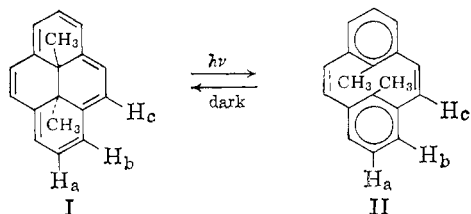


to *trans*-15,16-dimethyldihydropyrene.⁴ We wish now to report that *trans*-15,16-dimethyldihydropyrene is converted by visible light to its valence tautomer having the metacyclophane structure II. In the dark the metacyclophane isomer reverts back to the more stable dihydropyrene system. Furthermore, the interconversions of I and II by the photochemical and dark reactions can be carried out repeatedly without deterioration of the sample.



The photochemical transformation is best described by giving details for a particular experiment. A solution of 30 mg. of I in 1 l. of pentane was subjected to irradiation using four ordinary Mazda lamps (a total of 500 w.) for 6 hr. After concentration of the solution, a spectral comparison of the irradiation product with pure I showed the presence in the irradiation product of a photoisomer (II) which does not absorb above 300 μ . In this instance the ratio of I:II was roughly 1:1, although in other experiments employing other solvents the proportion of II in the irradiation product may be as high as 95%.

The n.m.r. spectrum of the product mixture after irradiation can be interpreted readily since the signals for the protons in II are quite distinct and do not overlap the signals for the protons present in I. Also, there is no evidence that by-products are formed to any extent. The n.m.r. signals observed are summarized in Table I in terms of the individual protons as denoted in structures I and II.

Table I. N.m.r. Signals of the Irradiation Product^a

I			II		
δ , p.p.m.			δ , p.p.m.		
H(CH ₃)	-4.20	Singlet	H(CH ₃)	1.52	Singlet
H _a	8.00	A ₂ B	H _a	6.95	AB ₂
H _b	8.50		H _b	6.56	
H _c	8.55	Singlet	H _c	6.24	Singlet

^a The spectrum was determined using a Varian A-60 and a Varian A-100 with carbon tetrachloride as solvent and tetramethylsilane as an internal standard.

The change in the n.m.r. spectrum in going from I to II is in good accord with what would be predicted. Thus, the signal at -4.20 p.p.m., corresponding to the internal methyl groups in I, is replaced by a signal at 1.52 p.p.m. as is appropriate for the internal methyls of a metacyclophane.⁵ In I the H_a and H_b protons form a A₂B system with a spin-coupling constant $J_{AB} = 7.5$ c.p.s. In II these protons form an AB₂ system with a spin-coupling constant of 7.2 c.p.s., the signals occurring in the usual benzene region but at much higher field than I. Thus, the n.m.r. spectrum is par-

(4) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

(5) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *ibid.*, **82**, 6302 (1960).

ticularly striking in supporting the conclusion that the photoisomer does indeed have the metacyclophane structure II.

The dark reaction by which II is converted back to I has been followed both by absorption spectroscopy and by n.m.r., the agreement between the two methods being excellent. The dark reaction follows first-order kinetics and its rate is temperature dependent. A convenient method for carrying out these studies is to dissolve I in a polyvinyl chloride foil, irradiate, and then observe the dark reaction. Under these conditions the half-life of II at 50° is about 2 hr.

Other derivatives of *trans*-15,16-dimethyldihydropyrene also show a similar photoisomerization. For example, the 2-nitro derivative is readily converted by visible light to the corresponding metacyclophane structure. In this case the dark reaction, when measured using a polyvinyl chloride foil at 50°, is about 40 times faster than that of the unsubstituted hydrocarbon.

The photochemical transformation of dihydropyrene derivatives to metacyclophanes and their spontaneous reversion back to the dihydropyrene structure is an unusual interconversion allowing temporary storage of photochemical energy. Further studies are underway investigating the fundamental details of both processes.

(6) Aided in part by a grant from the National Science Foundation and by the Schweizerische Nationalfonds (Projekt No. 2776).

