the wide range of reactions that could be induced by exposure of organic compounds to sunlight.

Magnetic resonance methods are well suited to probe the intermediacy of radicals or radical ions, radical (ion) pairs, biradicals, or carbenes, and have shed new light on many of the reactions explored by Ciamician and Silber. We have chosen representative reaction types studied by the Bologna group and will elaborate current research, particularly the application of magnetic resonance techniques, in these areas.

PHOTOINDUCED REACTIONS OF CARBONYL COMPOUNDS

The first photoreaction investigated by Ciamician was the photoreduction of benzoquinone in alcohol solution. He identified hydroquinone and acetaldehyde as complementary products of an oxidation-reduction reaction (ref. 1). These studies were carried out as early as 1886, but Ciamician did not continue this research because Heinrich Klinger had observed the same reaction type a few months before him (ref. 2) and had "reserved" the field for himself. Fifteen years later Ciamician and Silber returned to carbonyl photochemistry and investigated the irradiation of benzophenone in alcohol solution. They recognized the first example of photopinacolization (ref. 3). A thorough investigation of benzophenone photochemistry followed, which included the reaction with toluene. In this system, the full complement of geminate and free radical coupling products were isolated, 1,1,2-triphenylethanol, and benzpinacol and bibenzyl, respectively (ref. 4).

The photoreduction of ketones and quinones by a variety of substrates still is an important area of photochemical investigation. Interest has turned to the mechanistic aspects of the reaction, specifically to the question whether the net hydrogen abstraction is initiated by an electron transfer step. Several techniques have been brought to bear on this question. Electron paramagnetic resonance (EPR) has been used to characterize many semiquinone, semidione and ketyl radical anions, the species resulting from one-electron reduction of the carbonyl moiety. Time resolved EPR and chemically induced dynamic electron polarization (CIDEP) are used in several laboratories to probe the primary steps in the light induced reactions of various carbonyl compounds.

The photoreaction of the simplest ketone, acetone, with 2-propanol as hydrogen donor in the cavity of an ESR spectrometer gives rise to "multiplet" CIDEP induced by $S-T_0$ mixing in the resulting radical pair. The involvement of an additional polarization mechanism is indicated by the intensities of several lines, including the non-zero intensity of the center line (ref. 5). The interpretation of the resulting effects is impeded by the involvement of two identical radicals with different chemical histories. However, the polarization of the two radicals can be separated by employing different isotopically labeled reagents, e.g. acetone-d_6 with 2-propanol-h_8. The resulting CIDEP spectrum shows two components, a 7-line spectrum with a splitting near 18 G, and a more narrowly spaced spectrum, presumably a 13-line feature caused by coupling to six nuclei of spin 1. Both spectra are strongly enhanced and substantially distorted (ref. 6). For several other ketones net CIDEP effects provide insight into the rates of intersystem crossing from the excited-singlet state to individual triplet sublevels.
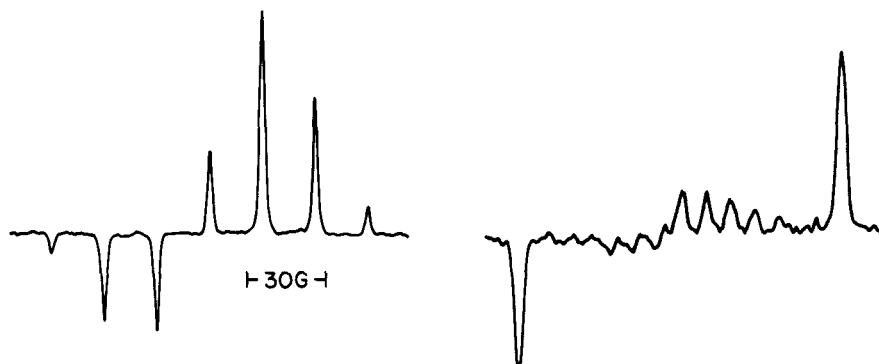

Fig. 1 CIDEP spectra resulting from laser excitation of acetone in 2-propanol; left: acetone-h_6; right: acetone-d_6.

