Organic and Biological Chemistry

The 7-Norbornadienyltricarbonyliron Cation[1,2]

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Abstract: 7-Tosyloxynorbornadienetricarbonyliron (**12**) solvolyzes in 80% aqueous acetone at least 1,000,000 times more slowly than uncomplexed 7-tosyloxynorbornadiene should. From this and other data it is concluded that the 7-norbornadienyltricarbonyliron cation (**6**) is much less stable than the 7-norbornadienyl cation itself. This is the first example of a carbonium ion which is destabilized by attachment of a transition-metal atom. Arguments are presented which attribute the destabilization of **6** to inhibition of the homoallylic interactions which stabilize the 7-norbornadienyl cation.

Stabilization of carbonium ions by formation of π bonds to transition-metal atoms is a well-documented phenomenon. π-Allyltricarbonyliron (**1**),[4] π-pentadienyltricarbonyliron (**2**),[5] the π-benzyl- and π-benzhydryltricarbonylchromium (**3**),[6] and the π-tropyliumtricarbonylchromium, -molybdenum, and -tungsten (**4**)[6] cations are all much more stable than their simple carbonium ion counterparts. The reduced electrophilicity of the complexed cations is striking; π-cyclohexadienyltricarbonyliron fluoroborate can even be recrystallized from water.[5a] Unusually stable organo-transition metal cations which have no exact metal-free counterparts include the ferrocenylcarbinyl[7] and π-cyclobutadienylcarbinyltricarbonyliron[8] ions and the ion derived from di-μ-chloro-(4-methoxybut-2-enyl)-dipalladium(II) by loss of methoxide ion (**5**).[9]

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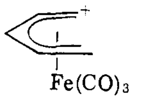

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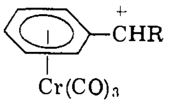
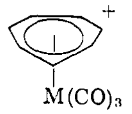
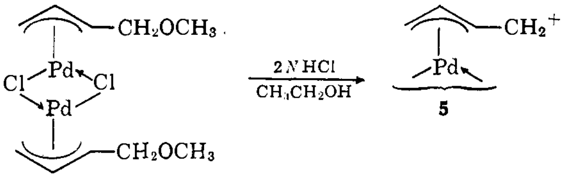


3, R = H, C_6H_5



4, M = Cr, Mo, W

All of these ions possess organic ligands with fully conjugated π-electron systems in which, at least conceivably, all carbons can be bonded directly to the metal atom.[10] The 7-norbornadienyltricarbonyliron cation (**6**) is a homoconjugated ion in which the nominally positive carbon, C_7, cannot interact directly with iron. Stabilization of the 7-norbornadienyl cation (**7**) by homoallylic interaction of at least one pair of π electrons with C_7 has been demonstrated by solvolysis rates[11] and direct observation of cation **7** by nmr spectroscopy.[12,13] Thus, it was of interest to see whether the tricarbonyliron group would stabilize the 7-norbornadienyl cation as it does allyl and pentadienyl cations.



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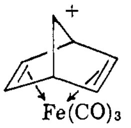

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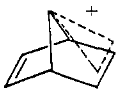

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Synthesis

Our initial goal was the synthesis of a 7-substituted norbornadienetricarbonyliron derivative which could serve as a precursor for cation **6**. Three 7-substituted norbornadienetricarbonyliron compounds, the *t*-butoxy,[14a] acetoxy,[14b] and hydroxy[14c] derivatives, have

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(1) Reported in part at the 3rd International Symposium on Organometallic Chemistry, Munich, Germany, Aug 28–Sept 1, 1967.

(2) Taken from the thesis of D. F. Hunt submitted to the University of Massachusetts in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

(3) National Science Foundation Graduate Teaching Fellow, summer 1964; University of Massachusetts Graduate Fellow, 1965–1966.

(4) (a) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962); (b) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind.* (London), 836 (1964).

(5) (a) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960); (b) J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963), and references therein.

(6) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.* (Amsterdam), **4**, 324 (1965), and references therein.

(7) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3484 (1959), and subsequent papers.

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

(9) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963).

(10) Traylor has recently suggested that the iron atom does not interact directly with the carbinyl carbon in the ferrocenylcarbinyl cation and has presented evidence in favor of this proposal: T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967), and previous papers. For a recent presentation of the opposite view see M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1695 (1966); M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966).

(11) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(12) P. R. Story and M. Saunders, *ibid.*, **82**, 6199 (1960); **84**, 4876 (1962).

(13) Brown prefers a classical structure for this and the 7-*anti*-norbornenyl cation; *cf.* H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(14) (a) R. Pettit, G. F. Emerson, and J. E. Mahler, *J. Chem. Educ.*, **40**, 175 (1963); (b) R. L. Collins and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2332 (1963); (c) R. Pettit, *Advan. Organometal. Chem.*, **1**, 1 (1964).

