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The Reaction of Disodium Tetracarbonylferrate(−II) with Carboxylic Esters and Carbothioic Esters[1)]

Yoshihisa WATANABE, Masakazu YAMASHITA, Mineo IGAMI,
Take-aki MITSUDO, and Yoshinobu TAKEGAMI

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

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The reaction of carboxylic and carbothioic esters with disodium tetracarbonylferrate has been studied. Aryl and thiolic esters reacted with the ferrate under mild conditions to give aldehydes after the reaction mixture had been quenched with acetic acid, but alkyl esters did not. 3-Benzylidenephthalide and phthalide gave 2-phenyl-1,3-indanedione and a dimeric product respectively.

Recently, several works have demonstrated that alkali metal tetracarbonylferrate, $[Fe(CO)_4]^{2-}$ (**1**), is useful for the syntheses of aldehydes,[2—5)] carboxylic acid derivatives,[6)] and ketones[7,8)] from alkyl halides, acid chlorides, carboxylic anhydrides, and carboxylic carbonic anhydrides. Though these carboxylic acid derivatives have great reactivities to **1**, little attention has been paid to other carboxylic acid derivatives. In this paper, we wish to report that the ferrate (**1**) also has some reactivities as a nucleophile to carboxylic esters and carbothioic esters, which can be transformed into the corresponding acyl tetracarbonylferrate (**2**). This is the first example of an anionic metal carbonyl reacting with an ester linkage.

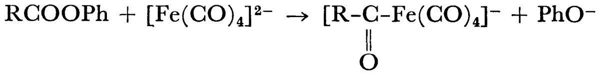
Results and Discussion

*Reactions of Carboxylic Esters with **1**.* Aryl esters, such as phenyl benzoate and phenyl propionate, reacted with a tetrahydrofuran(THF) solution of **1** at room temperature, and the corresponding aldehydes and phenols were formed after the treatment of the reaction mixture with glacial acetic acid.

$$RCOOPh \xrightarrow[\text{ii) } H^+]{\text{i) } Na_2Fe(CO)_4} RCHO + PhOH$$

Alkyl esters, such as ethyl propionate and benzyl benzoate, scarcely reacted at all with **1** even at rather higher temperatures. The results are summarized in Table 1.

In the case of the aryl esters, the infrared spectra of the reaction mixture show bands at 1890 and 1550—1600 cm^{-1} which are not detectable before the addition of the esters. This indicates that the corresponding acylcarbonylferrates (**2**) are formed as intermediates.[9)]



$$RCOOPh + [Fe(CO)_4]^{2-} \rightarrow [R\text{-}\underset{\underset{O}{\|}}{C}\text{-}Fe(CO)_4]^- + PhO^-$$

(**1**) (**2**)

2 is assumed to be formed by the uncleophilic attack of **1** on the carbonyl carbon of the ester. The remarkable difference in reactivity between the aryl esters and the alkyl ones appears to arise partly from the electronic effects of the phenoxyl and alkoxyl group. The electron-withdrawing property of the phenoxyl group is larger than that of the alkoxyl group. Therefore, the electron density on the carbonyl carbon of the aryl esters may be lower than that of alkyl carboxylates. This slight difference may make the aryl esters active in the nucleophilic attack of **1**. Such an influence of the electron density of the carbonyl carbon on the attack of **1** has also been observed in the reaction of mixed carboxylic anhydrides.[4)]

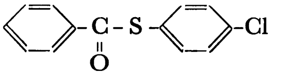
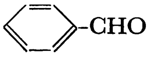
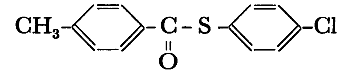
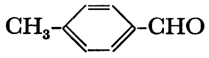
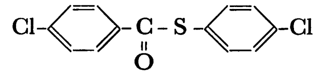
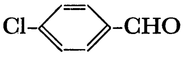
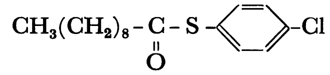
*Reaction of Carbothioic Esters with **1**.* Carbothioic esters such as *S*-*p*-chlorophenyl benzenecarbothioate reacted readily with **1** to give the corresponding

