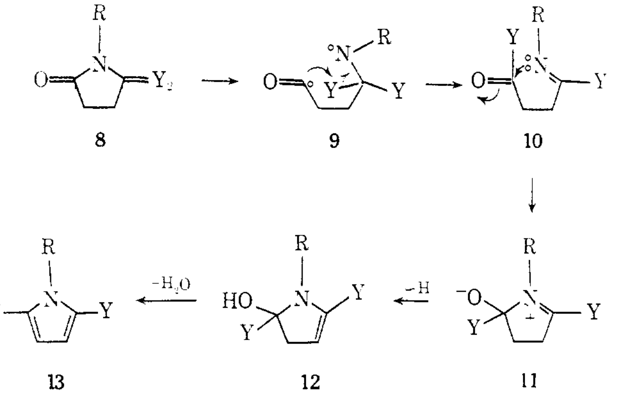
of **5**, **5a**, **6**, and **6a** isolated as **7** and **7a** was expected; *i.e.*, **4a** has two equivalent cleavage pathways: A, which would lead to **5a** and **6**, and B, which would lead to **5** and **6a**.

An infrared spectrum of the ethylene obtained on irradiation of **1a** showed absorptions at 3017, 2230, 1585, 1384, 943, and 751 cm^{-1}, identical with those reported[12] for **5a**. In addition, the nmr spectrum of the *s*-triazene obtained was identical with that of **7** indicating that there was no deuterium incorporation. Clearly, under these experimental conditions **4** is not an important intermediate to the formation of **5** and **6**.

Of particular interest is *N*-methylpyrrole (**13**) formation which formally corresponds to dehydration of **1**. *N*-Phenylpyrrole (**13b**) has been reported[3] as the sole product isolated from irradiation of **8b** in solution but its mode of formation was not commented on. The close analogy to the photochemistry of cyclopentanone, which affords 4-pentenal as a major product, led us to speculate on the absence and possible fate of the nitrogen analog of this material, **10**, in the present case. In fact, the route **10** → **13** appeared to be an attractive one for the formation of pyrrole.

Photolysis of material labeled in the 5 position provided a critical test for the intermediacy of **10** since this mechanistic scheme requires deuterium transfer (in **8a** or **8c**) from C_5 to C_2. Subsequent dark steps would result in α,α'-labeled pyrroles **13a** or **13c**.



8-13, $R = CH_3$; $Y = H$
8a-13a, $R = CH_3$; $Y = D$
8b-13b, $R = C_6H_5$; $Y = H$
8c-13c, $R = C_6H_5$; $Y = D$

The nmr spectrum of the volatile condensate obtained on direct irradiation of **8a**[13] showed the expected resonances at τ 6.59 (NCH_3) and 4.05 (β H) but the resonance at τ 3.65 present in the spectrum of **13** (α H) was absent. Similarly, the spectrum of the *N*-phenylpyrrole isolated from irradiation of **8c** in 2-propanol showed resonances at τ 2.72 (C_6H_5) and 3.85 (β H). These data are only consistent with the formation of **13a** and **13c** from **8a** and **8c**, respectively, and clearly demonstrate the intermediacy of **10** in the formation of **13**.

The vapor-phase photochemistry of *N*-methyl-2-pyrrolidone, at least with respect to product formation, is strikingly similar to that of cyclopentanone. Whether this close analogy holds for the quantitative aspects of this reaction is a question which must await the results of further studies.

Acknowledgment. We are indebted to the Center of Materials Research of the University of Maryland for partial support of this work.

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(12) W. J. Lehman, *J. Mol. Spectrosc.*, **7**, 3 (1961).

(13) Compounds **8a** and **8c** were prepared by heating the corresponding amine and butyrolactone-*4,4-d*$_2$ (prepared by $LiAlD_4$ reduction of succinic anhydride[14]) in sealed tubes.

(14) J. J. Bloomfield and S. L. Lee, *J. Org. Chem.*, **32**, 3919 (1967).

(15) National Science Foundation Science Faculty Fellow, 1970–1972.

