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Functionalization of styrene copolymers with $(Bu_4N)_2Fe(CO)_4$ in phase-transfer catalysis

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Summary

The use of tetracarbonylferrate dianion, $Fe(CO)_4^{2-}$, as reagent in the acid and aldehyde functionalization of chloromethylated and acid chloride groups containing styrene copolymers in phase-transfer catalysis has been investigated.

Introduction

There are many applications of $Na_2Fe(CO)_4$ in organic syntheses (1-5). Unfortunately, the synthetic application of disodium tetracarbonylferrate has hitherto been limited by its samewhat difficult preparation and handling. In an earlier paper we reported the results regarding the use of this reagent to the acid functionalization of chloromethylated polystyrene resins (5).

Extending these studies on application of tetracarbonylferrate dianion, we have investigated novel approaches to the application of ditetrabutylammonium tetracarbonylferrate in acid functionalization of chloromethylated polystyrene resins, and aldehyde functionalization of acid chloride groups containing resins under phase-transfer conditions.

Experimental

The syntheses were carried out in argon atmosphere, using careffuly purified solvents and reagents. Chloromethylated styrene-2%-divinylbenzene (SDVB-2), styrene-5%-divinylbenzene (SDVB-5), and styrene-10%-divinalbenzene (SDVB-10) microporous copolymers were prepared according to published methods (6). Acid chloride containing groups resin (SDVBA) was prepared by reaction of $SOCl_2$ with styrene-methacrylacid-divinylbenzene copolymer.

a) Acid functionalization

A calculated amount (corresponding to 3 meq Cl) of deaerated resin was moderately stirred in 100 ml benzene for 1 hour. After addition of 0.6 g $Fe(CO)_5$ to the vigorously stirred suspension, a solution of 1.1 g Bu_4NBr in 120 ml 40% NaOH aqueous solution was added in 10 hours, addition rate being controlled by a syringe pump. The stirring was

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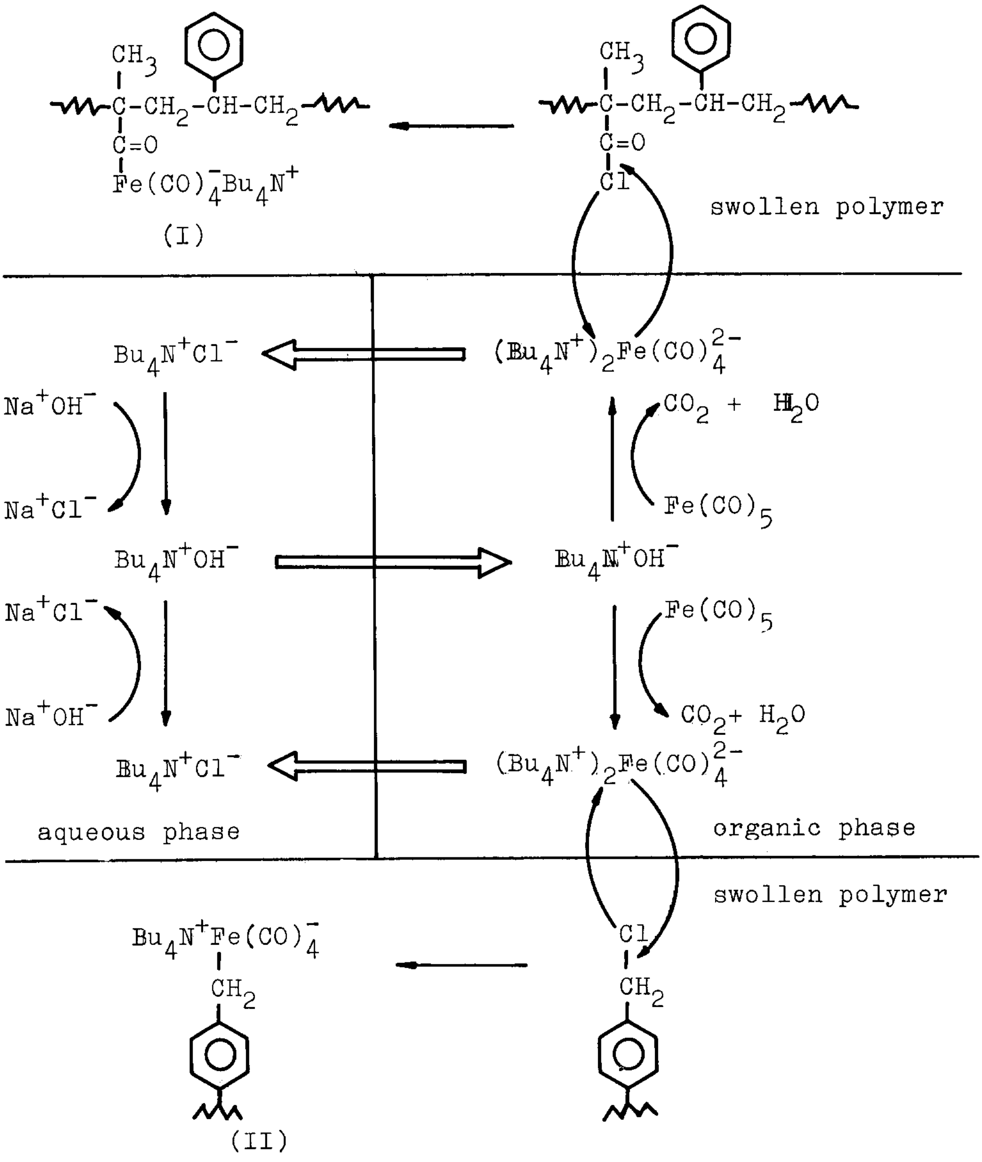