TABLE 1. REACTION OF CARBOXYLIC ESTERS WITH DISODIUM TETRACARBONYLFERRATE

Run	Carboxylic ester	Reaction conditions Temp (°C)	Time	Solvent	Aldehyde[a)]	Yield (%)[c)]
1	Phenyl benzoate	25	6 (day)	THF	Benzaldehyde	27
2	Phenyl benzoate	25	6 (day)	THF-NMP(1 : 1)	Benzaldehyde	20
3	Phenyl benzoate	60	8 (h)	THF	Benzaldehyde	Trace[b)]
4	Phenyl *p*-toluate	25	10 (day)	THF	*p*-Tolualdehyde	32
5	Phenyl *p*-chlorobenzoate	25	8 (day)	THF	*p*-Chlorobenzaldehyde	39
6	Phenyl propionate	25	7 (day)	THF	Propionaldehyde	40
7	Phenyl nicotinate	25	6 (day)	THF	3-Pyridinecarbaldehyde	22
8	*p*-Chlorophenyl benzoate	25	6 (day)	THF	Benzaldehyde	25
9	*p*-Chlorophenyl propionate	25	6 (day)	THF	Propionaldehyde	35
10	Benzyl benzoate	25	7 (day)	THF	——[b)]	
11	Benzyl benzoate	60	5 (h)	THF	——[b)]	
12	Ethyl propionate	25	5 (day)	THF	——[b)]	

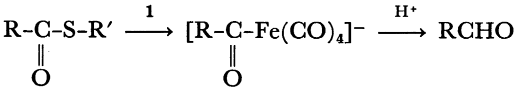
a) Product after the treatment of the reaction mixture with acetic acid. b) Almost quantitative amounts of starting materials were recovered. c) Based on the amount of esters used.

TABLE 2. REACTION OF CARBOTHIOIC ESTERS WITH DISODIUM TETRACARBONYLFERRATE[a)]

Run	Carbothioic ester	Aldehyde[b)]	Yield (%)[c)]
13			49
14			70
15			56
16		CH_3-(-CH_2-)$_8$-CHO	45

a) At 25 °C for 20 h in tetrahydrofuran. b) Product after the treatment of the reaction mixture with acetic acid. c) Based on the amount of esters used.

aldehydes in high yields after the treatment of the reaction mixture with glacial acetic acid. The results are shown in Table 2. In these reactions, the infrared spectra of the reaction mixture had bands at 1890 and 1550—1600 cm^{-1}. Therefore, the formation of the acyl tetracarbonylferrate (**2**) as an intermediate in this reaction is also strongly suggested.



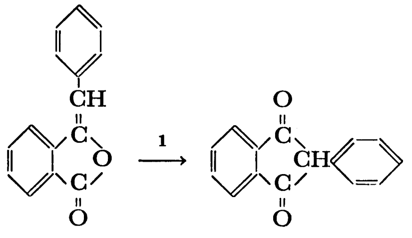
$$\mathrm{R\text{-}\underset{\underset{O}{\|}}{C}\text{-}S\text{-}R'} \xrightarrow{1} [\mathrm{R\text{-}\underset{\underset{O}{\|}}{C}\text{-}Fe(CO)_4}]^- \xrightarrow{H^+} \mathrm{RCHO}$$

(**2**)

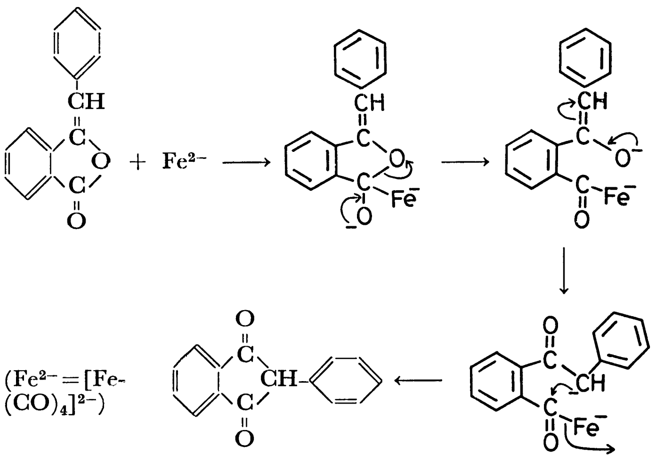
A comparison of the reaction conditions and the yields of the products in Tables 1 and 2 show that carbothioic esters have a greater reactivity to a nucleophilic attack of **1** than usual carboxylic esters. This agrees with the order of susceptibility of carboxylic acid derivatives to a nucleophilic attack.

