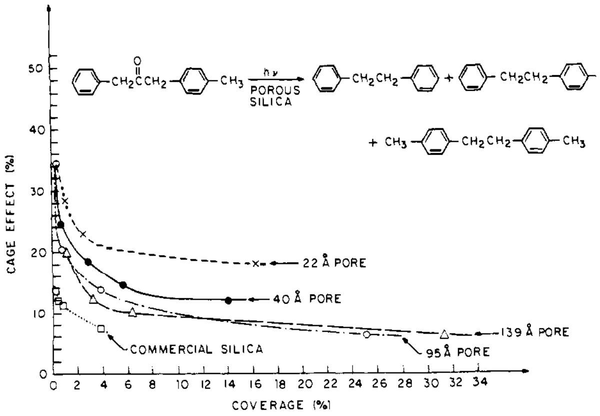

Figure 2. Cage effect as a function of coverage for the photolysis of **1** on porous silica of various pore sizes.

of radical pairs produced by photolysis of **1**.

High-purity silica of known median pore size and fairly narrow pore size distribution[6] (Figure 1) was employed for the photolysis. The % cage was determined for the photolysis of **1** as a function of coveage on porous silica of various pore sizes.[7] For comparison, a sample was photolyzed on commerical silica gel. The results are summarized in Figure 2.

For each of the silicas investigated, the profile of % cage as a function of coverage is qualitatively similar and consists of two distinct regions: (I) for "low" coverage (<5%) the % cage is substantial and decreases slowly with increasing coverage, and (II) for "high" coverage (>5%) the % cage reaches a limiting value, which is maintained to higher coverages. Significantly, the family of curves produced by a plot of % cage vs. coverage is correlated with pore size. The smaller the median pore size, the higher the limiting % cage at high coverage. For comparison, Baker silica is found to behave more similar to the largest pore silicas investigated.

An interpretation of the results in Figure 2 is possible by assuming there is an analogy between the properties of the reaction space provided by silica pores and the restricted reaction space provided by micelles.[3c,8] This analogy suggests that the larger the pore size, the lower the efficiency of return of geminate pairs to a common space which is needed for cage recombination and the more efficient escape of radicals from an initial pore. Once geminate radical pairs escape the pore in which they were generated, they are equivalent to "free radicals" and combine in a random fashin corresponding to 0% cage.

One of the consequences of the analogy between micelles and silica pores is the expectation that the % cage will be magnetic field dependent.[5] The expectation is realized experimentally. Significantly, a large magnetic field effect was found only in region I (low coverage). For 22- and 95-Å pores, the magnetic field effect becomes less significant for coverage about ca. 5%. There is only an insignificant effect in region II. There is no significant effect at any coverage for commerical silica. Our results may be most simply interpreted in terms of a two-site model for adsorption of **1** on silica which results in behavior characteristic of regions I and II, respectively. Such phenomenological behavior is well-known in the chromatographic literature,[7] but the interpretation of the molecular basis for the difference in sites has been the subject of controversy. For example, the difference has been ascribed to (a) differences in hydrogen bonding in the two sites, (b) differences in pore size distribution, and (c) differences in surface "viscosity". Although our results do not allow a distinction between these alternatives and other possibilities (e.g., pore shape) to be made at this moment, we believe that use of cage effects and magnetic effects can be developed into a powerful and normal tool to examine the behavior of radicals on silica and other porous surfaces, such as zeolites, and vice versa to study the properties of porous surfaces.

Acknowledgment. We at Columbia thank the National Science Foundation for their generous support of this research. The initial stages of this research were aided by the work of Dr. Chen-Ho Tung.

Registry No. 1, 35730-02-0; silica, 7631-86-9.

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[5] Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.

[6] The silica (surface area ca. 900 m^2/g and average pore diameter 20 Å) employed in this study was prepared by freezing poly(silic acid) (Mahler, W.; Bechtold, M. *Nature (London)* **1980**, *285*, 27). Silica with larger pores was obtained by soaking this material in 0.05 N NH_4OH for various periods of time, followed by washing with water and drying at 150 °C for 3 h. Surface areas and average pore diameter distributions were obtained by the conventional BET(N_2) method: Brunauer, S.; Emmett, P.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309. The BET(N_2) method does not reveal information concerning pore sizes smaller than 20 Å.

[7] For example, see: Snyder, L. R. *Sep. Sci.* **1966**, *1*, 191. Snyder, L. R.; Ward, J. W. *J. Phys. Chem.* **1966**, *70*, 3941.

[8] Tarasov, V. F.; Buchachenko, A. L.; Maltsev, V. I. *Russ. J. Phys. Chem.* **1981**, *55*, 1095.

