$f^+(\bar{r})$, η^+, $\bar{\eta}^+(\bar{r})$; when it is being subtracted one has μ^-, $f^-(r)$, η^-, $\bar{\eta}^-(\bar{r})$. One also has the averages μ^0, $f^0(\bar{r})$, η^0, $\bar{\eta}^0(\bar{r})$.

Extension of the local or point hardness to a regional or group hardness is immediate and provides the means for evaluating the hardness of a particular atom in a molecule, some group, or any specified region. We merely break eq 18 into regional components:

$$\eta = \sum_\Omega \eta_\Omega \tag{40}$$

$$\eta_\Omega = \int_\Omega \bar{\eta}(\bar{r}) f(\bar{r}) \, d\bar{r} \tag{41}$$

Equation 41 admits of calculation as desired.

It may be mentioned that eq 41 is a different definition of regional hardness than the one implied by the approach of Bader and colleagues,[16] who speculate that the hard–soft behavior can

be rationalized from the properties of the Laplacian $\nabla^2\rho$. They characterize a hard site in a molecule by the appearance of a large maximum (minimum) of $\nabla^2\rho$ which is tightly bound (occurs at small r); and they ascribe the soft behavior to a site with opposite characteristics. They then state the hope that chemical reactions can be predicted on the basis of "hard maxima reacting with hard holes and soft maxima with soft holes".

Generally, then, each atom has its own effective hardness in a molecule (whereas electronegativities of all atoms are the same). While a detailed discussion along these lines remains to be given, we may confidently expect, in accordance with the extended HSAB principle,[5] that a hard reactant will generally attack the hardest part of the partner, and similarly soft will prefer soft. Calculated group hardnesses should allow prediction of site selectivity in chemical reactions.

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Radical Cations of Fulvenes: Planar or Twisted?

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Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Received May 20, 1985

Abstract: The reactions of several fulvene derivatives with photoexcited electron acceptors (chloranil, anthraquinone) give rise to strong nuclear spin polarization effects. These results offer insight into the structures of the radical cation intermediates. For all systems studied, the spin density is restricted to the ring carbons. Electron-donating substituents in the exomethylene position affect the delocalization of the positive charge and the strength of the exocyclic bond in the radical cations. For example, the (Z)- and (E)-2-tert-butyl-6-(dimethylamino)fulvene radical cations rearrange readily, whereas the di-tert-butylfulvene
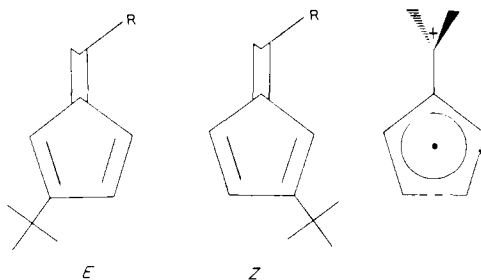
radical cations show no interconversion. The results are compatible with either planar or slightly twisted radical cations and preclude the intermediacy of perpendicular radical cations.

The fulvenes long have been a focus of interest as prototypes of cyclic, cross-conjugated molecules and because of their unique properties.[1] The electronic spectra of most fulvenes show transitions in the visible region as a result of a small HOMO–LUMO gap.[2] The comparatively large dipole moments of the parent molecule (0.42 D)[3] and simple derivatives (1.44 D for 6,6-dimethylfulvene)[4] attest to the importance of zwitterionic character in the ground state. The dipole moment can be understood as

resulting from intramolecular charge transfer from the exocyclic double bond to the five-membered ring thereby acquiring pseudoaromatic cyclopentadienide character. Substituents can affect the degree of zwitterionic character, and such perturbations manifest themselves as shielding effects in NMR spectra.[5] Furthermore, substituents which reinforce the zwitterionic structure, i.e. electron-releasing groups at C6 and/or electron-accepting groups on the ring, stabilize the fulvene and reduce its tendency for dimerization, polymerization, and oxygenation.[1]

We were attracted to the fulvenes as potential precursors of nonvertical radical cations, a concept we have introduced recently.[6]

