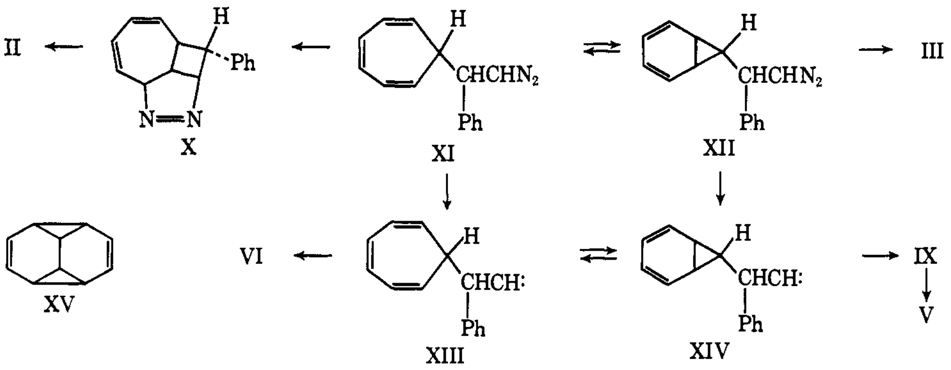

III by a high-pressure mercury lamp in dioxane in a Pyrex vessel afforded V (40%) supports structure III. The formation of V can be explained by the retro-Diels–Alder process of the severely strained intermediate IX, which is derived from III by photoelimination of the diazo group. Adoption of IX as the intermediate satisfies the stereochemistry of V in which the phenyl group is located *syn* to the C_7–C_8 double bond.

In contrast to the photolysis, thermolysis of III by refluxing in diglyme resulted in the formation of 2-phenylindene (IV; 48%) accompanied by a small amount of V.[13] In this decomposition of III, elimination of nitrogen may occur with cleavage of the cyclopropane ring and a hydrogen shift to afford 2-phenyldihydroindene, which, by air oxidation,[14] then leads to IV. On the other hand, heating V around 200° gave neither indene (IV) nor tricyclic diene (VI). It should also be noted that an attempted decomposition of III under the same conditions employed for the sodium salt of I resulted only in recovery of III. Therefore, III cannot be a general intermediate for the formation of II, IV, and V but is a potential intermediate, by which it is possible to clarify the reaction behavior of IX giving IV or V. For the formation of II, another hypothetical intermediate (X) may be proposed, arising from the 1,3-dipolar addition of the diazomethane group of XI to the C_1–C_2 double bond of the tropilidene.[15] Relief of strain by cleavage of the four-membered ring and the stabilization of the extended conjugated system including the pyrazole ring contribute the driving force for the rearrangement of X to II. On the other hand, the formation of III could be explained by the similar addition of the diazomethane group of XII, the valence isomer of XI, to the C_2–C_3 double bond of the norcaradiene. The predominant formation of V suggests that carbene XIV is formed prior to the formation of II (*i.e.*, X) and III, and XIV undergoes intramolecular addition to the double bond to give IX, which can easily isomerize to V.

Since intermediate IX has a close relationship with an intermediate (XV)[16] in bullvalene chemistry,[17,18] the present study on the isolation of the potential intermediate III should give information concerning the chemistry of C_9H_{10} and $C_{10}H_{10}$ hydrocarbons.

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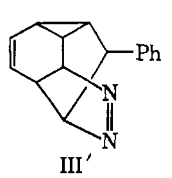
[13] This fact also ruled out another possible structure, III′, for the



III′

product III in addition to the above nmr evidence, because IV could not be derived from III′ without going through IX.

[14] The yield of IV is dropped to 5% in a nitrogen stream.

[15] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967).

[16] S. Masamune reported the existence of XV at low temperatures and thermal isomerization of XV to bicyclo[4.2.2]deca-2,4,7,9-tetraene (IUPAC Symposium on Valence Isomerization, Karlsruhe, Sept 10, 1968).

[17] W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, 88, 2078 (1966).

[18] E. Babad, D. Ginsburg, and M. B. Rubin, *Tetrahedron Letters*, 2361 (1968).