Photoinduced Electron-Transfer Reactions. Radical Cations of Methylenebicyclo[2.2.0]hexene Derivatives

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Nuclear spin polarization effects observed during the reactions of photoexcited electron acceptors (chloranil) with two derivatives of 5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hex-2-ene (**1**) allow the conclusion that radical cations of two principally different structure types are involved. In the case of the chloro derivative, **1a**, the available evidence supports a radical cation with a methylenecyclohexadiene skeleton (**2a**) whereas the effects observed for the methoxy derivative, **1b**, suggest that the interesting doubly allylic radical cation **3b** is an intermediate.

As part of a research program to elucidate the structures of radical cations derived from strained-ring hydrocarbons,[1-6] we have investigated the photoreactions of strong electron acceptors with two derivatives (**1a,b**) of methylenebicyclo[2.2.0]hex-2-ene.[7] This ring system has two different doubly allylic carbon-carbon bonds which may be involved in delocalizing spin and charge of the resulting radical cations. The transannular bond (|||||) appears to be essentially orthogonal to both π bonds whereas the doubly allylic bond (ΔΔΔ) of the methylenecyclobutane fragment may interact readily with the π bond of the cyclobutene fragment. Selective participation of one or the other of these bonds would generate radical cations with substantially different structures,

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[1] Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956-7958.

[2] Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 1246-1248.

[3] Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210-7217.

[4] Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027-1035.

[5] Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805-6808.

[6] Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253-255.

[7] Derivative **1a** is synthesized from hexamethyl(Dewar benzene)[8] by chlorination with *tert*-butyl hypochlorite. Derivative **1b** is one of two products obtained from **1a** by nucleophilic substitution with sodium methoxide in methanol. Both **1a** and **1b** have been demonstrated to have *exo* stereochemistry.[9]

[8] Shama, S. A.; Wamser, C. C. *Org. Synth.* **1983**, *61*, 62-64.

[9] Wamser, C. C.; Ngo, D.; Shama, S. A.; Tran, T., manuscript in preparation.

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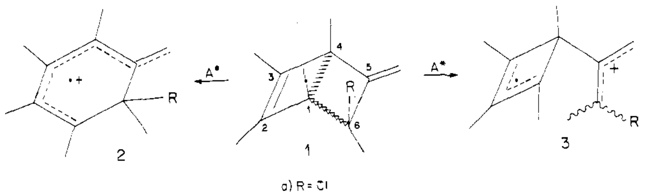
either a methylenecyclohexadiene cation (**2**) or the unique doubly allylic species 3. Previous experience in several systems[1-6,10]



a) R = Cl
b) R = OCH_3

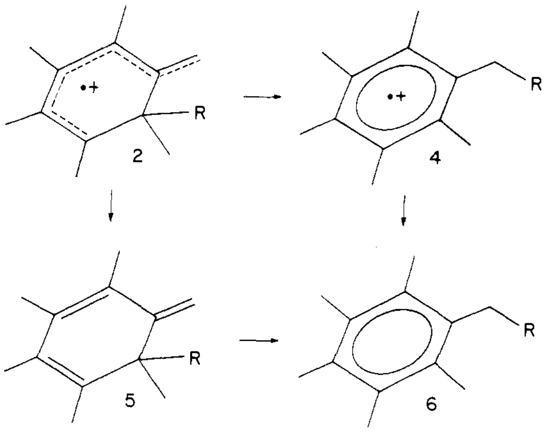
suggested that the CIDNP technique is well suited to differentiate between these structures and possibly to probe their simultaneous involvement.

The reaction of 6-chloro-5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hex-2-ene (**1a**, R = Cl) with photoexcited chloranil in acetone generates pentamethylbenzyl chloride (**6a**) efficiently. The formation of this product requires the opening of the transannular bond and a 1,3- (or 1,7-) chlorine migration. During this reaction, pronounced CIDNP effects are observed (Figure 1, upper), which allow an insight into the reaction mechanism. The signal at 2.2 ppm represents the *o*- and *p*-methyl groups of **6a**, which originate in the 2-, 4-, and 6-positions of **1a**. The observation of emission for this signal indicates that the polarized methyl protons have positive hyperfine coupling constants (hfcc's); at least one of these methyl groups must be adjacent to a carbon with positive spin density in the intermediate. The *m*-methyl groups of **6a** (2.3 ppm), which originate in the 1- and 3-positions of **1a**, also show emission; these protons, too, must have positive hfcc's. Finally, the benzylic methylene protons of **6a** (4.8 ppm), which originate in the methylene position of **1a**, show enhanced absorption. These protons must have a negative hfcc in the key intermediate indicating that the methylene carbon bears positive spin density.

