

A Route from Olefins to Cyclopentanones Induced by Iron Carbonyl Photolysis^{1,2}

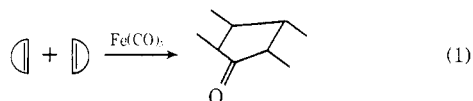
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Abstract: The mechanism by which pentacarbonyliron(0) photolytically couples olefins to carbon monoxide is discussed. The proposed mechanism involves trapping of photolytically generated Fe(CO)₄ followed by a reversible loss of carbon monoxide to vacate a coordination site on the monoolefintetracarbonyliron(0) intermediate. This tetracoordinate species adds a second olefin in an equilibrium step. Cyclization to a metallocycle followed by migratory insertion and product elimination are proposed.

Since Mond³ reported Ni(CO)₄ and began investigating the interaction between metal carbonyls and "organic bodies," organometallic reactions have received increasing attention. Several synthetically useful processes such as the oxo process⁴ and alkyl halide transformations with tetracarbonylferrate(-II)⁵ have been extensively studied. Recently Osborn⁶ has reported metallocycle and acyl intermediates found during dimerization of norbornadiene.

Our investigations of iron carbonyl induced olefin dimerization coupled to carbonyl insertion have led to a synthetically useful process,^{1,2} which is illustrated by reaction 1. While the reaction is general, strained ole-



fins are most susceptible to coupling. In the following discussion we propose a detailed mechanism for the photochemical process which is consistent with previously reported synthetic data and additional data presented herein.

Results and Discussion

Although the carbonyl insertion-cyclization reaction occurs both thermally and photochemically, the photochemical reaction permits a more detailed mechanistic investigation. In the absence of conflicting data, we assume that the thermal and photochemical mechanisms of ketone formation are similar although their initiation steps differ. Photochemical results are consistent with the proposed mechanism given in Scheme I; step 6 is thought to be a composite of at least three separate steps as discussed later in this communication. Selected olefin reagents and products are shown in Table I. A general feature which we have imposed upon the proposed mechanism is the 16-18 electron

(1) (a) For a preliminary account of this work, see J. Mantzaris and E. Weissberger, *Tetrahedron Lett.*, **28**, 2815 (1972). (b) Experimental details and nmr assignments of prepared compounds are reported in J. Mantzaris and E. Weissberger, *J. Amer. Chem. Soc.*, **96**, 726 (1974). (c) J. Mantzaris and E. Weissberger, *J. Org. Chem.*, **39**, 726 (1974).

(2) Taken in part from the Ph.D. Thesis of J. Mantzaris, Wesleyan University, Aug 1973.

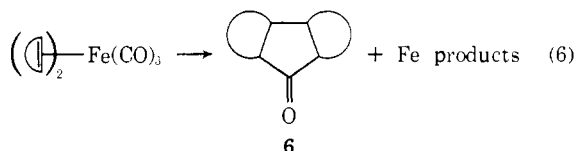
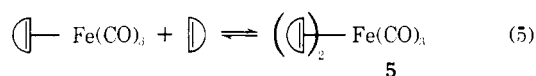
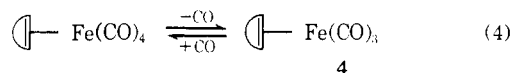
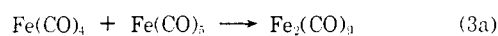
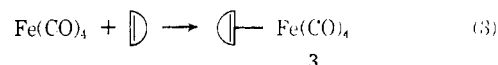
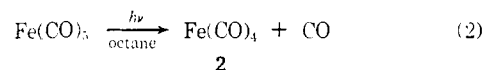
(3) L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, 749 (1890).

(4) A. J. Chalk and J. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968).

(5) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Amer. Chem. Soc.*, **94**, 1788 (1972).

(6) A. R. Fraser, P. H. Bird, S. A. Gegman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 579 (1973).

Scheme I



rule.⁷ Thus when appropriate, we assume the stability of 18-electron systems and kinetic reactivity of 16-electron systems.