H.-R. Blattmann, Doris Meuche, E. Heilbronner
Laboratorium für Organische Chemie, Eidg. Technische Hochschule
Zürich, Switzerland

R. J. Molyneux, V. Boekelheide⁶
Department of Chemistry, University of Oregon
Eugene, Oregon
Received November 16, 1964

Cyclobutadiene- and Benzocyclobutadiene-Iron Tricarbonyl Complexes¹

Sir:

Although the isolation of metal complexes of tetraphenylcyclobutadiene² and tetramethylcyclobutadiene^{3,4} may provide adequate verification of the prediction made by Longuet-Higgins and Orgel⁵ that cyclobutadiene might form stable metal complexes, nonetheless no complexes of cyclobutadiene itself have been prepared. A substance which initially appeared to be a silver ion complex of cyclobutadiene has recently been shown to be a complex of a dimer of cyclobutadiene.⁶

(1) This work was reported at the Regional Meeting of the Southeastern Section of the American Chemical Society, Charleston, W. Va., October 15-17, 1964.

(2) (a) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); (b) R. P. Dodge and V. Schomaker, *Nature*, **196**, 798 (1960); (c) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961); (d) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961); (e) L. Malatesta, G. Santarella, L. Vallarino, and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); (f) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); (g) P. M. Maitlis and M. L. Games, *ibid.*, **85**, 1887 (1963).

(3) (a) R. Criegee and G. Schroder, *Ann.*, **623**, 1 (1959); (b) J. D. Dunitz, H. C. Mey, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 627 (1962).

(4) A perfluorotetramethylcyclobutadiene-cobalt complex is stated not to have symmetrical bonding of the ligand: J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

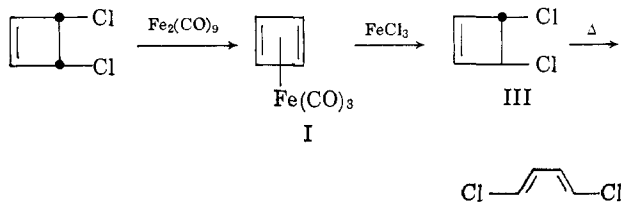
(5) H. C. Longuet-Higgins and L. E. Orgel, *ibid.*, 1969 (1956).

(6) M. Avram, H. P. Fritz, H. J. Keller, C. G. Kreiter, G. Mateescu, J. F. W. McOmie, N. Sheppard, and C. D. Nenitzescu, *Tetrahedron Letters*, 1611 (1963), and references therein.

We wish now to report the preparation of a stable complex of cyclobutadiene, namely cyclobutadiene-iron tricarbonyl (I), utilizing a reaction which offers promise of being of general utility for the preparation of complexes of other cyclobutadiene derivatives; we report here also the preparation of benzocyclobutadiene-iron tricarbonyl (II) using the same reaction sequence.

During initial studies we found that *trans*-acenaphthylene dibromide reacted with molar amounts of iron enneacarbonyl to yield acenaphthylene while with excess of the iron carbonyl the product obtained was an acenaphthylene-iron tetracarbonyl complex. This dehalogenation and complexation then suggested that similar reactions might be utilized to form complexes of unstable ligands.

Reaction of *cis*-3,4-dichlorocyclobutene⁷ with excess $\text{Fe}_2(\text{CO})_9$ has been found to produce cyclobutadiene-iron tricarbonyl (I) in yields of 40%.⁸ The complex I



crystallizes in pale yellow prisms from pentane, m.p. 26° , b.p. $68\text{--}70^\circ$ (3.0 mm.). *Anal.* Calcd. for $\text{C}_4\text{H}_4 \cdot \text{Fe}(\text{CO})_3$: C, 43.75; H, 2.08; Fe, 29.09; CO, 3.0. Found: C, 43.72; H, 2.22; Fe, 28.96; CO, 2.9. The infrared spectrum of the material shows strong carbonyl absorptions at 1985 and 2055 cm^{-1} ; the n.m.r. spectrum consists of a single sharp absorption at τ 6.09. The complex exhibits thermal stability comparable to that of other diene-iron tricarbonyl complexes.⁹

Strong evidence favoring structure I over a conceivable bis(acetylene)-iron tricarbonyl formulation is seen in the mass spectral cracking pattern. This displays strong peaks at values for m/e of 192, 164, 136, and 108 which correspond to the parent molecular ion and the derived species having one, two, and three fewer carbonyl groups, respectively; no peaks corresponding to the loss of C_2H_2 fragments were observed.