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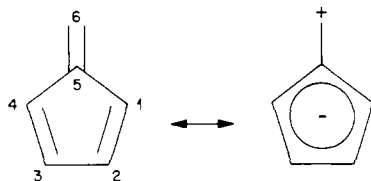
Several factors have been singled out which favor the formation of nonvertical structures: relief of ring strain, resonance stabilization, rehybridization at key centers, and separation of spin and charge. Only the latter can be relevant in the fulvene system. Although fulvenes possess planar π-systems, molecular orbital considerations suggest that spin and charge are restricted to the endocyclic diene portion.[2] However, the delocalization of spin and charge might be enhanced and the intermediate further stabilized by adopting a nonvertical structure with two orthogonal π-systems. We have reported similar stabilization by enhanced delocalization in several other systems.[7] All of these have in common that a σ-bond is broken, whereas the stabilization of the fulvene molecule requires that a π-bond be decoupled. To date only one radical cation of a remotely related structure type, the molecular ion of radialene, has been reported.[8] Radical cations of simple olefins, on the other hand, are thought to be slightly twisted ($25°$),[9] but this limited deviation from planarity is not sufficient to estabilish them as nonvertical radical cations. For example, CIDNP results obtained in the 1-phenylpropene system indicate the existence of two separate radical cations.[10]

In an attempt to gain insight into their structures we have generated the radical cations of several fulvene derivatives as short-lived intermediates by electron transfer to photoexcited chloranil and studied these reactions using the CIDNP technique.[11] This method has been useful as a tool in elucidating the structures of many hydrocarbons radical cations.[7,11,12] Basically, the CIDNP effects can be related to the signs and magnitudes of the hyperfine coupling patterns of the radical ion intermediates. This, in turn, reflects the spin density distribution which is an integral structural feature of the radical cation.

Experimental Section

Diphenylfulvene (Aldrich) was used without purification, wheras dimethylfulvene (Columbia Organics) required purification by gas chromatography (10%SE-30). Most of the fulvenes included in this study were prepd. according to published procedures by condensation of a cyclopentadiene with an aldehyde or ketone with either sodium methoxide (Method A)[13] or pyrrolidine (Method B).[14] 6-Phenylfulvene[13,14] was prepared by using Method B and purified by liquid chromatography (SiO$_2$, hexane, R_f 0.25). 6,6-Diphenylfulvene-6-^{13}C was prepared from benzophenone-^{13}CO (90% Merck, Sharp and Dohme) by Method A and purified by liquid chromatography (SiO$_2$, hexane, R_f 0.10). (Z)- and (E)-2,6-di-*tert*-butylfulvene were prepared from *tert*-butylcyclopentadiene[15] and trimethylacetaldehyde (Aldrich) by Method B. The mixture of isomers was isolated by liquid chromatography (SiO$_2$, hexane, R_f 0.20) and separated by gas chromatography (30% SE-30, 125 °C, 75
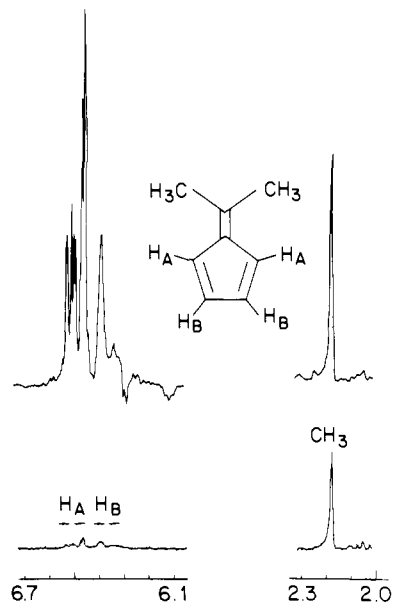
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Figure 1. ^{1}H NMR spectrum of a 0.02 M solution each of chloranil and 6,6-dimethylfulvene in acetone-d_6 in the dark (bottom) and during UV irradiation (top).
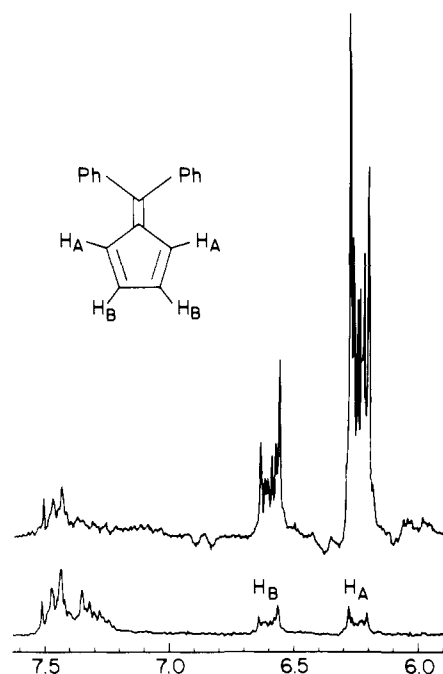