Chemically induced dynamic nuclear polarization (CIDNP) effects have proved useful in probing the initial step in the photoreduction of ketones and quinones by tertiary amines (ref. 7-9). We have found evidence for a two-step mechanism initiated by electron transfer and completed by proton transfer. We illustrate the effects that may be observed with four spectra of vinyldiethylamine, an unstable product formed during the irradiation of quinones in the presence of triethylamine. Spectra 1a (simulated) and 1d can be explained by the involvement of the aminium radical cation and the aminoalkyl radical, respectively. In contrast, spectra 1b and 1c require the cooperative involvement of both species. Interestingly, the simulation of some of the observed effects suggests that the proton is not transferred form the aminium radical cation to the semiquinone counter ion within the geminate radical ion pair. Rather, a proton from the aminium species is transferred to the bulk of the solution, and the semiquinone ion is protonated independently.
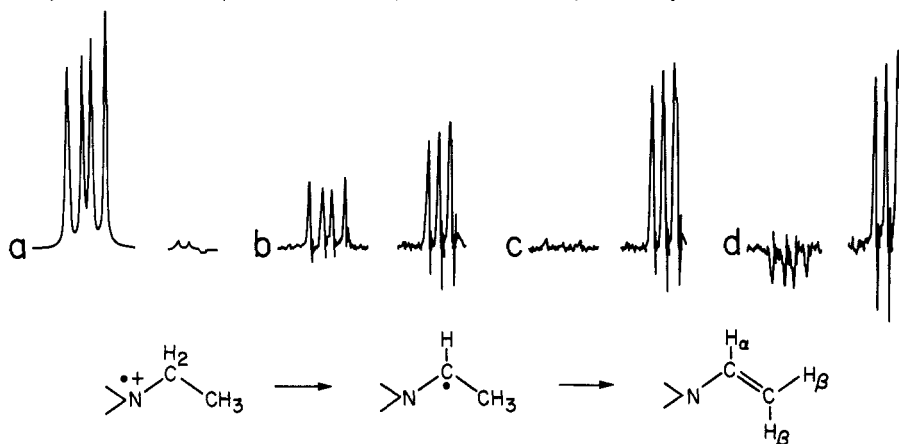

Fig. 2. CIDNP spectra of the α- (left) and β-protons (right) of vinyldimethylamine, simulated for the exclusive involvement of the aminium radical ion (a), and observed during the reaction of benzoquinone with triethylamine in acetonitrile (b) and acetone (c), and of anthraquinone with triethylamine in acetone (d).

In addition to intermolecular reactions of ketones Ciamician and Silber also observed cleavage reactions of aliphatic and cyclic ketones. For example, the photolysis of pinacolone led to acetaldehyde and isopropylene (ref. 10). They established the analogous conversion

of cyclohexanone to 5-hexenal (ref. 11) and of menthone (2-isopropyl-5-methylcyclohexanone) to 3.7-dimethyl-5-octenal (ref. 12). Based on this example, they concluded that the cleavage occured between the carbonyl group and the more highly substituted α-carbon. The irradiation of camphor produced campholenaldehyde and an unsaturated ketone (ref. 10); the former reaction is initiated by α-cleavage, whereas the latter involves intramolecular γ-hydrogen abstraction followed by β-cleavage. Thus, Ciamician and Silber deserve credit for discovering both types of cleavage reactions (though they did not find a kind biographer who would associate their names with these reactions).
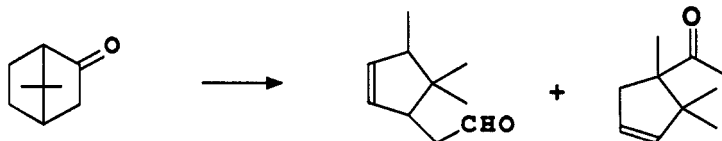

Fenchone, though closely related to camphor, suffered a seemingly different course of photochemical reaction, giving rise to carbon monoxide and an unsaturated hydrocarbon (ref. 10). With the advantage of 75 years of progress in photochemistry it is obvious that the two reactions are initiated by the same primary process and differ mainly in the ease of decarbonylation of the biradical intermediate.