The first mechanistic step depicted in eq 2 of Scheme I is the formation of the highly reactive Fe(CO)₄ intermediate 2. Evidence for the photolytic generation of 2 has been obtained⁸ from low-temperature studies. In general, M(CO)_n (M = Fe, Cr, Mo, W, Ni) systems have been shown to yield M(CO)_{n-1} species on photolysis.⁹

Tetracarbonyliron(0) is efficiently trapped by olefins yielding the monoolefin complex 3 as shown in eq 3. Formation of this intermediate is supported by the observation that in the absence of olefin, photolysis of Fe(CO)₅ in *n*-octane, saturated with either nitrogen or carbon monoxide, yields almost immediately insoluble Fe₂(CO)₉, whereas little or no Fe₂(CO)₉ is detected in the presence of olefins under similar conditions.

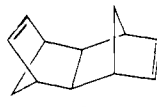
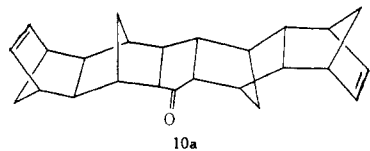
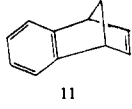
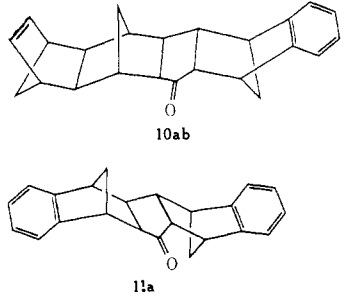
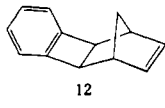
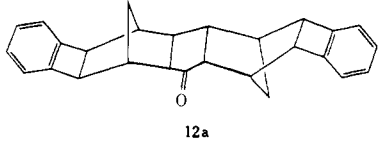
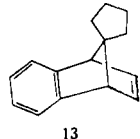
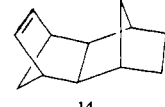
Sterically hindered olefins such as 13 and 14 or unstrained olefins such as cyclohexene are unreactive in the sense that they do not proceed to cyclopentanone products in appreciable yields. Nevertheless, these olefins do inhibit the formation of Fe₂(CO)₉ during photolysis under an N₂ atmosphere. Photolysis of Fe(CO)₅ may be carried out in the presence of 14 for 1 hr without formation of appreciable Fe₂(CO)₉ or ke-

(7) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

(8) I. W. Stolz, G. G. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **85**, 1013 (1963).

(9) M. F. A. El-Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, **1**, 525 (1962).

Table I. Selected^{1,2} Reagent Olefins and Corresponding Products

Reagent	Product
	
	
	
	
	

tonic products. If at the end of this period reactive olefin (**10** or **11**) is added in the dark, significant amounts of ketone (**10a** or **11a**) appear. (See experiments C and D, Table II.) Clearly, **14** is trapping a reactive species in a reaction far more efficient than $\text{Fe}_2(\text{CO})_9$ formation. When $\text{Fe}(\text{CO})_5$ is photolyzed in the presence of reactive olefin **10** under 1 atm of CO, no

Table II. Formation of Monoolefintetracarbonyliron(0) Intermediates^{a,b}

Expt	Olefin I ^c	Olefin II ^c	Ketone products ^c	Rel yield	% yield
A	10	11	10a	0.01	
			11a	2	
			10ab	1	
B	11	10	10a	0.01	
			11a	2	
			10ab	1	
C	14	10	10a		5
D	14	11	11a		25
E	Cyclohexene (excess)	11	11a		12
F ^d	Cyclohexene	11	11a		1-2
G ^d	13	11	1a		1

^a Yields were corrected for slow coupling of **11** to **11a**. ^b 0.1 M olefin and 0.05 M $\text{Fe}(\text{CO})_5$ in *n*-octane. ^c See Table I for structures corresponding to numbers. ^d $\text{Fe}_2(\text{CO})_9$ formed.

product is formed. However, if photolysis is ended after 1 hr and the solution is purged with N_2 , ketone appears. Conversely, if the photolyzed, CO saturated, solution is kept in the dark, neither ketone nor $\text{Fe}_2(\text{CO})_9$ appears, leading us to conclude that reaction 3 is irreversible. Similarly, $\text{Fe}_2(\text{CO})_9$ does not appear when photolysis is interrupted in the presence of unreactive olefin **14**. Attempts to form ketone *via* $\text{Fe}_2(\text{CO})_9$ photolysis under N_2 met with minimal success.