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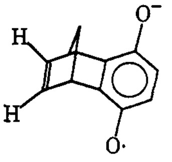
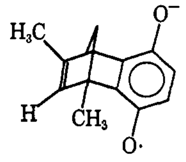
Long-Range Electron Paramagnetic Resonance Coupling in Bridged Anthracenes[1,2]

Sir:

Several interactions require consideration in the discussion of the mechanism of long-range coupling in epr spectroscopy. Recently we pointed out that the coupling constants for the vinyl hydrogen atoms of I and II were much greater than the coupling constants for the methyl hydrogen atoms of II.[3,4] The inference of this observation is that the coupling of the vinyl hydrogen atoms in compounds such as I and II does not involve the transfer of spin density from the aromatic π orbitals to the isolated double bond and thence to the vinyl proton. Rather, the data suggest that long-range coupling results from an interaction of the kind implicit in the extended Hückel theory[5] or from an interaction similar to the direct (through space) or indirect (through σ bond) spin polarization mechanism advanced to account for long-range nuclear couplings.[6]



I



II

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[1] Electron Paramagnetic Resonance Spectra of Semiquinones. VII.

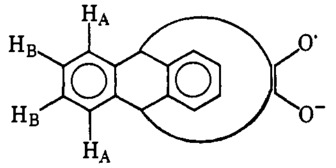
[2] This research was supported in part by the Petroleum Research Fund administered by the American Chemical Society and in part by the National Science Foundation.

[3] D. Kosman and L. M. Stock, *Chem. Commun.*, 551 (1968).

[4] D. Kosman and L. M. Stock, *J. Am. Chem. Soc.*, in press.

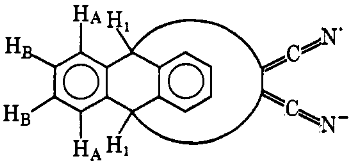
[5] The theory has been applied to some related bicyclic molecules: G. R. Underwood and R. S. Given, *ibid.*, 90, 3713 (1968).

Russell and his students report that the eight aromatic hydrogen atoms of III are coupled equally.[7] McKinney, on the other hand, reports that only four aromatic hydrogen atoms of IV are coupled.[8] The interaction responsible for the selective long-range coupling in IV is, apparently, similar to the interaction principally responsible for the coupling of the vinyl hydrogen atoms of I and II. This conclusion is based on the examination of several semifuraquinones[9] and semiquinones.[10] The results for V, shown in Figure 1, parallel the results for IV with only four of the eight hydrogen atoms bonded to the aromatic nuclei coupled detectably (Table I).



III

a_H = 0.15 G (8 H), H_A, H_B

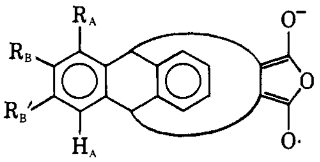


IV

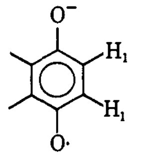
a_H = 0.15 G (6 H), H_1 H_B

a_N = 2.30 G

Table I. Hyperfine Coupling Constants for Bridged Anthracene Semifuraquinone and Semiquinone Derivatives



Semifuraquinone



Semiquinone

Compd	R_A	R_B	R_B'	Observations a, G	Observations Assignment
		Semifuraquinones			
V	H	H	H	0.12 (4 H)	H_B
VI	F	H	H	0.12 (4 H)	H_B
				0.12	F
VII	H	F	H	0.12 (3 H)	H_B
				0.62	F
VIII	H	CH_3	CH_3	0.11 (2 H)	H_B
		Semiquinones			
IX	F	H	H	2.37 (2 H)	H_1
X	H	F	H	2.40 (2 H)	H_1
				0.15	F

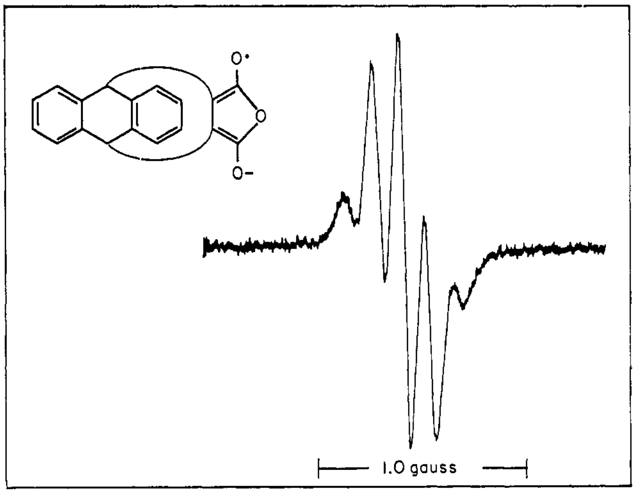


Figure 1. The spectrum of V in acetonitrile solution.