The study of cyclic ketones is currently focussed on the characterization of the optical and magnetic properties of the resulting biradicals and on their reactions upon excitation with a second photon (ref. 13). The biradical lifetimes have been determined for a series of medium-sized α-phenyl- and α,α'-diphenylcycloalkanones. The intersystem crossing in these species is magnetic field dependent and can be dissected into separate contributions due to spin orbit coupling and electron-nuclear hyperfine coupling. The relative importance of the two components varies with ring size. These studies further revealed the interesting formation of cyclophanes upon photolysis in polar media (ref. 14). Their formation can be rationalized via α-cleavage followed by radical addition to the para position of the aromatic moiety.

LIGHT INDUCED CYCLOADDITION REACTIONS OF OLEFINS

Ciamician and Silber studied several dimerization reactions both in the solid and liquid phase and they were the first to observe an intramolecular cycloaddition, the formation of carvone camphor upon irradiation of carvone (shown below). The solid state dimerization of cinnamic acid to α-truxillic acid had been observed as early as 1895 by Bertram and Kursten (ref. 15) and by Liebermann (ref. 16). In recent years an interesting complement to this reaction has been observed: irradiation of a metastable crystalline form of the acid was found to produce β-truxinic acid (ref. 17). This is an interesting manifestation of the kind of selectivity that may be observed in solid state photochemistry as a result of the highly ordered packing in the crystal (ref. 18).
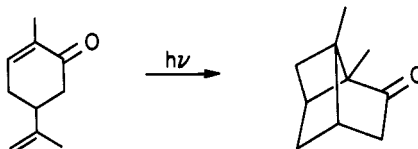
The solution photodimerizations studied in Bologna included those of stilbene and coumarin. Various mechanistic possibilities exist for these reactions, including the involvement of excited singlet or triplet states. Current interest in this area is focussed on electron transfer induced dimerizations and cycloadditions in general. We will discuss several radical cation cycloadditions, including an intramolecular cycloaddition and a radical cation Diels Alder reaction.

Reactions of this type can be initiated by chemical oxidations, for example by aminium salts (ref. 19), by pulse radiolysis of reactants in glassy matrices (ref. 20), or by photoexcitation of an electron acceptor in the presence of the olefin (ref. 21). The mechanism of these cycloadditions is of great interest, in particular the question whether the addition is concerted or stepwise. Molecular orbital considerations indicate that such a reaction may be orbital symmetry allowed (ref. 19) but state symmetry forbidden (ref. 20). The observation of stereoselective cycloadditions, especially the retention of dienophile stereochemistry, has been interpreted as evidence for a concerted mechanism (ref. 19). On the other hand, the existence of a singly linked doubly allylic radical cation derived from endo-dicyclopentadiene might be viewed as evidence for a stepwise mechanism (ref. 22). We have been able to demonstrate the involvement of a singly linked intermediate in the radical cation Diels Alder reaction of spiroheptadiene and, thereby, established a nonconcerted component in this cycloaddition and the corresponding cycloreversion (ref. 23,24).
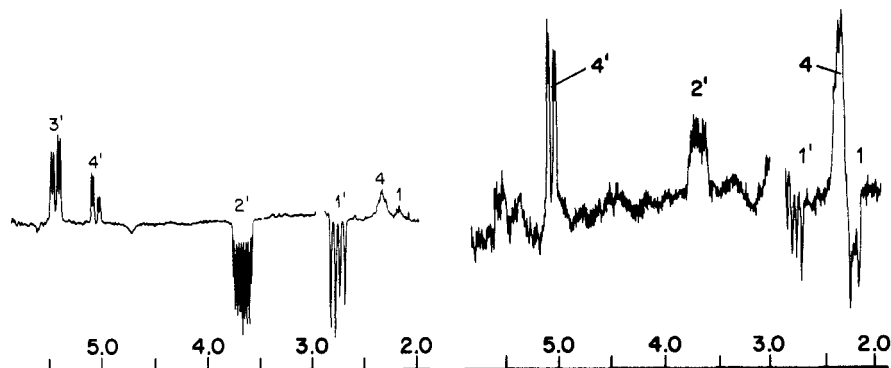
Fig. 3. CIDNP spectra observed 100µs after excitation of chloranil
solutions with the frequency tripled output of a Nd/YAG laser. Left:
solution containing bis(spiroheptadiene), 16 laser pulses. Right: solution
containing spiroheptadiene, 64 laser pulses. In this system, enhanced
absorption indicates that the corresponding protons are attached to carbons
with positive spin density.

