Oxidation of cymene with Mn(III) salt was carried out in the absence of sodium acetate and without removal of water, conditions favoring an electron transfer mechanism.[11] Even under such conditions, coupling of cymene radicals was the dominant course of the reaction. Some dimers could also be formed by gradual addition of diacetyl peroxide to boiling cymene.[18] Minor products consisted of 15 components (vpc), mostly esters and some acids. Only a trace or *p*-isopropylbenzaldehyde, its diacetate, and *p*-isopropylbenzyl acetate was detected. Analysis of the total product by nmr after removal of unreacted cymene by column chromatography showed that virtually all of the isopropyl groups had reacted.

Conclusion

Products formed in the oxidation of *p*-cymene using cobaltic or manganic salts alone or in conjunction with oxygen indicate operation of different mechanisms in the two cases studied. Electron transfer with cobalt and a free-radical path with manganese are in accord with our results as well as published data.

Experimental Section

Reactions with oxygen at elevated pressure were carried out as previously reported.[16] Experiments with metal salts alone were done in sealed tubes under nitrogen atmosphere. Concentrations of metal ions were determined by iodometric titration. After termination of the reaction, the mixture was taken up in ether and repeatedly extracted with cold water. The organic layer was dried ($MgSO_4$) and filtered, and the ether was removed. After addition of methyl palmitate as internal standard, the residue was analyzed by vpc (6 ft × 0.25 in., OV-1 column, programmed from 50 to 275° at 10°/min). Unreacted cymene was removed from the product by column chromatography over silica gel. Standard analytical procedures were then used for the characterization of the residual product mixture. Cobaltic acetate and manganic acetate were prepared by published procedures.[10,13]

Registry No.—*p*-Cymene, 99-87-6; Co(III) acetate, 917-69-1; Mn(III) acetate, 993-02-2.

[18] H. C. McBay and P. T. Groves, *J. Org. Chem.*, **21**, 691 (1956).

The Formation of 1,4 Diketones, Monoketones, and β-Epoxy Ketones by Reaction of Iron Pentacarbonyl with α-Halo Ketones. A Possible Mechanism for Iron Pentacarbonyl–Halide Reactions

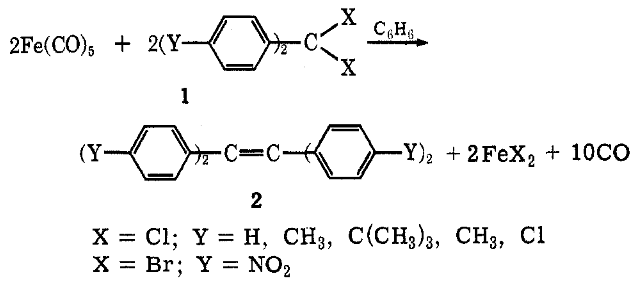
HOWARD ALPER* AND EDMUND C. H. KEUNG[1]

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

Received January 11, 1972

Iron pentacarbonyl reacts with a variety of primary, secondary, and tertiary aryl and alkyl α-halo ketones in refluxing 1,2-dimethoxyethane, followed by treatment with water, to generally give the coupled 1,4 diketones and the reduced monoketones. Use of deuterium oxide instead of water results in α-deuterio ketone formation. β-Epoxy ketones were produced in several instances. The reaction apparently occurs *via* organoiron tetracarbonyl halide and organoiron halide complexes. Some support is presented for the intermediacy of such complexes. The reactions of $Fe(CO)_5$ with sulfonyl chlorides and *gem*-dihalides likely proceed *via* similar intermediates.

A number of papers have appeared in the literature concerning the reaction of iron pentacarbonyl with halides. A simple preparation of tetraarylethylenes (2) was reported by Coffey,[2a] in 1961, by treatment of



X = Cl; Y = H, CH_3, $C(CH_3)_3$, CH_3, Cl
X = Br; Y = NO_2

certain *gem*-dihalides (1) with $Fe(CO)_5$ in refluxing benzene. Activating groups such as aryl, halo, cyano, and carbalkoxy must be attached to the halogen-bearing carbon in order for this thermal reaction to occur, but substituted ethylenes are not produced in all instances; *e.g.*, (i) although bisfluorenylidene was obtained by reaction of 9,9-dibromofluorene with the metal carbonyl in hot benzene, the alkene and 9,9′-dibromobisfluorenyl are formed by using dioxane as the solvent; (ii) diethyl dibromomalonate and dibromomalonitrile react with $Fe(CO)_5$ in benzene giving iron-containing materials of no apparent synthetic utility; (iii) some hexachloroethane, along with substantial amounts of tar, resulted when carbon tetrachloride was the starting halide.[2] Some *gem*-dihalides with other activating groups failed to react with the metal carbonyl (*e.g.*, dichloromethyl phenyl sulfone).[3] Vicinal dihalides are dehalogenated by $Fe(CO)_5$.[1,3]

Coffey observed no reaction between $Fe(CO)_5$ and any monohalide. Recently, Pankowski and Bigorgne reported that no reaction occurred when methyl iodide and $Fe(CO)_5$ were mixed at room temperature.[4] However, Bruce[5] showed that decafluorobenzhydryl bromide (3) reacts with $Fe(CO)_5$ in hot petroleum ether (bp 100–120°) to give the expected coupling product 4, in 37% yield, and small amounts of bis(pentafluorophenyl)methane (5), the formation of the latter attrib-

---

[1] Taken in part from the B.A. (Honors) thesis of E. C. H. Keung, May 1972; presented in part at the Third Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 1971, Abstract 172.

[2] (a) C. E. Coffey, *J. Amer. Chem. Soc.*, **83**, 1623 (1961); (b) A. Mittasch, *Angew. Chem.*, **41**, 827 (1928).

[3] H. Alper and E. C. H. Keung, unpublished results.

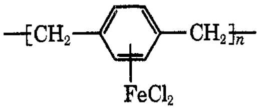
[4] M. Pankowski and M. Bigorgne, *J. Organometal. Chem.*, **30**, 227 (1971).

[5] M. I. Bruce, *ibid.*, **10**, 495 (1967).

