



Figure 1 summarizes Plattner's rules and gives the visible absorption maximum for each of five homoazulenes, two of which have been synthesized specifically for this project (see below). One can see immediately that homoazulene exhibits spectroscopic behavior toward substitution by a donor substituent which is decidely atypical of an alternant hydrocarbon and in this regard appears far more similar to azulene than to an alternant hydrocarbon. For example, depending on the point of attachment of a single OMe group to homoazulene, the absorption maximum can be shifted either toward longer wavelength (3 and 4) or toward shorter wavelength (5) and by differing amounts. When two strong donor groups are judiciously counterpoised (6), the absorption maximum moves hardly at all! These data provide compelling evidence for the fact that even homoconjugation between atoms of like parity can impart nonalternant character to a neutral hydrocarbon π -system.

Both 3-methoxyhomoazulene (3) and 1-methoxyhomoazulene (4) have been reported previously, the former from this laboratory^{4a,c} and the latter by Masamune et al.^{3a} The two new methoxyhomoazulenes (5 and 6) were synthesized⁹ from propellane 7, a key intermediate in our route to the parent homoazulene 2.4b,c



Photooxygenation of 7 gave the endoperoxide 8 $(61\%)^{10}$ and a minor amount of the ene reaction product 9 (4%), which was easily separated by chromatography on silica gel.

Isomerization of 8 with triethylamine at room temperature produced a 2:1 mixture of the γ -hydroxy enones 10 and 11 (89%).



This mixture was oxidized with pyridinium chlorochromate to give a single dione (12). A retro-Michael reaction then served to remove the superfluous propellane bond. Thus, bicyclic dione 13, our precursor to 4,7-dimethoxyhomoazulene (6), was obtained



(81% from the 10/11 mixture) simply by stirring tricyclic dione 12 with silica gel in methylene chloride for 4 h at room temperature. The release of strain accompanying rupture of the cyclopropane ring undoubtedly accounts for the unusual facility of this reaction in the present circumstance. Homotropone 14, our precursor to 4-methoxyhomoazulene (5), was obtained by dehydration of 10 via the corresponding mesylate (31% from 10).

Deprotonation of 13 with excess LiN(SiMe₃)₂ in 3:1 THF/ HMPA at 0 °C gave a cherry red solution of the bis enolate, which, on quenching at -78 °C with methyl fluorosulfonate ("Magic Methyl"), yielded 4,7-dimethoxyhomoazulene (6, 58%). The same procedure served to convert 14 into 4-methoxyhomoazulene (5, 61%). It should be noted that this latter transformation is initiated by deprotonation of a homocyclopentadiene ring.

These two new methoxyhomoazulenes (5 and 6) and the other compounds in Figure 1 vividly underscore the importance of cyclic homoconjugation in neutral organic molecules and provide the first clear-cut example of an alternant hydrocarbon π -system with nonalternant character.

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Application of Spin Trapping To Probe the Radical Pair Model in Magnetic-Field-Dependent Photoreduction of Naphthoquinone in SDS Micellar Solution

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The effects of magnetic field on photochemical reactions¹ have been successfully interpreted in terms of the radical pair model,² in which the intersystem crossing rate between triplet and singlet radical pairs is influenced by an external magnetic field (reaction scheme, eq 1, 2). To investigate the relevance of the radical pair model further, it is very important to detect the intermediates,³⁻⁵ preferably both of the radicals.

In this paper, we show that the spin trapping method⁶ can be used to detect the unstable radical intermediates (as the function

⁽⁸⁾ The proposal that homoazulene might obey Plattner's rules, at least qualitatively, was orginally based on quite limited data."

⁽⁹⁾ All new compounds were characterized by the usual spectroscopic methods; however, only 8 and 10-14 were sufficiently stable to give good high-resolution mass spectra or C,H analysis.

