

The STO-3G results for the same barrier but using a geometry derived from the optimized geometry of the ethyl cation are shown in Table II (2a, 2b). The barriers obtained with the two basis sets (2.52 and 2.26 kcal/mol) are in close agreement. Since the STO-3G calculations require about one-tenth the computer time of the extended basis set, the remaining calculations were performed at the STO-3G level.

The rotational barriers for four more carbonium ions held in their planar²⁴ conformations are presented in Table II. If the preference for the C-CH₃ bond to be coplanar with the "empty" p orbital in the *n*-propyl cation follows a simple twofold cosine potential function, *i.e.*, $V(\theta) = (V_2/2)(1 - \cos 2\theta)$, where V_2 is the twofold barrier, it is easy to show that the same function applied to the isobutyl cation predicts the conformation (3a) which has both C-CH₃ bonds forming dihedral angles of 30° with the "empty" p orbital to have the lowest energy and the barrier to be the same as in the *n*-propyl cation. Our calculated barrier and lowest energy conformation are in agreement with these predictions. As expected, the sixfold barrier in the planar²⁴ neopentyl cation (4) is indistinguishable from zero.

Incorporation of the two methyl groups of the isobutyl cation into increasingly smaller ring systems leads to an increasing preference of the cations for the "bisected" conformations (5a and 7a), the energy difference being 4.08 kcal mol⁻¹ in the cyclobutylcarbinyl (7) and 17.54 kcal/mol in the cyclopropylcarbinyl (5) systems. In going from the cyclopropyl (5) to the 1-methylcyclopropylcarbinyl (6) cation this rotational barrier is reduced²⁵ by 1.54 kcal/mol, analogous to the 1.77- and 2.68-kcal/mol drops in barriers in going from the cyclobutylcarbinyl to the 1-methylcyclobutylcarbinyl, and from the isobutyl to neopentyl cations, respectively. The preference of the cyclopropylcarbinyl cation for the bisected conformation has been shown in many ways.²⁶ Recent nuclear magnetic double resonance studies²⁷ have suggested the bisected conformation for the dimethylcyclopropylcarbinyl cation and a barrier to rotation of 13.7 kcal/mol in this tertiary system.

Many carbonium ions cannot achieve the preferred planar structure^{2,3,10} as, *e.g.*, bridgehead cations.²⁸ We have reported calculations which showed that the ethyl cation barrier increases significantly if the CH₂⁺ group is held in a tetrahedral geometry.⁶ In the *n*-propyl cation, this deformation leads to an increase of the barrier to 6.04 kcal/mol (STO-3G) with the preferred geometry (9a) having the "empty" sp³ lobe trans to the methyl group. The highest energy conformation (9b) has the hydrogens eclipsed.

(24) "Planar" refers to the arrangement of bonds at the positive carbon center. Such arrangements may not represent the most stable geometries.⁶

(25) Attempts to study this barrier in super acid solution are frustrated by ready interconversion between the 1-methylcyclopropylcarbinyl and 1-methylcyclobutyl cations. See M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **92**, 2548 (1970); G. A. Olah, C. J. Jewell, D. P. Kelley, and R. D. Porter, *ibid.*, in press.

(26) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); B. R. Ree and J. C. Martin, *ibid.*, **92**, (1970); G. A. Olah, D. P. Kelley, C. J. Jewell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

(27) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

(28) R. C. Fort and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

These results have rather startling implications which should be tested experimentally. Firstly, contrary to popular assumption²⁹ nonsixfold barriers in simple alkylcarbonium ions may be quite appreciable, on the order of 2.5–3.0 kcal/mol. An energy difference of this magnitude corresponds to a 100-fold variation in rate or equilibrium phenomena which should be readily detectable in rigid structures where cations are locked into favorable and unfavorable conformations. However, the effects in secondary and tertiary cation systems may be smaller than these calculated here for primary systems. Secondly, the "C-C hyperconjugation" conformations are preferred over the "C-H hyperconjugation" geometries.²² This contrasts with the usual assumption that C-H hyperconjugation is more favorable than C-C hyperconjugation.² Finally, the well-documented energy difference between the cyclopropylcarbinyl conformations 5a and 5b is revealed to be not a special case but only an extreme of a general phenomenon already present in the isobutyl cation (3a and 3b). When the C-C bonds are "bent" increasing their p character (as in 5 and 7) their C-C hyperconjugative ability increases,³⁰ but the enhancement in the rotational barrier only becomes really large when a three-membered ring is present.