The electron transfer reaction of spiro[2.4]heptadiene with photoexcited chloranil resulted
in strong nuclear spin polarization for the reactant and its [4+2] dimer. The monomer
polarization is compatible with a butadiene-like radical cation, which lacks appreciable
interaction with the cyclopropane fragment. The dimer polarization is significant since it
constitutes evidence for a rapid radical cation Diels Alder reaction. The polarization pat-
tern unambiguously identifies a dimer radical cation with appreciable spin density only on
two carbons of the dienophile fragment. This finding establishes the existence of a doubly
linked dimer radical cation (D) in which spin and charge are localized in the vinylcyclopro-
pane moiety. The same species is implicated in the electron transfer reaction of the dimer.

However, these results cannot be considered evidence for a concerted mechanism because of a
limiting feature inherent in the CIDNP technique. Nuclear spin polarization effects reflect
the electron spin density distribution of the intermediates which are present in solution
during the spin sorting process, typically 1-10 ns after the generation of the original
radical pair. In contrast, the structures of short-lived radical successors will not be
reflected in the polarization of the ultimate diamagnetic products. Accordingly, the above
results merely establish the existence of the doubly linked radical cation and the fact that
it suffers cycloreversion or reduction by the counter ion.
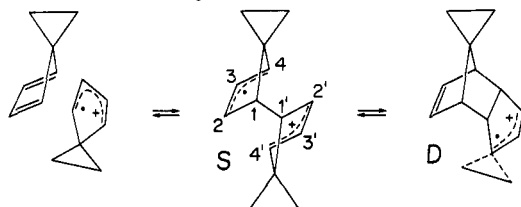
An experiment utilizing pulsed laser excitation allows a more detailed insight into the
mechanism of this cycloaddition. Under these conditions the reaction of the dimer still
produces evidence for the involvement of D (Figure 3, left). However, the reaction of the
monomer, especially at high monomer concentrations, provides evidence for a different dimer
radical cation. The nature of this intermediate is most clearly indicated by the enhanced
absorption signals observed for H_4 and H_2' (Figure 3, right), which are characteristic for a
singly linked radical cation (S). The high monomer concentration used in these experiments
favors the rapid interception of monomer radical cation and, likewise, the rapid reduction
of the doubly linked radical cation. On the other hand, the reduction of S to form a singly
linked biradical or zwitterion is less favorable, causing S to be the polarization deter-
mining intermediate.

An interesting intramolecular cycloaddition was observed during the photooxidation of
methylenebicyclo[4.2.1]nona-2,4,7-triene (B) (ref. 25). Because of the nature of its HOMO
it is reasonable to assume that this system initially forms a radical cation with spin and
charge restricted to the butadiene fragment (B+). This intermediate undergoes rapid intra-
molecular cycloaddition to generate a bishomoheptafulvene radical cation formally derived
from a highly strained tetracyclic structure (Q). The cycloaddition step must be fast even
at -50°C; the barrier is estimated to be 5 kcal/mol. The existence of Q+ is all the more
remarkable as the parent hydrocarbon can be detected by NMR only at -50°C; at temperatures
as low as -20°C it rearranges within seconds to B with a barrier near 15 kcal/mol. We
ascribe the relative stability of Q+ to its cyclic conjugated nature and to the fact that
the increase in strain energy relative to B+ is minimized as the two pivotal cyclopropane
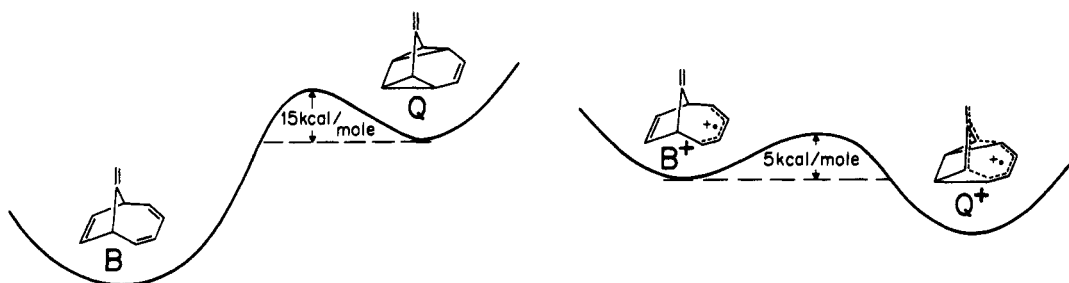bonds are only partially formed (ref. 25).