The latter result specifically rules out the benzyl chloride radical cation **4a** as the origin of the observed polarization since this cation cannot be expected to have spin density on the methylene carbon. Indeed, the photoreaction of chloranil with **6a** results in polarization for the methyl signals exclusively. This indicates that the radical cation **4a** can have spin and charge only in the methyl-substituted ring carbons.

The polarization observed for **6a** in the reaction of **1a** is compatible with a methylenecyclohexadiene radical cation, **2a**. The results suggest that the opening of the transannular bond is fast on the CIDNP time scale, i.e., relative to intersystem crossing (and spin sorting) in the intermediate radical ion pair, and that the chlorine migration is slower. The fact that spin density is indicated for C-7, requires that the chlorine remains at C-6 at least for a fraction of the pair lifetime (several nanoseconds; fast migration) but not longer than for a fraction of the spin lattice relaxation time (several seconds; slow migration). In the fast-migration limit, the chlorine migration would occur in the radical cation prior to recombination ("pair substitution").[11,12] In the slow migration limit, geminate electron return would generate polarized 6-chloro-5-methylene-1,2,3,4,6-pentamethylcyclohexadiene (**5a**), which then would rearrange to the observed polarized product **6a**. Time-resolved CIDNP experiments have the potential either to narrow substantially or to define exactly the time frame for the chlorine migration.[13]

Substantially different results are observed for the photoreaction of chloranil with a second methylenebicyclohexene, the methoxy derivative **1b** (R = OCH_3).[7] This reaction results in the formation of pentamethylbenzyl methyl ether (**6b**) in somewhat reduced quantum efficiency but does not give rise to CIDNP effects for this product. Instead, strong emission signals at 1.82 and 1.90



a) R = Cl
b) R = OCH_3

ppm, characteristic for allylic methyl groups, suggest the intermediacy of **5b**. Accordingly, the formation of **6b** can be explained by a mechanism analogous to that invoked for the formation of **6a**. The principal difference between the two reactions is the slower rate of the 1,3- (or 1,7-) migration of the methoxy group, which allows the observation of **5b**, though not its isolation.

Significantly, this reaction also gives rise to spin polarization for the reactant: one of the bridgehead methyl groups (1.04 ppm) and one of the olefinic methyl groups (1.51 ppm) show strong emission signals whereas the second bridgehead methyl (1.06 ppm) and the second allylic methyl group (1.58 ppm) show little or no polarization (Figure 1, lower). Although the radical cation **2b** is a plausible intermediate in the formation of the product **5b**, it can be ruled out as an intermediate in regenerating the starting material. This follows from the fact that the reclosure of the transannular bond is energetically unfavorable as well as from the observed polarization pattern.

The selective polarization of two methyl signals requires an alternative structure with high spin density in one olefinic and in one bridgehead position but low or negligible spin density in the adjacent olefinic and bridgehead positons. This spin-density distribution is consistent with radical cation **3b**, in which the perimetric doubly allylic bond of the methylenecyclobutane fragment (△△△) is broken. In the framework of this structure, the failure to observe polarization for the methylene group or the methyl group in the 6-position requires that the unpaired spin density be largely localized in the 1- and 3-positions of the cyclobutenyl fragment whereas the positive charge is largely localized in the methoxyallyl fragment. This assumption appears quite reasonable in view of the possibility for strong resonance electron donation by the methoxy group.[14]

In summary, the CIDNP effects observed for **5b** and for regenerated **1b** suggest that two different intermediates are involved, each of which gives rise to a specific product. The competitive involvement of the radical cation **3b** accounts for the diminished quantum efficiency for the formation of **6b**. The different structures derived from **1a** and **1b** illustrate the importance of substituent effects for the relative stabilities of these structures. For the formaton of **2a,b** from **1a,b** the relief of ring strain appears to be the predominant factor. The formation of **3b** from **1b**, on

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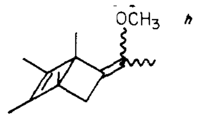
(10) Roth, H. D. In "Chemically Induced Magnetic Polarization"; Muus, L. T., et al., Eds.; Reidel: Dordrecht, The Netherlands, 1977; p 39–76.

(11) den Hollander, J. A. *Chem. Phys.* **1975**, *10*, 167–184.

(12) Kaptein, R. In "Chemically Induced Magnetic Polarization"; Muus, L. T., et al., Eds.; Reidel: Dordrecht, The Netherlands, 1977; p 257–266.