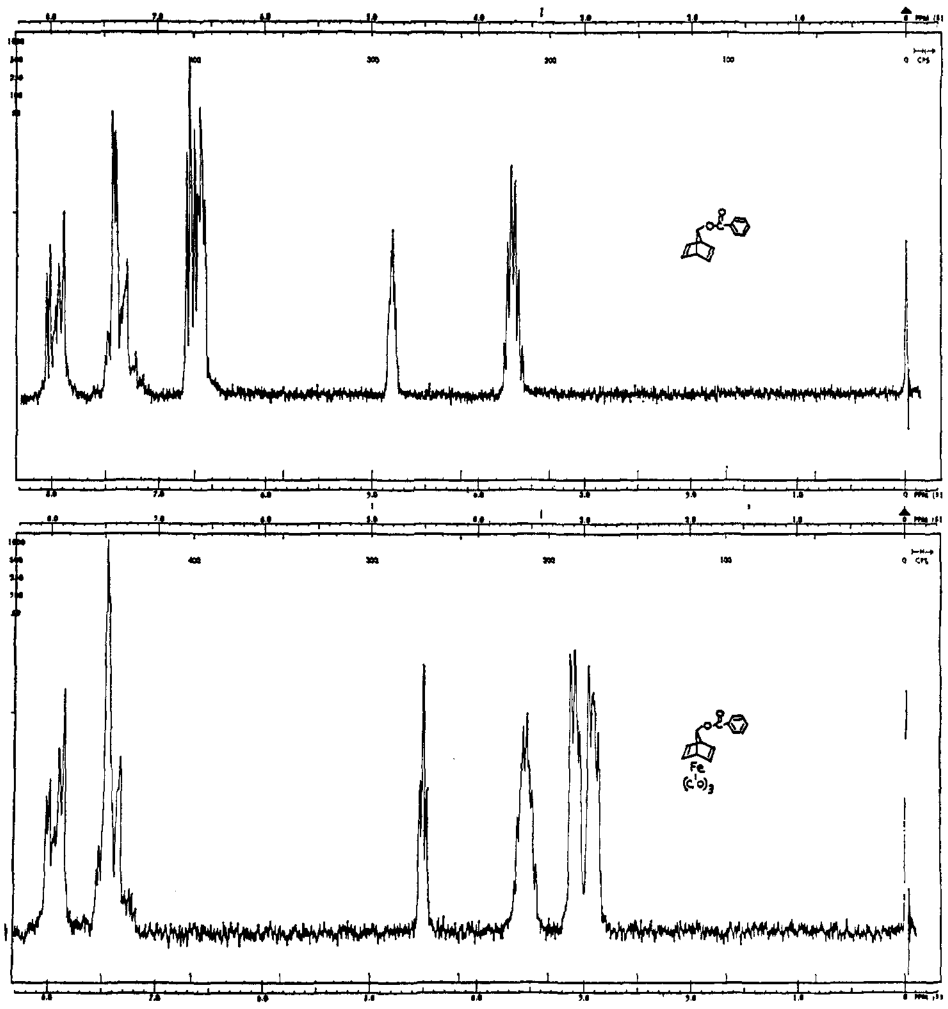
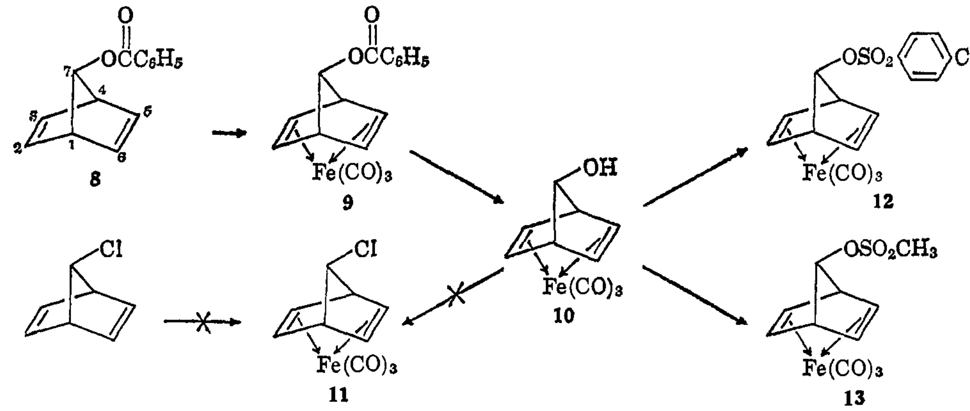


Figure 1. Nmr spectra of 7-benzoyloxynorbornadiene (**8**) (top) and 7-benzoyloxynorbornadienetricarbonyliron (**9**) (bottom).

been reported in the literature. The last of these, 7-norbornadienoltricarbonyliron (**10**), was chosen as our initial synthetic goal. Important synthetic transformations are summarized below in Scheme I.

Scheme I. Synthesis of Norbornadienetricarbonyliron Compounds



Treatment of 7-benzoyloxynorbornadiene (**8**)[15] with excess pentacarbonyliron in refluxing di-*n*-butyl ether gave 7-benzoyloxynorbornadienetricarbonyliron (**9**), isolated in 45% yield. This compound exhibits intense terminal carbonyl absorption at 2035 and 1965 cm^{-1} and strong ester carbonyl absorption at 1725 cm^{-1} in the infrared region. The nmr spectrum of **9** (see Figure 1) shows the aromatic hydrogens as two complex multiplets (5 H) from τ 2.0 to 2.8, H_7[16] as a triplet (1 H) at τ 5.50, the bridgehead hydrogens as an octet (2 H) at τ 6.45, and the *anti*- and *syn*-olefin hydrogens as two quartets (2 H each) at τ 6.91 and 7.08, respectively. This spectrum is compared with that of 7-benzoyloxynorbornadiene itself in Figure 1. Complexation to iron causes an upfield shift of the olefin protons of *ca.* 3.5

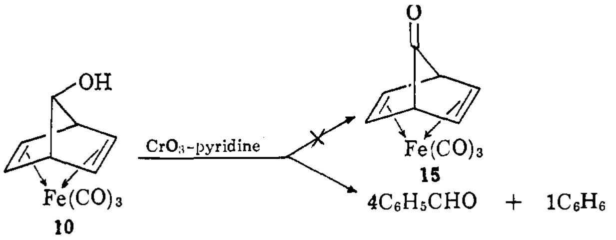
[15] H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964).

[16] The numbering system for the norbornadiene ring is shown in structure **9** in Scheme I.

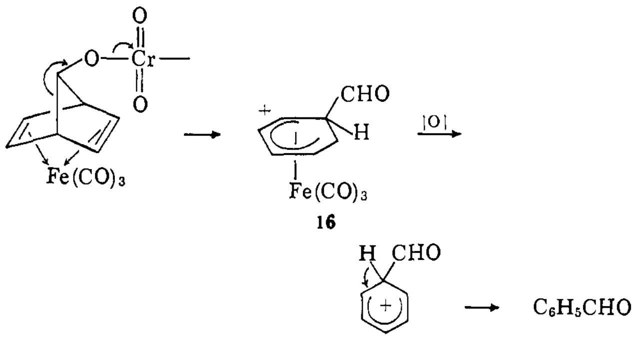
ppm. Such a shift is characteristic of olefin–transition-metal complexes[17] and leaves no doubt that the iron is bound to the diene unit. H_7 is shifted upfield by 0.32 ppm, and the bridgehead hydrogens undergo a smaller upfield shift. Similar shifts occur in the other tricarbonyliron derivatives prepared in this work. The long-range coupling, $J_{5,7}$, detected by Snyder and Franzus in uncomplexed 7-substituted norbornadienes[18] is not detectable in the spectra of this or other complexed norbornadienes. Treatment of **9** with a 1 M excess of phenylmagnesium bromide in ether afforded 7-norbornadienoltricarbonyliron (**10**) in 74% yield. This conversion was also effected smoothly and efficiently by alkali in aqueous alcohol.[19]

All attempts to convert alcohol **10** to the 7-chloro derivative **11** for solvolysis studies failed. Reagents used included thionyl chloride in pyridine or ethyl ether, triphenylphosphine dichloride,[20] and hydrogen chloride in sulfur dioxide. Preparation of **11** by direct combination of 7-chloronorbornadiene with iron carbonyls was also unsuccessful. Treatment of **10** with *p*-toluenesulfonyl chloride in pyridine[21] afforded a crystalline tosylate in 83% yield. The methanesulfonate (**13**) and 3,5-dinitrobenzoate (**14**) esters were prepared in a similar fashion; however attempts to prepare the methanesulfonate ester of 7-norbornadienol itself by the Tipson[21] and Hammond[22] procedures failed, probably because of the high reactivity of this ester.

