BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1339—1340 (1975)

# The Preparation of Aryl Heptafluoroisopropyl Ketones from Aroyl Chlorides and Hexafluoropropene in the Presence of Fluoride Ions

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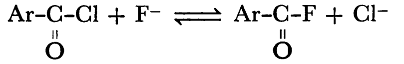
(Received November 25, 1974)

**Synopsis.** Aroyl chlorides and hexafluoropropene in the KF/DMF system gave aryl heptafluoroisopropyl ketones. The substituent effect on the yield was discussed.

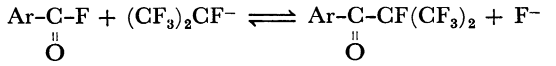
The hexafluoroisopropyl anion prepared from hexafluoropropene (HFP) and the fluoride ion in an aprotic polar solvent is known as a useful nucleophile for heptafluoroisopropylation.[1] As for the preparation of perfluoroisopropyl ketons, $(CF_3)_2CF\text{-}CO\text{-}R_f$, Smith *et al.*[2] have obtained perfluoroalkyl heptafluoroisopropyl ketones by the reaction of this nucleophile with various perfluoroacyl fluorides. In the aromatic series, Chambers *et al.*[3] have reported on the similar formation of perfluoro(isopropyl phenyl ketone) and perfluoro(isopropyl 4-pyridyl ketone) from pentafluorobenzoyl or tetrafluoroisonicotinoyl fluorides respectively. However, they mentioned that pentafluorobenzoyl chloride did not react with HFP under the same conditions.

We wish now to report a convenient method for the preparation of aryl heptafluoroisopropyl ketones in which aryl groups are the general substituted or unsubstituted phenyls. In this case, satisfactory yields were obtained by the reaction of aroyl chlorides with hexafluoropropene in the presence of the fluoride ion and it was not necessary to use aroyl fluorides as the starting material. The reactions were carried out in the potassium fluoride–dimethylformamide system at 120—130 °C under an autogeneous pressure. The amount of potassium fluoride must be present in excess, probably to convert the aroyl chloride into fluoride.

$$\mathrm{CF_3CF{=}CF_2 + F^- \rightleftharpoons (CF_3)_2CF^-} \qquad (1)$$



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{C}{-}Cl + F^- \rightleftharpoons Ar{-}\underset{\underset{O}{\|}}{C}{-}F + Cl^-} \qquad (2)$$



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{C}{-}F + (CF_3)_2CF^- \rightleftharpoons Ar{-}\underset{\underset{O}{\|}}{C}{-}CF(CF_3)_2 + F^-} \qquad (3)$$

For the purpose of checking the scope of this reaction, we also examined a similar reaction between substituted aroyl chlorides and HFP.

The effects of the substituents of the aroyl halides upon the yields of the heptafluoroisopropyl ketones were noteworthy. The strong electron-attractive *p*-nitro group and the strong electron-donative *p*-methoxy group both served to produce poor yields (Table 1). In the former case, it was assumed that the *p*-nitrophenyl heptafluoroisopropyl ketone formed must be very unstable thermodynamically, because the carbon atom of the carbonyl group is linked on both sides to the strong electron-attractive groups. Then the equilibrium of Eq. (3) becomes unfavorable for the formation of the ketone.

On the other hand, in the case of *p*-methoxybenzoyl halide, the electron-donative mesomeric effect of the methoxyl group increases the electron density on the carbon atom of the carbonyl group, thus making the nucleophilic attack of the heptafluoroisopropyl anion difficult. Consequently, the reaction of the *p*-nitrobenzoyl halide is controlled thermodynamically, whereas that of the *p*-methoxybenzoyl halide is controlled kinetically.

In order to improve our knowledge about the electronic effect of the $COCF(CF_3)_2$ group as a benzene substituent, we calculated the $\sigma$ values for this group from $^{19}F$ NMR according to Taft's equation.[4] Since the chemical shifts for the aromatic fluorine atoms of *m*- and *p*-fluorophenyl heptafluorisopropyl ketones in $CCl_4$ from fluorobenzene were observed to be $\delta_m = -2.50$ and $\delta_p = -12.13$ ppm, the $\sigma_R^0$ and $\sigma_I$ values for the heptafluoroisobutyryl group were determined to be 0.326 and 0.437 respectively. These figures suggest that the inductive and conjugative effects for the $COCF(CF_3)_2$ group are almost the same as those for the $COCF_3$ group ($\sigma_R^0=0.329$, and $\sigma_I=0.455$).[4]

Table 1. Preparation and spectral data for $Ar\text{-}CO\text{-}CF(CF_3)_2$

| Subst. or Ar | Preparation | | | | | Spectral data | | | |
|---|---|---|---|---|---|---|---|---|---|
| | KF/ArCOCl | Bp °C/mmHg | Yield % | F-Anal (%) | | IR (cm$^{-1}$) C=O | $^{19}F$ NMR[a] | | |
| | | | | Obsd | Calcd | | $CF_3$ | CF | Ar-F |
| H | 2 | 80—81/39 | 47 | 48.7 | 48.5 | 1700 | −39.0(d) | 64.5(m) | — |
| H | 4 | 80—81/39 | 66 | — | — | — | — | — | — |
| *p*-Me | 4 | 76—78/14 | 63 | 46.3 | 46.2 | 1700 | −37.8(d) | 66.0(m) | — |
| *p*-OMe | 4 | 84/5 | 14 | 43.4 | 43.8 | 1695 | −38.6(d) | 64.8(m) | — |
| *m*-F | 4 | 65/18 | 48 | 52.2 | 52.1 | 1700 | −38.5(d) | 66.4(m) | −1.4 |
| *p*-F | 4 | 68/19 | 48 | 51.9 | 52.1 | 1700 | −37.7(d) | 66·0(m) | −10.7 |
| *p*-Cl | 4 | 87—88/19 | 50 | 42.9 | 43.1 | 1700 | −38.9(d) | 65.8(m) | — |
| *p*-$NO_2$ | 4 | 103/8 | 3 | 41.3 | 41.7 | 1720 | −39.1(d) | 66.1(m) | — |

a) The chemical shifs are given in $\delta$ ppm from ext. PhF in $CCl_4$ or in neat.

## Experimental

*Phenyl Heptafluoroisopropyl Ketone.* A mixture of benzoyl chloride (2.81 g, 0.02 mol), dimethylformamide (10 ml), and finely ground potassium fluoride (4.64 g, 0.08 mol) was put into a glass tube vessel equipped with a mechanical stirrer. At −70 °C liquefied hexafluoropropene (0.045 mol) was added, and after having been sealed the vessel was brought to room temperature. The whole was then heated for 6 hr in an oil bath kept at 120—130 °C under mechanical stirring. The reaction mixture was then poured into water and the separated oily material was extracted with diethyl ether. The extract was washed with a dilute aqueous solution of potassium hydroxide and water successively, and then dried over magnesium sulfate. After the solvent had been removed, the residual oil was subjected to a vacuum distillation. Phenyl heptafluoroisopropyl ketone (bp 80—81 °C/39 mmHg) was thus obtained in a yield of 66%.

Other substituted aryl heptafluoroisopropyl ketones were prepared in a similar manner.

### References

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