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(29) As was pointed out by a referee, one of the authors of this paper has been a "prime perpetrator" of the idea the barriers in alkyl cations are near zero. See P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854 (1964); G. J. Gleicher and P. v. R. Schleyer, *ibid.*, **89**, 582 (1967).

(30) Cf. F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5686, 5688 (1969); N. A. Clinton, R. S. Brown, and T. G. Traylor, *ibid.*, **92**, 5228 (1970).

(31) Princeton University Fellow, 1968–1969; American Cyanamid Fellow, 1969–1970. Ph.D. Thesis, Princeton University, 1970.

* Address correspondence to either of these authors.

L. Radom, J. A. Pople*

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

V. Buss,³¹ P. v. R. Schleyer*

Department of Chemistry, Princeton University
Princeton, New Jersey 08547

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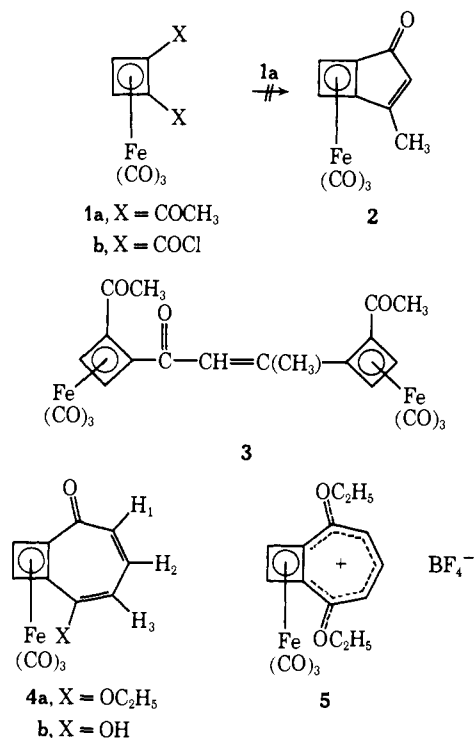
Evidence on the Scope and Limitations of Ring-Forming Reactions of Tricarbonyliron Complexes of Functional 1,2-Disubstituted Cyclobutadienes. Synthesis of Tricarbonyliron Complexes of Cyclobutadienocycloheptatrienyl Derivatives

Sir:

Recently we reported the synthesis of a series of tricarbonyliron complexes of functional 1,2-disubstituted cyclobutadienes and commented on the potential synthetic value of the latter as precursors to complexes of theoretically interesting fused-ring cyclo-

butadienoid systems *via* cyclization reactions involving adjacent substituents.¹ We now wish to report some results which partially delineate the scope and limitations of such an approach and to describe the synthesis of complexes of some cyclobutadienocycloheptatrienyl derivatives.

Numerous efforts to effect aldol cyclization of diketone **1a** as a route to cyclobutadienocyclopentadienone complex **2**² failed with a variety of acidic and basic catalysts. Some acidic catalysts [$\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, $(\text{C}_2\text{H}_5)_3\text{O}^+\text{BF}_4^-$], however, afforded two crystalline isomers separated by tlc, mp 162–164 and 191–193°, which on the basis of closely similar spectroscopic data are both products of linear bimolecular condensation corresponding to gross structure **3**. The stereochemical difference between the two isomers is of some interest since they do not appear to be olefinic *cis*–*trans* isomers as shown by failure to equilibrate either under original reaction conditions or with trifluoroacetic acid. Consequently, the two compounds most reasonably correspond to the two *dl* isomers arising from stereochemical variation of the asymmetry associated with each cyclobutadieneiron tricarbonyl unit in **3**.