These observations are amply explained by reactions 2, 3, and 4 of Scheme I. Reactive intermediate is generated in (2) and trapped in (3). In the absence of a trapping agent, $\text{Fe}_2(\text{CO})_9$ is formed according to (3a) or a related process.

When benzonorbornadiene (**11**) is the substrate, the rate of ketone formation under 1 atm of CO is reduced threefold compared with the rate under N_2 . Reversible step 4 is consistent with these semiquantitative data as it represents a reversible slow step in the reaction sequence. That the reaction is in fact being retarded at an intermediate stage by CO is indicated by photolysis interruption data cited above and by the increase in observed (glc) product yield from 13 to 22% upon purging in the dark a solution of **11** which has been photolyzed for 75 min. A similar inverse dependence is also noted for the thermal reaction; when *exo*-3,4-benzotricyclo[4.1.0^{2,5}]nona-3,7-diene (**12**) is heated with $\text{Fe}(\text{CO})_5$ in a closed system no dimer ketone is formed. However, heating the reaction mixture under an atmosphere of nitrogen in an open system gave the dimer ketone in 12% yield.

Trapping experiments indicate that the reaction shown in eq 5 is an equilibrium step in which olefin exchange occurs. This was demonstrated by performing a series of experiments in which $\text{Fe}(\text{CO})_5$ was photolyzed in the presence of olefin in *n*-octane while keeping the solution saturated with carbon monoxide. After 1 hr photolysis was ended, an equimolar amount of a second olefin was added and the solution was purged with nitrogen. The distribution of products formed during nitrogen purging is shown as experiments A and B in Table II.

The formation of the mixed ketone dimer **10ab** arises from reaction of the trapped monoolefin complex **4** with a second olefin. The fact that the final ratio of ketone **11a**/ketone **10ab** is the same regardless of the order of addition is indicative of olefin exchange in step 5 of the proposed mechanism. Furthermore, the yield of ketone **10a** is very low in experiments A and B suggesting that the binding constant of **10** is less than that of **11** in step 5. Indeed, assuming similar kinetics subsequent to step 5, the relative thermodynamic stabilities of the three possible bisolefintetracarbonyliron(0) complexes, **10-10**, **10-11**, and **11-11**, must be in the ratio of 0.01:1.0:2.0.

Additional evidence for equilibrium 5 is found in experiment E of Table II. Cyclohexene, which inhibits the formation of $\text{Fe}_2(\text{CO})_9$, less efficiently than more strained olefins, behaves similarly to monoene **14** in that it is not effectively coupled to form ketone. The concentration of the proposed reactive intermediate **4** depends upon the efficiency of trapping in eq 3 as well as the dissociation constant in eq 4. Experiments E and F confirm this conclusion. After photolysis of an approximately equimolar cyclohexene- $\text{Fe}(\text{CO})_5$ solu-

