BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(10), 2621—2622 (1974)

The Preparation of 3,5-Dichloro-2,4,6-trifluorophenyl(cyclopentadienyl)-dicarbonyliron and Its Derivatives

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(Received March 18, 1974)

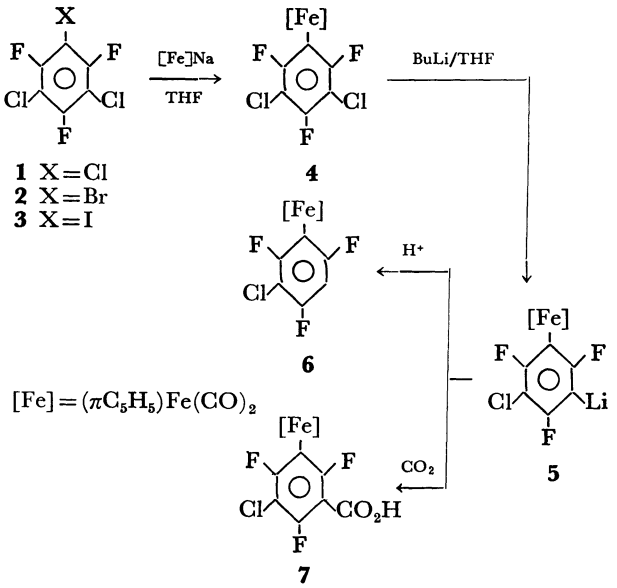
Synopsis. 3,5-Dichloro-2,4,6-trifluorophenyl(cyclopentadienyl)dicarbonyliron (**4**) was prepared by the nucleophilic substitution of *sym*-trichlorotrifluorobenzene with the (cyclopentadienyl)dicarbonyliron anion. One of the chlorine atoms of **4** was lithiated and the resulting lithio compound was hydrolyzed or carboxylated to give 3-chloro-2,4,6-trifluorophenyl(cyclopentadienyl)iron (**6**) or its 5-carboxylic acid (**7**) respectively.

A number of polyfluoroaryl(cyclopentadienyl)dicarbonylirons have recently been prepared by the nucleophilic substitution of a fluorine or other halogen atom of polyfluoro or monohalogenopolyfluoro aromatic compounds with the (cyclopentadienyl)dicarbonyliron anion.[1] For the preparation of further derivatives, however, polyfluoroaryliron compounds which carry other halogen atoms in addition to the fluorines on the aryl nucleus would seem to be more useful, because the halogen atom may be replaced by a functional group by means of the Grignard and similar reactions. As an example of such a kind of polyfluorohalogenoaryliron, bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron has been prepared by Cohen very recently.[2] We will here describe another compound of this type derived from *sym*-trichlorotrifluorobenzene (**1**).

The reaction between **1** and the iron complex anion, generated from the dimer of (cyclopentadienyl)dicarbonyliron and sodium amalgam, was carried out in tetrahydrofuran under a nitrogen atmosphere at −70 °C. At a higher temperature, only a tarry material resulted and no expected product was isolated, probably because of the formation of the (cyclopentadienyl)-dicarbonyliron dimer.[2]

In the usual nucleophilic reactions on *sym*-trichlorotrifluorobenzene, one or two fluorine atoms are replaced by the alkoxide ion or amines.[3,4] However, in the reactions between polyfluorohalogenobenzenes and the (cyclopentadienyl)dicarbonyliron anion, it is generally known that a chlorine or bromine atom is replaced in preference to a fluorine atom.[5] This can be explained by assuming that the elimination step of the halogen atom, and not the preceeding addition step of the anion, is the rate-determing step.[5] As expected, one chlorine atom of **1** was exclusively replaced by the (cyclopentadienyl)dicarbonyliron group to give 3,5-dichloro-2,4,6-trifluorophenyl (cyclopentadienyl) dicarbonyliron (**4**) in a yield of 14%.

The structure of **4** was evident from its ^{19}F NMR and mass spectra. In the ^{19}F NMR spectrum, two signals appeared, at +2.7 and +43.5 ppm,* in a 2 : 1 ratio of strength; those signals should be assigned to 2,6-F and 4-F respectively. These experimental values agree approximately with those calculated from the substituted shielding parameters of Bruce,[6] *i. e.*, +0.4 and +40.0 ppm. In the mass spectrum, *P* and *P*+2 peaks appeared at *m/e* 376 and 378 in a 100 : 65 ratio, as had been expected.



Bruce *et al.*[5] reported that the nucleophilic reactivity of the halogen atoms of polyfluorohalogenobenzenes towards the (cyclopentadienyl)dicarbonyliron anion increases in the order of Cl<Br<I. In order to have better yields, similar reactions with 3,5-dichloro-2,4,6-trifluorobromo- (**2**) and -iodobenzene (**3**) were examined. While a better yield (25%) was obtained from the bromo compound, **2**, the yield from the iodo compound, **3**, was poorer even than that from the chloro compound, **1**. We assumed that, while, in the cases of **1** and **2**, the elimination of the halogen atom is the rate-determining step, in the case of **3** it is the addition of the iron anion to the iodinated carbon atom.