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Figure 1. (A) Schematic diagram of the apparatus and (B) the timing chart of the spin trapping experiment. N_2 gas is bubbled to purge out the dissolved oxygen in the reactant solution involving the spin trap and naphthoquinone in SDS micellar solution. Two stopcocks are equipped to prevent the flow of the reactant solution during the photoirradiation and the ESR measurement. All the experiments were carried out with a timing as shown in diagram (B), where $B_1, B_2, \dots B_n$ represent the external magnetic field during the photoirradiation. After a constant waiting time, the ESR measurements were made.

of the static magnetic field) of field-dependent chemical reactions. An increase in the yield of a spin adduct of SDS radical, produced by spin trapping during the photoreduction of naphthoquinone (NQ) in sodium dodecyl sulfate (SDS) micellar solution, was shown with increasing the external magnetic field. Since the other radical of the postulated radical pair, naphthosemiquinone (NOH). has been shown to increase with increasing of the field,⁴ our observation may give the solid basis to the radical pair model for this kind of reactions.

Figure 1 shows the apparatus and the "timing chart" for the application of the spin trapping method to the study of magnetic-field-dependent photochemical reactions. An apparatus like a flow system was used to charge the sample solution without changing the filling factor of the sample solution in the ESR cavity. The light⁷ is kept on from time 0 to t_1 under a magnetic field which is set to one of the appropriate values. At time t_2 the field is changed to B_{ESR} . After a constant delay time (t_2-t_3) field scan for the ESR observation is started from B_{ESR} and the spectrum is recorded during the period of t_3-t_4 .

A set of the ESR spectra and the dependence of the "spin adduct" concentration on the magnetic field are shown in Figure 2A,B. The spin trap used was phenyl-tert-butylnitrone (PBN) and the spectrum shown in Figure 2A was assigned to the spin adduct of SDS radical based on the following reasons: (1) The hyperfine splitting constants (hfsc) for nitrogen (a_N) and β -hydrogen $(a_{\rm H})$ of 1.57 and 0.29 mT, respectively⁸ [1 T (tesla) = 10⁴ G], are reasonable for long-chain alkyl radical trapped by PBN.⁹ (2) The ESR spectrum shows that the radical center is highly immobilized and thus the spin adduct should have a large substituent group. This spectral pattern is similar to that of spin adduct bearing a dodecyl group as a substituent in SDS micellar solution¹⁰ and also similar to that of the SDS radical adduct of 2-methyl-2-nitrosopropane.¹¹ (3) A prolonged irradiation of PBN in aqueous SDS micellar solution gave a weak ESR signal which

A)



Figure 2. (A) ESR spectra observed after the photoreduction of naphthoquinone $(2.6 \times 10^{-4} \text{ M})$ in SDS (0.4 M) micellar solution in the presence of PBN (17 mM). Microwave power, 6.3 mW; modulation field (100 kHz), 1.0×10^{-4} T (1 T = 10⁴ G). The times $t_1 - t_4$, shown in Figure 1, were 60, 75, 120, and 240 s, respectively. The arrow indicates the direction and the scale of the field scan (to higher field). (B) Spin adduct concentration as the function of magnetic field under which the photoirradiations were made. The data shown are the averaged values with standard errors of three independent sets of observations. The magnetic field (B in units of tesla), under which the irradiations were made, was changed among nine values in a random order. The lowest field (1.6 mT) was achieved by pulling the whole microwave circuit (including ESR cavity) toward the outside of the magnetic field. The field of 7.5 mT was the residual magnetic field of our magnet.

is identical with the spectrum in Figure 2A.¹² It is known^{6b} that photolysis of PBN in a hydrogen-donating solvent (e.g., tetrahydrofuran) produces spin adducts derived from solvent radicals, and SDS may act as a hydrogen donor in the present reaction.^{4,5} (4) Another spin trap, perdeuterio sodium 2,4-dimethyl-3nitrosobenzenesulfonate (DMNS)¹³ was employed. A six-line ESR spectrum with the hyperfine splittings of 1.47 mT for a_N and 0.91 mT for $a_{\rm H}$ was observed (NQ, 1.6 × 10⁻⁴ M; SDS, 0.4 M; DMNS, 8.2 × 10⁻⁴ M) in phosphate buffer (50 mM, pH 7.4), and the yield of the adduct also showed almost identical dependence on the magnetic field. In this case the hydrogen hfsc is due to the hydrogen of trapped radical, therefore the structure of the original radical should be expressed as R1-CH-R2, i.e., SDS radical. All this information, (1)-(4), supports our assignment.