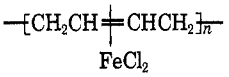
$$\underset{\mathbf{3}}{(C_6F_5)_2CHBr} + Fe(CO)_5 \longrightarrow \underset{\mathbf{4}}{(C_6F_5)_2CHCH(C_6F_5)_2} + \underset{\mathbf{5}}{(C_6F_5)_2CH_2}$$

uted to the presence of traces of moisture in the solvent or the metal carbonyl. Perfluoroalkyliron tetracarbonyl iodides have been obtained from reaction of perfluoroalkyl iodides with $Fe(CO)_5$.[6,7]

Thermal reaction of $Fe(CO)_5$ and some halides not having strongly electron-attracting groups results in the formation of polymeric materials. Reaction of benzyl chloride and the metal carbonyl in tetrahydrofuran at 30° gives $(C_6H_4CH_2)_n$ where $n \sim 62$.[8] α,α-Dichloro-*p*-xylene and 1,4-dichloro-2-butene (of unspecified stereochemistry) react with $Fe(CO)_5$ in xylene at 100–110° to give, it is claimed, **6** and **7**,



6



7

respectively.[9] Other allyl halides usually form allyl halide–iron tetracarbonyl complexes[10] or π-allyliron-tricarbonyl halides.[11,12] Aryl halides show low thermal reactivity toward $Fe(CO)_5$. Iodobenzene, for example, fails to react with the metal carbonyl at temperatures of 30–60°.[8]

Koerner von Gustorf and coworkers[13-15] have investigated the irradiation of $Fe(CO)_5$ with a number of simple saturated halides. Coupling or photoelimination products were obtained from these reactions, subject to the nature of the organic reactant. An iron tetracarbonyl complex has been isolated from photolysis of $Fe(CO)_5$ in dibromodifluoromethane.[16] Ferraindene–iron carbonyl complexes have been obtained by a novel 1,4-dehydrobromination of *o*-bromostyrene, on irradiation of the latter with $Fe(CO)_5$.[17] Vinyl halides react with $Fe(CO)_5$ on irradiation to form iron tetracarbonyl complexes.[15,18,19]

Fluorinated nitrogen compounds such as tetrafluorohydrazine, perfluoroethylenediamine, and *N,N*-dichlorotrifluoromethylamine undergo dehalogenation upon reaction with $Fe(CO)_5$ in a sealed tube.[20-23] Treatment of sulfonyl halides with a 1:1 mixture of $Fe(CO)_5$ and boron trifluoride etherate in preferably dipolar aprotic solvents provides a convenient preparation of thiosulfonate esters.[24] Disulfides have been obtained from the coupling reaction of some sulfenyl halides and $Fe(CO)_5$ in tetrahydrofuran in the cold.[25] In some instances (perchloro- or perfluoroalkanesulfenyl chlorides) partial dehalogenation of the coupled product occurs. The tin halide, tri-*n*-butyltin chloride, reacts with the metal carbonyl to form di-*n*-butyl ketone in low yield (among other products).[26] Finally, acid halides form a variety of products (coupling,[27] solvent incorporation[28]) upon reaction with $Fe(CO)_5$, the nature of the products depending on the reaction conditions and the type of acid halide.

Recently, Noyori and coworkers[29] reported a new route to troponoid compounds by reaction of α,α′-dibromo ketones with diiron enneacarbonyl at 60° in the presence of 1,3-dienes. The authors briefly noted that $Fe(CO)_5$ was not as useful for effecting this cyclization reaction. Their communication prompts us to present our results on the reaction of α-halo ketones and $Fe(CO)_5$. The purpose of this investigation was to attempt to answer the following: (a) what products are formed in these reactions (coupling, dehalogenation, other)?; (b) what are some of the possible mechanisms for the reactions?; (c) if coupling products are obtained as in several other halide–$Fe(CO)_5$ reactions, is the reaction pathway unique to a given type of halide or perhaps common to all?

Results and Discussion

Reaction of $Fe(CO)_5$ with α-halo ketones [**8**, 2:1.14 ratio of **8**:$Fe(CO)_5$] in refluxing anhydrous 1,2-dimethoxyethane [DME] for 5–19 hr, followed by treatment with water, gave 1,4 diketones (**9**), monoketones (**10**), and/or β-epoxy ketones (**11**). The reaction time, yields, melting points of new compounds, and pertinent nmr data for the reaction products are listed in Table I.

In general, 2-bromoacetophenone and its *p*-phenyl- and *p*-methoxy-substituted derivatives gave the 1,4 diketone as the major product with the methyl ketone formed as the by-product. The presence of strongly electron-attracting para substituents (Br, F) on the benzene ring results in the formation of β-epoxy ketones (**11**) and **10**, but little, if any, 1,4 diketone. Rather surprisingly, the secondary and tertiary halides, **8**, $R = C_6H_5$, $R' = CH_3$, $R'' = H$, and **8**, $R = C_6H_5$, $R' = R'' = CH_3$, respectively, gave **9** in moderate

---

(6) T. A. Manuel, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 249 (1961).

(7) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3604 (1961).

(8) I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 361 (1967).

(9) M. Asfazadourian and M. Prilleux, French Patent 1,418,851 (1965); *Chem. Abstr.*, **65**, 10747*ef* (1966).

(10) E. K. von Gustorf, M. C. Henry, and C. di Pietro, *Z. Naturforsch.*, **21b**, 42 (1966).

(11) R. F. Heck and C. R. Boss, *J. Amer. Chem. Soc.*, **86**, 2580 (1964).

(12) R. F. Heck, U. S. Patent 3,338, 936 (1967); *Chem. Abstr.*, **68**, 49788f (1968).

(13) E. K. von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969).

(14) E. K. von Gustorf, M.-J. Jun, H. Hun, and G. O. Schenck, *Angew. Chem.*, **75**, 1120 (1963).

(15) (a) E. K. von Gustorf, F.-W. Grevels, and J. C. Hogan, *Angew. Chem., Int. Ed. Engl.*, **8**, 899 (1969); (b) J. C. Hogan, Ph.D. Thesis, Boston College, Boston, Mass., 1969.

(16) F. Seel and G.-V. Roschenthaler, *Angew. Chem.*, **82**, 182 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 166 (1970).

(17) R. Victor, R. Ben-Shoshan, and S. Sarel, *Chem. Commun.*, 1241 (1971).

(18) E. K. von Gustorf, M. C. Henry, and D. J. McAdoo, *Justus Liebigs Ann. Chem.*, **707**, 190 (1967).

(19) R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggans, *J. Chem. Soc. A*, 1969 (1970).

(20) M. A. Englin and A. S. Filatov, *Zh. Obshch. Khim.*, **39**, 1214 (1969); *J. Gen. Chem. USSR*, **39**, 1184 (1969).

(21) A. S. Filatov, M. A. Englin, and V. I. Yakutin, *Zh. Obshch. Khim.*, **39**, 1325 (1969); *J. Gen. Chem. USSR*, **39**, 1295 (1969).

(22) M. Green and A. E. Tipping, *J. Chem. Soc.*, 5774 (1965).

(23) V. A. Ginsburg and K. N. Smirnov, *Zh. Obshch. Khim.*, **37**, 1413 (1967); *J. Gen. Chem. USSR*, **37**, 1343 (1967).