In contrast to the foregoing results are some facile cyclization reactions which have led to complexes of cyclobutadienocycloheptatrienyl derivatives and thus afford a promising entry for elaboration of the chemistry of 4,7-fused systems. The first example was inadvertently discovered during exploratory work on the chemistry of diketone **1a** when treatment with ethyl orthoformate and 95% sulfuric acid afforded in 72%

(1) B. W. Roberts, A. Wissner, and R. A. Rimerman, *J. Amer. Chem. Soc.*, **91**, 6208 (1969).

(2) The ring system of **2**, in various modifications, has been the subject of much current interest: (a) R. Breslow, W. Washburn, and R. G. Bergman, *ibid.*, **91**, 196 (1969); (b) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *ibid.*, **91**, 2787 (1969); (c) M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. G. Glick, *ibid.*, **91**, 2379 (1969); (d) M. B. D'Amore and R. G. Bergman, *ibid.*, **91**, 5694 (1969); (e) R. Breslow and W. Washburn, *ibid.*, **92**, 426 (1970).

yield a crystalline reddish-brown compound, mp 126–127°, $\text{C}_{14}\text{H}_{10}\text{FeO}_5$,³ which has been identified as tropolone ether **4a** on the basis of spectral data. The pmr spectrum⁴ revealed an ethoxy group [δ 1.38 (t, 3 H), 4.10 (q, 2 H), $J = 7.0$ Hz], two nonequivalent cyclobutadiene ring protons [δ 4.82, 4.95 (s's, 1 H each)],⁵ and three protons appearing as a complex eight-line pattern in the region δ 5.73–6.87. The chemical shifts and coupling constants [δ_{H_1} 6.02, δ_{H_2} 6.73, δ_{H_3} 5.78; $J_{12} = 13.0$ Hz, $J_{23} = 9.5$ Hz, $J_{13} \leq 0.4$ Hz] extracted from the latter by computer simulation⁶ were assigned by correlation of the magnitudes of the larger coupling constants with those expected for vicinal coupling across formal double and single bonds.⁷ The infrared spectrum (CHCl_3) was consonant with the presence of olefinic, ketone carbonyl, and metal carbonyl groups [1520, 1592, 1620, 1995, and 2060 cm^{-1}]. Chemically **4a** was also consistent with the tropolone ether formulation in forming the crystalline violet-black diethoxytropylium fluoroborate **5** [mp 159–161°; $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ 5.66 (s, 2 H) and 6.88–8.06 (AB₂, δ_{A} 7.94, δ_{B} 6.94, $J_{\text{AB}} = 11.3$ Hz)] with triethyloxonium fluoroborate and in hydrolyzing to tropolone **4b**, dec pt 170°, with 50% aqueous sulfuric acid.^{8,10}

The mechanism of formation of **4a** probably involves condensation of an enol ether of **1a** with ethyl orthoformate¹¹ to give, after elimination of ethanol, cation **6** or a functional equivalent. Cyclization of the latter in the manner shown followed by loss of ethanol would then afford the cation of **5**, which would lead to **4a** on aqueous work-up. To our knowledge the foregoing type of reaction represents a new γ -tropolone synthesis, the scope and limitations of which deserve further study.

Construction of 4,7-fused systems was also realized in Friedel–Crafts reactions of bis(acid chloride) **1b**¹ with naphthalene and acenaphthene (AlCl_3 – CS_2) to give diketones **7**^{8b} (yellow leaves, mp 166–176°) and **8**^{8b}

(3) (a) Compositional analyses of all new compounds reported herein for carbon, hydrogen, and iron agreed within 0.3% of values expected of assigned structures; (b) molecular weight determined by mass spectrometry.

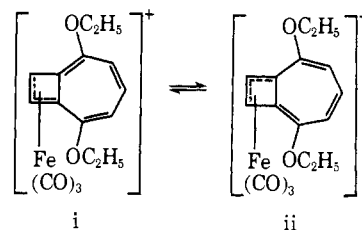
(4) All pmr spectra were recorded at 100 MHz at ambient temperatures. Chemical shifts are reported as parts per million downfield from internal TMS.