Substituted derivatives of V were studied to define the nuclei involved and the origin of the coupling. The spectrum of VI is a simple sextet suggesting that the fluorine atom, F_A, and the four hydrogen atoms, H_B, are coupled. The spectrum of VII exhibits one major doublet, further split into quartets. This observation is consistent with the coupling of the fluorine atom, F_B, and the three remaining H_B. In accord with this interpretation, the spectrum of VIII in which two H_B are replaced by methyl groups is a triplet indicative of the coupling of the two remaining H_B. The results for the corresponding fluorosemiquinones derived from triptycene, IX and X, confirm the view that B nuclei, rather than the A nuclei, are coupled. In these molecules, the coupling constants for the H_B are below the detectable limit.[11] However, the spectra of IX and X indicate that F_B is coupled, whereas the coupling of F_A is below the detectable limit (line width 0.15 G). The coupling patterns for these semifuraquinones and semiquinones are similar to the results for the dicyanoacetylene adduct IV and clearly different from the observation for the related semidione III. Differences of this kind have been noted previously.[4,7-9] Moreover, the rather specific coupling of the B nuclei suggests that spin density is not transferred to these nuclei *via* the aromatic π system. The spectrum of VIII with three narrow lines (separation between derivative extreme 0.075 G) indicates the absence of a significant coupling of the six methyl hydrogen atoms. Inasmuch as a coupling mechanism involving spin density in the aromatic orbitals would lead to equal coupling of H_B and the methyl hydrogen atoms,[3,4] we infer that the data for V and VIII require an interpretation based on a long-range interaction such as that implicit in an extended Hückel model or spin polarization. The difference between the results for the semiquinones, semifuraquinones, and dicyanoacetylene adducts and for the semidiones presumably originates in their different symmetry characteristics.[4] The first group is alike with the highest occupied molecular orbital of the spin label antisymmetric with respect to a plane bisecting the spin label, *i.e.*, a plane perpendicular to the quinone bisecting C_2C_3 and C_5C_6. The highest occupied orbital of the

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(6) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

(7) G. A. Russell, G. Holland, and K.-Y. Chang, *J. Am. Chem. Soc.*, **89**, 6629 (1967).

(8) T. M. McKinney, *ibid.*, **90**, 3879 (1968). The assignment shown is based, in part, on the results of this study.

(9) S. F. Nelsen and E. D. Seppanen, *ibid.*, **89**, 5740 (1967).

(10) The new compounds prepared in this investigation were characterized by conventional methods. The spectra of the semifuraquinones were obtained in dilute (about 10^{-3} *M*) acetonitrile using customary procedures.[9] The semiquinones were generated from the hydroquinones by air oxidation in basic acetonitrile.[4]

(11) L. M. Stock and J. Suzuki, *J. Am. Chem. Soc.*, **87**, 3909 (1965).

semidione, on the other hand, is symmetric with respect to this symmetry element.

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Catalytic Dimerization of Ethylene and Propylene by Nitrogentris(triphenylphosphine)cobalt Hydride

Sir:

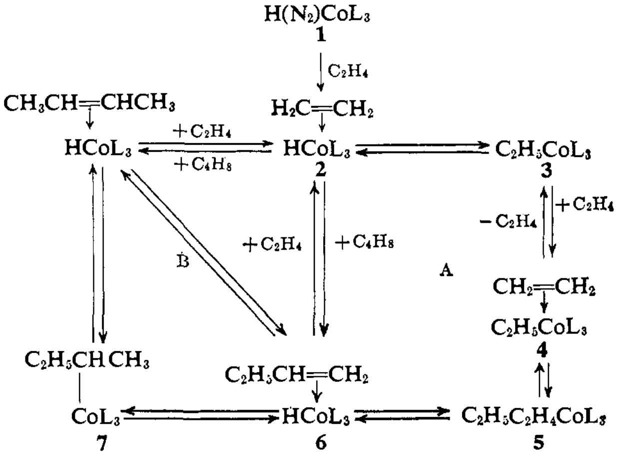
Nitrogentris(triphenylphosphine)cobalt hydride ($H(N_2)Co(PPh_3)_3$,[1] **1**) exhibits remarkably versatile chemical properties. It combines reversibly with H_2,[2,3] C_2H_4,[2] and NH_3,[2] forms a carbonyl complex by reaction with carbon monoxide[2,3] or by abstraction of CO from aldehydes,[3] and reacts with CO_2 to give a formate complex, $HCO_2Co(PPh_3)_3$.[4] The cobalt complex also catalyzes the hydrogenation of ethylene,[5] oxidation of triphenylphosphine to triphenylphosphine oxide,[5,6] and reduction of N_2O.[6] We wish to report now another example of catalytic activities of the complex, dimerizations of ethylene and propylene.