(24) H. Alper, *Tetrahedron Lett.*, 1239 (1969).

(25) E. Lindner and G. Vitzthum, *Angew. Chem.*, **81**, 706 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 518 (1969).

(26) J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 264 (1967).

(27) A. S. Filatov and M. A. Englin, *Zh. Obshch. Khim.*, **39**, 533 (1969); *J. Gen. Chem. USSR*, **39**, 502 (1969).

(28) H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1623 (1970).

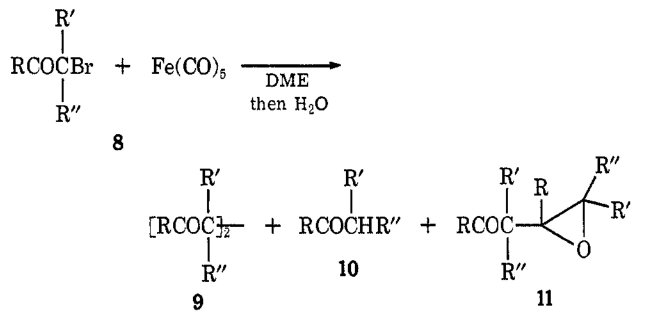
(29) R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).

TABLE I

PRODUCTS OBTAINED FROM REACTION OF $Fe(CO)_5$ WITH α-HALO KETONES IN DME[a]

α-Halo ketone (**8**)	Registry no.	Reaction time, hr	Products[b]	Registry no.	New compd[c] mp, °C	Yield, %	Pertinent nmr data,[d] ppm
2-Bromoacetophenone	70-11-1	5	**9**, R = C_6H_5; R′ = R″ = H			35	3.45 (s, CH_2, DMSO-d_6)
			10, R = C_6H_5; R′ = R″ = H			25	2.59 (s, CH_3, $CDCl_3$)
2-Bromo-4′-phenylacetophenone	135-73-9	5	**9**, R = p-$C_6H_5C_6H_4$; R′ = R″ = H	34733-52-3	200–202	63	3.31 (s, CH_2, DMSO-d_6)
			10, R = p-$C_6H_5C_6H_4$; R′ = R″ = H			30	2.59 (s, CH_3, DMSO-d_6)
2,4′-Dibromoacetophenone	99-73-0	5	**9**, R = p-BrC_6H_4; R′ = R″ = H			5.3	3.29 (s, CH_2, DMSO-d_6)
			10, R = p-BrC_6H_4; R′ = R″ = H			17	2.47 (s, CH_3, CCl_4)
			11, R = p-BrC_6H_4; R′ = R″ = H	34733-53-4	92 dec	20	3.06 (m, CH_2 chain, $CDCl_3$) 2.58 (m, CH_2 ring, $CDCl_3$)
2-Bromo-4′-fluoroacetophenone	403-29-2	5	**9**, R = p-FC_6H_4; R′ = R″ = H			Trace	3.28 (s, CH_2, $CDCl_3$)
			10, R = p-FC_6H_4; R′ = R″ = H			34	2.46 (s, CH_3, CCl_4)
			11, R = p-FC_6H_4; R′ = R″ = H	34733-54-5	93–94	21	3.41 (m, CH_2 chain, $CDCl_3$) 2.55 (m, CH_2 ring, $CDCl_3$)
2-Bromo-4′-methoxyacetophenone	2632-13-5	12	**9**, R = p-$CH_3OC_6H_4$; R′ = R″ = H			51	3.37 (s, CH_2, $CDCl_3$)
			10, R = p-$CH_3OC_6H_4$; R′ = R″ = H			25	2.47 (s, CH_3CO, CCl_4)
α Bromopropiophenone	2114-00-3	5.5	**9**, R = C_6H_5; R′ = CH_3; R″ = H	34733-55-6	85–86	46	1.23 (d, CH_3, $CDCl_3$) 3.92 (m, CH, $CDCl_3$)
			10, R = C_6H_5; R′ = CH_3; R″ = H			31	1.16 (t, CH_3, CCl_4) 2.85 (q, CH_2, CCl_4)
α-Bromoisobutyrophenone	10409-54-8	5	**9**, R = C_6H_5; R′ = R″ = CH_3	34733-56-7	113–115	47	1.38 (s, CH_3, $CDCl_3$)
			10, R = C_6H_5; R′ = R″ = CH_3			14	1.20 (d, CH_3, $CDCl_3$) 3.51 (se, CH, $CDCl_3$)
α-Bromo-2′-acetonaphthone	613-54-7	19	**9**, R = 2-$C_{10}H_7$; R′ = R″ = H	34733-57-8	213–215	6.0	e
			10, R = 2-$C_{10}H_7$; R′ = R″ = H			24	2.57 (s, CH_3, $CDCl_3$)
α-Bromo-9′-aceto-1,2,3,4,5,-6,7,8-octahydroanthrone	34733-51-2	5.5	**9**, R = 9-Anthryl; R′ = R″ = H	34733-58-9	235–237	15	3.49 (s, CH_2, DMSO-d_6)
			10, R = 9-Anthryl; R′ = R″ = H			13	2.42 (s, CH_3, $CDCl_3$)
1-Adamantyl bromomethyl ketone	5122-82-7	14′	**9**, R = 1-Adamantyl; R′ = R″ = H	34733-59-0	220–222	4.6	e
			10, R = 1-Adamantyl; R′ = R″ = H			25	2.08 (s, CH_3, $CDCl_3$)

[a] 2:1.14 mole ratio of **8**:$Fe(CO)_5$. [b] Satisfactory analytical data were obtained for C and H. [c] The melting point or boiling point and spectral data for known products were in good agreement with data reported in the literature. [d] s = singlet, d = doublet, t = triplet, q = quartet, se = septet, m = multiplet. [e] Insufficiently soluble for nmr purposes.



yields along with smaller amounts of **10** (no elimination products were observed). 1-Adamantyl bromomethyl ketone and *d*-3-bromocamphor (to be considered in detail in a forthcoming publication) gave low yields of **9** and **10** when treated with $Fe(CO)_5$.

Variations of the reaction conditions were studied using 2-bromo-4′-phenylacetophenone as the reactant α-halo ketone. 2-Deuterio-4′-phenylacetophenone was obtained when the reaction mixture (in DME) was poured into deuterium oxide rather than water, indicating that this reaction may provide for a simple synthesis of α-deuterio ketones. If the reaction mixture was not poured into water, then no methyl ketone formation occurred, clearly showing that the hydrogen for **10** arises from water and not from DME. The presence of water inhibited reaction, since only starting material was recovered when the α-halo ketone and $Fe(CO)_5$ were refluxed in DME–water (9:1). The reaction is not catalytic in $Fe(CO)_5$ and is not affected by the addition of azobisisobutyronitrile, a radical initiator.[30] Dipolar aprotic solvents such as *N*,*N*-dimethylacetamide and tetramethylurea could be used but yields were lower than when DME was the reaction solvent.