In an attempt to prepare norbornadienonetricarbonyliron (**15**) we studied oxidation of alcohol **10**. Compound **15** was of interest as a derivative of and precursor to the yet unknown norbornadienones[23] and as a model for the 7-norbornadienyltricarbonyliron cation. Oxidation of **10** with chromium trioxide in pyridine[24] afforded, instead of **15**, benzaldehyde and benzene in approximately a 4:1 mole ratio.



Formation of benzaldehyde can be pictured as proceeding through a stable pentadienyltricarbonyliron cation (**16**) formed by fragmentation of the intermediate chromate ester.



Presence of manganous ions, which are reported to suppress C–C bond cleavage in chromic acid oxidations,[25] had no apparent effect on the course of this reaction, however. Benzene may be a decomposition product of **15**, but no direct evidence for norbornadienone formation by the action of CrO_3–pyridine or several other oxidizing agents on **10** has been observed. Oxidation of 7-norbornadienol itself with chromium trioxide in pyridine produced benzaldehyde and benzene as well, but in roughly a 1:3 mole ratio.

Attempted Generation of Cation 6

Treatment of norbornadienetricarbonyliron[26] in methylene chloride or nitromethane with triphenylmethyl fluoroborate[27] gives a dramatic color change from yellow to black. This observation must be attributed to formation of a charge-transfer complex, since hydrolysis of the reaction mixture gave only **17** and triphenylcarbinol. Treatment of 7-norbornadienoltricarbonyliron (**10**) in liquid sulfur dioxide at −60° with antimony pentafluoride and fluorosulfonic acid[28] changed the color of the solution from deep red to pale yellow green. This solution gave a complex nmr spectrum in which all signals had shifted downfield and a broad signal near τ 0.0, which might be caused by OH_2^+ hydrogens,[29] appeared. Quenching of this solution in cold methanol regenerates only starting alcohol; thus, extensive C_7–O bond cleavage does not occur.

Intramolecular Hydrogen Bonding in 10

Several workers have noted that 7-norbornadienol (**18**) can form an unusually strong intramolecular hydrogen bond.[30] We have studied dilute solutions of **18** and its tricarbonyliron derivative **10** in carbon tetrachloride by infrared spectroscopy. As can be seen from the data in Table I, $\Delta\nu$ is much smaller for **10** than it is for **18**, implying that **10** forms a much weaker intramolecular hydrogen bond.[31,32] In agreement

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[17] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

[18] E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964). This coupling was the basis of assignment of the *syn*- and *anti*-olefin hydrogen signals by Snyder and Franzus. Lacking this guide in the complexed dienes, we have assigned the signal at higher field to the *syn*-hydrogens in analogy to uncomplexed norbornadienes.

[19] Direct combination of 7-norbornadienol and iron carbonyls gave no **10**.

[20] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

[21] R. S. Tipson, *J. Org. Chem.*, **9**, 239 (1944).

[22] J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3443 (1953).

[23] Norbornadienones decompose spontaneously to arenes and carbon monoxide at room temperature or above; *cf.* C. F. H. Allen, *Chem. Rev.*, **62**, 653 (1962), and P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Am. Chem. Soc.*, **86**, 4211 (1964).

[24] This reagent has been used successfully to oxidize a dienoltricarbonyliron complex to the corresponding ketone; *cf.* J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

[25] J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, **78**, 306 (1956); J. J. Cawley and F. H. Westheimer, *ibid.*, **85**, 1771 (1963).

[26] R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *Chem. Ind.* (London), 1592 (1958).

[27] H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

[28] G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).

[29] G. A. Olah and E. Namanworth, *ibid.*, **88**, 5327 (1966); G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

[30] R. Picolini, unpublished work quoted in ref 11 and R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

[31] For a review of infrared studies of intramolecular hydrogen bonding see M. Tichy in "Advances in Organic Chemistry: Methods and Results," Vol. 5, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 115.

[32] During the course of this work we learned that R. Pettit, D. A. K. Jones, and G. F. Emerson had studied these alcohols and obtained results similar to ours: personal communication from G. F. Emerson.

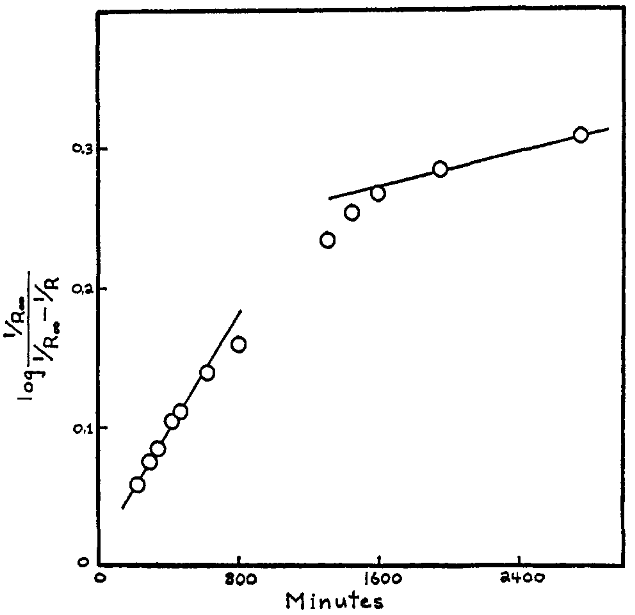


Figure 2. Solvolysis of 7-tosyloxynorbornadienetricarbonyliron (**12**). The slope of the initial line corresponds to a first-order rate constant of 7.7 × 10^{-6} sec^{-1} while the line drawn through the last three points gives a rate constant of 1.1 × 10^{-6} sec^{-1}.

with this, the relative intensities of the O–H stretching bands suggest that **18** exists almost completely in the hydrogen-bonded form in dilute carbon tetrachloride solution, while the nonhydrogen-bonded form of **10** predominates under the same conditions.

Table I. O–H Stretching Frequencies in Dilute CCl_4 Solution[a]

Compd	Free OH, cm^{-1}	H Bonded OH, cm^{-1}	Δ, cm^{-1}	Rel intensity free:H bonded
18	3628	3555	73	1:9
10	3628	3582	46	3:2

[a] Values are the average of three separate determinations.

Solvolysis Experiments

We undertook a study of the solvolysis rates of **12** and **13** in 80% aqueous acetone in order to assess the relative stabilities of cations **6** and **7**. The yellow color of the iron derivatives in aqueous acetone prevented accurate determination of titration end points using visual acid–base indicators, so the conductometric method[33] was used to follow the reactions. The rate constant data are presented in Table II.