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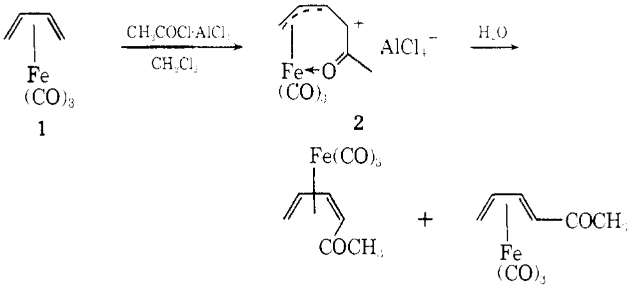
Reactivity of Tricarbonyl(diene)iron Compounds toward Electrophiles and Charge Distribution in Tricarbonyl(π-allyl)iron Cations

Sir:

Tricarbonyl(diene)iron compounds undergo facile Friedel–Crafts acylation to give *cis*- and *trans*-tricarbonyl(dienone)iron compounds.[1-3] Acetylation of tricarbonyl(butadiene)iron (**1**) was shown to proceed *via* the isolable ionic intermediate **2**.[2a] Lack of substitution at internal diene carbons is attributable to the relative instability of the requisite tricarbonyl(π-homoallyl)iron cation intermediate.[2,4] Rate-determining electrophilic attack of the methyloxocarbonium tetrachloroaluminate ion pair[5] should proceed *via* a transition state which resembles a tricarbonyl(π-allyl)iron cation.[6] Substituent effects on electrophilic reactivity of the diene complexes[7] would provide a basis for determining charge distribution in tricarbonyl(π-allyl)iron cations and for evaluating the general synthetic utility of the acylation reaction.



We have assessed the relative reactivity in acylation of several substituted diene complexes by allowing each to

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(1) G. G. Ecke, U. S. Patent 3,149,135 (1964). Acylation at C_2 reported in this patent has been shown to be in error.[2]

(2) (a) E. O. Greaves, C. R. Knox, and P. L. Pauson, *Chem. Commun.*, 1124 (1969); (b) R. E. Graf as quoted by N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 3065 (1970).

(3) A. N. Nesmeyanov, K. N. Anisimov, and G. K. Magomedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 715, 959 (1970).

(4) Evidence for existence of this type of cation has been described recently: R. E. Graf and C. P. Lillya, submitted for publication.

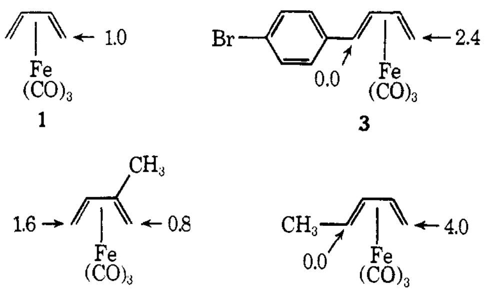
(5) (a) H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, **81**, 3310 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959); (c) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 2203 (1964).

(6) *Cf.* G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

(7) Nesmeyanov, *et al.*,[3] have commented that the 2,3-dimethylbutadiene derivative is significantly more reactive than **1** but give no quantitative estimate of the difference or experimental basis for their conclusion.

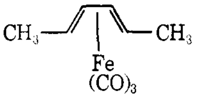
compete with *m*-xylene for a limited amount of acetyl chloride–aluminum chloride complex in dichloromethane.[5a] Product analysis was carried out using high-speed liquid chromatography.[8,9] In agreement with the qualitative observations of Knox, *et al.*,[2a] we find **1** to be 3800 times as reactive as benzene. Partial rate factors[10] relative to **1** for acetylation are listed in Chart I. Substitution of a terminal carbon decreases its reactivity dramatically. Thus, neither compound **6** nor **7** yielded an acyl derivative under conditions in which acylation of **1** was complete in less than 1 min.

Chart I. Partial Rate Factors[a] for Acetylation with Acetyl Chloride–Aluminum Chloride in Dichloromethane at 25°[b]



1 **3** **4** **5**

[a] See ref 10 for definition. [b] Values are the average of four or five determinations. Individual values were always within ±5% of the average except for **1** where the deviation was up to ±9%.



