

ketones, **9**. The effect on the π -system is illustrated by the measured ionization potentials, I_π , of vinyl and allyl halides **10**¹⁶ and **11**.^{16,17} Increased π -donation ($F \rightarrow I$) in **10** raises the energy of the π level in **10**, just as decreased σ withdrawal ($F \rightarrow I$) in **11** accomplishes the same.

The relative roles of the alternating charge effect and the conjugative through-bond interaction remain to be elucidated in both theoretical and experimental studies.

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(16) G. W. Mines and H. W. Thompson, *Spectrochim. Acta, Part A*, **29**, 1377 (1973).

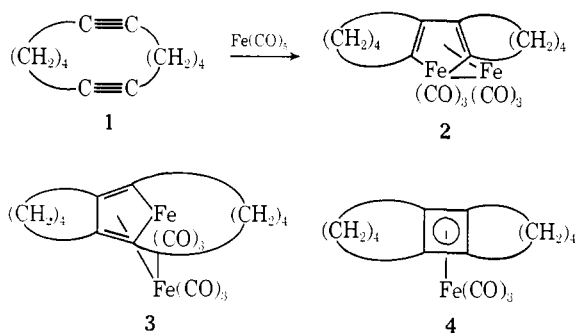
(17) H. Schmidt and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **12**, 307 (1973).

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sym- and *unsym*-Benzoferroles. Ferroles from a Cyclobutadieneiron Tricarbonyl

Sir:

It has recently been reported¹ that the reaction of 1,7-cyclododecadiyne (**1**) with $\text{Fe}(\text{CO})_5$, unexpectedly, affords the ferrole **2**, rather than the ferrole **3** which had been proposed² earlier and which could have been more reasonably expected.



One possible mechanism for the conversion of diyne **1** to the ferrole **2** involves initial formation of the isomeric ferrole **3**, then isomerization of **3** to **2**, perhaps through a cyclobutadiene diiron complex. There exists, however, no experimental evidence for the interconversion of metalocycles of type **2** and **3**.

An alternative explanation for the appearance of **2** involves formation of the cyclobutadieneiron tricarbonyl complex³ **4** from **1** and $\text{Fe}(\text{CO})_5$, and further reaction of the cyclobutadiene- $\text{Fe}(\text{CO})_3$ complex with $\text{Fe}(\text{CO})_5$ to yield **2**.

In support of this latter proposal we now report evidence indicating that in fact cyclobutadieneiron tricarbonyl compounds can be converted to ferroles

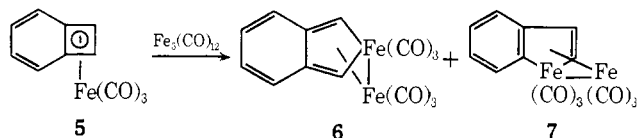
(1) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5068 (1973).

(2) R. B. King and I. Haiduc, *J. Amer. Chem. Soc.*, **94**, 4044 (1972).

(3) A trace amount of the cyclobutadieneiron tricarbonyl complex was in fact obtained.²

under conditions comparable to those employed for the conversion of diyne **1** to ferrole **2**. Furthermore, two isomeric ferroles have been isolated and have been found not to interconvert under similar conditions.

Benzocyclobutadieneiron tricarbonyl (**5**) and excess $\text{Fe}_3(\text{CO})_{12}$ in hydrocarbon solvents react at 120° to afford a mixture of the *sym*- and *unsym*-benzoferroles, **6** and **7**, respectively.⁴ *sym*-Benzoferrole (**6**) forms orange crystals from pentane: mp $86\text{--}87^\circ$, ir (Skelly B) 2078, 2043, 2005, 2000, 1955 cm^{-1} , nmr (CS_2) τ 2.7 (s), 2.55–2.8 (m).⁵ *unsym*-Benzoferrole (**7**) has been recently prepared by alternative routes,⁶ and our physi-



cal and spectroscopic data are in agreement with those reported. X-Ray crystallographic analysis confirms the proposed structures.