Reaction of Cyclic Carboxylic Esters with 1. The reaction of **1** with carboxylic esters was applied to cyclic esters. As the esters, phthalide, coumarin, 3,4-dihydrocoumarin, 3-benzylidenephthalide, and γ-butyrolactone were employed. If the reaction proceeds as expected, the corresponding aldehydes with a hydroxyl group will be produced, but the aldehydes were not obtained in these reactions. When coumarin, 3,4-dihydrocoumarin, and γ-butyrolactone were treated with **1**, some reaction took place, with a color change in the reaction mixture from pale-yellow to reddish-black. However, the formation of acyl carbonylferrate as an intermediate is not clear; the infrared absorption bands characteristic of the acyl carbonylferrate (**2**) were not detectable. In these reactions, only a black, tarry material was obtained even after treatment with acetic acid or methyl iodide.

3-Benzylidenephthalide gave 2-phenyl-1,3-indanedione in *ca.* a 50% yield by a reaction with **1**.



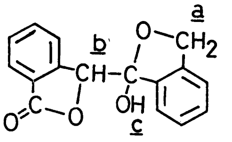
The reaction mechanism is not completely clear at the present time, but a plausible reaction scheme is that described in Scheme 1.



Scheme 1.

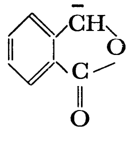
In this scheme, an acyl carbonylferrate is also considered to be an intermediate. Such a transformation of 3-benzylidenphthalide takes place in the presence of sodium alkoxide as the catalyst.[10)]

Phthalide also reacted with **1** to give white crystals in a 71% yield (based on the amount of phthalide); these crystals are soluble only in acetone and dimethyl sulfoxide. The infrared spectra of this compound had absorption bands at 3400 and 1740 cm^{-1}, characteristic of the hydroxyl group and of a carbonyl in a strained ring respectively. Thermolysis under reduced pressure (180 °C 1 Torr) and hydrolysis in a hot 3.5 M NaOH alcoholic solution gave phthalide in 85 and 70% yields respectively. From these results and elemental analysis, the structure of this compound is considered to be **3**.



(**3**)

The mass spectrum did not exhibit a peak corresponding to the parent molecular ion, but the following peak assignments were made: *m/e* 251$[M-OH]^+$, 135$[M-\overline{C_6H_4COOC}H]^+$, 134$[\overline{C_6H_4CH_2OC}O]^+$, 133$[M-135]^+$, 118$[135-OH]^+$. **3** may be a mixture of two diastereomers. In the NMR spectra, there are three types of signals besides that of the benzene ring: i) τ 5.04 and 4.90, both the AB type, assigned to $\underline{a}$ in **3**, ii) τ 4.09 and 4.25, both signlets, assigned to $\underline{b}$, and iii) τ 3.75 and 3.70, both singlets, assigned to $\underline{c}$, which disappeared upon the addition of D_2O. The fractional recrystallization of **3** from an acetone–water solution gave white needles (**4**), which have a similar infrared spectrum to, and the same composition as **3**. The NMR spectrum of **4** showed signals at τ 4.90 (AB type, 2H), 4.25 (singlet, 1H), and 3.70 (singlet, 1H). These results show that **4** is the one of the diastereomers of **3**, although its steric configuration is unknown at the present time.



(5)

The mechanism of the formation of **3** is not clear at present, but the phthalide anion (**5**) is assumed to be formed by the reaction of phthalide with **1**; the anion will attack a carbonyl carbon of the second phthalide to give **3** after protonation. The phthalide anion (**5**) is also suggested to be formed by the treatment of phthalide with a basic reagent and to react with carbonyl compounds to give cross-adducts.[11] However, in the reaction of phthalide with **1** in the presence of such carbonyl compounds as benzyl benzoate, the cross-adducts were not obtained.

Experimental

The NMR spectra were obtained on a JEOL JNM-PMX 60 NMR spectrometer and a Varian Model HR-220 NMR spectrometer. The infrared spectra were measured on a Hitachi model 215 grating infrared spectrometer. The mass spectra were recorded on a JMS=OISG mass spectrometer. The melting points are uncorrected.