One particularly interesting reaction of the complex I is that with FeCl_3 in ethanol or with ceric ammonium nitrate in acetone saturated with LiCl . Normally these oxidizing agents degrade diene- $\text{Fe}(\text{CO})_3$ complexes with liberation of the free diene ligand⁹; however, in the present instance, these reactions lead to the formation of the hitherto unknown *trans*-3,4-dichlorocyclobutene (III). The structure of this product is established by elemental analysis, n.m.r. spectrum (two absorptions of equal intensity centered at τ 3.82 and 5.32) and by ozonolysis to produce *rac*-dichlorosuccinic acid. As suggested by Nenitzescu and co-workers⁷ the dichloride III is found to undergo facile thermal

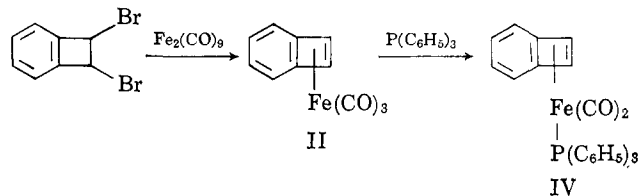
(7) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

(8) (a) It is not considered necessary that a free cyclobutadiene molecule appear as an intermediate in the reaction. (b) The experimental conditions employed for the formation of complexes I and II involve stirring a suspension of $\text{Fe}_2(\text{CO})_9$ with a solution of the appropriate dihalide in pentane at 30° for about 2 hr. followed by filtration, then distillation *in vacuo* after removal of the solvent.

(9) R. Pettit and G. F. Emerson, "Advances in Organo-metallic Chemistry," F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964, pp. 1-46.

rearrangement to form *trans,trans*-1,4-dichlorobutadiene.

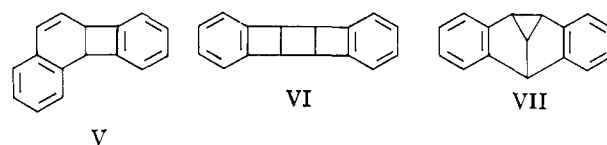
Benzocyclobutadiene-iron tricarbonyl (II) has been prepared in an analogous manner from *trans*-dibromobenzocyclobutene,¹⁰ or the corresponding diiodide,¹¹ and excess $\text{Fe}_2(\text{CO})_9$. The complex II forms orange prisms from pentane, m.p. 25° , b.p. $73\text{--}78^\circ$ (0.1 mm.).



Anal. Calcd. for $\text{C}_8\text{H}_6 \cdot \text{Fe}(\text{CO})_3$: C, 54.49; H, 2.50; mol. wt., 242. Found: C, 54.46; H, 2.54; mol. wt., 250. The infrared spectrum displays strong absorption at 1978 and 2047 cm^{-1} while the n.m.r. spectrum shows absorption at τ 3.05 (multiplet, four protons) and 5.98 (singlet, two protons). Reaction of the complex II with triphenylphosphine at 140° for 6 hr. effects replacement of one carbonyl ligand by triphenylphosphine to give the complex IV.

In the complexes II and IV involvement of two electrons from the aromatic ring is required in order that the inert gas structure of krypton is formally attained by iron. From the n.m.r. spectrum this does not appear to affect markedly the aromaticity of the benzene ring.