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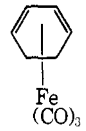

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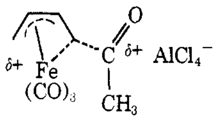
The substituent effects are small, even somewhat smaller than those observed in ferrocene acylation,[11] and dramatically smaller than those in uncomplexed benzenes.[5] Replacement of a terminal hydrogen in **1** by methyl to give **5** increases the partial rate factor for acetylation at C$_1$ by a factor of only 4, while the partial rate factor for para acetylation to toluene (relative to benzene) is 770.[5b] The data require a transition state for electrophilic attack with very little net positive charge at the allyl carbons (**8**).



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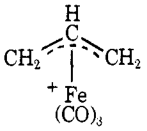
The observed directive effects are also consistent with this transition state. Lack of substitution at substituted terminal carbons is attributable to steric hindrance. Steric effects are characteristically large for acylation.[5a] Similarity of partial rate factors for electrophilic attack at C$_1$ and C$_4$ in **4** is not caused by cancellation of large activating electronic and deactivating steric effects at C$_1$. Such an explanation is inconsistent with the uniformly small substituent effects, particularly the modest reactivity of **5**. Significant steric effects have been ruled out in acylation of tricarbonyl(alkylcyclobutadiene)iron compounds in which similar directive effects have been observed.[12] Thus, in contrast to uncomplexed allyl cations,[13] there is no evidence for charge alternation in these complexed allyl cations.

The structure of tricarbonyl(π-allyl)iron cations which emerges is one in which virtually all the positive charge resides on the tricarbonyl iron moiety **9**. Such



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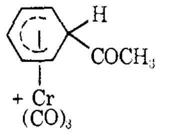
a structure is consistent with their unusually high terminal carbonyl infrared stretching frequencies[6] and with the relative electronegativities of carbon and iron. It can be accommodated by the MO model of metal carbon bonding in terms of donation of electrons from filled orbitals on iron into the nonbonding and antibonding MO's of the allyl ligand.[14] Jackson and Jennings have reported negligible substituent activating effects and unusually large ortho–para and meta–para ratios in acylation of tricarbonylchromium complexes of monosubstituted benzenes.[15] They have demonstrated that steric interactions involving the tricarbonylchromium group play a role in these reactions and have discussed their data in these terms. We would like to point out that these data suggest strongly a tricarbonyl(π-arene)chromium cation intermediate in which little or no positive charge resides on the hexadienyl ligand **10**. This charge distribution is obviously similar to



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that which we have found in tricarbonyl(π-allyl)iron cations.

Details of acylation reactions of diene complexes as well as an assessment of relative reactivity for a wider variety of diene types will be presented in a full paper.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant.

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(8) *Cf.* J. J. Kirkland, Ed., "Modern Practice of Liquid Chromatography," Wiley-Interscience, New York, N. Y., 1971. We employed a 50 cm × 2.0 mm (i.d.) column packed with Du Pont ODS Permaphase with 20% aqueous methanol as mobile phase. We determined a toluene–benzene reactivity ratio of 140 in dichloromethane similar to the value of 128 observed in 1,2-dichloroethane.[5b] Details of our method will be published elsewhere.

(9) Products were also isolated and new compounds were characterized by ir, nmr, and mass spectrometry as well as elemental analysis.

(10) *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, New York, N. Y., 1953, Chapter 6.

(11) R. A. Benkeser, Y. Nagai, and J. Hooz, *J. Amer. Chem. Soc.*, **86**, 3742 (1964).

(12) R. Pettit in "Plenary Lectures at the Third IUPAC International Symposium on Organometallic Chemistry, Munich, 1967," Plenum Press, New York, N. Y., 1968, pp 262–263. Both methyl- and isopropylcyclobutadiene complexes give 2- and 3-acetyl products in a 1:2 ratio. Reactivities relative to the parent complex were not reported.

(13) *Cf.* N. C. Deno in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 783.

(14) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(15) W. R. Jackson and W. B. Jennings, *J. Chem. Soc. B*, 1221 (1969). See also G. E. Herberich and E. O. Rischer, *Chem. Ber.*, **95**, 2083 (1962).

(16) Alfred P. Sloan Foundation Research Fellow, 1969–1971.

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