(13) Schäublin, S.; Wokaun, A.; Ernst, R. R. *J. Magn. Reson.* **1977**, *27*, 273–302.

(14) Intermediate **3b** could be expected to give rise to a pair of stereoisomeric rearranged methylenebicyclohexenes i upon electron return. That



i

these products were not isolated may reflect their preferential reaction, since they should be better electron donors than **1b**. However, we note that the strong emission signal at 1.1 ppm may well represent the bridgehead methyl group of such an intermediate.

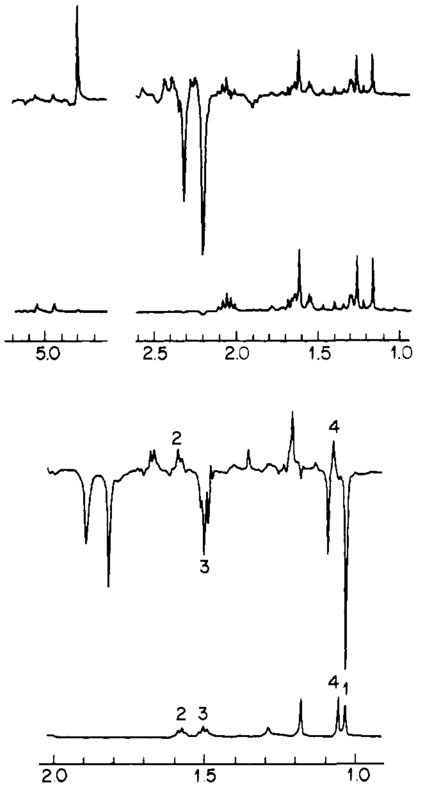


Figure 1. (Upper section) ^{1}H NMR spectra (90 MHz) of 0.02 M chloranil solutions in acetone-d_6 containing 0.02 M 6-chloro-5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hex-2-ene (**1a**) in the dark (bottom) and during UV irradiation showing the formation of polarized pentamethylbenzyl chloride (top). (Lower section) ^{1}H NMR spectra (90 MHz) of 0.02 M chloranil solutions in acetone-d_6 containing 0.02 M 6-methoxy-5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hex-2-ene (**1b**) in the dark (bottom) and during UV irradiation (top).

the other hand, indicates that the stabilization of the cationic allyl fragment by the methoxy group may partially compensate for the presence of the more highly strained cyclobutenyl fragment.

Registry No. 1a, 91281-46-8; **1b**, 91281-47-9; chloranil, 118-75-2.

Synthesis of Doubly Orthogonal Hexa-1,3,5-trienes: 11,12-Dimethylbicyclo[5.3.2]dodeca-1,6,11-triene

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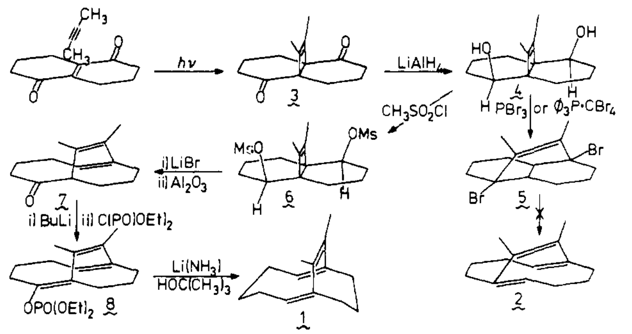
A fundamental property of butadiene and its higher vinylogues relates to changes in energy as the planes of two adjacent double bonds are twisted from 0° (s-trans) to 180° (s-cis). Extensive theoretical[1] and experimental[2] investigations over many years attest to the significance attached to the problem.

The present purpose is the first synthesis of a structure containing conjugated double bonds permanently fixed at nearly right angles to each other. To construct such a permanently orthogonal butadiene, so much structural complexity is required that it is just as easy to incorporate a doubly orthogonal hexatriene unit, which has the virtue of amplifying any thermochemical differences associated with orthogonality.

Scheme I



Triene **1**, for example, may be viewed as a near model of the transition state for the disrotatory interconversion of the s-trans,s-trans conformation of hexa-1,3,5-triene into its hypothetical s-cis,s-cis conformation, whereas triene **2** represents a model of the corresponding conrotatory transition state.

The first two steps toward a synthesis of the original target, **2**, proceeded smoothly. Reduction of the known[3] tricyclic dione **3** gave a mixture of diols. The major isomer, mp 171–174 °C, was assigned structure **4** of C_{2v} symmetry on the basis of a proton-decoupled ^{13}C NMR having seven instead of 14 peaks. The suggested configuration of the hydroxyl groups was based on steric considerations of hydride delivery. Attempted conversion to the corresponding dibromide led via profound rearrangement to **5**, the structure of which was determined by X-ray crystallographic analysis (details to be published elsewhere). Although **5** can still be imagined to give **2** by fragmentation of the Grob type, all efforts to realize that transformation failed.