It should be pointed out that only in the case of the 2-bromo-4′-phenylacetophenone–$Fe(CO)_5$ reaction was experimentation carried out toward determining the optimum reaction conditions (93% total product yield). Hence, it is likely that the total yields for some of the other reactions could be improved using more suitable reaction conditions. Many of the 1,4 diketones,[31] produced in this simple reaction, are new compounds (see Table I) and may be precursors to as yet unknown, but potentially useful, five-membered ring heterocycles *via* the well-known Paal–Knorr[32a–c] synthesis and to cyclopentenones *via* treatment with base.[32d]

A possible mechanism (Scheme I) for the α-halo ketone–$Fe(CO)_5$ reaction involves initial oxidative addition to give **12**. The latter can lose carbon monoxide to form **13**, which can then be converted to **10** by cleavage of the iron–carbon bond (addition of water or deuterium oxide), and to **9** and/or **11** by reaction with more **8**. It is also possible that **12** can react directly with additional **8** to give the coupled products or with H_2O or D_2O to form **10**.

An alternative mechanism (Scheme II) proposes radical generation *via* reaction of **12** with **8**. The radical could then give **9** by dimerization, **10** by hydrogen abstraction from solvent, and **11** by attack on **8** followed by cylization. However, some evidence against a radical process was noted earlier (the failure of a radical initiator to affect the reaction).

In order to determine the validity of the mechanism outlined in Scheme I as a possible rationale for the α-halo ketone reaction, we treated 2-bromo-4′-phenylacetophenone with the more reactive diiron ennea-

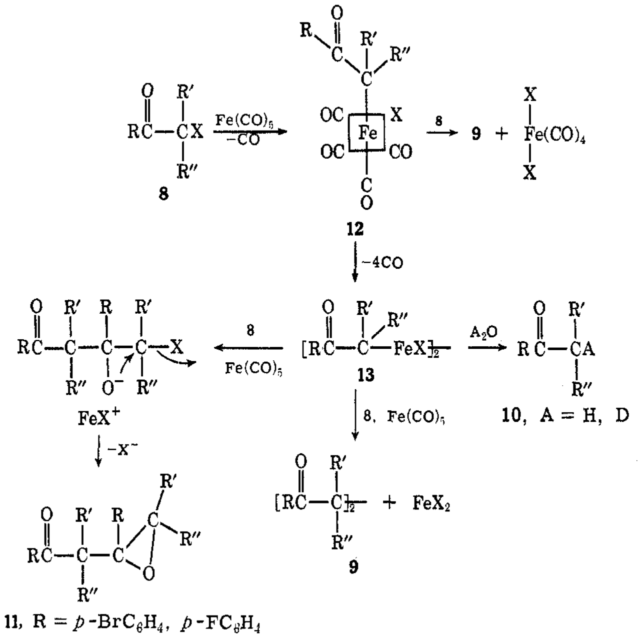
---

[30] C. Walling and E. S. Huyser, *Org. React.*, **13**, 115 (1963).

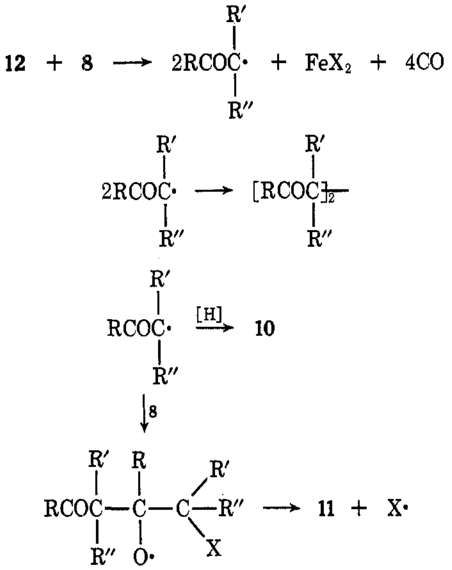
[31] For a review of synthetic approaches to 1,4-diketones see E. Ritchie and W. C. Taylor, *Aust. J. Chem.*, **24**, 2137 (1971).

[32] (a) C. Paal, *Chem. Ber.*, **17**, 2757 (1884); (b) L. Knorr, *ibid.*, **17**, 2863 (1884); (c) E. E. Campaigne and W. O. Foye, *J. Org. Chem.*, **17**, 1405 (1952); (d) *e.g.*, J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971). A study of the cyclization reactions of some of the 1,4 diketones prepared in this study is currently in progress.

Scheme I

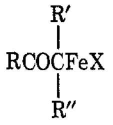


Scheme II

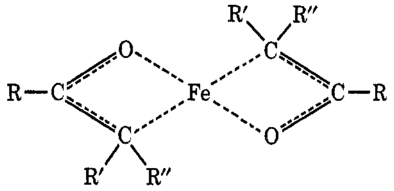


carbonyl at room temperature. In this manner, we succeeded in isolating **12** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$; $X = Br$), identified by elemental analysis and mass spectral data (parent peak at m/e 443; important fragments at m/e 415, 387, 359, 331). Complex **12** has the cis configuration, since the ir spectrum shows three bands in the terminal metal carbonyl stretching region at 2104, 2041, and 1982 cm^{-1} (KBr, four bands in methylene chloride). The trans isomer would have given only one band in this region.[33] Cis oxidative addition has also been observed in the addition of halogen to the trigonal bipyramidal *trans*-$Os(CO)_3[P(C_6H_5)_3]_2$.[34]

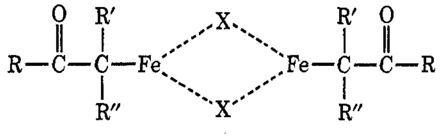
Complex **12** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$; $X = Br$) was only moderately stable under nitrogen and slowly decarbonylated to **13** by standing at room temperature, or rapidly when heated in DME. We had hoped to prepare a more stable analog of **12** by reaction of **8** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) with triphenylphosphineiron tetracarbonyl, but only starting material] were recovered when the reactants were refluxed in DME.[35] A number of structures (**13a–d**) could be assigned to **13**. Structures **13a** and **13b** were eliminated since the molecular weight of the compound was 644 as determined by vapor phase osmometry. The molecular weight (662) of **13c** or **13d** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) was in reasonable accord with the osmometrically determined value. We favor **13d** rather than **13c** as the structure for the organoiron halide, since the carbonyl stretching frequency was shifted from 1687 (for **8**) to 1577 cm^{-1} (for **13**), thereby indicating coordination of the keto group to the metal in some manner. Bennett and coworkers[36] have recently suggested that decomposition (loss of carbon monoxide) of octahedral Fe(II) and Ru(II) carbon σ-bonded chelate complexes (**14**) may result in the formation of halogen-bridged dimers.