(5) Lack of observable vicinal coupling of ring protons appears to be a consistent feature of cyclobutadieneiron tricarbonyl complexes (see ref 1, footnote 16).

(6) LAOCN3, A. A. Bothner-By and S. Castellana, Program III, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(7) D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *J. Amer. Chem. Soc.*, **91**, 5286 (1969).

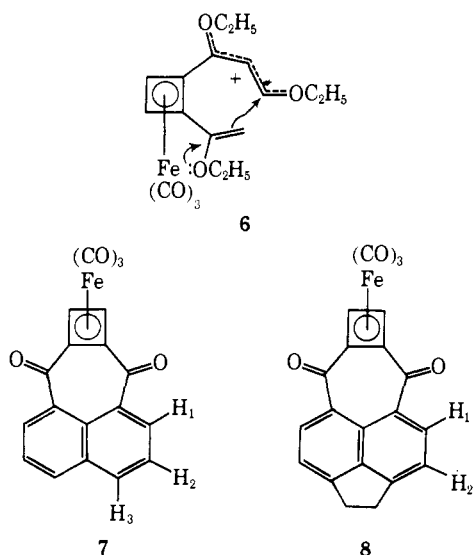
(8) While our formulation of **5** as a cyclobutadiene complex is consistent with all spectral data, it should be pointed out that certain alternate structures are not necessarily excluded, *viz.*, rapidly interconverting π -allyl complexes i and ii.⁹



(9) J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Lett.*, 1299 (1966).

(10) The propensity of **4a** (and **4b**) toward tropylium ion formation was also reflected in pmr spectra in trifluoroacetic acid, which indicated essentially complete protonation.

(11) For a review of condensation of enol ethers with acetals and related compounds, see L. S. Povarov, *Russ. Chem. Rev.*, **34**, 639 (1965).



(golden plates, dec pt 230–240°) in 75 and 42%¹² yields, respectively. The pmr spectra⁴ (CDCl₃) were particularly valuable in establishing that cyclization had taken place across peri positions. Thus the cyclobutadiene protons in each appeared as a singlet (**7**: δ 5.18; **8**: δ 5.16] while the naphthalenic protons appeared as incipient AMX [δ_{H_1} 8.89, δ_{H_2} 7.64; δ_{H_3} 8.17; $J_{12} = 7.7$ Hz, $J_{13} = 1.9$ Hz, $J_{23} = 7.6$ Hz] and AX [δ_{H_1} 8.90, δ_{H_2} 7.48 (somewhat broadened, $W_h = 2.0$ Hz); $J_{12} = 7.5$ Hz] patterns in **7** and **8**, respectively.¹³ Chemical shifts were assigned on the basis that the lowest field absorption in each compound corresponds to H₁, which is situated for effective deshielding by a carbonyl group.¹⁴ The ethano protons in **8** absorbed as a broadened singlet at δ 3.47 ($W_h = 2.0$ Hz). In addition the infrared spectrum (CHCl₃) of each diketone [**7**: 1508, 1563, 1601, 1637, 2006, and 2066 cm⁻¹; **8**: 1505, 1566, 1587, 1600, 1626, 2002, and 2064 cm⁻¹] was consonant with the indicated functionality.¹⁵

The foregoing results are especially useful in defining some of the limitations of approach to fused-ring cyclobutadienes from 1,2-disubstituted complexes. In the case of diketone **1a**, the stereochemical disposition of substituents is undoubtedly a crucial factor in the failure to cyclize. X-Ray crystallographic studies of tetramethylcyclobutadiene nickel dichloride dimer¹⁷ and tetraphenylcyclobutadiene iron tricarbonyl¹⁸ have shown that external ring-substituent angles are close to 135°. If this structural feature be maintained in **1a**, ring closure would be inhibited because of the large distance to be overcome between interacting centers of sub-

(12) This is a minimum yield after one recrystallization. The total yield is significantly higher, but an unidentified side product has prevented complete separation.

