

NOTE

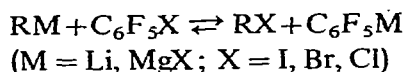
PERFLUOROARYLMETAL-HALIDE EXCHANGE REACTIONS

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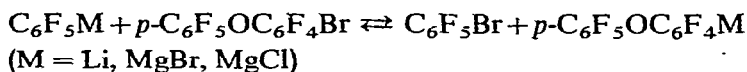
Halogen-metal exchange is a common phenomenon in organometallic reactions. Alkyl lithium⁻¹ and Grignard²-haloaromatic exchange reactions have recently gained recognition in perfluoroaromatic chemistry.



This reaction is an effective method for preparing perfluoroarylmethyl intermediates since the polarizability of the perfluoroaromatic carbon-halogen (I, Br, Cl) bond makes the reaction fast while the anion stabilizing effect of the fluoroaromatic ring shifts the equilibrium far to the right.

Studies involving alkyl lithium-alkyl halide³ and alkyl Grignard-alkyl halide⁴ exchange reactions have been reported. To our knowledge, little information is available concerning aryllithium-aryl halide* and aryl Grignard-aryl halide exchange reactions. Recently⁶, it has been reported that certain perfluoroaryllithium compounds exchange with some perfluoroaryl halides. We too have noted and are now reporting such exchange reactions and have extended these observations to the perfluoroaryl Grignard-perfluoroaryl halide reactions.

The following system was chosen for study:

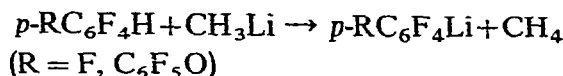


It was assumed⁷ that a change in the organometallic's *para* substituent from F to C₆F₅O would have a minor stabilizing effect on the organometallic so that the equilibrium constant would be approximately 1. This choice of reactants would facilitate the study of equilibria from either side and afford ease of analysis of the volatile reactants and products by use of vapor phase chromatography (VPC).

ORGANOLITHIUM-HALIDE EXCHANGE

Essentially pure perfluoroaryllithium compounds were prepared through the acid-base reaction between methyl lithium and the monohydroperfluoroaromatic compound in tetrahydrofuran at -70°.

* It has been qualitatively reported⁵ that phenyllithium and *p*-iodotoluene exchange in diethylether solution.

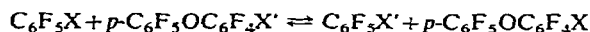


This convenient preparative reaction went to completion in less than 5 min. Attempts to prepare the pure perfluoroaryllithium compounds by the more commonly used preparative methods, reaction between *n*-C₄H₉Li and either C₆F₅X¹ or C₆F₅H⁸, were not satisfactory. Under these preparative conditions, alkylation of the perfluoroaryl group was noted as a minor but definite side reaction.

After the perfluoroaryllithium compound was prepared, the appropriate perfluoroaryl bromide was rapidly introduced while keeping the reaction temperature constant. Aliquot samples were periodically withdrawn, hydrolyzed and analyzed by VPC for C₆F₅Br, *p*-C₆F₅OC₆F₄H and *p*-C₆F₅OC₆F₄Br* (see Table 1). The observation that the amount of *p*-C₆F₅OC₆F₄H initially present after equilibration corresponds with the amount of C₆F₅Br and then decreases while the ratio of C₆F₅Br

TABLE 1

PERFLUOROARYLMETAL-HALIDE EXCHANGE IN THF



X	X'	<i>p</i> -C ₆ F ₅ OC ₆ F ₄ H ^a (%)	C ₆ F ₅ Br ^a (%)	<i>p</i> -C ₆ F ₅ OC ₆ F ₄ Br ^a (%)
Br	Li ^b	65 ^d , 28 ^e	65	35
Li ^b	Br	54 ^d , 39 ^e	54	46
Br	MgCl ^c	56	56	44
MgCl ^c	Br	56	56	44
Br	MgBr ^c	56	56	44

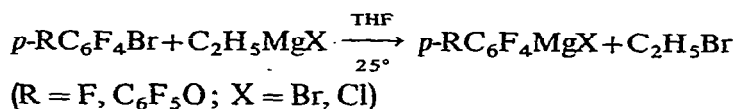
^a Calculated by VPC using an internal standard, $\pm 3\%$ averaged from 4 aliquots. ^b $-70 \pm 2^\circ$. ^c $+25 \pm 1^\circ$.

^d Initial value. ^e Final value.

and *p*-C₆F₅OC₆F₄Br remains constant suggests that the equilibrating organolithium species are decomposing at comparable rates. This is probably the reason that the observed values depend on the direction from which equilibration is approached. At the conclusion of the experiment, insoluble polymeric material was detected indicating the decomposition of the organolithium species as has been observed and described previously⁹. Trial experiments demonstrated that equilibration was complete within 5 min at -70° indicating the ease of perfluoroaryllithium-halogen exchange.