Many papers have been published reporting the ethylene dimerization by soluble catalysts based on Ti,[7,8] Ni,[8] Rh,[9] Ru,[9] and Pd[10] compounds and on mixed systems of cobalt and organoaluminum compounds.[11] However no report has been made, to our knowledge, on the catalytic dimerization using an isolated cobalt complex. Concerning the dimerization of propylene, only a few catalyst systems based on $RhCl_3$[9] and nickel compounds[8] have been reported.

The catalytic dimerizations of ethylene and propylene by **1** take place at ambient temperature and pressure and proceed with substantial rates even at 0°. In a typical example of the ethylene dimerization, 192 mmol of ethylene with an initial pressure of 710 mm was brought in contact with 10 ml of a *m*-xylene solution containing 0.55 g (0.63 mmol) of **1** at room temperature (25–30°). The solution absorbed ethylene with an initial rate of *ca.* 100 cc (NTP)/hr, but the rate of ethylene absorption decayed with time under this condition, accompanied by the color change of the original solution to dark brown, presumably by the partial decomposition of the catalyst. The deterioration of the catalyst was less marked at 0°. The products were separated by distillation and preparative vapor phase chromatography and identified by vpc, ir, and mass spectroscopy. After the reaction time of 32 hr, 41 mmol of butenes was produced, consisting of 72% *trans*-2-butene, 26% *cis*-2-butene, and 2% of 1-butene. In addition to butenes, small amounts of ethylene trimers and ethane (0.57 mmol) were found. This system also catalyzes the isomerization of 1-butene to 2-butenes. The isomerization takes place very rapidly at room temperature and gives a butene mixture with the same composition as obtained in the ethylene dimerization by **1**.

The propylene dimerization was carried out in a similar manner as ethylene. Complex **1** (0.23 g, 0.32 mmol) in 7 ml of *m*-xylene was stirred at 25° in contact with 190 mmol of propylene with an initial pressure of 753 mm for 47 hr. About 17 mmol of propylene dimers was produced, containing 2-methyl-1-pentene as the main product with two other unidentified dimers of minor quantities. The addition of 3 mol of tri-*n*-butylphosphine/mol of **1** reduced the dimerization rate considerably, but triphenylphosphine had little effect on the rate.

The mechanisms of ethylene dimerization and butene isomerization by $RhCl_3 \cdot 3H_2O$ were discussed in detail by Cramer. The dimerization mechanism by the present cobalt complex appears to be simpler compared with the one by $RhCl_3 \cdot 3H_2O$, where the activation of $RhCl_3 \cdot 3H_2O$, the presence of a cocatalyst such as HCl, and the formal change of the oxidation state of Rh are required. Since the presence of a cobalt–hydride bond in the original complex (**1**) has been established,[4,12,13] the following mechanism involving the insertion of ethylene between Co–H bond seems to be reasonable for the ethylene dimerization. Evidently complex **1** is only a precursor of the active species, and the coordinated N_2 is displaced by ethylene from **1** as confirmed by the examination of the ir spectrum of the catalyst solution.[2] An unstable crystalline complex which releases on pyrolysis 0.9 mol of C_2H_4/g-atom of cobalt with a small amount of C_2H_6 and has a composi-



L = triphenylphosphine

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[1] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); A. Sacco and M. Rossi, *ibid.*, 316 (1967); A. Misono, U. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967).

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[6] Submitted for publication.

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[11] G. Hata, *Chem. Ind.* (London), 223 (1965); M. Iwamoto and I. Shionoya, *Kogyo Kagaku Zasshi*, **70**, 1207 (1967).

[12] J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Commun.*, 96 (1968).

[13] G. W. Parshall, *J. Am. Chem. Soc.*, **90**, 1669 (1968).