Compound **6**, crystallized from pentane, is triclinic $P1$, $a = 8.734$, $b = 14.926$ Å, $c = 12.174$ Å, $\alpha = 99.04^\circ$, $\beta = 102.06^\circ$, $\gamma = 68.96^\circ$, and $Z = 4$. Of the 5057 independent reflections whose intensities measured ($2\theta(\text{max}) = 50^\circ$ with Mo $K\alpha$ radiation), 3337 were used in the structure solution and refinement. This structure, which includes two molecules per crystallographic asymmetric unit, has been refined to $R = 0.063$, $R_w = 0.055$.

Crystals of **7** from pentane are monoclinic $P2_1/c$, $a = 8.076$ Å, $b = 14.188$ Å, $c = 12.408$ Å, $\beta = 113.57^\circ$, and $Z = 4$. Three-dimensional single-crystal intensity data were collected with Mo $K\alpha$ radiation to the limit $2\theta = 52.5^\circ$. Of the 2854 independent reflections measured, 2093 were included in the refinement. The structure was refined to $R = 0.072$, $R_w = 0.058$.

The two benzoferroles are not interconverted or decomposed in hydrocarbon solvents at 120° , suggesting that in the diyne work ferrole **3** is probably not being converted to ferrole **2** under the reaction conditions. Instead, our results suggest that the formation of ferrole **2** from diyne **1** could more reasonably stem from the conversion of a transient cyclobutadieneiron tricarbonyl complex to the observed ferrole in the presence of $\text{Fe}(\text{CO})_5$.

If indeed the results of the diyne studies and of our present work can be extended to a discussion of the mechanism of alkyne disproportionation ($R_1\text{C}\equiv\text{CR}_1 + R_2\text{C}\equiv\text{CR}_2 \rightleftharpoons 2R_1\text{C}\equiv\text{CR}_2$),⁷ we conclude that cyclobutadiene metal complexes could conceivably be involved in this latter process. Such species, however, could be formed directly and reversibly (leading to disproportionation), and the intermediate formation or

(4) (a) With a reaction time of 7 hr the relative yields of **5**, **6**, and **7** were 24, 38, and 38%, respectively; no other products were observed. (b) Complex **6** and **7** have also been obtained from **5** by photolysis with pentacarbonyliron: R. Victor and R. Ben-Shoshan, *J. Chem. Soc., Chem. Commun.*, 93 (1974).

(5) (a) R. Victor and Ben-Shoshan^{4b} report mp $79.5\text{--}80.5^\circ$. (b) Compound **6** can also be prepared by treatment of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo- δ -xylene with disodium tetracarbonylferrate.

(6) R. Victor, R. Ben-Shoshan, and S. Sarel, *Chem. Commun.*, 1241 (1971); D. Ehntholt, A. Rosan, and M. Rosenblum, *J. Organometal. Chem.*, **56**, 315 (1973).

(7) F. Pennella, R. L. Banks, and G. C. Bailey, *Chem. Commun.*, 1548 (1968).

interconversion of metallocycles need not perforce be involved.

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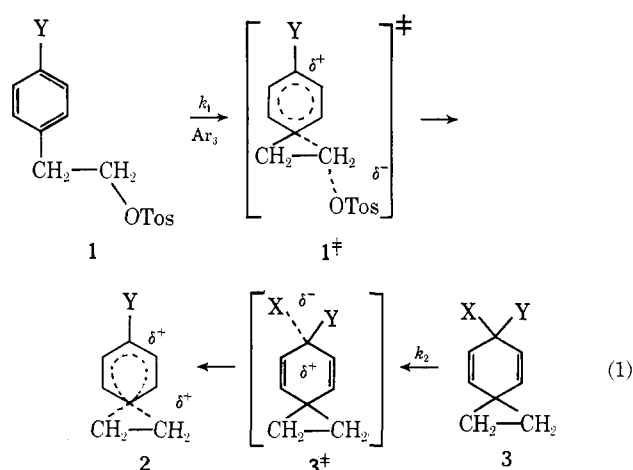
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Distortional Stabilization in Phenyl Participations¹

Sir:

There is a wealth of kinetic, product, and theoretical evidence for the direct formation of phenonium ions through transition states closely resembling the ions in eq 1.²⁻⁴ This implies that the accelerated k_2 in-



volves little change in the geometry of the three-membered ring in going to 2^{5,6} and that acceleration of k_2 requires extensive movement in the direction of cyclopropane ring formation. Recent calculations of Hehre⁴ on this system agree with this postulate.