(I)
swollen polymer
$Bu_4N^+Cl^-$
$(Bu_4N^+)_2Fe(CO)_4^{2-}$
Na^+OH^-
Na^+Cl^-
CO_2 + H_2O
$Fe(CO)_5$
$Bu_4N^+OH^-$
$Bu_4N^+OH^-$
Na^+Cl^-
Na^+OH^-
$Fe(CO)_5$
CO_2+ H_2O
$Bu_4N^+Cl^-$
$(Bu_4N^+)_2Fe(CO)_4^{2-}$
aqueous phase
organic phase
swollen polymer
$Bu_4N^+Fe(CO)_4^-$
CH_2
Cl
CH_2
(II)

Scheme 1

continued for 10 hours at room temperature. After filtration the resin beads were suspended in 75 ml THF at $-15\,^{\circ}C$, and 10 ml of water were added folowed by 2.5 g iodine dissolved in 25 ml THF. After stirring for 2 hours at this temperature,the mixture was filtered, and the resin beads were sequentially washed with THF, ether, 1 N HCl, and water. The resin beads were then dried in vacuo to constant weight and analysed.

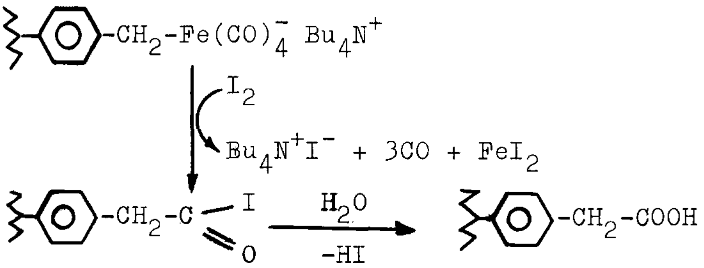
b) Aldehyde functionalization

A calculated amount (corresponding to 3 meq Cl) of deaerated acid chloride containing groups resin SDVBA was treated with 0.6 g of iron pentacarbonyl as above. After stirring for 10 hours at room temperature, the mixture was filtered, and the resin beads were treated with 20 ml of glacial acetic acid. The mixture was stirred for additional 2 hours, then poured into 100 ml of water and filtered. The resin beads were then sequentially washed with THF, ether, and water, dried in vacuo to constant weight, and analysed.

Results and discussion

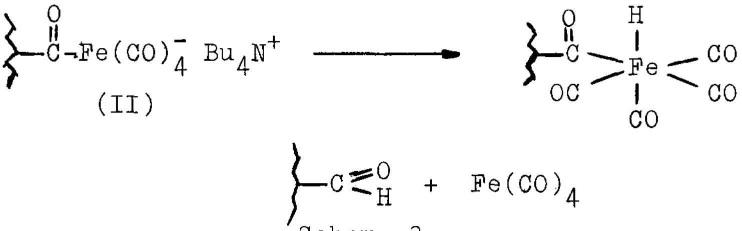
Our system consists of a polymer phase swollen in benzene with an aqueous solution of NaOH to which iron pentacarbonyl and tetrabutylammonium bromide are added (Scheme 1). The $Bu_4N^+OH^-$ ion pair produced in the aqueous phase is extracted by benzene and reacts with iron pentacarbonyl. The ferrate ion pair $(Bu_4N^+)_2\ Fe\ (CO)_4^{2-}$ thus produced in the organic phase is transfered to the swollen polymer and reacts with with a benzylchloride group to afford anionic benzyltetracarbonyl complex I or with an acid chloride group to afford acyl complex II.

Carboxylic groups are produced in high yields by treating the alkyl complex I with iodine as oxidizing agent ,apparently through the intermediacy of an acid iodide as follows :



Scheme 2

Only the acyl route has been found to afford aldehyde groups by cleavage with acetic acid. The aldehyde group arises through protonation of anion II followed by reductive elimination of the aldehyde from the intermediate acyl iron hydride III (Scheme 3)



Scheme 3

As it can be seen in Table 1, the acid functionalization of chlormethylated polystyrene resins, and aldehyde functionalization of acid chloride groups conaining resins in phase-transfer catalysis were successful. Complete displacement of chlorine was not achieved, however, when carried out with highly cross-linked polymers even at low content of clorine.

Table 1

Functionalization of polystyrene resins, and acid chloride groups containing styrene-methacrylicacid-divinylbenzene copolymer

Semple	Initial chlorine content%	Residual chlorine content%	Functionalization[(a)] yield%
SDVB-2	4.20	0.25	96
SDVB-2	9.22	0.56	94
SDVB-2	22.00	2.20	90
SDVB-5	6.10	0.85	86
SDVB-5	12.40	2.10	83
SDVB-5	20.20	4.84	76
SDVB-10	5.20	0.90	82
SDVB-10	9.10	2.28	75
SDVB-10	20.00	6.00	70
SDVBA	32.10	-	94

(a) Yields were calculated from ionic total exchange capacity data, and aldehyde groups determination(7).

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