Several anomalies quickly became apparent when the solvolyses of the two organometallic compounds were attempted. The rates were sensitive to the presence of air; thus when nondegassed solvents were used, straight-line, first-order plots corresponding to rate constants about a factor of 10 larger than those listed in Table II were observed. These solvolysis mixtures darkened considerably, and an orange precipitate formed in the conductance cell. When degassed solvents were used and precautions were taken to exclude air from the cell, discoloration did not occur. However, the reaction rates decreased noticeably, as shown in Figure 2, after about 30% of the theoretical acid had been liberated. The tosylate required *ca.* 48 hr to liberate 50% of the calculated acid, but when this solution was exposed to air, the rest of the calculated acid was produced in a few hours.

Table II. Reaction Rates in 80% Aqueous Acetone

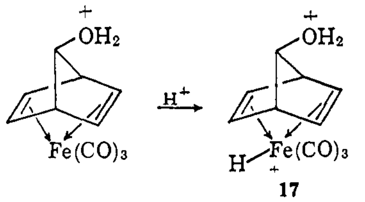
Compound	Temp, °C	k_1, sec^{-1}
7-Norbornadienyl chloride	25	$(1.33 \pm 0.1) \times 10^{-3}$ [a–c]
	25	$(1.30 \pm 0.1) \times 10^{-3}$
	25	$(1.37 \pm 0.1) \times 10^{-3}$
	35	$(2.91 \pm 0.2) \times 10^{-3}$
	50	$(9.2 \pm 0.3) \times 10^{-3}$
	50	$(9.8 \pm 0.3) \times 10^{-3}$
	50	$(9.5 \pm 0.3) \times 10^{-3}$
12	25	$(7.7 \pm 0.4) \times 10^{-6}$ [d,f]
		$(1.1 \pm 0.4) \times 10^{-6}$ [e,f]
13	25	$(9.5 \pm 0.4) \times 10^{-6}$ [d,f]

[a] Winstein and Ordronneau[11] report a rate of $(6.12 \pm 0.8) \times 10^{-4}$ sec^{-1} for this compound under the same conditions. Our value, obtained both by conductometric and titrimetric methods using vpc-purified norbornadienyl chloride and carefully purified acetone (see Experimental Section), is higher by a factor of 2. The discrepancy is too small to affect any conclusions drawn here, but is larger than experimental error. [b] A rate constant of $(1.1 \pm 0.1) \times 10^{-3}$ sec^{-1} was determined titrimetrically. [c] We calculate $H^{\ddagger} = 15 \pm 1.5$ kcal/mol and $S^{\ddagger} = -22 \pm 4$ eu. [d] Initial rate. [e] Rate after 40% of the theoretical acid was liberated. [f] In degassed solvents.

A study of the solvolysis products showed that none of the expected product, 7-norbornadienoltricarbonyliron (**10**), was produced. Direct analysis of the solvolysis mixture by thin layer chromatography showed, in addition to unreacted tosylate, only 7-norbornadienol and an unidentified yellow-orange compound which is probably organometallic. Attempted preparative work-up of the solvolysis mixtures resulted in extensive decomposition as evidenced by tlc. Unreacted tosylate was the only compound which could be isolated in a pure form. Solvolysis in the presence of excess sodium carbonate gave similar results.

Discussion

Protonation of alcohol **10** to give an oxonium ion without C–O bond cleavage is characteristic of alcohols which cannot give stable carbonium ions,[29] and contrasts with that of 7-norbornadienyl chloride which gives the stable 7-norbornadienyl cation when treated with silver fluoroborate in liquid sulfur dioxide.[12] Interpretation of this experiment is complicated, however, by possible protonation at iron[34] to give a dication **17** which would be less likely to undergo C_7–O bond cleavage.



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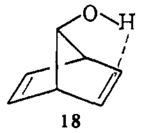
[33] V. J. Shiner and C. J. Verbanic, *J. Am. Chem. Soc.*, **79**, 369 (1957); W. M. Schubert and R. G. Minton, *ibid.*, **82**, 6188 (1960).

[34] Norbornadienetricarbonyliron undergoes protonation at iron in fluorosulfonic acid–liquid sulfur dioxide to give a yellow-green solution with an nmr signal at τ 17.3: D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *ibid.*, **89**, 6387 (1967). No high-field signal is observed in the case of **10**; however, this could be due to rapid exchange of the proton on iron with excess fluorosulfonic acid.

Extensive C_1–C_7 bond cleavage in oxidation of 7-norbornadienoltricarbonyliron cannot be taken as evidence for instability of ketone **15**, and indirectly cation **6**, for the striking stability expected of the possible intermediate **16** could itself account for the course of this reaction.

Our infrared data show that the hydrogen bond in 7-norbornadienol (**18**) is considerably stronger than that in its tricarbonyliron derivative **19**. Owing to iron–carbon bonding, π-electron density in **19** is probably greatest between the *endo* side of norbornadiene and iron, leaving that available for hydrogen bonding on the *exo* side severely reduced.



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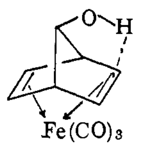

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Smooth saponification of 7-benzoyloxynorbornadienetricarbonyliron is significant in view of Story's report that saponification of 7-acetoxynorbornadiene gave no 7-norbornadienol.[35] Failure of Story's reaction may have been caused by *endo* attack of hydroxide ion at one of the olefinic carbons. Several workers have reported that nucleophiles attack 7-substituted norbornadienes in this way to give tricyclic products.[13,36] The tricarbonyliron ester should not behave in a similar fashion because *endo* attack at C_2 would require breaking of an iron–carbon bond and would be sterically inhibited by the tricarbonyliron group. The reluctance of the complexed alcohol **10** to undergo nucleophilic substitutions is also consistent with noninvolvement of the π electrons.

Solvolysis experiments are also in accord with this picture. The initial relatively rapid reaction (see Figure 2) is almost certainly caused by oxidative decomposition of the complex with production of acid. More rapid reaction of the mesylate than the tosylate is inconsistent with a solvolysis mechanism,[37] and none of the expected solvolysis product **10** could be detected. Depletion of residual oxygen in the system would cause the rate of acid production to decrease as is observed. Thus, we consider the slower rates to be more characteristic of solvolysis in a truly oxygen-free environment. The actual solvolysis rate may be, of course, much slower than this.[38] Formation of 7-norbornadienol (**18**) suggested that rate-determining dissociation of the iron complex to give 7-tosyloxynorbornadiene might be occurring. This mechanism was tested by solvolyzing **12** in the presence of excess norbornadiene to trap any Fe(CO)$_3$ species. However, no norbornadienetricarbonyliron could be detected in the products.[39]

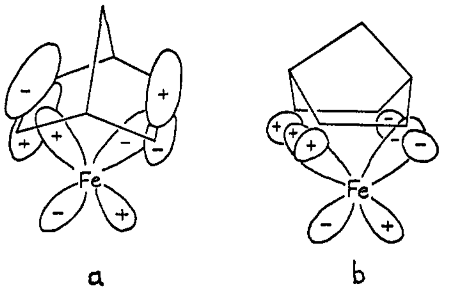
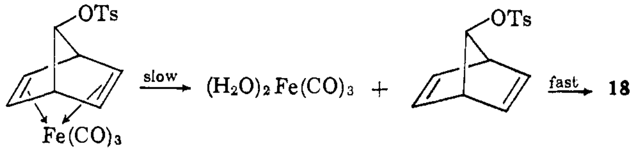


Figure 3. Iron–carbon bonding in norbornadienetricarbonyliron: (a) forward coordination, (b) back coordination (lobes of the antibonding π orbital which lie on the *exo* side of the norbornadiene ligand are not shown).