Figure 2. ^{1}H NMR spectrum of a 0.02 M solution of chloranil and 0.01 M 6,6-diphenylfulvene in acetone-d_6 in the dark (bottom) and during UV irradiation (top).

cm^3/min, Z: 23 min, E: 27 min). The individual isomers are characterized as follows. Z: ^{1}H NMR (acetone-d_6, 500 MHz) δ 6.45 (ddd, J = 5.2, 1.6, 0.6 Hz, 1 H), 6.28 (ddd, J = 2.1, 1.6, 0.7 Hz, 1 H), 6.25 (br s, 1 H), 6.12 (dd, J = 5.2, 2.1 Hz, 1 H), 1.26 (s, 9 H), 1.18 (s, 9 H). E: ^{1}H NMR (acetone-d_6, 500 MHz) δ 6.65 (dd, J = 1.9, 1.0 Hz, 1H), 6.64 (d, J = 2.1 Hz, 1H), 6.29 (br d, J = 1.0 Hz, 1 H), 5.76 (ddd, J = 2.1, 1.9, 0.3 Hz, 1 H), 1.26 (s, 9 H), 1.16 (s, 9 H), mp 54–55 °C. (Z)- and (E)-6-*tert*-butyl-2-(dimethylamino)fulvene were prepared from *tert*-butycyclopentadiene and dimethylformamide diethyl acetal (Aldrich) and purified by sublimation, mp 44–45 °C. The ^{1}H NMR signals (acetone-d_6) are assigned as follows. Z: δ 7.04 (br s, 1 H), 6.41 (m, 2 H), 5.95 (br t, J = 2.2 Hz, 1 H), 3.20 (s, 6 H), 1.16 (s, 9 H). E: δ 7.01 (br s, 1 H), 6.23–6.16 (m, 3 H), 3.21 (s, 6 H), 1.20 (s, 9 H).

The CIDNP experiments were carried out in acetone-d_6 (Aldrich) or acetonitrile-d_3 (Merck, Sharp and Dohme). Samples containing 0.02 M each of chloranil (Eastman Organics) and fulvene were dearated by purging with Ar for 3 min and irradiated through Pyrex in the probe of a Bruker WH-90 FT NMR spectrometer with the collimated beam of
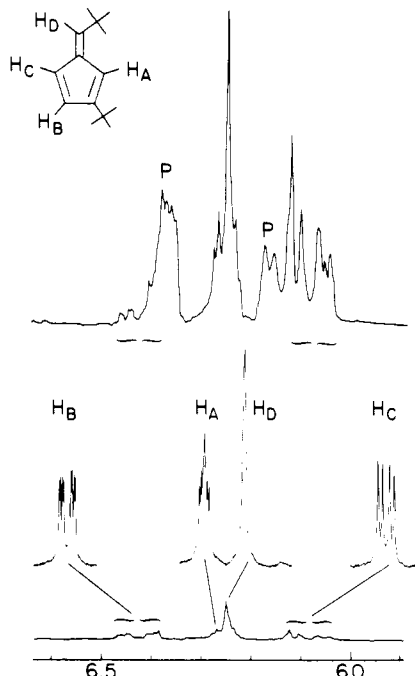
Figure 3. ^{1}H NMR spectrum of a 0.02 M solution each of chloranil and (E)-2,6-di-*tert*-butylfulvene in acetone-d_6 in the dark (bottom) and during UV irradiation (top). The individual resonances, recorded at 500 MHz, are shown as insets. The enhanced signals labeled P represent a reaction product but not the E-isomer (cf. Figure 4).

an Osram 200W high-pressure mercury lamp.