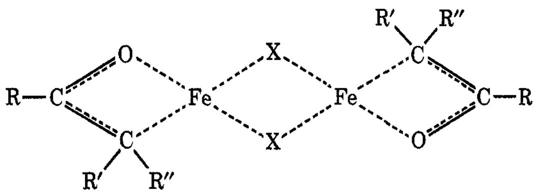
13a



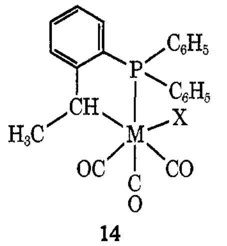
13b



13c



13d



14

M = Fe, Ru

X = Cl, Br

Complex **13** could be converted to **10** by treatment with water, the latter cleaving the Fe–C σ bond. When **13** was heated with **8** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) under conditions described for the $Fe(CO)_5$ reaction [*i.e.*, refluxing DME for 5 hr], only traces of the

---

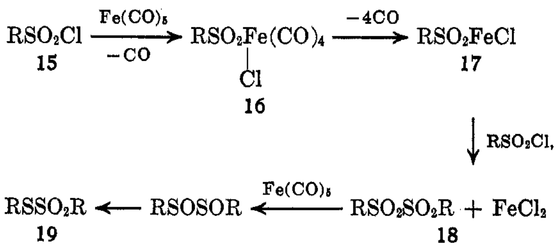
[33] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

[34] J. P. Collman and W. R. Roper, *ibid.*, **88**, 3504 (1966).

[35] C. H. Bamford and W. R. Maltman, *Trans. Faraday Soc.*, **62**, 2823 (1966), found that triphenylphosphineiron tetracarbonyl is more active than $Fe(CO)_5$ in producing the trichloromethyl radical from treatment with carbon tetrachloride and methyl methacrylate. These results are opposite to those observed with **8**.

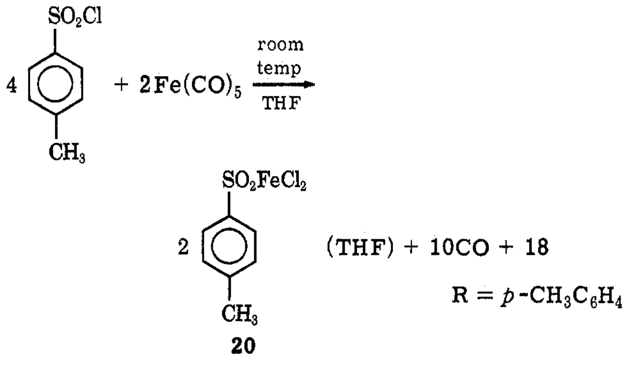
[36] M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *J. Organometal. Chem.*, **32**, C19 (1971).

SCHEME III



1,4 diketone were produced. However, if the metal carbonyl was present in catalytic amounts, **9** (R = p-$C_6H_5C_6H_4$; R′ = R″ = H) was obtained in good yield. An unsymmetrical 1,4 diketone resulted when **13** (R = p-$C_6H_5C_6H_4$; R′ = R″ = H) was treated with **8** (R = C_6H_5; R′ = R″ = H) in the presence of $Fe(CO)_5$. The formation of β-epoxy ketone **11** depends on R being an effective electron-attracting group, thereby making the carbonyl carbon of **8** more positive and hence more susceptible, than the halogen-bearing carbon, to attack by **13** (treating this step as a displacement).

Now that the reaction pathway as outlined in Scheme I had been established, we next considered whether coupling products obtained from several other $Fe(CO)_5$–halide reactions were formed *via* the same or a similar process. The postulated mechanism for the formation of thiolsulfonate esters, from treatment of sulfonyl chlorides **15** with $Fe(CO)_5$ in various solvents, invoked initial iron incorporation into the sulfur–chlorine bond (**16**).[24] The resulting organometallic could then react with additional sulfonyl chloride to give an α disulfone and $Fe(CO)_4Cl_2$. The α disulfone, as shown independently,[24] could be deoxygenated by more $Fe(CO)_5$ to the thiolsulfonate ester. This proposed mechanism, with minor modifications (Scheme III, decarbonylation of **16** prior to reaction with more **15**), is supported by the following results. (a) Treatment of **15** (R = CF_3) with $Fe(CO)_5$ in *n*-heptane at temperatures below −20° gave **16** (R = CF_3) in 80% yield.[37] If allowed to warm to room temperature, **16** was decarbonylated to **17** (R = CF_3). Treating **15** (R = CF_3) with $Fe(CO)_5$ in tetrahydrofuran (THF) at −20° gave solvated **17** (R = CF_3) directly. (b) *p*-Toluenesulfonyl chloride is substantially less reactive toward $Fe(CO)_5$ than **15** (R = CF_3 or CCl_3),[24,37] and gives the iron halide **20** as well as the α disulfone (in unspecified yield) when treated in THF at room temperature for 4 days.[37,38]



(c) Reaction of **20** with **15** (R = p-BrC_6H_4) in *N,N*-dimethylacetamide under conditions employed for the $Fe(CO)_5$ reaction gave no α disulfone or thiolsulfonate. However, as observed before with α-halo ketones, the presence of $Fe(CO)_5$ resulted in rapid formation of the unsymmetrical thiolsulfonates, p-$BrC_6H_4SSO_2C_6H_4CH_3$-*p* and p-$CH_3C_6H_4SSO_2C_6H_4Br$-*p*. The vigorous reaction was so rapid that we could isolate but traces of the expected α disulfone. Ferric chloride was also formed in the reaction.

Coffey[1] proposed that the *gem*-dihalide–$Fe(CO)_5$ reaction giving substituted ethylenes proceeds *via* a carbene intermediate. We believe, on the basis of preliminary experiments, that a mechanism similar to that outlined in Schemes I and III is operative here (Scheme IV). Our support for this mechanism is based on the following results. (a) As previously noted, treatment of 9,9-dibromofluorene with $Fe(CO)_5$ in refluxing dioxane gave both the alkene and 9,9′-dibromobisfluorenyl, corresponding to **23**. (b) Reaction of **1** (X = Cl; Y = H) and $Fe(CO)_5$ in benzene at 5° for 4 days gave **2** (X = Cl; Y = H) and a purple-red complex, probably the halogen-bridged dimer of **22** (X = Cl; Y = H). In addition, the unstable *cis*-dichlorotetracarbonyliron was formed in the reaction and identified by comparison of its physical properties with those reported in the literature.[39] That the source of *cis*-$Fe(CO)_4Cl_2$ was the dehalogenation of **23** was demonstrated by its formation, along with tetraphenylethylene, when **23** (X = Cl; Y = H) was treated with $Fe(CO)_5$ in benzene at 5°. The formation of both **22** and CO in the reaction of **1** (X = Cl; Y = H) with $Fe(CO)_5$ indicated that **21** was produced but that it was probably too unstable to permit isolation.