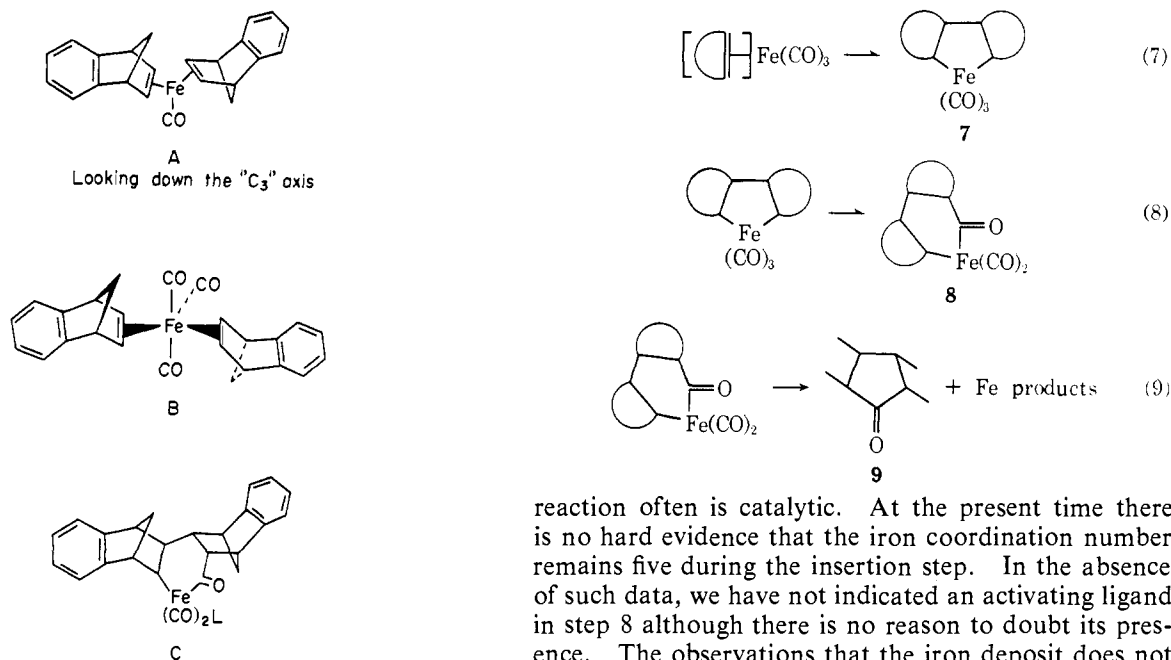


Figure 1. Structure of intermediates discussed in text.

tion, addition of **11** produced very little benzonorbornadiene ketone dimer while $\text{Fe}_2(\text{CO})_9$ precipitated from solution. When cyclohexene is present in large excess a significant quality of ketone **11a** is formed upon addition of **11** and $\text{Fe}_2(\text{CO})_9$ does not appear.

The relative ease with which these olefins form the corresponding bisolefintricarbonyliron(0) complexes is probably a function of strain energy as well as steric factors. It is known that the binding constant of olefins to low oxidation state metal systems increases as olefin ring strain increases.^{10a,b} Thus cyclohexene gives only trace amounts of a ketonic product, and norbornene gives only slightly higher yields. Norbornadiene is reported¹¹ to give a maximum yield of 16%. The strain energies of these three-ring systems are given¹² as 2.5, 27.2, and 34.7 kcal/mol, respectively. The importance of steric factors becomes apparent when considering the results of experiment G. These results suggest that formation of the monoolefintetracarbonyliron(0) complex of **13** is hindered by the presence of bulky groups at the bridge position, thereby favoring formation of $\text{Fe}_2(\text{CO})_9$. The spiropropyl olefin analogous to **13** is reactive and prevents $\text{Fe}_2(\text{CO})_9$ formation at similar concentrations.

Taken together, these data suggest a mechanism involving the stepwise formation of the bisolefin complex **5**. In order to account for the formation of ketone, step 6 is further broken into three steps. These are shown in eq 7–9. Oxidative coupling to form a metallocycle **7** followed by migratory insertion yielding acyl complex **8** and elimination to form the ketone-product complete the sequence from reactant to product. As a general observation, migratory insertion steps such as reaction 8 require the presence of an activating ligand. If this ligand is carbon monoxide the

reaction often is catalytic. At the present time there is no hard evidence that the iron coordination number remains five during the insertion step. In the absence of such data, we have not indicated an activating ligand in step 8 although there is no reason to doubt its presence. The observations that the iron deposit does not form under an atmosphere of carbon monoxide when benzonorbornadiene is the reactive olefin but does form under nitrogen suggest that step 8 may proceed with or without an external ligand source.

The probable direction of attack becomes clear when one considers the relative yields of ketone derived from coupling of compounds **11**, **13**, and the spiropropyl derivative analogous to **13**. The almost complete lack of reactivity of **13** is consistent with exo attack by a reactive iron carbonyl moiety. The methylene hydrogens adjacent to the bridge in **13** are in close proximity to the double bond and thus effectively block exo attack. Models show that the analogous methylene hydrogens on the cyclopropyl ring of the spiropropyl derivative offer less steric hindrance to exo attack, and the compound reacts in good yield. Thus the numerous observations made by Brown,¹³ that norbornyl systems are subject to exo attack by reagents unless bulky substituents are present at the bridge position, applies to reactions involving transition metals. The lack of reactivity of **14** is probably due to steric repulsion between protons on the double bond and the opposing syn-bridge proton, which arises when the iron moiety attacks exo at this double bond. While this repulsive interaction is insufficient to prevent formation of two strong σ bonds or to prevent trapping by $\text{Fe}(\text{CO})_4$, it does present a barrier to exo attack and restricts the formation of intermediate **5**. Steric compression between this double bond and the opposing syn-bridge proton has been demonstrated.^{1b,c}