Results

All fulvenes studied give rise to strong CIDNP effects. The most intense polarization is observed for the protons in the 1 and 4 positions (α-protons), whereas the protons in the 2 and 3 positions (β-protons) show somewhat weaker effects. This pattern is illustrated most clearly in the CIDNP effects for dimethylfulvene (Figure 1) and diphenylfulvene (Figure 2). Phenylfulvene shows a similar pattern, although the NMR spectrum does not allow ready differentiation between the α- and β-protons. Similar effects are observed in the isomeric di-*tert*-butylfulvenes, in spite of the presence of the ring substitutents. The Z-isomer shows strong enhancement for both α-protons and also for two other resonances representing a reaction product, but not the E-isomer (Figure 3). One of the product signals obscures the polarization of the β-proton. The E-isomer also shows enhancement for at least one α-proton, a triplet at 5.8 ppm (Figure 4). The other α-proton, a doublet at 6.6 ppm, coincides in chemical shift and coupling constant with the β-proton. The strong polarization observed for this feature must be ascribed to the second α-proton rather than to the β-proton.

In contrast to the ring protons, protons and/or substituents of the *exo*-methylene group show weaker effects. A methyl group at C6 shows enhanced absorption (Figure 1), whereas a phenyl group in this position shows net emission (Figure 2). The *exo*-methylene proton of (E)-2,6-di-*tert*-butylfulvene shows emission, whereas the polarization of the corresponding protons in the Z-isomer and 6-phenylfulvene cannot be determined. Finally, diphenylfulvene-6-^{13}C (90% enriched) shows weakly enhanced ^{13}C absorption.

In addition, two pairs of geometrically isomeric fulvenes were investigated: (Z)- and (E)-di-*tert*-butylfulvene, which are readily separable by gas chromatography, and (Z)- and (E)-*tert*-butyl-6-(dimethylamino)fulvene, which have eluded separation in our hands. The assignment of the di-*tert*-butylfulvene isomers is based on the following considerations. The method of synthesis strongly suggests substitution at the 6-position and in the ring. The facile photochemical interconversion (vide infra) suggests that they are geometrical isomers. We assume 2,6-disubstitution based on steric grounds and on the analogous substitution observed in the oxidative
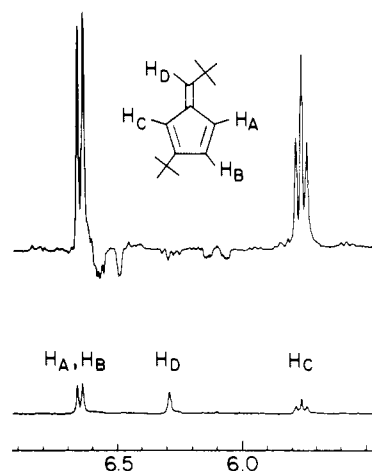

Figure 4. ^{1}H NMR spectrum of a 0.02 M solution each of chloranil and (Z)-2,6-di-*tert*-butylfulvene in acetonitrile-d_3 in the dark (bottom) and during UV irradiation (top).