The amplitude of the spectrum changed dramatically by applying the magnetic field, and the magnetic field effect almost saturated above 0.1 T which is a typical value for this kind of saturation.14 The reaction scheme may be as follows: where RH

$$NQ \longrightarrow NQ^{*1} \longrightarrow NQ^{*3} \qquad (1)$$

$$NQ^{*3} + RH \longrightarrow (NQH \cdot R)^{3} \longrightarrow (NQH \cdot R)^{1}$$

$$NQH \cdot + \cdot R \qquad \text{product} \quad (2)$$

$$I \longrightarrow NQ + \cdot R \longrightarrow I \longrightarrow N(P)Q \cdot \qquad (3)$$

represents a hydrogen donor. Steps 1 and 2 are based on the mechanism postulated by the former researchers.³⁻⁵ In step 3, the intermediate radical (R) derived from the hydrogen donor, SDS radical in the present case, reacts with the spin trap (T-NO) and yields a spin adduct (T-N(R)O).⁶

⁽⁷⁾ The sample solutions were photolyzed in a ESR flat cell, which is set in the cavity of Varian E-3 spectrometer, by ultrahigh pressure mercury lamp (Ushio UH-500D, Japan, 500 W). A $CuSO_4$ solution filter (1.2 M), which cuts UV light 50% at 330 nm and 90% at 320 nm, was used for the filter.

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The concentrations of the spin adduct of SDS radical (Figure 2B) were determined by comparing the double integration of the first-derivative ESR spectra of the spin adduct with that of tetramethylpiperidine-1-oxyl (TEMPO) in SDS micellar solution. The maximal concentration of the spin adduct was 2.4×10^{-5} M (Figure 2B), which corresponds to 9.2% of the initial concentration of naphthoquinone. As shown in the reaction scheme, (1) escaping of the SDS radical from the triplet radical pair $(NQH \cdot R)^3$ is competing with the product (nonradical species) formation via singlet radical pair $(NQH \cdot R)^{1}$. (2) SDS radical is an alkyl radical and very reactive. Therefore, before being trapped by PBN, some part of the radical may react with other components, such as naphthosemiquinone, other SDS radical, etc. Besides, (3) the UV light was irradiated through the grid of the ESR cavity wall: i.e., only 50% of the reactant solution was irradiated. Taking into account these yield-determining factors, (1)-(3), the yield of the spin adduct (about 9% of the initial NQ) is quite large, thus the trapped SDS radical is not due to a side reaction which does not appear in the reaction scheme. Because the spin trapping process may not likely have dependence on magnetic field strength, we conclude that the yield of SDS radical itself have a dependence on the magnetic field strength qualitatively in the same manner as Figure 2B.

A slight increase in the yield of the spin adduct from 0.14 to 0.5 T was noticed. Sakaguchi and Hayashi⁴ also observed a steady increase in the UV absorption of naphthosemiquinone up to 1.4 T, and they interpreted this phenomenon with the spin relaxation effect.

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The hydrogenation of CO over supported metal catalysts to form simple hydrocarbons and oxygen-containing products appears to proceed by the elementary steps outlined in Scheme I.¹ The step requiring the largest ensemble of contiguous surface metal atoms is the dissociation of adsorbed CO (1).² Oxygenates appear to result from migratory insertion between a surface alkyl and surface CO (3).³ The generation of hydrocarbons by H addition or β -H elimination of surface alkyl groups (5) competes with the migratory CO insertion process (3).³

High yields of oxygen-containing products are achieved with supported rhodium, which has been promoted by cations of certain electropositive metals. The mode of action of these promoters on the elementary steps in CO hydrogenation is a topic of con-



Figure 1. Rates of product formation $(mmol/min/g \text{ of catalyst}) C_2H_5$ -CHO (O), C_3H_7OH (O), and C_2H_6 (×), by changing Zn contents (Zn/Rh atomic ratios) in SiO₂-supported Rh-Zn catalysts. Catalyst; 4.0 wt % Rh loading, 0.4–0.5 g. Reaction conditions: C_2H_4 :CO:H₂ = 10:10:10 mL/min, 180 ± 2 °C, 1 atm, SV = 1200 L/L/h.

Scheme I



siderable interest and debate.^{3,4} It has been proposed that (a) the electropositive promoter ion stabilizes a catalytically active oxidation state of rhodium,^{4a,5} (b) the promoter blocks sites that

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