In summary, this paper has described a simple, and useful, synthesis of 1,4 diketones, monoketones, and α-deuterio ketones, subject to reaction conditions. We have shown that the mechanisms for the reactions of $Fe(CO)_5$ with α-halo ketones, sulfonyl chlorides, and probably *gem*-dihalides are similar and we believe that some of the other halide reactions, *e.g.*, sulfenyl halides,[25] proceed by an analogous pathway. An important step of this mechanism, the reaction of the organoiron halide intermediate with additional reactant halide, requires the presence of $Fe(CO)_5$. It should be noted that involvement of radicals at some stage(s) of the reaction pathway outlined in Schemes I, III, and IV has not, as yet, been ruled out.

Studies in progress with optically pure α-halo ketones [*d*-3-bromocamphor, enantiomers of desyl chloride] are directed toward determining the stereochemical consequences of the α-halo ketone reaction, insofar as the halogen-bearing carbon is concerned.

Experimental Section

General.—Melting points were determined on a Fisher-Johns or Gallenkamp apparatus and are uncorrected. Elemental analysis (Table II) were carried out by A. Bernhardt, West Germany, and PCR, Inc., Gainesville, Fla. Infrared spectra were obtained on Perkin-Elmer 457 and 521 spectrophotometers; the wavelength readings were calibrated with a polystyrene film. Nmr spectra were obtained on a Varian A-60 spectrometer, employing tetramethylsilane as the internal standard. Mass spectra were recorded using an Atlas CH-5 spectrometer.

---

[37] E. Lindner, H. Weber, and G. Vitzthum, *J. Organometal. Chem.*, **13**, 431 (1968).

[38] We recovered starting materials, along with small amounts of polymer, when triphenylphosphineiron tetracarbonyl and **15**, R = p-BrC_6H_4–, were allows to react in *N,N*-dimethylacetamide at 80°.

[39] R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, **3**, 584 (1964).

SCHEME IV

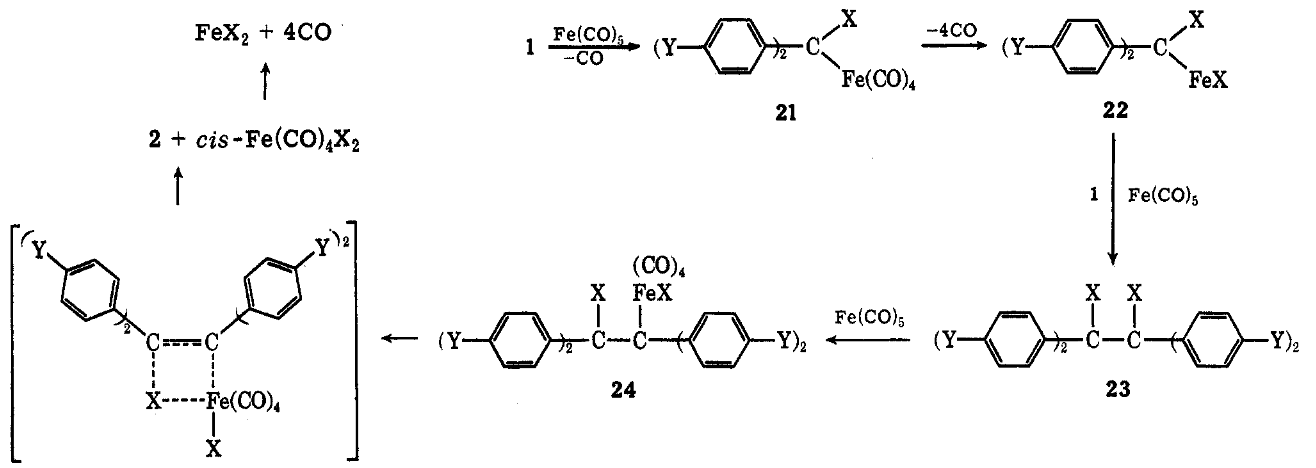


TABLE II

ANALYTICAL DATA

Compd	Formula	Calcd, % C	Calcd, % H	Calcd, % Fe	Found, % C	Found, % H	Found, % Fe
9, R = *p*-$C_6H_5C_6H_4$; R′ = R″ = H	$C_{28}H_{22}O_2$	86.12	5.68		86.30	5.53	
11, R = *p*-BrC_6H_4; R′ = R″ = H	$C_{16}H_{12}Br_2O_2$	48.52	3.05		48.87	3.00	
11, R = *p*-FC_6H_4; R′ = R″ = H	$C_{16}H_{12}F_2O_2$	70.07	4.41		70.03	4.51	
9, R = C_6H_5; R′ = CH_3; R″ = H	$C_{18}H_{18}O_2$	81.17	6.87		80.94	6.67	
9, R = C_6H_5; R′ = R″ = CH_3	$C_{20}H_{22}O_2$	81.60	7.53		81.26	7.26	
9, R = 2-$C_{10}H_7$; R′ = R″ = H	$C_{24}H_{18}O_2$	85.18	5.36		85.11	4.98	
9, R = 1,2,3,4,5,6,7,8-octahydroanthryl; R′ = R″ = H	$C_{32}H_{38}O_2$	84.54	8.42		84.61	8.47	
9, R = 1-Adamantyl; R′ = R″ = H	$C_{24}H_{34}O_2$	81.31	9.67		81.57	9.32	
12, R = *p*-$C_6H_5C_6H_4$; R′ = R″ = H; X = Br	$C_{18}H_{11}BrFeO_5$			12.60			12.69
13, R = *p*-$C_6H_5C_6H_4$; R′ = R″ = H; X = Br	$C_{28}H_{22}Br_2Fe_2O_2$	50.80	3.35	16.87	51.12	3.53	16.38
1-Phenyl-4-*p*-phenylphenyl-1,4-butanedione	$C_{22}H_{18}O_2$	84.05	5.77		83.75	5.96	

Iron pentacarbonyl and diiron enneacarbonyl (Pressure Chemical Co.) were used as received. The α-halo ketones were commercial products and were recrystallized or distilled prior to use. Solvents were dried and purified by standard methods. All reactions were run under a dry nitrogen atmosphere.