coupling of lithium *tert*-butylcyclopentadiene to 2,2'-di-*tert*-butylpentafulvene.[16] The CIDNP patterns (vide supra) are also consistent with the assumed regiochemistry. The stereochemical assignment is based on the ^{1}H NMR spectrum of 6-*tert*-butylfulvene.[5b] In this monosubstituted fulvene the Z-α-proton is most strongly deshielded, whereas the E-α-proton is most strongly shielded. A *tert*-butyl substituent in the β-position should result in greater shielding of the adjacent α-proton. Therefore, we identify the molecule with the most highly shielded olefinic proton as the E-isomer. The remaining chemical shifts are consistent with this assignment if a deshielding effect is assumed for the protons on the unsubstituted double bond. This assignment is further supported by the relatively large long-range coupling constant between the β- and 6-protons ($^5J = 1.0$ Hz) of the E-isomer, which arises from the zigzag bonding relationship between these nuclei.
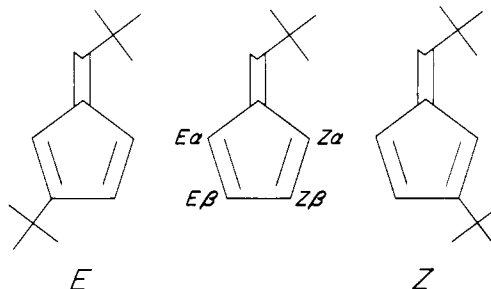
These pairs of isomers are photochemically reactive. In the presence of electron-transfer sensitizers such as chloranil the di-*tert*-butylfulvenes show strong CIDNP effects but no interconversion. On the other hand, direct irradiation in acetonitrile results in facile interconversion. Under our reaction conditions a photostationary Z:E mixture of 40:60 is achieved from either isomer. In contrast, the *tert*-butyl-6-(dimethylamino)fulvenes show interconversion upon direct irradiation as well as electron transfer sensitization. With anthraquinone as a sensitizer a photostationary Z:E mixture of 55:45 is attained. The CIDNP effects of the E-isomer, which is enriched during irradiation, are opposite in sign to those of the Z-isomer, which is depleted during irradiation (Figure 5). The polarization patterns of these pairs of isomers are consistent with the other fulvenes studied.

Discussion

The CIDNP effects can be interpreted in terms of the spin density distribution in the fulvene radical cations. The results show clearly that in all fulvenes examined the unpaired electron resides largely at C1 and C4 and to a smaller degree at C2 and

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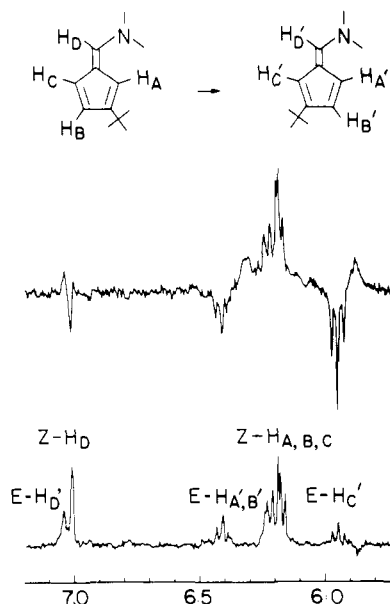
Radical Cations of Fulvenes: Planar or Twisted?

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Figure 5. ^{1}H NMR spectrum of a 0.01 M solution each of anthraquinone and a mixture of (Z)- and (E)-tert-butyl(dimethylamino)fulvene in acetone-d_6 in the dark (bottom) and during UV irradiation (top). The average of the spectra recorded before and after UV irradiation was subtracted from the CIDNP spectrum. The ring protons of the principal starting material, (Z)-tert-butyl(dimethylamino)fulvene, appear in enhanced absorption, whereas those of the principle product appear in emission. The single methylene protons of the two isomers show the opposite signal directions.

C3. The disposition of spin density in the exocyclic double bond is more difficult to assess, especially for the quaternary carbon (C5) for which direct evidence could be obtained only by ^{13}C labeling. The delocalization of positive spin density onto the methylene position (C6) would result in predictable polarization patterns. For example, a ^{13}C in this position would display emission, a ^{1}H nucleus attached to this carbon would show enhanced absorption, a methyl group emission, and the o- and p-hydrogens of a phenyl group enhanced absorption. Experimentally, only weak effects are observed, and they are opposite in all cases to those expected for positive spin density at C6. Accordingly, significant spin density at this position is ruled out.

Because of the ambiguity concerning spin density at C5, the CIDNP effects do not lead to an unambigous structure for the radical cations. The simplest structure would be one in which an electron is removed from the HOMO of fulvene. This orbital has coefficients principally at C1 and C4 and a nodal plane through C5 and C6.[2] Removal of an electron from this orbital would give rise to a structure in which spin and charge are localized in the endocyclic diene. A radical cation with this spin density distribution is consistent with the observed effects. The substituents at C6 would interact only weakly with the unpaired spin.