Estimates of the relative solvolysis rates of tosylates and chlorides give values for $k_{\mathrm{Ts}}/k_{\mathrm{Cl}}$ of 700 to 3500.[40] Using a value of 1000 we can estimate a solvolysis rate constant of 1.33 sec^{-1} for solvolysis of 7-tosyloxynorbornadiene in 80% aqueous acetone at 25°. Since the maximum possible rate constant for the tricarbonyliron tosylate is *ca.* 1×10^{-6}, *the tricarbonyliron group decreases the solvolysis rate by a minimum factor of* 10^6. Clearly, in contrast to all other known cases, the 7-norbornadienyl carbonium ion is destabilized by the transition-metal group.



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Using the scheme suggested originally by Dewar for silver ion–olefin complexes[41] and applied to dienetricarbonyliron complexes primarily by Pettit,[14a] iron–carbon bonding in norbornadienetricarbonyliron complexes can be pictured as arising by two processes. Electrons in bonding π orbitals on the diene are donated to unoccupied d orbitals on iron (forward donation), and electrons are donated back to the diene's antibonding π orbitals from occupied d orbitals on iron (back donation) as pictured in Figure 3. Electron density in the diene's bonding π orbitals is decreased, and that in the antibonding π orbitals is increased, but relatively little net charge transfer occurs. The π-electron clouds of norbornadiene will be polarized so that a disproportionate amount of electron density is situated between the ligand and iron, leaving that on the *exo* side of the ligand reduced.

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(35) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(36) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966); G. W. Klumpp and F. Bickelhaupt, *Tetrahedron Letters*, 865 (1966).

(37) Isopropyl tosylate solvolyzes at roughly twice the rate of isopropyl mesylate in water at 30°: K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *Can. J Chem.*, **38**, 1505 (1958). *p*-Toluenesulfonic acid (pK_a = −1.3) is a stronger acid than methanesulfonic acid (pK_a = −0.6); *cf.* J. Berkowitz and E. Grunwald, *J. Am. Chem. Soc.*, **83**, 2956 (1961), and K. N. Bascome and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(38) Professor Joseph Landesberg at Adelphi University has also prepared tosylate **12** and observed that its oxidation is more rapid than solvolysis in aqueous ethanol and acetic acid: personal communication from Professor Landesberg.

(39) Chromium and molybdenum tetracarbonyl species from the dissociation of 7-chloronorbornadienetetracarbonylchromium and -molybdenum in 80% aqueous acetone have been trapped successfully in this fashion: D. F. Hunt, C. P. Lillya, and M. D. Rausch, unpublished work.

(40) Isopropyl tosylate solvolyzes faster than isopropyl chloride in 80% aqueous ethanol at 50° by a factor of 3500: A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 82. Use of Swain and Lohmann's leaving group constant, *L*, with γ = 1.58 gives a ratio of 3600; see C. G. Swain and K. H. Lohmann as quoted by E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, pp 164–165. Calculations based on data from J. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953), and J. Hine and D. E. Lee, *ibid.*, **73**, 22 (1951), give a ratio of 700:1 for benzyl tosylate and chloride in 50% aqueous ethanol at 30°.

(41) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C79 (1951).


a. b.

Figure 4. Homoallylic bonding in the 7-norbornadienyl cation (view from above C_7): (a) overlap of an orbital at C_7 with a bonding π orbital, (b) symmetry-forbidden interaction between C_7 and an antibonding π orbital.

We can define destabilization of an organic cation, R^+, by an attached transition metal, M, in terms of eq 1 and 2 as $K_1 > K_2$.

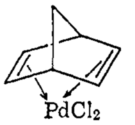
$$\text{R-X} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{R}^+ + \text{X}^- \qquad (1)$$

$$\text{M-R-X} \underset{}{\overset{K_2}{\rightleftharpoons}} \text{M-R}^+ + \text{X}^- \qquad (2)$$

Destabilization could result from a decrease in the M-R bond strength on going from M-R-X to $M\text{-}R^+$ or from interdiction of a stabilization mechanism which operates in R^+ owing to the requirements of M-R bonding. It seems clear that the 7-norbornadienyl cation derives most of its unusual stability through homoallylic interaction of the π electrons of one of its double bonds with C_7.[12,42] Interaction between the bonding π orbitals and C_7 (Figure 4a) should be considerably reduced owing to the reduction of electron density in this orbital on the *exo* side of the ligand. Population of the antibonding π orbitals by back coordination should not help to stabilize positive charge at C_7 since the overlap required for this is symmetry forbidden (Figure 4).[43] Thus, the simple Dewar-type bonding picture accommodates our results nicely.

Several other possible explanations for the low solvolytic reactivity of **12** should be considered here. A field-induced[44] rate retardation caused by interaction of the dienetricarbonyliron dipole[45] with the developing C_7-O dipole in the transition state may contribute to the rate retardation. A comparison of Streitwieser's data on polar retardation of solvolysis rates[46] with the expected moment and distance for **12** suggests that this effect will be small compared to a factor of 10^6, however. Enhancement of the electron-withdrawing inductive effect of the double bonds[47] by complexation to iron, on the other hand, does not seem likely. This would require that the olefin carbons become electrically positive in the complex, which is inconsistent with the high-field nmr signals of the olefin hydrogens.