Further, the exo stereochemistry of the ketone products is indicative of exo attack by iron carbonyl moieties to form exo-bound intermediates. Two geometric extremes must be considered for bisolefin intermediate **5**. In order to facilitate carbon-carbon coupling, the π systems of the two olefinic ligands must be directed toward one another; such a reactive intermediate is depicted in Figure 1A. The π systems are directed toward one another and the full organic ligands are antiparallel to one another in order to minimize steric interaction with an individual CO

(10) (a) C. A. Tolman, private communication. (b) M. Englert, P. W. Jolly, and G. Wilkie, *Agnew Chem.*, **83**, 84 (1971).

(11) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, **11**, 373 (1961).

(12) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(13) H. C. Brown, W. R. Heydkamp, E. Brewer, and W. S. Murphy, *J. Amer. Chem. Soc.*, **86**, 3565 (1964).

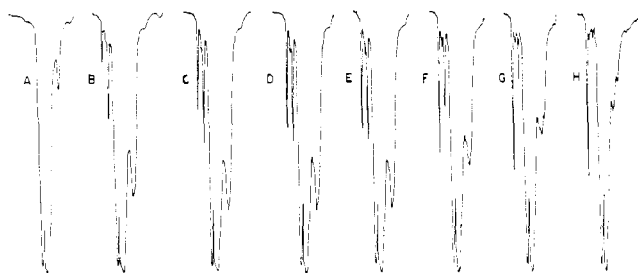


Figure 2. Infrared spectra of benzonorbornadiene- $\text{Fe}(\text{CO})_5$ reaction mixture in *n*-octane ($2200\text{--}1900\text{-cm}^{-1}$ region): (A) spectrum of reaction mixture before photolysis; (B-E) photolysis under 1 atm of CO, 15, 30, 45, and 60 min, respectively; (F-H) solution corresponding to E purged with N_2 in dark, 15, 30, and 60 min, respectively.

ligand. The trans stereochemistry is a consequence of this orientation.

However, the expected thermodynamically stable bisolefin intermediate places the olefin carbons in planes containing the axial carbonyl groups and perpendicular to the basal plane, as seen in Figure 1B. This expectation is consistent with observed olefin complexes and maximal metal-ligand π -bonding.¹⁴ Such an intermediate places the organic π systems antiparallel to one another in an unreactive configuration. If indeed this is the thermodynamically preferred form of the bisolefin intermediate, rearrangement to a species more closely akin to the reactive form (Figure 1A) will involve significant activation. Since reaction 7 is slow, sufficient time is available for the establishment of equilibrium 5.

Migratory insertion from metalocycle 7 to acyl intermediate 8 must take place with retention of exo geometry as depicted in Figure 1C. Recently, Osborn⁶ has reported the formation of a compound similar to 7 from the reaction of $[\text{Ir}(1,5\text{-cyclooctadiene})\text{Cl}]_2$ with norbornadiene. Furthermore, treatment of the iridocycle with carbon monoxide produced an acyl product analogous to 8.

The possibility that bisolefin intermediate 5 is similar to species present during olefin metathesis^{6,15} must be considered. Data presently at hand give no indication as to whether or not cyclobutane derivatives may form directly from 5. While one may easily imagine that the benzonorbornadiene dimer, formed during the coupling reaction,^{1,2} corresponds to a metathesis intermediate which was prevented from going on to products, evidence does not support or refute this hypothesis. Indeed, the yield of benzonorbornadiene dimer depends upon product work-up and the degree to which homogeneity is maintained. Until an understanding of dimerization is available, it seems inappropriate to claim a similarity between dimerization and metathesis.

In a recent review¹⁶ von Gustorf reported that dimethyl cyclobutene-3,4-dicarboxylate reacts with $\text{Fe}(\text{CO})_5$ to give an intermediate analogous to the proposed metalocycle. Upon addition of carbon monoxide or triphenylphosphine as activating ligands, the corresponding ketone was formed. No specific data were

(14) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

(15) N. Calderon, *Accounts Chem. Res.*, **5**, 127 (1972).

(16) E. K. von Gustorf and F. W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1970).