Reaction of $Fe(CO)_5$ with α-Halo Ketones.—A mixture of the α-halo ketone (11.6 mmol) and $Fe(CO)_5$ (6.61 mmol) in anhydrous DME (15–30 ml) was refluxed (95–100° oil bath temperature) with stirring. At the end of the reflux time (see Table I), the reaction mixture was heated to an oil bath temperature of 140° for 5 min, cooled, and then poured into 250–350 ml of cold water. The resulting precipitate was filtered and dried. Work-up was effected in the following manner for the various reactions.

A. 8 (R = C_6H_5; R′ = R″ = H).—The red-brown solid was treated with chloroform (30 ml) and filtered through Celite, and the filtrate was evaporated *in vacuo* to give a dark red oil. Crystallization from pentane afforded 9 (R = C_6H_5; R′ = R″ = H), which was recrystallized from 70% aqueous ethanol.

The aqueous filtrate was extracted six times with ether (100 ml), and the ether extract was dried and distilled to give **10** (R = C_6H_5; R′ = R″ = H).

B. 8 (R = *p*-$C_6H_5C_6H_4$; R′ = R″ = H).—The solid was continuously extracted (Soxhlet) with pentane. Evaporation of pentane extract gave 10 (R = *p*-$C_6H_5C_6H_4$; R′ = R″ = H). The residue in the thimble was treated with hot acetone. Gradual evaporation of the solvent deposited crude 1,4 diketone, which was filtered. The filtrate was evaporated to dryness, pentane was added, and additional precipitated 1,4 diketone was filtered. The two fractions of 9 (R = *p*-$C_6H_5C_6H_4$; R′ = R″ = H) were combined and recrystallized from benzene.

C. 8 (R = *p*-BrC_6H_4; R′ = R″ = H).—The yellow-brown solid was continuously extracted (Soxhlet) with pentane. Removal of pentane gave 10 (R = *p*-BrC_6H_4; R′ = R″ = H). The nonextractable material was now continuously extracted with tetrahydrofuran. Removal of solvent gave an oil which was treated with hot benzene and filtered through Celite, and the filtrate was gradually reduced to give crystalline 9 (R = *p*-BrC_6H_4; R′ = R″ = H). The β-epoxy ketone 11 (R = *p*-BrC_6H_4; R′ = R″ = H) was obtained by evaporation of the mother liquor.

D. 8 (R = *p*-FC_6H_4; R′ = R″ = H).—The pale brown solid was treated repeatedly with ether and filtered. The residue from evaporation of the filtrate was chromatographed on Florisil using carbon tetrachloride as eluent. The methyl ketone 10 (R = *p*-FC_6H_4; R′ = R″ = H) was eluted first, followed by recovered starting material and then 11 (R = *p*-FC_6H_4; R′ = R″ = H). Elution with chloroform gave traces of 1,4 diketone. Purification of the methyl ketone was effected by vacuum distillation, while the β-epoxy ketone was recrystallized from hexane.

E. 8 (R = *p*-$CH_3OC_6H_4$; R′ = R″ = H).—The aqueous filtrate was extracted with ether, and the ether extract was dried and evaporated to an oil. Crystallization from pentane gave 10 (R = *p*-$CH_3OC_6H_4$; R′ = R″ = H).

The water-insoluble solid was continuously extracted with pentane–benzene (1:1) to give additional methyl ketone. Extraction of the residual solid with ether–methylene chloride (1:2) gave 9 (R = *p*-$CH_3OC_6H_4$; R′ = R″ = H).

F. 8 (R = C_6H_5; R′ = CH_3; R″ = H).—In this case, a yellow oil resulted when the reaction mixture was poured into water. It was extracted six times with ether (100-ml portions), and the ether extract was dried and evaporated. Pentane was added to the resulting oil and white crystals of 9 (R = C_6H_5; R′ = CH_3; R″ = H) crystallized out when the solution was chilled in an ice bath. The 1,4 diketone was filtered, and the filtrate was distilled to give 10 (R = C_6H_5; R′ = CH_3; R″ = H).

G. 8 (R = C_6H_5; R′ = R″ = CH_3).—A gummy substance was obtained when the reaction mixture was poured into water. The aqueous solution was decanted and pentane was added to the gum to give, on cooling, 9 (R = C_6H_5; R′ = R″ = CH_3), which was recrystallized from benzene.

The ketone 10 (R = C_6H_5; R′ = R″ = CH_3) was obtained by extracting the aqueous solution with ether, combining the ether and pentane extracts, and fractionally distilling the mixture.

H. 8 (R = 2-$C_{10}H_7$; R′ = R″ = H).—The solid was treated with hot chloroform and filtered, and the filtrate was evaporated *in vacuo*. Sublimation of the resulting solid gave 10 (R =

$2\text{-}C_{10}H_7$; $R' = R'' = H$). Recrystallization of the sublimation residue gave the 1,4 diketone.

I. 8 (R = 1,2,3,4,5,6,7,8-Octahydroanthryl; $R' = R'' = H$).—The gray-green paste was continuously extracted with pentane. Removal of the solvent gave a brown paste which nmr indicated to be a mixture of methyl ketone and starting material. The paste was treated with hot methanol (200 ml), the solution was decanted, and the volume of methanol was reduced until crystals of starting material began to appear. The methanol-insoluble solid was recrystallized from hexane to give pure methyl ketone.

Further extraction of the gray-green paste with methylene chloride gave the 1,4 diketone, which was purified by recrystallization from hexane-benzene (7:3).

J. 8 (R = 1-Adamantyl; $R' = R'' = H$).—The semisolid was treated with chloroform and methanol was added slowly. A white precipitate of 9 (R = 1-adamantyl; $R' = R'' = H$) was isolated by filtration. Starting material and the methyl ketone were obtained by evaporation of the filtrate *in vacuo*.

Reaction of 8 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) under Different Conditions. A. Adding the Reaction Mixture to Deuterium Oxide.—By pouring the reaction mixture into deuterium oxide (99.8%) rather than water, 2-deuterio-4′-phenylacetophenone was obtained using the work-up conditions described above. Mass spectral analysis indicated >95% monodeuteration.

B. Anhydrous Reaction Conditions.—After refluxing for 5 hr, the reaction mixture was cooled and the solvent was removed *in vacuo*. Work-up according to part B of the previous section gave 1,4 diketone but no methyl ketone.

C. Using DME-Water as Solvent.—The α-halo ketone and $Fe(CO)_5$ were refluxed in a mixture of DME (27 ml) and water (3 ml). Work-up as above gave recovered starting materials along with a small amount of triiron dodecacarbonyl.