Another possibility is that complex formation narrows the C_1-C_7-C_4 bond angle which destabilizes the 7 cation. Dependence of solvolysis rates on bond angle is well authenticated.[48] Values for this bond angle in norbornadiene and norbornadiene transition metal complexes are listed in Table III. No limits of confidence are available for the work in footnote *d*, Table III, so it is not possible to know how much weight to give this value. The other four angles are close in value; however, the angle in norbornadienepalladium dichloride[49] is larger than that in norbornadiene[50] by slightly more than three standard deviations. Thus, the angle at C_7 does not decrease on complexation and may even increase.[50a]



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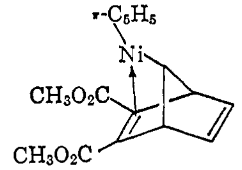

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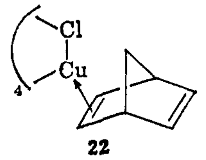

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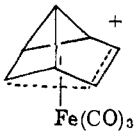
Table III. Bond Angle at C_7 in Norbornadienes

Compound	Angle at C_7, deg	σ, deg	Method	Ref
20	94.5[a]	0.4	X-ray	49
21	94.8	1.1	X-ray	*b*
22	93.3	0.6	X-ray	*c*
Norbornadiene	92.0	0.8	Elect. diff	50
	96.7		Elect. diff	*d*

[a] Calculated from atom position parameters in ref 49. [b] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963). [c] N. C. Baenziger, H. L. Haight, and J. R. Doyle, *ibid.*, **3**, 1535 (1964). [d] V. Schomaker and W. C. Hamilton as quoted by W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

Homoallylic interaction of π electrons with C_7 to stabilize the 7-norbornadienyltricarbonyliron cation implies resonance structure **23**, a homoallyltricarbonyliron cation. We have attempted to generate the closely related cation **24** by protonation of norbornadienetricarbonyliron. Unlike conjugated dienetricarbonyliron compounds which protonate on carbon to give allyltricarbonyliron cations,[4] the norbornadiene derivative in strong acids acquires a proton at iron.[34] Clearly, homoallyltricarbonyliron cations do not possess the same unusual stability as do their conjugated analogs. This observation is in accord with the apparent reluctance of the π electrons of norbornadienetricarbonyliron compounds to participate in reactions at C_7.



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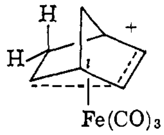

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(42) R. Hoffmann, *J. Am. Chem. Soc.*, 86, 1259 (1964); *J. Chem. Phys.* 40, 2480 (1964).

(43) Brown's classical 7-norbornyl cation,[13] in which C_7 interacts with only one end of the double bond, would permit interaction with the antibonding orbital as far as symmetry is concerned. Nevertheless, this interaction should be relatively unimportant because of the polarization of the antibonding orbital toward iron, its high energy, and its low electron density. We do not feel that our results can be interpreted either in favor of or against the classical 7-norbornadienyl cation.

(44) *Cf.* R. K. Bly and R. S. Bly, *J. Org. Chem.*, 31, 1577 (1966). We are indebted for this suggestion to Profesor Bly.

(45) Butadienetricarbonyliron has a dipole moment of 2.15 D; its positive end is believed to be the diene: H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1156 (1962); 46, 1558 (1963).

(46) A. Streitwieser, Jr., ref 40, pp 122–125.

(47) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(48) H. C. Brown, *J. Chem. Soc.*, 1248 (1956); P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961); C. S. Foote, *ibid.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).

(49) N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Acta Cryst.*, **18**, 924 (1965).

(50) Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Japan*, 40, 1552 (1967).

(50a) NOTE ADDED IN PROOF. Professor L. F. Dahl has undertaken the X-ray diffraction study of compounds **8** and **9** to provide further information on this point.

Experimental Section

Melting points were determined using a Mel-Temp[51] apparatus and are uncorrected. Infrared spectra were recorded using a Beckman IR-10 instrument and were calibrated with the 1603-cm^{-1} polystyrene band. Nmr data were obtained at 60 Mc with a Varian Associates A-60 spectrometer. Tetramethylsilane was employed as an internal standard, and signal positions are reported in τ units. All microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

7-Benzoyloxynorbornadienetricarbonyliron (9). Iron pentacarbonyl (90 ml, 0.68 mol) and 7-benzoyloxynorbornadiene (**8**) (34 g, 0.16 mol) were heated under nitrogen at reflux in 200 ml of di-*n*-butyl ether for 15 hr. Evaporation of the solvent at 40° (0.1 mm) left a dark solid which was dissolved in benzene and chromatographed on alumina. The first band gave a yellow-orange solid which contained **8**, **9**, and small amounts of di-*n*-butyl ether. Elution with acetone afforded two additional bands which gave a red oil and a yellow solid, respectively. Both of these products were formed in minor amounts and were not characterized further. Purification of the first band was accomplished by fractional sublimation. 7-Benzoyloxynorbornadiene and di-*n*-butyl ether were removed at 65° (0.1 mm); continued heating at 110° (0.1 mm) gave 25 g (45%) of **9** as yellow needles, mp 100–101° (under nitrogen).

In an alternative procedure, the crude products were dissolved in benzene and filtered through alumina packed in a large Büchner funnel. Evaporation of the filtrate followed by recrystallization of the residue from Skellysolve B at −78° gave pure **9**. The infrared spectrum showed ν (CCl_4) 2035, 1965, 1725, 1365, 1110, and 712 cm^{-1}. (See Figure 1 and discussion for nmr spectrum.)

Anal. Calcd for $C_{17}H_{12}O_5Fe$: C, 57.99; H, 3.44; Fe, 15.86. Found: C, 58.22; H, 3.41; Fe, 15.72.

7-Norbornadienoltricarbonyliron (10). a. Cleavage of 9 Using Phenylmagnesium Bromide. Phenylmagnesium bromide, prepared from bromobenzene (8.94 g, 57 mmol) and magnesium metal (1.38 g, 57 mg-atom) in 16 ml of anhydrous ether, was added slowly under nitrogen to a stirring solution of 7-benzoyloxynorbornadienetricarbonyliron (**9**) (8.0 g, 22.8 mmol) in 100 ml of anhydrous ether. The reaction mixture was allowed to stand at room temperature for 4 hr and was heated at reflux for an additional hour. The reaction mixture was poured into cold, saturated aqueous ammonium chloride, and the organic layer was separated and dried over magnesium sulfate. The solvent was then evaporated under reduced pressure, and the residue was taken up in benzene and chromatographed on alumina. Elution with benzene removed unreacted ester and small amounts of side products, and subsequent elution with ether afforded crude **10**. Sublimation at 70° (0.1 mm) gave 4.14 g (74%) of 7-norbornadienoltricarbonyliron (**10**) as dark yellow crystals. Recrystallization from methylene chloride–Skellysolve B at −78° followed by sublimation afforded an analytical sample as pale yellow needles, mp 95–96.5° (under nitrogen), ν (CCl_4) 3620, 3580, 3410, 2035, 1965, 1085, 1060 cm^{-1}; τ ($CDCl_3$) (relative intensity): 3.68 (1, broadened doublet, J = 7.5 Hz) H_7, 6.72 (2, septet) $H_{1,4}$, 6.98 and 7.08 (4, overlapping triplets) $H_{2,3,5,6}$, and *ca.* 8.0 (1, doublet J = 7.5 Hz) O*H*.