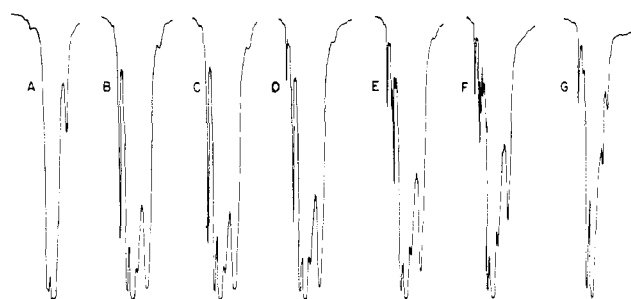


Figure 3. Infrared spectra of olefin-10- $\text{Fe}(\text{CO})_5$ reaction mixture in *n*-octane ($2200\text{--}1900\text{-cm}^{-1}$ region): (A) spectrum of reaction mixture before photolysis; (B and C) photolysis under 1 atm of CO, 30 and 60 min; (D-F) solution corresponding to C purged with N_2 in dark, 10, 30, and 45 min, respectively; (G) solution F placed under 1 atm of N_2 for 16 hr.

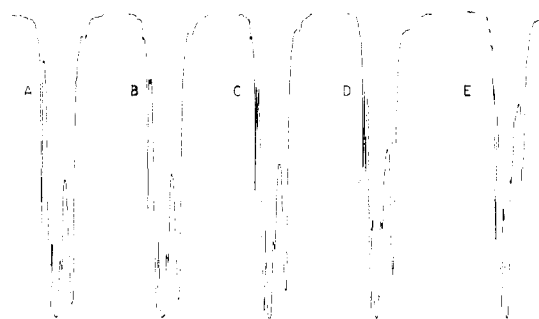


Figure 4. Infrared spectra of $\text{Fe}(\text{CO})_5$ -monoene 14 reaction mixture in *n*-octane ($2200\text{--}1900\text{-cm}^{-1}$ region): (A) photolysis for 30 min in CO atm; (B-E) solution corresponding to A purged with N_2 in dark, 15, 45, 60, and 90 min, respectively.

presented regarding the reaction or its products. The exo-trans-exo stereochemistry was, however, depicted without explanation.

Laszlo¹⁷ has reported the thermal coupling of 7,7-dimethoxybenzonorbornadiene with $\text{Fe}(\text{CO})_5$ in di-*n*-butyl ether. In contrast to the exo-trans-exo stereochemistry found for other systems he reports exclusive formation of the exo-trans-endo product. Since olefin 13 is thermally unreactive, we conclude that the methoxy groups are participating directly in the reaction and that the dimethoxy compound couples by a significantly modified mechanism. Evidence for both methoxy complexation and endo complexation induced by the presence of the methoxy group is taken from analogous chromium compounds reported by Wege.¹⁸

Infrared Studies

Although isolation of reaction intermediates has not been possible, infrared studies indicate their presence. The thermodynamic stability of these complexes is probably small; known monoolefintetracarbonyliron(0) complexes are unstable unless electron-withdrawing groups are attached to the olefinic function.^{19,20} Figures 2-4 show the results of the infrared studies. Spectra recorded for $\text{Fe}(\text{CO})_5$ and its derivatives prior

(17) A. Speert, J. Gelan, M. Anteunis, A. P. Marchand, and P. Laszlo, *Tetrahedron Lett.*, **25**, 2271 (1973).

(18) D. Wege and S. P. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1335 (1972).

(19) M. J. Newlands and J. F. Ogilvie, *Can. J. Chem.*, **49**, 343 (1970).

(20) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **46**, 1588 (1963).

to reaction with olefin are in agreement with published spectra.²¹ Photolysis of Fe(CO)₅-olefin mixtures produces two new bands, a pair of absorptions with maxima at 1980 and 1983 cm⁻¹, and a sharp band at 2083 cm⁻¹. Saturating Fe(CO)₅ solutions with carbon monoxide prior to photolysis does not produce any changes in these spectra.

The metal carbonyl region of the infrared spectra recorded during the photolysis of Fe(CO)₅-benzonorbornadiene solutions in *n*-octane are shown in Figure 2. Figures 2B-E show the changes occurring in the iron carbonyl region of the spectrum during photolysis under one atmosphere of CO. Two distinct sharp bands appear at 2065 and 2100 cm⁻¹ while a band at 1972 cm⁻¹ appears and masks the original 1970-cm⁻¹ band. The intensity of these bands increases with time until 45 min when a steady-state condition is attained. No further increase in intensity is noted, although ketonic product continues to form. Once steady state was obtained, the solution was purged with nitrogen in the dark. As shown (Figures 2F-G), the bands at 1972 and 2065 cm⁻¹ decrease and after 60 min of nitrogen purging the 2100-cm⁻¹ band reaches a maximum intensity.