Materials. *p*-Chlorophenyl benzoate, *p*-chlorophenyl propionate, phenyl *p*-chlorobenzoate, phenyl *p*-toluate, *S*-*p*-chlorophenyl benzenecarbothioate, *S*-*p*-chlorophenyl *p*-toluenecarbothioate, *S*-*p*-chlorophenyl decanethioate, and *S*-*p*-chlorophenyl *p*-chlorobenzenecarbothioate were prepared according to the usual manner from acid chlorides and phenol, *p*-chlorophenol, or *p*-chlorothiophenol. The pentacarbonyliron, acetic acid, and other compounds employed in this study were all commercial products; their purities were checked by GLPC and found to be satisfactory for the reaction. Tetrahydrofuran was dried over lithium aluminium hydride and distilled before use.

Preparation of Disodium Tetracarbonylferrate (1). All the reactions were carried out in a 200-ml, three-necked flask equipped with a gas buret and a magnetic stirrer under an argon atmosphere. $Na_2[Fe(CO)_4]$ (**1**) was prepared according to the method described in a previous paper.[3] Six mmol of **1** in 30 ml of tetrahydrofuran were used in each run.

General Reaction Procedures and Analyses. To a solution of 6 mmol of **1** in tetrahydrofuran, an equimolar amount of an ester compound was added, and the reaction mixture was agitated at a desired temperature. After a certain reaction time, 0.6 ml of glacial acetic acid was poured in by means of a syringe and the mixture was stirred for an additional five minutes. A 0.2-ml sample of the solution was taken off and then submitted to GLPC analyses; column (3 mmϕ, 1.5 m) packed with Diethylene Glycol Adipate Polyester on chromosorb. The aldehydes were identified by a comparison of their retention times in GLPC with those of authentic samples, and the yields of the aldehydes were determined using internal standards.

Reaction of 3-Benzylidenephthalide with 1. 3-Benzylidenephthalide (11 mmol) was added to a tetrahydrofuran solution of **1** (11 mmol) under an argon atmosphere, and the mixture was stirred for about 5 h at 40 °C. The mixture was acidified with 30 ml of 25% sulfuric acid, the tetrahydrofuran was removed *in vacuo*, and the residue was shaken with 100 ml of diethyl ether. The clean aqueous layer was discarded, and the green-black ether layer was shaken with two 70-ml portions of a 20% sodium cabonate solution. The acidification of the sodium carbonate solution with hydrochloric acid furnished white solids. The solid was terated with about 200 ml of diethyl ether, and the yellow-brown ether solution was left overnight at room temperature over sodium sulfate and then dried. After the removal of the solvent, 2-phenyl-1,3-indanedione (1.2 g, yield *ca.* 50%) was obtained and recrystallized from ethanol; mp 148 °C (literature mp 147—148 °C).[12] Found: C, 81.23; H, 4.34%. Calcd for $C_{15}H_{11}O_2$: C, 81.06; H, 4.54%. The IR and NMR spectra are identical with those of an authentic sample.

The Reaction of Phthalide with 1. Into a tetrahydrofuran solution of **1** (11 mmol), we stirred 1.34 g (10 mmol) of phthalide in tetrahydrofuran at room temperature under argon. After 24 h, to the reaction mixture we added 3 ml of glacial acetic acid and the solvent was distilled off under reduced pressure. A 100-ml portion of a mixture of acetone and water, (5 : 1 v/v) was poured into the residue, and then 100 more ml of water were added. Diethyl ether (50 ml) was poured into the solution, and the organic layer was separated after vigorous shaking with the spearatory funnel. The organic solution was dried over sodium sulfate overnight, and the solvent was evaporated under reduced pressure. The white solids (**3**) thus obtained were recrystallized from acetone (0.95 g; yield 71% based on phthalide); mp 149.5—150.5 °C. Found: C, 71.52; H, 4.40%. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51%. Mass; *m/e* 251, 135, 134, 133, 118, 105. The fractional recrystallization of **3** was conducted as follows. 105 mg of **3** were dissolved in 15 ml of an acetone–water mixed solution (5 : 1 v/v), and the solution was permitted to stand in the open air. After about one week, the precipitated white crystals (**4**) were collected(28 mg). Found: C, 71.59; H, 4.61%.

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