D. Using Catalytic Quantities of $Fe(CO)_5$.—The reaction is not catalytic, as treatment of 8 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) with $Fe(CO)_5$ in a 20:1 ratio gave almost complete recovery of α-halo ketone accompanied by small amounts of **9** and **10**.

E. Presence of Azobisisobutyronitrile.—The procedure described for 2-bromo-4′-phenylacetophenone was repeated in the presence of azobisisobutyronitrile (1.0 mmol). The product yields were not altered and neither did the reaction appear to proceed any faster.

F. Solvent Variation.—Using dry *N*,*N*-dimethylacetamide or tetramethylurea as solvents gave the 1,4 diketone and 4-phenylacetophenone in 10–15% lower yields than obtained when DME was the reaction solvent.

Reaction of 8 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) with Diiron Enneacarbonyl.—A mixture of 8 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) (3.19 g, 11.6 mmol) and diiron enneacarbonyl (4.22 g, 11.6 mmol) in anhydrous benzene (55 ml) was stirred at room temperature for 6 hr. The solution was filtered to give 2.94 g of 12 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$). The ir and mass spectral data for this complex are given in the text. Evaporation of the filtrate *in vacuo* gave 13 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$).

Complex 13 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$).—The decarbonylated product was obtained in quantitative yield by heating 12 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) in DME at reflux temperature for 3 hr. Reaction of the α-halo ketone with diiron enneacarbonyl in benzene for 4 days at room temperature gave **13** as the sole product.

Reaction of Triphenylphosphineiron Tetracarbonyl with 8 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$).—Triphenylphosphineiron tetracarbonyl[40] [4.30 g, 10.0 mmol] and 2-bromo-4′-phenylacetophenone (4.81 g, 17.5 mmol) were refluxed in DME (35 ml) for 5 hr. The solution was evaporated *in vacuo* and continuous ether extraction of the resulting solid gave the two starting materials.

Conversion of 13 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) to Organic Products. A.—To DME [15 ml] was added 5.0 mmol of **13** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) followed by water (100 ml) and the mixture was stirred for 4 hr. Work-up as described above gave 10 ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$).

B.—A mixture of **13** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) and 2-bromo-4′-phenylacetophenone in DME (15 ml) was refluxed for 5 hr and then poured into ice-water (150 ml). Only trace amounts of 1,4 diketone (*p*-phenylacetophenone was the principal product) were isolated using the work-up conditions described in part B. However, repeating the reaction in the presence of $Fe(CO)_5$ gave the 1,4 diketone in 80% yield with the monoketone **10** formed as a by-product. Ferrous chloride was also obtained.

C.—When **13** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$) was treated with 2 equiv of **8** ($R = C_6H_5$; $R' = R'' = H$) in the presence of 1–2 drops of $Fe(CO)_5$, under the same conditions as above, 1-phenyl-4-*p*-phenylphenyl-1,4-butanedione, mp 183–185°, was isolated in 74% yield.

Reaction of 20 with *p*-Bromobenzenesulfonyl Chloride.—A mixture of complex **20** (1.24 g, 3.50 mmol) and **15** ($R = p\text{-}BrC_6H_4$) (0.894 g, 3.50 mmol) in *N*,*N*-dimethylacetamide (14 ml) was heated with stirring at 60° for 8 hr. The solution remained dark red-brown in color. Work-up gave starting materials. When the reaction was repeated with dropwise addition of $Fe(CO)_5$ at 60°, the solution immediately turned from dark red-brown to pale yellow. The solution was cooled and poured into water [350 ml], and the resulting solid was filtered to give 0.946 g (79%) of a mixture of thiosulfonate esters, recrystallized from *n*-heptane or isopropyl ether. Trace quantities of α disulfone were insoluble in hot *n*-heptane. Chromatography of the mixture on silica gel using benzene-hexane as eluent gave pure *p*-bromophenyl *p*-toluenethiolsulfonate, mp 92.0–94.0° (lit.[41] mp 93.5–94.5°), and *p*-tolyl *p*-bromophenylthiolsulfonate, mp 124–125° (lit.[41] mp 122–123°). The aqueous solution contained ferric chloride.

Reaction of Dichlorodiphenylmethane (1, X = Cl; Y = H) with $Fe(CO)_5$ at Room Temperature.—To a 5° solution of dichlorodiphenylmethane (7.11 g, 30.0 mmol) in dry benzene (20 ml) was added $Fe(CO)_5$ (2.03 ml, 15.0 mmol) and the reaction mixture was stirred for 4 days. During this time, a yellow solid precipitated out of solution. The yellow compound was filtered under nitrogen. It proved to be extremely air sensitive and gradually decomposed to ferrous chloride and carbon monoxide even when kept in the refrigerator under N_2. The ir spectrum ($CHCl_3$) shows terminal metal carbonyl stretching bands at 2173 (w), 2132 (vs), and 2087 cm^{-1} (s) in reasonable agreement with the values reported by Taylor and Horrocks[39] for *cis*-$Fe(CO)_4Cl_2$ [$\nu_{C\equiv O}$ at 2166.9 (w), 2125.8 (vs), and 2081.7 (s), solvent not stated].

The deep purple filtrate was evaporated *in vacuo*, the residue was treated repeatedly with 50-ml portions of petroleum ether (bp 38–51°) and filtered, and this filtrate was evaporated to a white solid and a liquid. The liquid was decanted from the solid and identified as unreacted dichlorodiphenylmethane. The petroleum ether insoluble solid was then treated with carbon tetrachloride and filtered, and the filtrate was evaporated *in vacuo* to give 0.93 g of tetraphenylethylene, mp 226–227° (lit.[1] mp 224–226°). The carbon tetrachloride insoluble solid was red-purple in color and displayed modest air stability. The ir spectrum lacked any bands due to terminal metal carbonyl stretching but did show the typical benzene ring absorptions. The molecular weight was 535 (vapor phase osmometry) compared to a calculated value of 586 for dimeric **22**.

Tetraphenylethylene and *cis*-$Fe(CO)_4Cl_2$ were obtained when a mixture of 1,2-dichloro-1,1,2,2-tetraphenylethane and $Fe(CO)_5$ was allowed to react at 5° as described for 1 (X = Cl; Y = H).

Registry No.—$Fe(CO_5)$, 13463-40-6; **12** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$; X = Br), 34728-92-2; **13d** ($R = p\text{-}C_6H_5C_6H_4$; $R' = R'' = H$; X = Br), 34728-93-3; 1-phenyl-4-*p*-phenylphenyl-1,4-butanedione, 34733-60-3.

Acknowledgments.—Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society.

---

[40] We thank Mr. R. A. Partis for providing us with generous quantities of this compound.

[41] J. Weidner and S. S. Block, *J. Med. Chem.*, **10**, 1167 (1967).