Fig. 4. Comparison of relative energies between methylenebicyclo[4.2.1]-nonatriene and its quadricyclic valence isomer and the corresponding radical cations.

Electron transfer induced olefin dimerizations and the reverse dimer cleavage have received much attention in recent years. Again, the question is being raised whether the addition is concerted, or whether it proceeds via a singly linked intermediate. Some dimers, for example that of dimethylthymine, are cleaved with a high degree of efficiency (ref. 26,27). Thus, no evidence was observed for any kind of dimer cation. In other systems, however, evidence for dimer cations is indeed observed. We discuss a system that shows particularly interesting effects, the electron transfer induced cleavage of the trans-head-to-head dimer of dimethylindene.
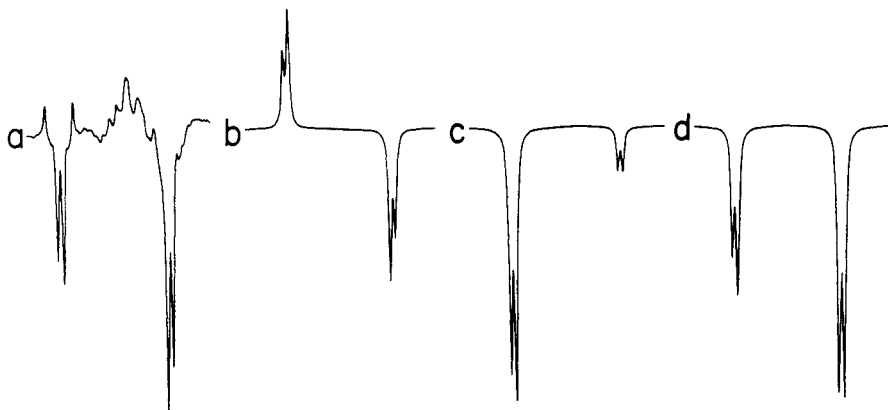

Fig. 5. CIDNP effects observed during the electron transfer induced cleavage of dimethylindene dimer (a) and simulated spectra assuming the involvement of a localized dimer radical cation (b), a singly linked dimer radical cation (c), and the cooperative involvement of both species (d).

During irradiation of an electron acceptor in the presence of this dimer the benzylic and non-benzylic cyclobutane protons of the dimer showed emission with comparable intensities. This polarization pattern is seemingly incompatible with either of the "logical" intermediates one might envision for the cycloaddition. It seems to suggest an intermediate that fails to utilize any element of benzylic stabilization. The observed polarization can be explained, however, as the sum of two contributions from the doubly and singly linked radical cation intermediates. This assignment implies an equilibrium between the two species and requires that both have comparable lifetimes. The observed effects can be simulated as "cooperative" effects induced in consecutive radical ion pairs (ref. 9).
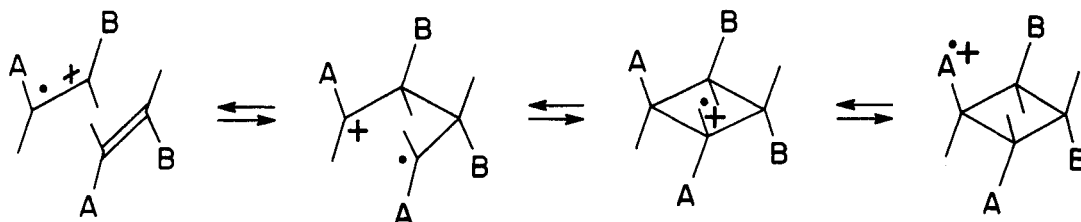

The dimer radical cation derived from tetramethylethylene was reported recently by Desrosiers and Trifunac based on Fluorescence Detected Magnetic Resonance results (ref. 28).

At low olefin concentrations a spectrum with the splitting of the known monomer radical cation (17 G) was observed. At higher olefin concentrations a new spectrum with reduced splitting (8.5 G) appeared, which was assigned to the dimer cation. The assignment rests on the magnitude of the coupling, as the intensities of seven (or nine) center lines cannot distinguish a 13- from a 25-line spectrum.