(13) A singlet at δ 8.57 in the spectrum of **7** suggested the presence of a very minor and as yet unidentified side product.

(14) D. J. Pasto and C. R. Johnson, "Organic Structural Determination," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, pp 170–171.

(15) Diketones **7** and **8** are of special interest in being potential precursors of cyclobutadiene analogs of pleiadene,^{16a} acepleiadene,^{16b} and acepleiadylene.^{16c} Hopefully, the chemistry of the cyclobutadienoid counterparts can be developed for comparison with that of the benzo forms.

(16) (a) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965); (b) M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3051 (1965); (c) M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3065 (1965).

(17) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).

(18) R. P. Dodge and V. Schomaker, *Nature (London)*, **186**, 798 (1969).

stituents and because of angle strain generated during product formation. Although alternate experimental conditions for effecting the closure have not been exhausted, this particular approach would appear to hold little promise for the synthesis of cyclobutadienocyclopentadienyl derivatives without serious modification.

On the other hand facile fusion of a cycloheptatrienyl ring to a complexed cyclobutadiene suggests the efficacy of the general approach and presents the possibility that substituent geometry may facilitate fusion of medium rings. We are currently testing the latter suggestion as a route to larger cyclobutadienopolynes and derivatives.

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* Address correspondence to this author.

Bryan W. Roberts,* Allan Wissner

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104

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The Possible Determination of Iron Coordination in Nonheme Iron Proteins Using Laser-Raman Spectroscopy. Rubredoxin

Sir:

The isolation¹ from *Clostridium pasteurianum* of ferredoxin, the initial member of the class of nonheme iron proteins that participate in electron-transfer reactions, has generated substantial interest in the structure and biochemistry of proteins of this type.^{2–5} Of particular importance is the nature of iron coordination in these proteins, since this may be a primary determinant of their apparently unique metabolic and photosynthetic roles.^{6,7} Briefly summarized, it is generally thought that sulfhydryl groups from cysteinyl residues and inorganic sulfides⁸ (with the exception of rubredoxin)⁹ constitute at least part of the iron environment.^{6,7} Electron paramagnetic resonance^{10–13} techniques have been applied to the problem, but so far with little success. Circular dichroism studies did not

(1) L. E. Mortenson, R. C. Valentine, and J. E. Carnahan, *Biochem. Biophys. Res. Commun.*, **7**, 448 (1962).

(2) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967).

(3) A. San Pietro, Ed., "Non-heme Iron Proteins: Role in Energy Conversion," Antioch Press, Yellow Springs, Ohio, 1965.

(4) B. B. Buchanan, *Struct. Bonding (Berlin)*, **1**, 109 (1966).

(5) R. C. Valentine, *Bacteriol. Rev.*, **28**, 497 (1964).

(6) J. C. M. Tsibris, Department of Chemistry, University of Illinois, Biochemistry Division, Urbana, Illinois; *Struct. Bonding (Berlin)*, in press.

(7) T. Kimura, *ibid.*, **5**, 1 (1968).

(8) W. Lovenberg, B. B. Buchanan, and J. C. Rabinowitz, *J. Biol. Chem.*, **238**, 3899 (1963).

(9) W. Lovenberg and B. E. Sobel, *Proc. Natl. Acad. Sci., U. S.*, **54**, 193 (1965).

(10) G. Palmer, R. H. Sands, and L. E. Mortenson, *Biochem. Biophys. Res. Commun.*, **23**, 357 (1966).

(11) H. Beinart and G. Palmer, *Advan. Enzymol.*, **27**, 105 (1965).

(12) H. Beinart in ref 3, p 23.

(13) W. Lovenberg "Protides of the Biological Fluids (Proceedings of the Fourteenth Colloquium, Bruges, Belgium, 1966)," H. Peeters, Ed., Elsevier, Amsterdam, 1967, p 165.