Anal. Calcd for $C_{10}H_8O_4Fe$: C, 48.43; H, 3.25. Found: C, 48.43; H, 2.85.

b. Saponification of 9. 7-Benzoyloxynorbornadienetricarbonyliron (**9**) (1.0 g, 3.0 mmol) was dissolved in a solution composed of 40 ml of 95% ethanol, 40 ml of ether, and 10 ml of 10% aqueous sodium hydroxide. Tlc analysis indicated that reaction was complete in 0.5 hr at room temperature. The reaction mixture was extracted with four 100-ml portions of ether, and the combined extracts were dried over anhydrous sodium sulfate. Evaporation of the dry extracts followed by recrystallization of the residue gave 0.51 g (70%) of **10**.

7-Tosyloxynorbornadienetricarbonyliron (12). 7-Norbornadienoltricarbonyliron (**10**) (1.0 g, 4.0 mmol) was added to a solution of *p*-toluenesulfonyl chloride (1.0 g, 5.25 mmol) in 5 ml of pyridine in a round-bottomed flask at −20°. The flask was tightly stoppered and allowed to stand for 24 hr at this temperature. Evaporation of pyridine at 0.1 mm left a yellow-brown solid which was taken up in methylene chloride. Pyridine hydrochloride was precipitated by addition of Skellysolve F to this solution and was separated by filtration. Cooling of the filtrate to −78° caused the tosylate to crystallize. The crude tosylate was further purified by filtration through Florisil in 2:1 benzene–ether. Evaporation of the filtrate gave 1.3 g (83%) of 7-tosyloxynorbornadienetricarbonyliron (**12**). Recrystallization from Skellysolve F–ether at −78° afforded an analytical sample as pale yellow needles, mp 120–121° dec (under nitrogen); ν ($CHCl_3$) 2040, 1975, 1370, 1190, 1180, 975 cm^{-1}; τ ($CDCl_3$) (relative intensity): 2.17 and 2.27 (4, multiplets) Ar–H, 5.90 (1, triplet) H_7, 6.55 (2, multiplet) $H_{1,4}$, 6.99 (2, triplet) $H_{2,3}$, 7.19 (2, triplet) $H_{5,6}$, and 7.50 (3, singlet) CH_3.

Anal. Calcd for $C_{17}H_{14}O_6S_6Fe$: C, 50.77; H, 3.51; S, 7.97; Fe, 13.89. Found: C, 50.54; H, 3.57; S, 7.99; Fe, 13.84.

7-Mesyloxynorbornadienetricarbonyliron (13). The mesylate derivative was prepared by a procedure identical with that described for preparation of the tosylate **12**. 7-Norbornadienoltricarbonyliron (1.0 g, 4.0 mmol) was converted to 0.65 g (50%) of mesylate **13**. Recrystallization from Skellysolve F–ether at −78° afforded an analytical sample as straw yellow needles which melted with decomposition at 92–92.5° under nitrogen, ν ($CHCl_3$) 2040, 1975, 1370, 1350, 1176, 971 cm^{-1}; τ ($CDCl_3$) (relative intensity): 6.75 (1, triplet) H_7, 6.38 (2, multiplet) $H_{1,4}$, 6.85 (2, triplet) $H_{2,3}$, 7.03 (5, multiplet) $H_{5,6}$ (SO_2CH_3).

Anal. Calcd for $C_{11}H_{10}O_6SFe$: C, 40.51; H, 3.09; S, 9.83; Fe, 17.13. Found: C, 40.46; H, 3.13; S, 10.16; Fe, 17.26.

7-(3,5-Dinitrobenzoyloxy)norbornadienetricarbonyliron (16). 7-Norbornadienoltricarbonyliron (**10**) (0.10 g, 0.40 mmol) and 3,5-dinitrobenzoyl chloride (0.10 g, 0.44 mmol) in 2 ml of dry pyridine were stirred in a tightly stoppered flask for 13 hr at room temperature. Evaporation of pyridine at 0.1 mm left an orange solid which was dissolved in benzene. The benzene solution was washed with 1 *N* hydrogen chloride and 1 *N* ammonium hydroxide and was dried over magnesium sulfate. Evaporation of benzene under reduced pressure left a dull orange solid which was recrystallized from ether–Skellysolve F at −78° to give 0.10 g (57%) of **16**, mp 144–144.5° dec (under nitrogen); ν ($CHCl_3$) 2040, 1975, 1740, 1655, 1354, 1275, and 1164 cm^{-1}; τ ($CDCl_3$) (relative intensity): 0.75 (1, triplet) H_{para}, 0.92 (2, doublet) H_{ortho}, 5.3 (1, triplet) H_7, 6.25 (2, multiplet) $H_{1,4}$, 6.77 (2, triplet) $H_{2,3}$, 6.94 (2, triplet) $H_{5,6}$.

Anal. Calcd for $C_{17}H_{10}N_2O_9Fe$: C, 46.18; H, 2.28; N, 6.34; Fe, 12.63. Found: C, 46.12; H, 2.31; N, 6.36; Fe, 12.85.

7-Norbornadienyl Chloride.[11,52] A cold solution of thionyl chloride (19.8 g, 0.164 mol) in 25 ml of anhydrous ethyl ether was added dropwise over a period of 30 min to a stirring solution of 7-norbornadienol (**18**) in 25 ml of anhydrous ether maintained at −5°. The reaction mixture was allowed to warm to room temperature and then was heated on a steam bath until evolution of sulfur dioxide ceased (*ca.* 45 min). The reaction mixture was protected at all times from atmospheric moisture by a calcium chloride drying tube. Evaporation of the ether and distillation of the residue under reduced pressure gave 15.2 g (84%) of 7-norbornadienyl chloride, bp 79–82° (63 mm). Further purification was accomplished by preparative vpc at 100° using a 20 ft × 0.25 in. column packed with diisodecyl phthalate (20%) on Chromosorb P (60–80 mesh).

Oxidation of 7-Norbornadienoltricarbonyliron (10) and 7-Norbornadienol (18). 7-Norbornadienoltricarbonyliron (0.5 g, 2 mmol) was added to a slurry of chromium trioxide (0.6 g, 5 mmol) in 11 ml of pyridine, and the mixture was allowed to stand under nitrogen at room temperature for 5 days. Distillation of the reaction mixture to dryness left an inorganic residue. Benzaldehyde was detected in the distillate by nmr and ir spectroscopy and by means of thin layer chromatography.

Direct vpc analysis of the reaction mixture or analysis of the distillate at 100° on a 7 ft × $^3/_8$ in. column packed with 20% diisodecyl phthalate on Chromosorb W showed that both benzaldehyde and benzene were formed in the approximate mole ratio of 4:1. A similar vpc analysis indicated that oxidation of 7-norbornadienol (**18**) under the same conditions produced benzaldehyde and benzene in a mole ratio of 1:3. The proportion of benzene may be higher in this case, however, since the starting samples of norbornadienol always contained small amounts of benzaldehyde.