One of the most interesting radical cation cycloadditions is observed upon one-electron oxidation of appropriate derivatives of 1,5-hexadiene (ref. 29,30) and 1,6-heptadiene (ref. 31). Photoinduced electron transfer of these diolefins proceeds via short-lived monoolefin radical cations, which add to the second olefinic moiety in intramolecular fashion. ESR results, CIDNP effects, and trapping experiments with oxygen clearly establish the existence of ring-closed bifunctional intermediates with spin and charge densities, respectively, in the 2 and 5 (2 and 6) positions. Because of the ring strain of the potential bicyclic product ion the cycloaddition is "arrested" at the state of the monocyclic bifunctional intermediate.
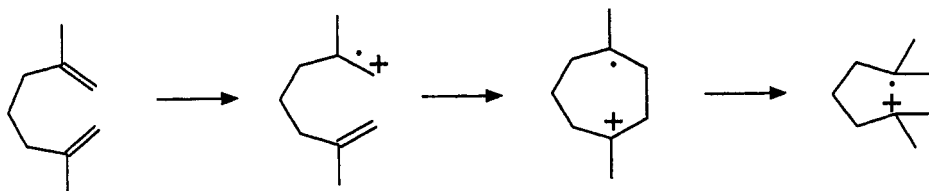

The bifunctional intermediate is of special interest, because of its relation to the transition structure for the Cope rearrangement of hexadiene. Here as in several other systems (ref. 32-34) the radical cation potential hypersurface has a minimum at a geometry corresponding to a saddle point on the hypersurface of the parent molecule. In principle, this electrocyclic reaction can be envisioned via three mechanistic extremes: a) addition might preceed cleavage; b) cleavage might preceed addition; c) bond making and bond breaking might occur in concerted fashion. Radical cations corresponding to key geometries of all three mechanistic extremes have been characterized. For the singly linked intermediate derived from dicyclopentadiene, cleavage is achieved without appreciable bonding; for the radical cation of hexadiene, addition is complete without any fragmentation; and finally, the radical cations of barbaralane derivatives represent intermediates, in which addition and cleavage are "frozen" at a stage permitting cyclic delocalization of five π-electrons.
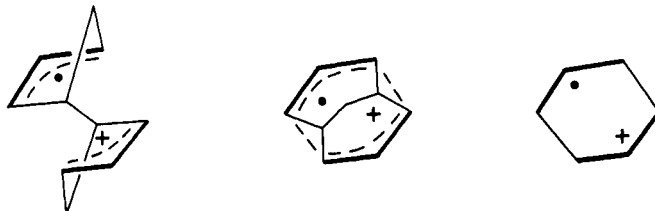
The doubly linked intermediates have been approached also by cerium (IV) and by photosensitized oxidation of 2,3-diazabicyclo [2.2.2] oct-2-ene derivatives (ref. 35,36). Under these conditions deprotonation and dehydrogenation of the intermediate is observed, leading to olefinic and aromatic products.

LIGHT INDUCED ISOMERIZATIONS

Geometric isomerizations induced by the action of light were first observed by Perkin in 1881 (ref. 37) and the scope of the reaction was expanded by Liebermann (ref. 16). The Bologna group investigated several isomerizations and detected even the direct interconversion of maleic and fumaric acids (ref. 38), which in sunlight proceeds very slowly. Various mechanisms have been documented for geometric isomerizations of unsaturated moieties, including: rotation in the excited singlet state; the intermediacy of a perpendicular triplet state, populated either by intersystem crossing, by triplet energy transfer, or by recombination of a triplet radical ion pair; rotation in a biradical adduct; and rotation in a radical cation generated by electron transfer to a photoexcited acceptor (ref. 39).
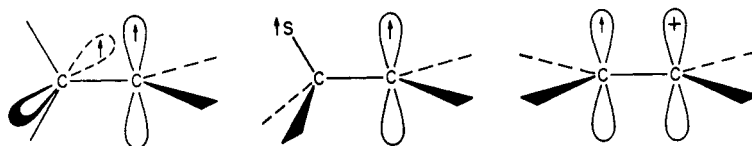
Many of the photoisomerizations proceeding via excited singlet or triplet states lead to photostationary states. In contrast, the isomerizations of radical cations often occur as one-way isomerizations in which the more stable isomer is formed exclusively. This is found particularly for the cis-isomers of styrene derivatives, viz. anethole and 1-phenyl-1-propene. Irradiation of an electron acceptor in the presence of these olefins causes complete conversion within seconds. The fact that the isomerization is unidirectional requires that the barrier to cis→trans isomerization is small compared to the free energy difference between the isomeric radical cations. The high efficiency is best explained by a radical ion chain mechanism involving electron transfer from the cis-substrate to the rearranged (trans-) radical cation (ref. 39). Isomerizations via this type of mechanism have been established, for example, for the electron transfer induced rearrangement of Dewar-benzene (ref. 40).

