The Reaction of Disodium Tetracarbonylferrate(−II) with Phthaloyl Dichloride. The Formation of Biphthalidylidene

Take-aki Mitsudo, Yoshihisa Watanabe, Masato Tanaka, Kazuo Yamamoto,
and Yoshinobu Takegami

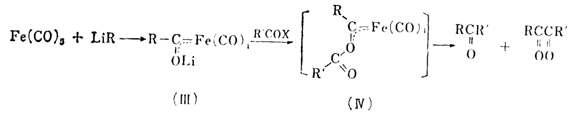
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received September 16, 1971)

Previously we reported that acyl halides react with disodium tetracarbonylferrate(−II) (I) to give the acyl tetracarbonylferrates (II), which are then hydrolyzed to the corresponding aldehydes in high yields.1)

$$\underset{(\mathrm{I})}{\mathrm{Na_2Fe(CO)_4}} + \mathrm{RCOCl} \longrightarrow \underset{(\mathrm{II})}{\mathrm{Na^+[RCOFe(CO)_4]^-}} \xrightarrow{\mathrm{H^+}} \mathrm{RCHO}$$

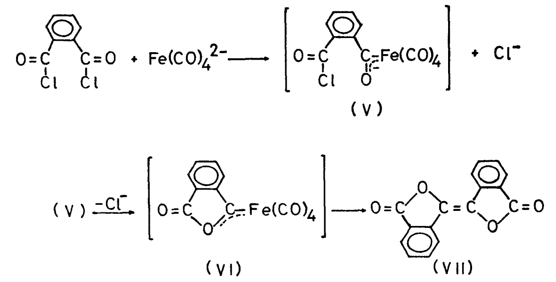
On the other hand, Sawa and his co-workers2) reported that lithium acyltetracarbonylferrates (III), which are prepared from $Fe(CO)_5$ and organolithium compounds, react with acyl halides to give ketones and/or α-diketones. It is strongly suggested that the reaction proceeds *via* the aryl- or alkylacyloxycarbene iron complex (IV):



In this communication we wish to report that $Fe(CO)_4^{2-}$ reacts with phthaloyl dichloride to give biphthalidylidene possibly *via* the cyclic carbene iron complex.

The reaction was carried out as follows. Into $Na_2Fe(CO)_4$3) (11 mmol) in tetrahydrofuran, we added 1.6 m*l* (11 mmol) of phthaloyl dichloride with stirring at −40°C under argon. After 1 hr, the mixture was warmed to 40°C and stirred for 2 hr. Then the solvent was distilled off and the residue was washed with water, 6N HCl, water again, and then ethyl ether. The orange-yellow precipitate (0.81 g) thus obtained was recrystallized twice form chloroform to give yellow biphthalidylidene (0.33 g). Yield, 23%. Mp 340—341°C (339—341°C4)). Found: C, 72.25; H, 3.17%; mol wt (mass) 264. Calcd for $C_{16}H_8O_4$: C, 72.73; H, 3.05%; mol wt 264.22. IR(KBr): 3085 (ν_{C-H}), 1785 ($\nu_{C=O}$), 1605, 1590, 1478 (benzene ring), 1190 (ν_{C-O}), 758 (*o*-disubstituted benzene) cm^{-1}. UV: $\lambda_{\max}^{\mathrm{CH_3CN}}$ mμ (log ε); 221(4.35), 226(4.38), 257(4.09), 293(4.02), 304(4.07), 356(4.39). These spectra are identical with those of *trans*-formed biphthalidylidene reported previously.4)

The reaction mechanism is not completely clear at the present time, but a plausible reaction scheme may be presented. First, $Fe(CO)_4^{2-}$ attacks one of the acyl halide groups in phthaloyl chloride to give an acyl carbonylferrate (V). Then the oxygen atom of the acyl group attached to the iron attacks another acyl carbon atom nucleophilically to form a lactonic carbene carbonyliron complex (VI),5) which then decomposes thermally to biphthalidylidene (VII). Fischer reported that the pyrolysis of a phenylalkoxycarbene-chromium complex gives the dimer of the carbene ligand.6)



It should be noted that it may be difficult to form the cyclic carbene complex by the reaction of organolithium compounds with metal carbonyls and that two carbene ligands are introduced into this product, biphthalidylidene. In contrast to the present results, only one ligand is introduced into the products in the reaction of lithium tetracarbonylferrate (III) with acyl halide.2) Further studies of the reaction mechanism are required to explain the difference between these reactions.

The reaction of diacyl halides with metal dianion complexes, $M(L)_n^{2-}$, can possibly be utilized for the preparation of other organic compounds or cyclic carbene metal complexes. We are now investigating these reactions; the results will be published in the near future.

---

1) Y. Watanabe, T. Mitsudo, M. Tanaka, K. Yamamoto, T. Okajima, and Y. Takegami, This Bulletin, **44**, 2569 (1971).

2) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183 (1970).

3) M. P. Cooke, Jr., *J. Amer. Chem. Soc.*, **92**, 6080 (1970); V. W. Hieber and G. Braun, *Z. Naturforsch.*, **14b**, 132 (1959).

4) J. C. Sauer, R. D. Cramer, V. A. Engelhardt, T. A. Ford, H. E. Holmqust, and B. W. Howk, *J. Amer. Chem. Soc.*, **81**, 3677 (1959).

5) Lactonic carbene cobalt complex has been prepared by the reaction of $Co_2(CO)_8$ with acetylene and carbon monoxide; H. W. Sternberg, J. G. Shukys, C. D. Donne, R. Markby, R. A. Friedel, and I. Wender, *ibid.*, **81**, 2339 (1959).

6) E. O. Fischer, B. Heckl, K. H. Dötz, J. Müller, and H. Werner, *J. Organometal. Chem.*, **16**, P 29 (1969).