GRIGNARD-HALIDE EXCHANGE

The perfluoroaryl Grignard compounds were quantitatively prepared as described by the following reaction^{2,9}.



* C₆F₅H, the other product of equilibration, was not analyzed since our analytical VPC techniques were not capable of resolving it completely from the solvents present in the reaction.

The above exchange reaction is complete in less than 30 min. After the Grignard was prepared, the perfluoroaryl halide was rapidly added, aliquot samples were periodically withdrawn, hydrolyzed and analyzed by VPC. Equilibration from either side of approach was complete in a few minutes. The greater stability of the perfluoroarylmagnesium compounds as compared to the lithium compounds made it possible to study equilibration at 25°. Unlike the perfluoroaryllithium compounds, the equilibrium values (see Table 1) corresponded regardless of the side of approach, and the quantity of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ did not decrease during the duration of the experiment*.

From these experiments, the equilibrium constant for the lithium-halogen exchange can be roughly estimated at 1.4–3.5 (-70°) while for the Grignard-halide exchange reaction, the equilibrium constant for $\text{C}_6\text{F}_5\text{MgX} \rightleftharpoons p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgX}$ can be estimated at 1.6 (25°). The relationship between these constants and anion stability may depend on further equilibria, *i.e.*, organometallic association³ and Schlenk** equilibria.

Although the perfluoroaryllithium-halide exchange reactions present a problem due to the instability of certain perfluoroaryllithium compounds, the perfluoroaryl Grignard-halide exchange reactions merit further consideration. The magnitude and direction of the perfluoroaryl Grignard-halide exchange constant is approximately what one would expect from substituent free-energy correlations⁷. The insensitivity of the constant to changes in the counterion ($-\text{MgCl}$ or $-\text{MgBr}$) seems to substantiate this notion. Further studies comparing our approximate equilibrium constants with carbon-hydrogen acidity measurements¹¹ may shed light on the processes that are pertinent to the Grignard-halogen exchange equilibria.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. All starting materials were shown to be at least 99% pure by VPC analysis. Solvents were purified and dried by conventional methods and distilled prior to use. Products were analyzed by VPC on an F&M Model 500 gas chromatograph. A 6-ft. Apiezon L on Chromosorb W (60–80 mesh) column using helium carrier gas at about 60 ml/min was used. The temperature was programmed from 100–275° at 21°/min.

$p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$

To $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (1.62 g, 4.86 mmole) dissolved in 25 ml of THF was added tert-butylbenzene (0.50 g) as an internal standard. The solution was cooled to $-70 \pm 2^\circ$ and maintained at this temperature for all subsequent reactions. To this cooled solution CH_3Li (30 ml of 1.60 *N* in diethyl ether, 4.86 mmole) was added slowly and allowed to stir for 0.5 h. Two aliquot samples were removed. One was hydrolyzed and indicated >98% $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ while the other was derivatized with excess $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Cl}$ and yielded besides the expected $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{OC}_6\text{F}_5$ less than 1% $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$.

* Similar to the lithium reagent decomposition is observed with further reaction times as seen by the decrease in $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ after hydrolysis.

** NMR studies indicate that Schlenk equilibria occur for pentafluorophenylmagnesium halides in diethyl ether solutions¹⁰.

Exchange reaction between $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ and $\text{C}_6\text{F}_5\text{Br}$

$\text{C}_6\text{F}_5\text{Br}$ (1.20 g, 4.86 mmole) was added rapidly to $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ (4.86 mmole) prepared as described above. There was no noticeable temperature rise. Over a 1 h period 5 aliquot samples were withdrawn every 12 min from the reaction mixture maintained at $-70 \pm 2^\circ$. Each aliquot was hydrolyzed, extracted with pentane, dried and analyzed by VPC (Table 1). The first aliquot sample indicated a 65 mole% concentration for $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$. This value slowly decreased in time until the final sample indicated only a 28 mole% concentration. The experimental error was estimated at $\pm 3\%$. The procedure for the preparation of $\text{C}_6\text{F}_5\text{Li}$ and its exchange with $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ was the same as described above.

 $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgCl}$

To $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (2.00 g, 4.86 mmole) dissolved in 25 ml of THF was added 0.5 g of tert-butylbenzene as a standard. A THF solution of ethylmagnesium chloride (2.86 N, 4.86 mmole) was then added to the above solution maintained at $25^\circ \pm 1$.

Exchange reaction between $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgCl}$ and $\text{C}_6\text{F}_5\text{Br}$

$\text{C}_6\text{F}_5\text{Br}$ (1.20 g, 4.86 mmole) was added rapidly to the $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgCl}$ as described above. Four aliquots were withdrawn at 5 min intervals, hydrolyzed, extracted with pentane and analyzed by VPC. The preparation of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ and its exchange with $\text{C}_6\text{F}_5\text{Br}$ was the same as described above. The preparation of $\text{C}_6\text{F}_5\text{MgCl}$ and its exchange with $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ was the same as described above.

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