This simple description of the fulvene radical cation is unappealing both intuitively and on experimental grounds. One would expect that delocalization of spin and charge throughout the entire molecule would result in a more stable structure. Indeed, the effect of substituents on the photoelectron spectra (PES) of 6-alkyl-fulvenes[17] might be interpreted as evidence for such delocalization. The first ionization potentials of these fulvenes are substituent dependent, an observation which precludes a HOMO without an appreciable coefficient at C6. Rather, these results support a more extended HOMO and suggest that spin and/or charge density exists at C6 of the corresponding radical cations. Our CIDNP results clearly eliminate the possibility of significant spin density at C6 but do not rule out charge density at this carbon. The spin density distribution of a radical cation with spin density in the ring and charge density at C6 can be derived by considering the

effect of a positively charged substituent on the spin density distribution in the cyclopentadienyl radical.
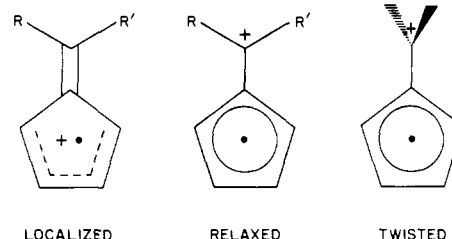
The two highest lying orbitals of this radical are degenerate. However, the degeneracy can be removed by interaction with a positively charged substituent, which lowers the energy of the symmetric orbital (S). As a result, the unpaired spin resides in the antisymmetric orbital (A), giving the "relaxed" radical cation a spin density distribution similar to that of the "localized" structure. The above analysis is born out by an ESR study of the effect of various substituents on the cyclopentadienyl radical.[18]
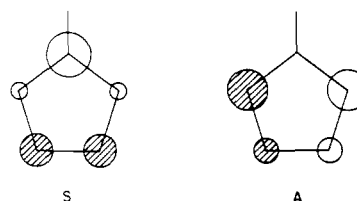
We have also considered whether the fulvene radical cations could be stabilized by twisting the exocyclic C–C bond, either to the extent postulated for olefin radical cations[19-22] or to a fully orthogonal position. The latter would effectively separate spin and charge. The polarization pattern expected for the involvement of this structure is very similar to those expected for the "localized" and "relaxed" radical cations. Accordingly, the CIDNP effects do not allow an unambiguous differentiation of the structure types discussed here.

The existence of perpendicular (nonvertical) radical cations was explored via pairs of geometrical isomers, (Z)- and (E)-2,6-di-tert-butylfulvenes and (Z)- and (E)-2-tert-butyl-6-(dimethylamino)fulvenes. Nonvertical, fully perpendicular radical cations should give rise to a mixture of Z- and E-isomers upon electron return, whereas radical cations with a lesser degree of twist need not result in any interconversion of geometrical isomers. In addition, the CIDNP effects are expected to show characteristic differences depending on the type of radical cation involved. If fully perpendicular (nonvertical) radical cations were involved, the CIDNP effects should be the same for both isomers with either isomer as reactant. In contrast, nearly planar or slightly twisted radical cations would result in opposite signal directions for reactant and product isomer, if isomerization is indeed observed. This prediction is based on the recognition that the reactant molecule can be regenerated readily from a planar or slightly twisted radical cation, whereas the formation of a rearranged product requires prior rotational isomerization of the radical cation. The nuclear spin polarization observed for the two types of products should be that of recombination and cage escape products, respectively.[10]

The experimental results obtained for the isomeric di-tert-butylfulvenes clearly eliminate the intermediacy of a perpendicular (nonvertical) species. This conclusion is based on the failure of the electron transfer sensitized reaction to give rise to any isomerization. Moreover, the reaction of each isomer resulted in a

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unique polarization pattern (Figures 3 and 4). The *tert*-butyl-(dimethylamino)fulvenes, on the other hand, show evidence for geometric isomerization under electron transfer conditions. However, the two isomers show opposite polarization (Figure 5). This result indicates clearly that the reactant and the product are (re)generated by different pathways. Such a finding precludes the involvement of a fully perpendicular radical cation as the key intermediate.