The aryliron, **4**, is a very stable compound forming orange crystals; mp>200 °C (dec.); recrystallizable from various organic solvents including dimethylformamide. No chemical change occurred upon boiling in a methanolic solution either with sodium hydroxide or with concentrated hydrochloric acid for a long period. Concentrated sulfuric acid, however, hydrolyzed the C–Fe bond even at room temperature, giving 1,3-dichloro-2,4,6-trifluorobenzene.

One of the chlorine atoms of **4** could be lithiated with *n*-butyllithium in hexane–tetrahydrofuran, and from the resulting monolithio compound, **5**, 3-chloro-2,4,6-

* All ^{19}F NMR chemical shifts in this article are given in δ ppm from ext. CF_3CO_2H in tetrahydrofuran.

trifluorophenyl-(**6**) and 3-chloro-2,4,6-trifluoro-5-carboxyphenyl(cyclopentadienyl)dicarbonyliron (**7**) were derived by treatment with water and carbon dioxide respectively. The further lithiation of **6**, or dilithiation of **4**, to obtain a bifunctional aryliron compound was unsuccessful.

Experimental

*3,5-Dichloro-2,4,6-trifluorophenyl(cyclopentadienyl)dicarbonyliron (**4**).* A mixture of the dimer of (cyclopentadienyl)-dicarbonyliron (7.08 g, 20.0 mmol), 0.9% sodium amalgam (155 g, 60 mmol), and tetrahydrofuran (200 ml) was stirred for 1.5 hr at room temperature under a nitrogen atmosphere. The resulting solution of the (cyclopentadienyl)dicarbonyliron anion was cooled to −70 °C in a dry ice-acetone bath, into which a solution of *sym*-trichlorotrifluorobenzene (6.27 g, 26.7 mmol) in tetrahydrofuran (80 ml) was then added, drop by drop; the mixture was then gradually brought to room temperature, after which stirring was continued overnight. The tetrahydrofuran was evaporated at 0 °C under reduced pressure, and from the residue the product was extracted with benzene. The extract was passed through a column of activated alumina, and the first yellow band was eluted with benzene The eluate was concentrated to dryness to give a crude product of **4** (1.43 g, 14%). Recrystallization from tetrahydrofuran gave pale orange crystals, which gradually darkened and decomposed above 200 °C, without any definite melting or decomposing point. Found: C, 42.14; H, 1.30; Cl, 18.9; F, 15.3%. Calcd for $C_{13}H_5Cl_2F_3O_2Fe$: C, 41.42; H, 1.33; Cl, 18.8; F, 15.1%.

From the eluate of the second band, the dimer of (cyclopentadienyl)dicarbonyliron (3.60 g, 51%) was recovered.

1-Bromo-3,5-dichloro-2,4,6-trifluorobenzene and 1-iodo-3,5-dichloro-2,4,6-trifluorobenzene reacted in a similar manner to give **4** in yields of 25 and 12% respectively. In these cases, the dimer of (cyclopentadienyl)dicarbonyliron was also recovered in 56 and 79% yields.

*3-Chloro-2,4,6-trifluorophenyl(cyclopentadienyl)dicarbonyliron (**6**).* Into a solution of **4** (1.00 g, 2.66 mmol) in tetrahydrofuran (25 ml), a solution of *n*-butyllithium in hexane (2.39 M, 1.50 ml, 3.59 mmol) was added at −66 °C and stirred for 1 hr. The reaction mixture was thrown onto ice, and the resulting yellow precipitate (0.84 g, 92%) was collected by filtration. Recrystallization from *n*-hexane gave pale orange crystals; mp 151—153 °C. Found: C, 45.85; H, 1.76; F, 16.2%. Calcd for $C_{13}H_6ClF_3O_2Fe$: C, 45.59; H, 1.77; F, 16.6%. ^{19}F NMR*: 2-F, −1.1; 4-F, +41.5; 6-F, −0.5. Calcd:[6] 2-F, −1.8; 4-F, +37.9; 6-F, −1.7.

*3-Chloro-2,4,6-trifluoro-5-carboxyphenyl(cyclopentadienyl)dicarbonyliron(**7**).* Through a lithiated solution prepared as has been described above, carbon dioxide was bubbled in a course of 2 hr, with mechanical stirring. The reaction mixture was thrown onto ice water and made acidic with concd hydrochloric acid. Resulting yellow precipitate was collected by filtration and dissolved in a dilute aqueous solution of sodium hydroxide. After filtering to remove a small amount of an insoluble material, the carboxylic acid was reprecipitated with conc. hydrochloric acid to give **7** (0.87 g, 84%) as yellowish brown crystals; mp 181 °C (dec.). Found: C, 44.17; H, 1.61; F, 15.0%. Calcd for $C_{14}H_6ClF_3O_4Fe$: C, 43.50; H, 1.57; F, 14.8%. ^{19}F NMR*: 2-F, −4.2; 4-F, +40.8; 6-F −1.8. Calcd:[6] 2-F, −4.7; 4-F, +38.0; 6-F; −1.6.

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