Another interesting isomerization studied by Ciamician and Silber was that of several oximes, a reaction type that was first described by Liebermann in 1895 (ref. 16) even before the cis-trans isomerism of oximes had been established. Ciamician and Silber found that irradiation caused the conversion of a photolabile oxime isomer into a photostable one, whereas the reverse conversion was observed upon heating (ref. p.38). On the other hand, irradiation of oximes in solid matrices gives rise to radicals. For example, ESR spectra recorded after irradiation of biacetylmonoxime at 5 and 77K show typical powder patterns with splittings characteristic for an iminoxyl radical. The spectra recorded at the two temperatures differ mainly by the presence of four lines in the spectrum recorded at lower temperature. Subtraction of the 77K from the 5K spectrum reveals the corresponding transient as the methyl radical by the characteristic splitting of 31 G (Fig. 6). Apparently, this species is trapped at the lower temperature but gains sufficient mobility at 77K to allow it to migrate and react. The difference between solution and the glassy matrix must be ascribed to the much slower dissipation of excess energy in the latter.
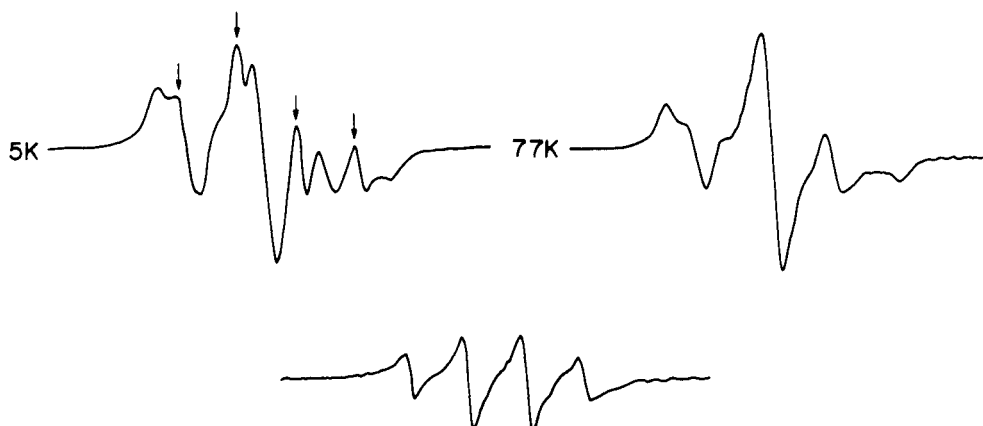

Fig. 6. EPR spectra observed after UV irradiation of biacetylmonoxime in a methyltetrahydrofuran matrix at 5K and 77K (top) and difference spectrum (bottom).

While the irradiation of oximes causes syn-anti isomerization, the closely related oxime esters suffer bond homolysis (ref. 41). Thus, appropriately substituted biacetylmonoxime esters have been used as photo-polymerization initiators. The fragmentation mechanism has been formulated as involving N-O cleavage followed by loss of acetonitrile and decarbonylation. However, EPR spectra observed upon photolysis of substituted dicarbonylmonoxime esters in rigid matrices fail to support the involvement of iminyl radicals and support only the formation of the ultimate decarbonylation product (ref. 9). These results indicate that additional decomposition pathways need to be cnsidered.

CONCLUSION

Ciamician and Silber have left a rich legacy of interesting photochemical systems, involving both intra- and intermolecular reactions of ketones, oximes, and olefins. The application of magnetic resonance techniques in their photochemistry aloows insight into mechanistic details of these reactions. Still, the information gained in some systems remains insufficient; further studies and poosibly new techniques are required to fully elucidate thier mechanisms.

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