Following earlier studies of Cava and Nenitzescu and their co-workers, it was of interest to attempt the liberation of benzocyclobutadiene from the complex II and study the fate of this hydrocarbon. Cava and Napier report¹⁰ that reaction of dibromobenzocyclobutene with Zn dust in ethanol gave the dimeric compound V. Nenitzescu and co-workers found¹² the same result upon dehalogenation using Li or Na



amalgam; however, if the reaction was conducted in the presence of $\text{Ni}(\text{CO})_4$ ^{12,13} then the dimer VI was produced. The dimer VI, upon heating, isomerized to 1,2,5,6-dibenzocyclooctatetraene.

Decomposition of the benzocyclobutadiene complex II with FeCl_3 or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ gave mainly polymeric material; however, oxidative decomposition with AgNO_3 produced metallic silver and a new dimeric compound to which we ascribe the structure VII. The dimeric product forms colorless needles from pentane, m.p. 105° . *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}$: C, 94.07; H, 5.93; mol. wt., 204. Found: C, 93.90; H, 5.83; mol. wt. (mass spectrum), 204. The structure VII is suggested from the n.m.r. spectrum which shows absorption at τ 3.0 (multiplet, 8 protons), 5.68 (doublet,

(10) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

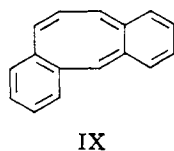
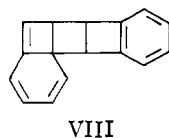
(11) F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

(12) M. Avram, D. Dinu, and C. D. Nenitzescu, *Chem. Ind. (London)*, 257 (1959).

(13) G. D. Mateescu, M. Avram, D. Dinu, and C. D. Nenitzescu, *Rev. Chim.*, **8**, 13 (1963).

1 proton), 6.47 (multiplet, 1 proton),¹⁴ and 7.10 (doublet, 2 protons). No evidence for the formation of the other dimeric products mentioned above was obtained.

The formation of the dimer VII may be rationalized in a manner similar to that postulated for the formation of V.¹⁰ Both reactions could lead to an intermediate VIII but having different configurations of the central four-membered ring. The *cis* isomer, presumed to be formed in the present instance, could rearrange to



1,2,4,5-dibenzocyclooctatetraene (IX) which then undergoes an internal Diels-Alder reaction to give VII. Whatever the mechanism of the dimerization, it is apparent that the presence of transition metals has a profound effect upon the course of these reactions.

The scope of the reactions of 3,4-dihalocyclobutenes with $\text{Fe}_2(\text{CO})_9$ and further reactions of cyclobutadiene-iron tricarbonyl complexes will be reported in later papers.

Acknowledgment. We wish to thank the National Science Foundation and the Robert A. Welch Foundation for financial assistance. We are also grateful to Antara Chemicals for a gift of iron pentacarbonyl.

(14) Models suggest that this nonbenzylic proton of the three-membered ring lies almost in the plane of each of the two benzene rings; this would explain its absorption at an abnormally low τ -value.

(15) University of Texas Socony-Mobil Fellow, 1964-1965.

G. F. Emerson, L. Watts,¹⁵ R. Pettit
Department of Chemistry
University of Texas, Austin 12, Texas
Received November 5, 1964

Hydrophobic Bonding. Its Detection by Nuclear Magnetic Resonance Spectroscopy and Its Effect on the Chemical Shifts of Internal Standards

Sir:

There has been a great deal of recent interest in hydrophobic bonding¹ (the formation of inter- or intramolecular aggregates of the nonpolar portions of molecules surrounded by highly ordered solvent molecules in aqueous medium) due to the recognition that this phenomenon plays an important role in the behavior of proteins.² We now wish to report the utilization of nuclear magnetic resonance spectroscopy for the study of hydrophobic bonding and to point out the implications of this phenomenon with regard to the chemical shifts of internal standards in aqueous solution.

(1) W. Kauzmann, *Advan. Protein Chemistry*, **14**, 1 (1959); G. Némethy and H. A. Scheraga, *J. Phys. Chem.*, **66**, 1773 (1962); E. E. Schrier, M. Pottle, and H. A. Scheraga, *J. Am. Chem. Soc.*, **86**, 3444 (1964).