An alternative suggestion of through-space⁹ inter-

(1) Supported by the National Science Foundation, Grant GP 27361.

(2) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952); (b) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957); (c) A. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969), and references cited there.

(3) (a) C. I. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1971, p 1347; (b) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949); (c) *ibid.*, **74**, 2129 (1952); (d) J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969).

(4) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 5919 (1972).

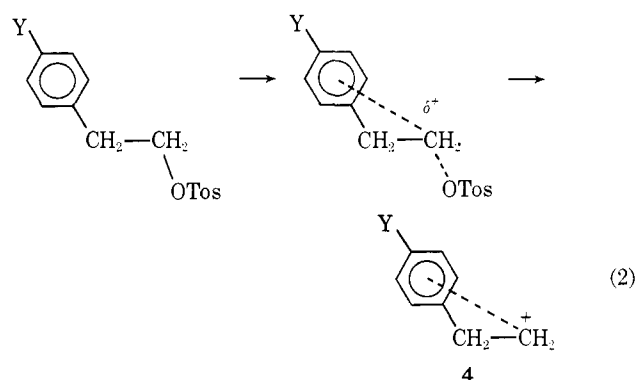
(5) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970); (b) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971); (c) K. Munk, J. Maier, D. W. Turner, and T. G. Traylor, submitted for publication; (d) J. M. Jerkunica and T. G. Traylor, *J. Amer. Chem. Soc.*, **93**, 6278 (1971).

(6) Charge-transfer data^{5a} and additivity effects also give excellent evidence against vertical stabilization in the phenethyl system. Two neighboring phenyl groups in (PhCH₂)₂CHOTos give additive k effects⁷ whereas two vertical stabilizing groups such as cyclopropyl⁸ or Me₃SnCH₂^{8d} in (Δ)₂CHX or (Me₃SnCH₂)₂CHX give additive log k effects.

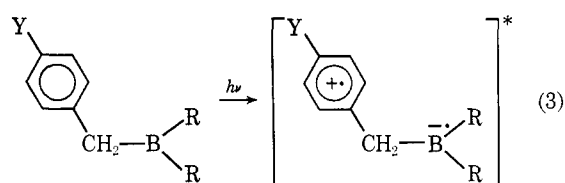
(7) C. J. Lancelot and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291 (1969).

(8) H. Hart and G. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959).

actions between the phenyl ring and the incipient cation center and requiring little advancement toward 2 has been made by Brown and Kim.¹⁰

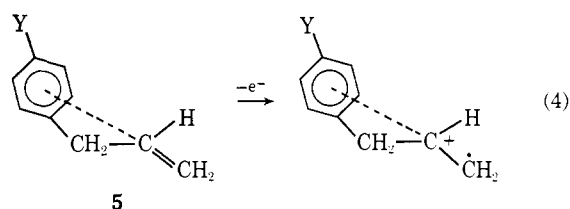


Ramsey and Das¹¹ observed a correlation between the uv transition energy identified as reaction 3 and



−log k of the corresponding reaction 1. This, and the fact that both these quantities were in turn proportional to the first ionization potentials of the corresponding substituted benzenes, PhY, were interpreted as evidence for the through-space stabilization suggested by Brown and Kim. It should be pointed out that such charge-transfer spectra will correlate even if the acceptor (in this case R₃B) is 3 Å away as in external charge-transfer complexes.^{5a} This evidence therefore reveals little about the geometry of transition states of eq 1.

It is possible to probe directly for stabilizing interactions in such molecular geometry as that shown in 4 by using photoelectron spectroscopy.¹² If the interaction as shown in 4 is significant, then the π orbitals in 5 should reveal such interaction.¹² In fact, we can



quite generally conclude that any neighboring group will interact strongly with such a π system if vertical

(9) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 706 (1970).

(10) H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, **93**, 5765 (1971).

(11) B. G. Ramsey and N. K. Das, *J. Amer. Chem. Soc.*, **94**, 4233 (1972).

(12) We tentatively concluded^{5a} that such an interaction as shown in eq 4 was absent in diphenylmethane, a conclusion corroborated by photoelectron spectroscopy.¹³ However, the expected interaction is small, and these results are therefore rather inconclusive.

(13) S. Pugnataro, V. Mancini, J. N. A. Ridyard, and H. J. Lempka, *Chem. Commun.*, 142 (1971).