Treatment of 7-Norbornadienoltricarbonyliron with SbF_5–FSO_3H. 7-Norbornadienoltricarbonyliron (**10**) (0.1 g) was added to 0.5 ml of liquid sulfur dioxide at −78° to give a deep red solution containing some undissolved **10**. A second cold solution of equal weights of fluorosulfonic acid and antimony pentafluoride in liquid sulfur dioxide was added dropwise to the first until **10** had completely dissolved and the color of the solution had changed to a pale yellow green. The nmr spectrum of this solution was recorded at low temperatures in a sealed tube with TMS as an internal standard.

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(51) Laboratory Devices, Cambridge, Mass.

(52) We are indebted to Professor Louis A. Carpino for furnishing us with the details of the reaction with thionyl chloride.

This solution was poured into methanol containing sodium carbonate at −78°. After the methanol solution had warmed to room temperature, it was poured into water and extracted with several portions of ethyl ether. The combined extracts were washed with 10% sodium carbonate and dried over sodium sulfate. Evaporation of the extracts left a yellow solid which was identified as **10** by means of tlc and nmr spectroscopy. No traces of 7-methoxynorbornadienetricarbonyliron could be detected.

Hydrogen Bonding Study of 10 and 18. Spectra were recorded on a Perkin-Elmer Model 237B grating infrared spectrometer, by scanning the region between 3800 and 3000 cm^{-1} at a rate of 340 cm^{-1}/min. The matched silica cells (Precision Cells, Inc., Model S18-260) with a path length of 1 cm exhibited a broad absorption themselves at 3680 cm^{-1} (40% absorption at ν_{max}); however, a carbon tetrachloride *vs.* carbon tetrachloride spectrum gave a perfectly flat base line; the instrument response was good at 3680 cm^{-1} under these conditions. Concentrations of 0.0025–0.07 *M* were used. The spectra were calibrated with the 2851-cm^{-1} polystyrene absorption, and the reported values of ν_{max} are the average of three scans.

Kinetic Measurements. The reaction solvent, 80% aqueous acetone, was prepared by mixing four volumes of acetone with one volume of water at 20° by means of pipets calibrated for delivery at this temperature. Reagent grade acetone was dried over calcium sulfate, treated with potassium permanganate, and subsequently distilled;[24] distilled water was used without further treatment. The conductance of the solvent was always less than 2.5×10^{-5} ohm^{-1}. Both the acetone and water were degassed by five freeze–pump–thaw cycles and then stored under nitrogen, and all solvent transfers were carried out under a stream of nitrogen.

Rates were measured by a conductance method similar to that described by Schubert and Minton.[33] A Beckman[53] conductivity bridge, Model RC-18, operating at 1000 cps, was used to measure the resistance of the solvolysis mixtures. A Beckman[53] Model CEL-AOl conductivity cell (cell constant 0.1) with shiny platinum electrodes was equipped with a 29/26 inner joint. This cell fit into a small vessel, equipped with a 29/26 outer joint and two side arms with stopcocks for flushing with nitrogen, to form an air-tight conductivity cell of 100-ml capacity. All connections were made with shielded cable, and the shields were carefully grounded. The cell was immersed up to the joint in an insulated Sargent water bath, the temperature of which was controlled to within ±0.04° by a Sargent "Thermonitor." Conductance measurements on standard solutions in 80% aqueous acetone verified that the conductance varied in a linear fashion with HCl concentration below 10^{-3} *M* at 25, 35, and 50°. Similar results were obtained with standard solutions of *p*-toluenesulfonic acid. Tests with 7-benzoyloxynorbornadienetricarbonyliron (**9**) in 80% aqueous acetone showed that the presence of an organometallic compound over a period of several days did not change the resistance of the solution significantly.

Compounds to be solvolyzed were weighed to the nearest 0.1 mg and placed in the conductance cell which was evacuated and refilled with nitrogen several times. Following the addition of 5 ml of acetone under nitrogen, the solution was allowed to equilibrate in the water bath for 15 min. The remainder of the solvent, 75 ml of acetone and 20 ml of water, equilibrated in the water bath under nitrogen, was transferred to the conductance cell under nitrogen to start the reaction. The 7-norbornadienyl chloride solvolyses were followed for six half-lives while the solvolyses of the iron compounds were followed for somewhat longer than one half-life. In the latter cases the infinity resistance was reached only after the conductance cell was opened to the atmosphere. The infinity resistance measurements agreed with the initial values calculated from the initial weights within at least 8% even when considerable decomposition had occurred. The resistance data were handled using the first-order rate law in the following form

$$k = \frac{2.303}{t} \log \frac{A}{A - X} = \frac{2.303}{t} \log \frac{1/R_\infty}{(1/R_\infty) - (1/R_t)}$$

where A = concentration of RX at $t = 0$, concentration of HX at $t = \infty$; X = concentration of HX at time t; $1/R_\infty$ = conductance at $t = \infty$; and $1/R$ = conductance at time t. The rate constants for 7-norbornadienyl chloride were determined by a least-squares fit of the data while the rough rate constants for the iron compounds were determined by eye.

Product Studies. 7-Tosyloxynorbornadienetricarbonyliron (**12**) (1.0 g) was dissolved in 100 ml of 80% aqueous acetone and allowed to stand under nitrogen at room temperature for 15 hr. The initial pale yellow solution darkened substantially over this period and an orange precipitate formed. Gas evolution was observed throughout the reaction period. Tlc analysis (silica gel, 2:1 benzene–ethyl ether) of the solvolysis mixture at this time revealed considerable amounts of norbornadienol (**18**) and unreacted tosylate **12**, identified by comparison with authentic samples chromatographed alongside, and a third yellow component which had a slightly higher R_f than the expected complexed alcohol. No traces of complexed alcohol could be detected. Following the addition of water and sodium carbonate to the reaction mixture, it was extracted with ether. Evaporation of the extracts left a red oil which showed five spots on a thin layer chromatogram in addition to spots for norbornadienol and unreacted tosylate. The original third component had disappeared, and no traces of **10** were observed. Chromatography of the ether extracts from a 10-hr solvolysis run gave a sample of unreacted tosylate.

Trial product studies were also run in 50% aqueous acetone and, since the expected alcohol **10** was shown to be unstable in aqueous acetone in the presence of *p*-toluenesulfonic acid, in 80% aqueous acetone containing excess sodium carbonate. The results obtained in these experiments, however, were similar to those described above.

Acknowledgments. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants in partial support of this work. We are grateful to Mr. Robert E. Graf for his assistance in carrying out the saponification of **9**.

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[53] Beckman Instruments Ind., Cedar Grove Operations, Cedar Grove, N. J. (formerly Industrial Instruments, Ind.).