In an attempt to prepare unrearranged dibromide, the mixture of diols **4** was converted to dimesylate **6**, which was treated with LiBr/THF. The resulting mixture afforded **7**, mp 68.5–70.0 °C, by chromatography on basic alumina. Its structure was deduced by spectral analysis[4] and confirmed by X-ray analysis[5] to be 11,12-dimethylbicyclo[5.3.2]dodeca-1,11-dien-6-one. The unanticipated formation of **7** opened the way to **1**, a target closely related in structure to **2** but, according to molecular mechanical calculations (MMPI),[6] even more closely approaching the desired ideal model (dihedral angles calculated for **1**, 87.5°, for **2**, 76°).

Base-catalyzed, deuterium exchange of **7** (0.048 M **7**, 0.48 M $NaOCH_3$, MeOD, 22 °C, 22 h) resulted in greater than 95% exchange at the bridgehead (C-7) hydrogen atom.[7] Advantage was taken of this unexpected behavior by converting **7** to its bridgehead enolate with butyllithium, trapping with diethyl chlorophosphate to give enol phosphate **8**,[8] and reduction of **8** with lithium in liquid ammonia. This sequence generated triene **1**, mp 36–38 °C, 78% theoretical yield based on **7** (Scheme I). Assignment of structure followed from the presence of two vinyl

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[1] Two recent theoretical papers also serve as a source of earlier references: (a) Breulet, J.; Schaefer, H. F., III. *J. Am. Chem. Soc.*, in press. (b) Bock, C. W.; George, P.; Trachtman, M. *Theor. Chim. Acta* (*Berlin*) **1984**, *64*, 292–311.

[2] (a) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657–3659. (b) Carreira, L. A. *J. Chem. Phys.* **1979**, *62*, 3851–3854.

[3] Peet, N. P.; Cargill, R. L. *J. Org. Chem.* **1973**, *38*, 4281–4285.

[4] IR (film) 1695 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.14 (t, 1 H, J = 4.0 Hz), 2.46–2.55 (m, 3 H), 2.17–2.24 (m, 4 H), 1.85 (q, 3 H, J = 0.99 Hz), 1.79 (q, 3 H, J = 0.99 Hz), 1.76–2.06 (m, 2 H), 1.50–1.59 (m, 2 H), 1.32–1.41 (m, 2 H); ^{13}C NMR ($CDCl_3$) 213.7 (s), 144.0 (s), 134.5 (s), 129.1 (s), 127.4 (d), 58.1 (d), 39.4 (t), 31.5 (t), 31.1 (t), 29.4 (t), 24.6 (t), 22.7 (t), 20.1 (q), 17.3 (q); ms, m/e 204 (calcd for $C_{14}H_{20}O$ 204).

[5] Crystal data for **7**: $C_{14}H_{20}O$, $M_r = 204.34$; monoclinic, space group $P2_1/n$, $a = 8.122$ (7) Å, $b = 12.071$ (4) Å, $c = 12.574$ (8) Å, $\beta = 105.21$ (1)°, $V = 1190$ (7) Å^3, $D_c = 1.140$, $Z = 4$, λ(Mo Kα) (graphite monochromator) = 0.71073 Å. The intensity data were measured on a Nicolet R3M diffractometer using a crystal, with approximate dimensions of 0.42 × 0.35 × 0.30 mm, mounted in a sealed capillary. From a total of 2040 unique reflections ($3.0 \leq 2\theta \leq 48.0°$) measured, 1221 ($I > 2\sigma(I)$) were used to solve (Oxford CRYSTALS package) and refine (SHELXTL) the structure to give final results $R = 0.0872$ and $R_w = 0.1003$. All bond lengths and angles are reasonable with the exception of those involving the bridgehead double bond, which differ from expected values, apparently due to minor disorder. The final difference map has no peaks greater than ±1 e Å^{-3}.

[6] Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907.

[7] ^{1}H NMR shows simplification of the multiplet at 2.46–2.55 ppm, while ^{13}C NMR shows loss of intensity at 58.1 ppm. Mass spectrographic analysis indicates d_0 0.6%, d_1 91.9%, d_2 6.2%, d_3 0.9%, and d_4 0.4%.

[8] Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098–5100.

0002-7863/84/1506-5025$01.50/0