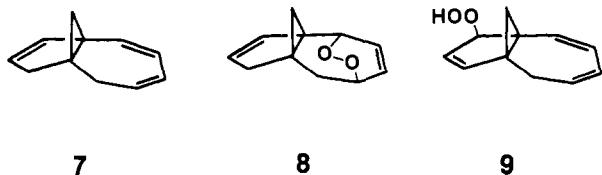


Figure 1. Visible absorption spectral maxima and Plattner's rules for the effects of alkyl substituents on the azulene absorption maximum.

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 decidedly 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.⁸

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

(8) The proposal that homoazulene might obey Plattner's rules, at least qualitatively, was originally based on quite limited data.^{4c}

(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.

(10) Stereochemistry previously shown to be anti: Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659-3664.

(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 $\text{LiN}(\text{SiMe}_3)_2$ 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

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(1) Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609-621.

(2) (a) Ward, H. R. *Acc. Chem. Res.* **1972**, *5*, 18-24. (b) Lawler, R. G. *Acc. Chem. Res.* **1972**, *5*, 25-33.

(3) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tanimoto, Y.; Weed, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574-4576.

(4) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1984**, *88*, 1437-1440.

(5) Tanimoto, Y.; Udagawa, H.; Ito, M. *J. Phys. Chem.* **1983**, *87*, 724-726.

(6) (a) Janzen, E. G. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1980; Vol. 4, pp 115-154. (b) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31-40.

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 ($\text{NQH}\cdot\text{R}$)³ is competing with the product (nonradical species) formation via singlet radical pair ($\text{NQH}\cdot\text{R}$)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 naphthoquinone, 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 naphthoquinone up to 1.4 T, and they interpreted this phenomenon with the spin relaxation effect.

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Selective Hydroformylation of Ethylene on Rh-Zn/SiO₂. An Apparent Example of Site Isolation of Rh and Lewis Acid Promoted CO Insertion

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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-

mmol/min/g-cat X 10²

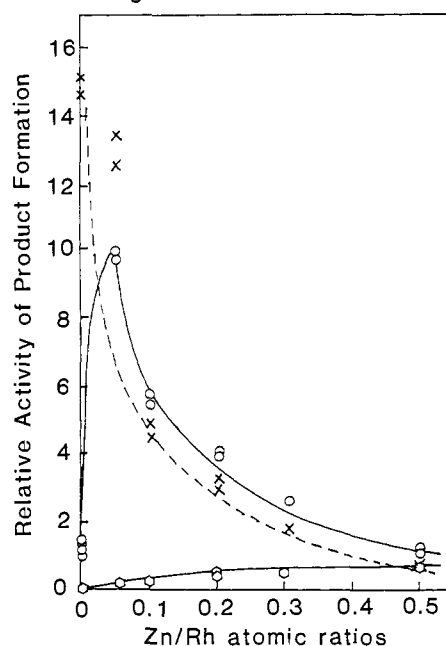
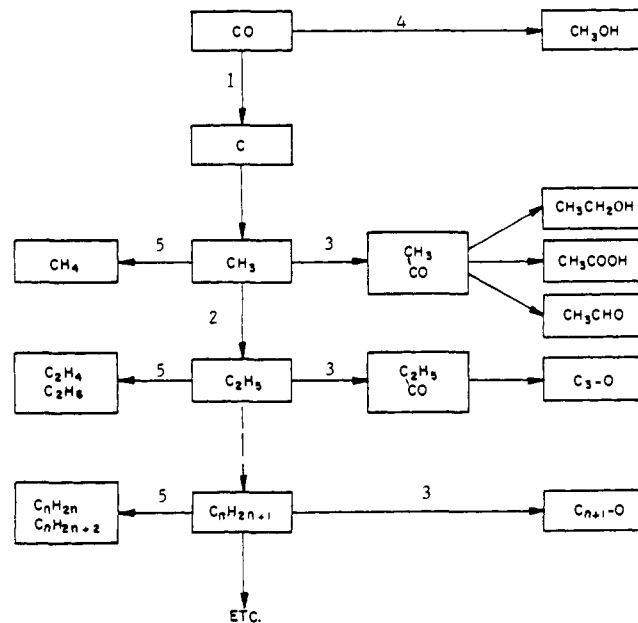


Figure 1. Rates of product formation (mmol/min/g of catalyst) $\text{C}_2\text{H}_5\text{-CHO}$ (O), $\text{C}_3\text{H}_7\text{-OH}$ (O), and C_2H_6 (X), by changing Zn contents (Zn/Rh atomic ratios) in SiO_2 -supported Rh-Zn catalysts. Catalyst: 4.0 wt % Rh loading, 0.4–0.5 g. Reaction conditions: $\text{C}_2\text{H}_4\text{:CO:H}_2 = 10\text{:}10\text{:}10$ 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

(1) (a) Sachtler, W. M. H. *Proc. 8th ICC*, Vol. I-151 1984. (b) van den Berg, F. G. A.; Glezer, J. H. E. *Proc. K. Ned. Akad. Wet., Ser. B: Palaeontol., Geol., Phys., Chem., Anthropol.* **1983**, *86*, 227.

(2) (a) Araki, M.; Ponc, V. *J. Catal.* **1976**, *44*, 439. (b) Biloen, P.; Helle, J. N.; Sachtler, W. M. H. *J. Catal.* **1976**, *43*, 363. (c) Sachtler, W. M. H. *Discuss. Faraday Soc.* **1982**, *72*, 7. (d) Rabo, J. A.; Risch, A. P.; Poutsma, M. L. *J. Catal.* **1979**, *58*, 95. (e) Delmon, J. A.; Martin, G. A. *J. Catal.* **1983**, *84*, 45.

(3) (a) Takeuchi, A.; Katzer, J. R. *J. Catal.* **1983**, *82*, 351. (b) Orita, H.; Naito, S.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1984**, 150. (c) Ichikawa, M.; Fukushima, T. *J. Chem. Soc., Chem. Commun.* **1985**, 321.

(4) (a) Driessen, J. M.; Poels, E.; Hinderman, J. P.; Ponc, V. *J. Catal.* **1983**, *82*, 26. (b) Wilson, T. P.; Kasai, P. H.; Ellgen, P. C. *J. Catal.* **1981**, *69*, 193. Bhasin, M. M.; Bartley, W. J.; Ellgen, P. C.; Wilson, T. P. *Ibid.* **1978**, *54*, 120. (c) Ichikawa, M. *CHEMTECH* **1982**, *674*; *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2273, 2268. Ichikawa, M.; Sekizawa, K.; Shikakura, K.; Kawai, M. *J. Mol. Catal.* **1981**, *11*, 167. (d) Hicks, R. F.; Bell, A. T. *J. Catal.* **1984**, *90*, 205. Ryndin, Y. A.; Hicks, R. F.; Bell, A. T.; Yermakov, Y. I. *J. Catal.* **1981**, *70*, 287. (e) Orita, H.; Naito, S.; Tamaru, K. *J. Catal.* **1984**, *90*, 183. (5) Kawai, M.; Uda, M.; Ichikawa, M. *J. Phys. Chem.* **1985**, *89*, 1654. Watson, P. R.; Somorjai, G. A. *J. Catal.* **1981**, *72*, 282. van den Berg, F. G. A.; Glezer, J. H. E.; Sachtler, W. M. H. *J. Catal.* **1985**, *93*, 340.