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REACTION OF HEPTAFLUORO-1-METHYLETHYLZINC IODIDE WITH HALIDES AND ANHYDRIDES OF CARBOXYLIC ACIDS

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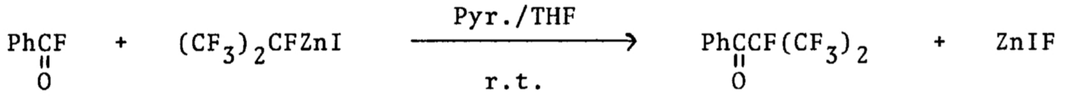
The reactions of heptafluoro-1-methylethylzinc iodide (1) with fluorides or anhydrides of carboxylic acids were smoothly induced in the presence of pyridine, and aryl or alkyl heptafluoro-1-methylethyl ketones were obtained in good yields. Although the reactivities of benzoyl halides in this reaction were in the order PhCOF > PhCOCl > PhCOBr, benzoyl chloride reacted with 1 smoothly in the presence of zinc fluoride, which converted benzoyl chloride to fluoride in situ.

Preparation and reactions of perfluoroalkylzinc iodides have been reported in several papers.[1-5] Although these perfluoroalkylzinc compounds are usually more stable and easier to handle at room temperature than the corresponding magnesium compounds,[3,6] which readily decompose into perfluoroolefins and magnesium halide, it has been reported that their low reactivity reduces their synthetic value. Acyl chlorides and acid anhydrides were reported to be unreactive,[3,5] or to react giving only poor yields of perfluoroalkyl ketones.[1,2]

We now found that the presence of pyridine induces smoothly the reaction of heptafluoro-1-methylethylzinc iodide (1) with benzoyl fluoride in tetrahydrofuran, affording heptafluoro-1-methylethyl phenyl ketone (2) in a quantitative yield. In the same manner, the reaction with benzoyl chloride and bromide gave 2 in yields of 64 and 4%, respectively.



$$\mathrm{Ph}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{F} + (\mathrm{CF_3})_2\mathrm{CFZnI} \xrightarrow[\text{r.t.}]{\text{Pyr./THF}} \mathrm{Ph}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{CF(CF_3)_2} + \mathrm{ZnIF}$$

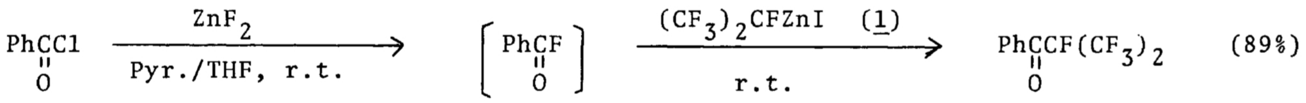
1 2

Thus, the reactivities of benzoyl halides toward 1 are in the order PhCOF > PhCOCl >

PhCOBr, which is in contrast to their reactivities toward usual nucleophiles.[7)]

A typical procedure of the reaction with benzoyl fluoride is as follows: In tetrahydrofuran[8)] (6 ml), 2-iodoheptafluoropropane (5.9 g, 0.02 mol) was allowed to react at 25 - 30°C with freshly purified zinc powder (1.7 g, 0.026 g-atom) in the usual manner.[3)] At the end of the reaction, ~60% conversion of 2-iodoheptafluoropropane into 1 was observed by ^{19}F nmr, and the rest of heptafluoro-2-iodopropane was converted into 2-H-heptafluoropropane and oligomers of hexafluoropropene, mainly pentamers. To this solution was added dropwise a solution of benzoyl fluoride (1.24 g, 0.01 mol) in pyridine (10 ml) at 25 - 30°C with stirring. After stirring for 1 h, ^{19}F nmr showed ca. 100% conversion of benzoyl fluoride into 2. Then, the solution was poured into hydrochloric acid, and a liberated oil was extracted with diethyl ether. The etheral solution was washed with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Evaporation of ether gave 2 (2.22 g) as an oil, which was distilled to give pure heptafluoro-1-methylethyl phenyl ketone, bp 85 - 86°C/ 48 mmHg (lit[9)]: bp 80 - 81°C/ 39 mmHg). When triethylamine, N-methylpiperidine or N,N-dimethylaniline was used instead of pyridine, no formation of 2 was observed. It was also noticeable that heptafluoropropylzinc iodide prepared from heptafluoropropyl iodide was innert to benzoyl fluoride.

In view of the lower reactivity of benzoyl chloride relative to benzoyl fluoride, the effect of the presence of certain metal fluorides in the reaction with benzoyl chloride was examined. For the conversion of benzoyl chloride into benzoyl fluoride zinc fluoride in pyridine was found to be surprisingly effective, resulting in quantitative conversion at 25 - 30°C within 20 min. Thus, the reaction of benzoyl chloride with 1 in pyridine-THF in the presence of an equimolar amount of zinc fluoride[10)] resulted in the formation of 2 in 89% yield.