Similar results are found for compound **10** as the reactive olefin (Figure 3). However, in this case ketone formation is initiated after a longer photolysis time than with benzonorbornadiene as the reactive olefin. This is in accord with the relative reactivities found for these two olefins in competition experiments. One observation of particular importance is that the band at 2100 cm⁻¹ does not appear until the onset of ketone formation; the band at 2065 cm⁻¹ begins to decrease at this time (Figure 3).

The spectra recorded during photolysis of Fe(CO)₅ in the presence of monoene **14** are shown in Figure 4. Photolysis of the solution for 30 min produces a spectrum identical with that in Figure 3B. Purging the solution with nitrogen in the dark causes a steady de-

crease in the 2065-cm⁻¹ band; however, no band at 2100 cm⁻¹ appears. In addition, the solution changes from homogeneous yellow to green during this time, indicating the presence of Fe₃(CO)₁₂. Continued purging with nitrogen steadily decreases the bands at 2065, 1965, and 1987 cm⁻¹; the band corresponding to Fe₃(CO)₁₂ (2055 cm⁻¹) increases.

These observations are consistent with the mechanism proposed as steps 1-9. The infrared bands appearing during photolysis in the presence of a carbon monoxide atmosphere (2065, 1987, and 1965 cm⁻¹) correspond to the monoolefintetracarbonyliron(0) complex (**3**). The presence of additional bands may be masked by the absorption bands of Fe(CO)₅ (*ca.* 2030 and 2000 cm⁻¹). The carbonyl stretching frequencies reported¹⁶ for C₂H₄Fe(CO)₄ are 2088, 2007, 2013, and 1986 cm⁻¹. In the absence of a reactive olefin, intermediate **4** proceeds to Fe₃(CO)₁₂. The band which appears at 2100 cm⁻¹ may correspond to the bisolefin complex **5**, the metallocycle **7**, the acyl complex **8**, or the final iron carbonyl following elimination. Careful inspection of the infrared spectra indicate the appearance of other absorption bands in addition to the 2100-cm⁻¹ band, *viz.*, 2018 and 2040 cm⁻¹.

Further similar experiments have shown that cyclohexene behaves as monoene **14**; however, the absorption intensity associated with the cyclohexenetetracarbonyliron(0) complex was much lower after equal photolysis times. These results are also consistent with those found in the competition experiments. Photolysis of Fe(CO)₅ in the presence of monoene **14** in a carbon monoxide atmosphere, followed by addition of equimolar benzonorbornadiene and purging with nitrogen in the dark, yielded ketone **11a**. Infrared spectra recorded during this experiment showed the same changes as those found during photolysis of Fe(CO)₅ in the presence of benzonorbornadiene alone.

Acknowledgment. Financial support from Wesleyan University and a Fellowship to one of us (J. M.) from the National Science Foundation are gratefully acknowledged.

(21) C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

Chromic Acid Oxidation of Isopropyl Alcohol. Oxidation by Chromium(IV)¹

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*Contribution from the Department of Chemistry, Yale University,
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Abstract: Experimental evidence is presented for the oxidation of isopropyl alcohol by chromium(IV) as being an essential step in the chromium(VI) oxidation of this substrate. Equilibrium constants for the formation of mono- and diesters, as well as rate constants for the decomposition of the esters and for the oxidation of isopropyl alcohol by chromium(V) in 97% acetic acid, have been reevaluated and are summarized.

The role of chromium(IV) in chromic acid oxidation has been the subject of a number of investigations. Roček and Radkowsky² found that chromium(IV)

generated by the reaction of vanadium(IV) with chromium(VI) causes oxidative cleavage of cyclobutanol. Similarly, Rahman and Roček^{2b} showed that

(1) This investigation was supported by a grant from the National Science Foundation.

(2) (a) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968); (b) M. Rahman and J. Roček, *ibid.*, **93**, 5455, 5462 (1971).