# Alkali-metal Tetrafluorocobaltates(III) and their Use as Fluorinating Agents for Organic Compounds: Direct Conversion of Benzene into Hexafluorobenzene

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*Summary* Lithium, sodium, rubidium, and caesium tetrafluorocobaltates(III) have been prepared and used to convert benzene into a mixture of cyclic polyfluorides; caesium tetrafluorocobaltate yields a mixture of polyfluoroaromatic compounds including hexafluorobenzene.

The difference in reactivity between cobalt trifluoride and potassium tetrafluorocobaltate(III)[1] as exhaustive fluorinating agents for organic compounds in the vapour phase has led to several developments in the preparation of per- and poly-fluoroheterocycles.[2]

We now describe syntheses of the previously unknown tetrafluorocobaltates(III) of lithium, sodium, rubidium, and caesium, and their use as fluorinating agents. In one case, that of caesium tetrafluorocobaltate(III), a polyfluoroaromatic compound is produced directly from a hydrocarbon precursor; such a direct preparation has not been recorded previously.

The tetrafluorocobaltates(III) were prepared by elemental fluorination at temperatures between 250 and 500°. Starting materials were the trichlorocobaltates(II) for the lithium, rubidium, and caesium salts, and the trifluorocobaltates (II) for those of sodium and potassium.[1] The salts were characterised by elemental analysis and by *X*-ray powder photography. The unit cell dimensions of the potassium, rubidium, and caesium salts are related closely to those of the corresponding[3] tetrafluoroferrates(III). The compounds have magnetic moments at room temperature around 3·5 B.M., values between those[4] of cobalt trifluoride and potassium hexafluorocobaltate(III).

The reactivity of these compounds towards benzene at elevated temperatures was studied. Large excesses of benzene reduced each tetrafluorocobaltate(III) to the correponding trifluorocobaltate(II) from which the higher valent fluoride was regenerated reproducibly with elemental fluorine.

Benzene was converted by lithium tetrafluorocobaltate(III) at low temperature (100—130°) into 3,3,6,6-tetrafluorocyclohexa-1,4-diene (>90% purity), a key intermediate in pathways suggested[5] for exhaustive fluorinations with transition-metal fluorides, and isolated[1] in small yield from the reaction of benzene with potassium tetrafluorocobaltate(III). However, with longer contact times or higher temperatures (250°) fluorination afforded 3,3,6,6-tetrafluorocyclohexa-1,4-diene (32%), monofluorobenzene (3%), 1*H*,4*H*/2*H*-nonafluorocyclohexane (2%), 1*H*,2*H*,4*H*-heptafluorocyclohexene (21%), 1*H*,2*H*,4*H*/5*H*-hexafluorocyclohexene (20%), 1*H*,2*H*,4*H*,5*H*/-hexafluorocyclohexene (2%), unchanged benzene (18%), and several minor unidentified compounds. This fluorination pattern is different from that of potassium tetrafluorocobaltate(III).[1]

Sodium and rubidium tetrafluorocobaltates(III) react with benzene at temperatures between 150—400° to give mixtures of known polyfluorocyclohexenes, but offer no practical advantage as fluorinating agents over potassium tetrafluorocobaltate(III).

The behaviour of caesium tetrafluorocobaltate(III) is different. It is unreactive towards benzene at temperatures below 250°, but at this temperature a mixture containing decafluorocyclohexene (6%), hexafluorobenzene

(4%), pentafluorobenzene (9%), unchanged benzene (14%), 3,3,6,6-tetrafluorocyclohexa-1,4-diene (26%), monofluorobenzene (32%), 1,2,4-trifluorobenzene (1%), *p*-difluorobenzene (1%), 1,2,3,4-tetrafluorobenzene (2%), and a few minor unidentified products is formed. This is the first example of the direct preparation of a perfluoroaromatic compound from a hydrocarbon, albeit in poor yield, by a high valent metal fluoride system. In other examples being studied at present aromatic products are formed directly, *e.g.* naphthalene yields a mixture of hexadecafluorobicyclo[4,4,0]dec-1(6)-ene (63%), perfluorotetralin (27%), and unchanged naphthalene (10%).

The differences in degree of fluorination brought about by the various cobalt(III) reagents cannot yet be explained. The behaviour would seem to depend very much on changes in the structure of the fluorides caused by varying the alkali-metal component. Recently potassium hexafluorocobaltate(III) was shown[6] to be incapable of fluorinating organic compounds under comparable conditions.

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