Conclusions

The results presented here fail to support the existence of perpendicular (nonvertical) radical cations in the systems studied. The lack of isomerization observed for the di-*tert*-butylfulvenes is not surprising in view of the fact that a partially or fully twisted structure would contain a poorly stabilized positive charge. The

isomerization observed in the *tert*-butyl(dimethylamino)fulvenes may indicate some degree of twisting, though certainly far short of the perpendicular conformation. Diaryl substitution in the 6-position would offer more extended delocalization of the positive charge. However, this possibility does not lend itself as readily to experimental verification. We are actively exploring other molecules as precursors to this elusive nonvertical structure type.

Registry No. 6,6-Dimethylfulvene, 2175-91-9; 6,6-diphenylfulvene, 2175-90-8; (*E*)-2,6-di-*tert*-butylfulvene, 98678-03-6; (*Z*)-2,6-di-*tert*-butylfulvene, 98678-04-7; (*Z*)-*tert*-butyl(dimethylamino)fulvene, 62667-49-6; (*E*)-*tert*-butyl(dimethylamino)fulvene, 62667-50-9; chloranil, 118-75-2; anthraquinone, 84-65-1.

Reaction of 6-yl Radicals of Uracil, Thymine, and Cytosine and Their Nucleosides and Nucleotides with Nitrobenzenes via Addition To Give Nitroxide Radicals. OH⁻-Catalyzed Nitroxide Heterolysis

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Contribution from the Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim, West Germany. Received March 26, 1985

Abstract: The 6-yl radicals produced by addition of OH to C(5) of the C(5)/C(6) double bond of naturally occurring pyrimidine bases, nucleosides, and nucleotides, or those formed by H-abstraction from C(6) of 5,6-dihydropyrimidines, react with para-substituted nitrobenzenes by addition ($k \approx 6 \times 10^6$ to 2×10^9 M^{-1} s^{-1}) to yield nitroxide-type radicals which were characterized by electron spin resonance and optical detection techniques. In basic solution the nitroxide radicals deprotonate: with the radicals derived from the free bases deprotonation occurs at N(1), with those from the nucleosides and nucleotides of uracil deprotonation at N(3) is observed. The ionized 6-yl radicals react with the nitrobenzenes also by addition with rate constants considerably higher ($k = 1 \times 10^8$ to 1×10^9 M^{-1} s^{-1}) than those for the case of the neutral radicals. The neutral nitroxide radicals react with OH⁻ to give the nitroxide radical anion which is able to undergo a unimolecular heterolysis reaction which results in the formation of the nitrobenzene radical anion. In the case of the nitroxide radicals having N(1)–H (the radicals derived from the free bases), the OH⁻ catalysis of nitroxide heterolysis proceeds via deprotonation at N(1) and the unimolecular rates are comparatively high (2.4×10^5 s^{-1} for the 5-hydroxy-6-yl radical adduct from uracil/4-nitroacetophenone). On substitution of N(1) by a methyl or (deoxy)ribosyl(phosphate) group the site of OH⁻ attack is changed to N(3)–H (with the uracils) or to N′(4)–H (with the cytosines). With radicals from N(1)-alkylated pyrimidines the rates of heterolysis of the nitrobenzene adducts are considerably lower (e.g., 4.5×10^3 s^{-1} for that from deoxyuridylic acid) than if N(1) is ionized. The addition/OH⁻ catalyzed elimination sequence of interaction of pyrimidin-6-yl radicals and nitrobenzenes results in the ultimate transfer of an electron from the pyrimidine radical to the nitrobenzene and is therefore an example of a one-electron redox reaction.

Nitro compounds have received a large amount of attention as a result of their (potential) use as sensitizers in the radiotherapy of cancer.[2-6] In the course of these investigations numerous

radicals, derived from molecules of importance in biological systems and also from model compounds, have been reacted with representative nitro compounds[7-11] with the aim of contributing to the understanding of in vivo radiation sensitization. An important result of these studies is that it is the redox potential of

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