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# THE REACTION OF DISODIUM TETRACARBONYLFERRATE(-II) WITH 1,3-DIBROMOPROPANE. THE FORMATION OF A NOVEL 2-FERRACYCLOPENTANONE COMPLEX

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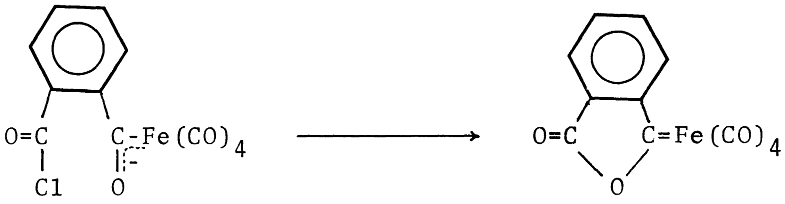
Disodium tetracarbonylferrate reacts with 1,3-dibromopropane in the presence of phosphine to give a 2-ferracyclopentanone complex, $\overline{CH_2CH_2CH_2COFe}(CO)_3PR_3$.

Previously, we reported that phthaloyl dichloride reacts with disodium tetracarbonylferrate to give biphthalidylidene possibly via a cyclic carbene iron complex (II), which is derived from an acylcarbonylferrate (I) by an intramolecular electrophilic reaction.$^{1)}$



(I) (II)

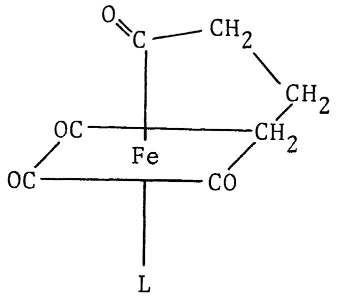
On the other hand, Collman and his co-workers reported that disodium tetracarbonylferrate reacts with alkyl halides to give aliphatic ketones via an acylalkylcarbonylferrate, though it has not been isolated.$^{2)}$

In this communication, we wish to report the reaction of disodium tetracarbonylferrate with 1,3-dibromopropane in the presence of phosphines. The purpose of this investigation is to examine the intramolecular electrophilic reaction on acylcarbonylferrates.

The typical reaction was carried out as follows. Into a solution of $Na_2Fe(CO)_4$ (11 mmol) in tetrahydrofuran was added 2.88 g (11mmol) of triphenylphosphine and then 2.22 g (11 mmol) of 1,3-dibromopropane; the mixture was stirred for 10 hr at room temperature under argon. The solvent was distilled off and the residue was extracted with 30 ml of methylene chloride. The extract was chromatographed over silicagel and yellowish-brown precipitates thus obtained were recrystallized twice from a mixed solvent of petroleum ether and methylene chloride to give pale-yellow crystals (yield ∿10 %), mp 141-142°C (dec.) in a sealed tube under argon.

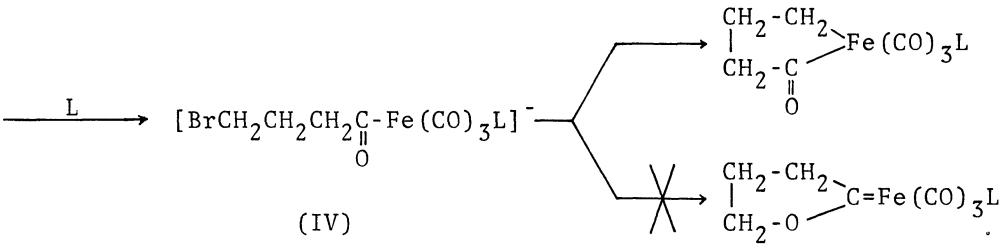
This compound was established to be the 2-ferracyclopentanone complex (V), where L is triphenylphosphine; IR (KBr): $\nu(CO)_{acyl}$ 1670(s) $cm^{-1}$. PMR (in $C_6D_6$): τ 7.59(triplet, 2H, J=7.5 Hz), 8.09(doublet of triplet, 2H, $J_{P-H}$=6.5[3] Hz), and 8.27(quintet, 2H, J=7.5 Hz). Found: C, 63.87; H, 4.59 %; mol wt (Rast), 465. Calcd for $C_{25}H_{21}FeO_4P$: C, 63.58; H, 4.48 %; mol wt, 472.3. The reduction of this compound with sodium borohydride gives 1-butanol, supporting this conclusion

When dimethylphenylphosphine was used instead of triphenylphosphine, a similar compound was obtained; PMR (in $C_6D_6$): τ 9.05(doublet, $2CH_3$, $J_{P-H}$=8.0 Hz). The compounds of this type were strongly suggested to have a configuration (III) from their nmr spectra.


(III)

A plausible reaction scheme may be presented;

$$BrCH_2CH_2CH_2Br + Fe(CO)_4{}^{2-} \longrightarrow [BrCH_2CH_2CH_2Fe(CO)_4]^- + Br^-$$


$$\xrightarrow{L} [BrCH_2CH_2CH_2\underset{\underset{O}{\Vert}}{C}\text{-}Fe(CO)_3L]^-$$

(IV)

(V)

(VI)

From the acyl iron complex (IV), two complexes (V) and (VI) are expected to be formed by the intramolecular electrophilic reaction. The carbene iron complex (VI), however, was not isolated in this reaction, suggesting that the reaction to 2-ferracyclopentanone complex (V) readily occurs.

Further studies are required to explain the difference between these two electrophilic reactions.

## REFERENCES

1) T. Mitsudo, Y. Watanabe, M. Tanaka, K. Yamamoto, and Y. Takegami, Bull. Chem. Soc. Japan, 45, 305 (1972).

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

3) This coupling constant shows that the phosphine is cis to the methylene group. See, F. L'Eplattenier, Inorg. Chem., 8, 965, (1969).

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