(2) Hydrophobic bonding almost certainly has considerable implications also for organic chemistry. Note, for example, the decrease in the rate of reaction of hydroxide ion with imido ester caused by the addition of various amines to the aqueous reaction medium: E. S. Hand and W. P. Jencks, *J. Am. Chem. Soc.*, **84**, 3505 (1962), or the selective terminal epoxidation of squalene in highly polar medium: E. E. van Tame- len, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 10F.

When 0.8 *m* (1.5 mole %) aqueous solutions of 1,3-naphthalenediol (I), naphthalene-2-sulfonic acid (II), or phenanthrene-3-sulfonic acid (III) are diluted, their n.m.r. spectra shift to lower field (relative to external TMS). Since the appearance of the spectra also changes markedly upon dilution, it is evident that the chemical shifts of different protons of the same substance are affected to different extents. For example, a fourfold dilution of the 0.8 *m* solution of I results in downfield shifts of *ca.* 10 c.p.s. for the peaks due to the AB system of H-2 and H-4, and of *ca.* 20 c.p.s. for the multiplet due to the remaining protons. Since the water peak does not shift within experimental error (relative to external TMS) during these dilutions, bulk diamagnetic susceptibility changes are probably not large at these concentrations.³ Similar dilution of a solution of I in acetone or methanol, solvents in which hydrophobic bonding cannot occur, causes a small (3 c.p.s.) shift of the aromatic spectrum in the opposite direction (up-field).

These results can be explained by the existence of a concentration controlled association of the organic molecules in aqueous solution, but not in the organic solvents. Such an association would cause the observed effect since the proximity of an aromatic molecule is known to cause protons of another molecule to experience a net shielding effect.^{4,5}

If hydrophobic bonding, rather than a more specific attractive interaction among the aromatic molecules, is responsible for this aggregation, unfavorable interactions of the solvent water with other organic compounds should lead to coaggregation of these and the aromatic species. The proton chemical shifts of such compounds in the presence of the aromatics should therefore also be displaced to higher field. In Table I

Table I. N.m.r. Shifts of Aliphatic Protons in the Presence of Aromatics^a

	I ^{b,c}	II ^{c,e}	III ^{c,e}	IV ^{c,e}	
CH ₃ OH		5		4.5	
(HOCH ₂) ₂		9		5	
CH ₃ CH ₂ OH	-4	10.5	10.5	13.5	3.5
CH ₃ CH ₂ OH	-4.5	11	11	13.5	3.5
(CH ₂) ₃ CCH ₂ OH	-2.5	25	19.5	34	7
(CH ₂) ₃ CCH ₂ OH	-5.5	23.5	19	30.5	7.5
CH ₃ CN		28.5	18	22	8
DSS ^d		48	21	31	9.5

^a Shifts in c.p.s. of aliphatic protons in the presence of 0.8 *m* aromatics relative to their absorption in solvent alone. ^b In acetone. ^c In water. ^d Sodium salt of 4,4-dimethyl-4-silapentane-1-sulfonic acid. ^e I, 1,3-naphthalenediol; II, naphthalene-2-sulfonic acid; III, phenanthrene-3-sulfonic acid; IV, resorcinol.

are listed the shifts observed for a number of aliphatic compounds (1.5-3.0 wt. %) when the medium is changed from pure water to water which is 0.8 *m* in the aromatic

(3) The water peak does shift upon dilution of solutions of II or III, but these shifts are in the opposite direction from those of the aromatic protons. These shifts are primarily due to the change which dilution causes in the acidity of the solutions, since the same shifts for water are observed upon dilution of a sulfuric acid solution of corresponding normality.

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 424-428.

(5) Benzene, when added to micellar solutions, has been reported to cause shielding of the protons of the soap: J. C. Eriksson, *Acta Chem. Scand.*, **17**, 1478 (1963).