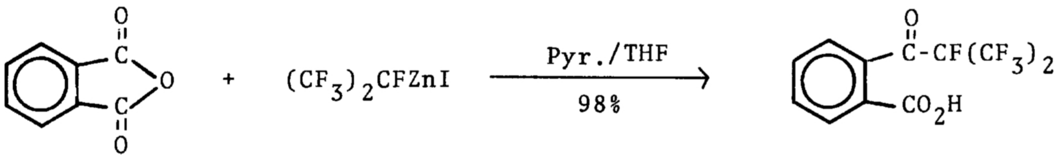
$$\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Cl} \xrightarrow[\text{Pyr./THF, r.t.}]{ZnF_2} \left[\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{F}\right] \xrightarrow[\text{r.t.}]{(CF_3)_2CFZnI\quad(1)} \mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CF}(\mathrm{CF}_3)_2 \quad (89\%)$$

2

Next the reaction of 1 in pyridine-THF with benzoic anhydride instead of benzoyl fluoride was undertaken. By a procedure similar to that described above, the reaction of 1 with benzoic anhydride gave 2 in a 92% yeild. However, no reaction was observed with heptafluoropropylzinc iodide.

When isobutyryl fluoride, an example of an aliphatic acid fluoride, was employed in place of benzoyl fluoride, the yield of heptafluoro-1-methylethyl 1'-methylethyl ketone was only 41% (^{19}F nmr analysis). A reaction of isobutyryl chloride in the presence of zinc fluoride gave the same product similarly in a low yield (38%). However, the reaction with isobutyric anhydride resulted in the formation of the ketone in comparatively higher yield (54%). This shows that acid anhydrides are more reactive than acid halides in this reaction.

Using phthalic anhydride and succinic anhydride, the reaction was successfully extended to the preparation of perfluoroalkyl keto carboxylic acids, o-carboxyphenyl heptafluoro-1-methylethyl ketone (3), mp 89 - 90°C (98% yield) [IR (KBr): 1755, 1745 (C=O), and 1310-1140 cm^{-1} (C-F); ^{19}F NMR (in Et_2O, ppm from ext. CF_3CO_2H): δ -6.0 (2 CF_3) and 102.5 (CF); ^{1}H NMR (in $(CD_3)_2SO$): δ 7.7-8.2 (4 Ar-H) and 9.7 (COOH)] and 5,6,6,6-tetrafluoro-5-(trifluoromethyl)-4-oxohexanoic acid (4), bp 92 - 93°C/ 2 mmHg (74% yield) [IR (neat): 1750, 1715 (C=O), and 1300-1150 cm^{-1} (C-F); ^{19}F NMR (neat from ext. CF_3CO_2H): δ-2.5 (2 CF_3) and 107.7 (CF); ^{1}H NMR (neat): δ 2.83, 3.15 (CH_2, CH_2) and 11.72 (COOH)], respectively.



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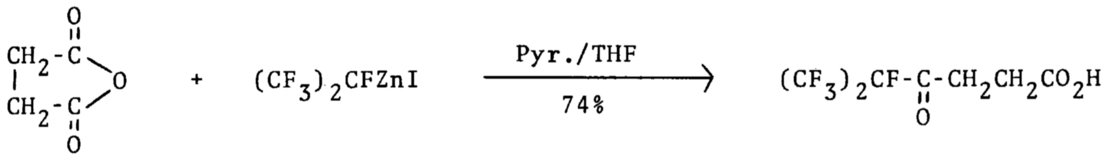
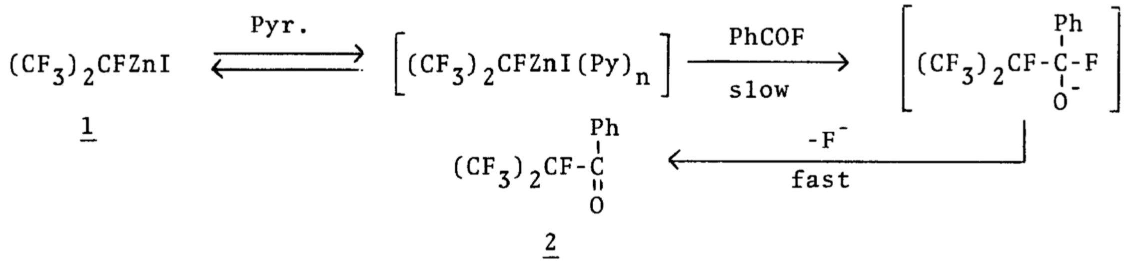


$(CF_3)_2CF\text{-}\overset{}{\underset{\|}{\underset{O}{C}}}\text{-}CH_2CH_2CO_2H$

4

Taking into account the order$^{7)}$ of reactivities of benzoyl halides and the similarity in reactivities$^{7)}$ between benzoyl fluoride and benzoic anhydride, the reaction reported here is assumed to proceed through an addition-elimination mechanism. Pyridine probably accelerates the addition step by coordination to the zinc atom of 1 and eases the releasing of heptafluoro-1-methylethanide ion.



1

2

Inertness of heptafluoropropylzinc iodide in the reaction may be ascribed to the difficulty of releasing unstable heptafluoropropanide ion.

References and notes

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8) Dioxane could be employed instead.
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10) Even without zinc fluoride, benzoyl fluoride seemed to exist in considerable amount, since a THF solution of 1 is contaminated with zinc fluoride formed through a 1,2-elimination side reaction. This was evidenced by the appearance of a ^{19}F nmr signal characteristic to the -CO-F group during the course of the reaction.

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