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Preliminary communication

Phenyl(iodobromochloromethyl)mercury and phenyl(dibromofluoromethyl)-mercury: two new highly reactive divalent carbon transfer reagents

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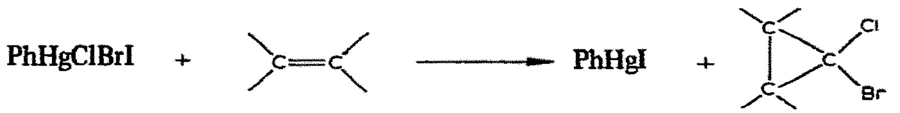
We have reported recently concerning phenyl(iododichloromethyl)mercury, a reagent which is a very effective room temperature source of dichlorocarbene[1] and thus nicely complements $\mathrm{PhHgCCl_2Br}$, which releases $\mathrm{CCl_2}$ rapidly at 80° but only slowly at room temperature[2]. We recognized that further development of such a 'second generation' of highly reactive organomercury carbene precursors may represent a valuable addition to the reagent resources of carbene chemistry and have continued our research in this direction. We report here concerning two new mercurials, PhHgCClBrI[★] and $\mathrm{PhHgCFBr_2}$[★★], which, although somewhat less reactive than $\mathrm{PhHgCCl_2I}$, find useful application at room temperature.

Phenyl(iodobromochloromethyl)mercury was prepared in 76% yield by treating a reagent solution of 1.6 (molar) equivalents of PhHgCl in diethyl ether and 2.2 equivalents of unsolvated $\mathrm{Me_3COK}$ in THF at −65° with 1.8 equivalents of HCClBrI. As in the case of $\mathrm{PhHgCCl_2I}$, a minimal reaction time and rapid work-up were essential to obtain good yields. PhHgCClBrI, bright yellow crystals, m.p. 78° (dec), was obtained in analytical purity. A survey of its reactivity as a divalent carbon transfer agent using olefins as substrates (3 molar equivalents of olefin to one of PhHgCClBrI in benzene solution, with stirring under nitrogen) showed that phenylmercuric iodide elimination was by far the most favored mode of reaction:



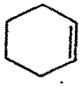
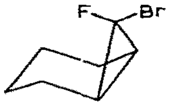
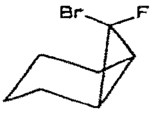
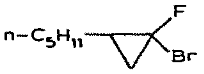
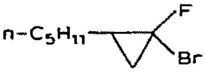
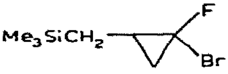
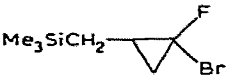
At room temperature a reaction time of about four days was required; at 80°, the reagent was consumed within 3–4 minutes, as indicated by discharge of its yellow color or by thin layer chromatography. When cyclohexene was the olefin used, 7-bromo-7-chloronorcarane was produced in 75% yield after 4 days at room temperature, in 81%

[★] Experiments by Carol K. Haas.
[★★] Experiments by Steven P. Hopper.

yield after 3 min. at 80°. Room temperature reactions of PhHgCClBrI with cyclooctene and with allyltrimethylsilane under similar conditions gave 9-bromo-9-chlorobicyclo-[6.1.0]nonane in 83% yield and 1-bromo-1-chloro-2-(trimethylsilylmethyl)cyclopropane in 78% yield. Insertion of CClBr into the Si–H bond of triethylsilane, giving Et$_3$SiCHBrCl, was achieved in 60% yield using this mercurial at room temperature.

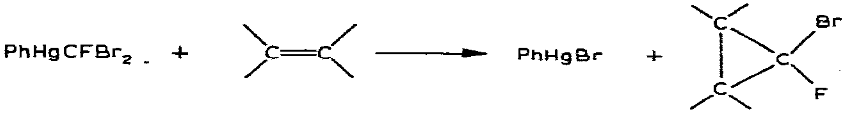
TABLE 1

REACTIONS OF PHENYL(DIBROMOFLUOROMETHYL)MERCURY[a]

Substrate	Reaction temp. (°C/time)	Product[b]	Yield (%)
	25°/ 3 days	 (I)	32
		 (II)	58
	80°/20 min.	I II	30 58
n-C$_5$H$_{11}$CH=CH$_2$	25°/ 3 days	 (mixed isomers)	78
n-C$_5$H$_{11}$CH=CH$_2$	80°/20 min.	 (mixed isomers)	72
Me$_3$SiCH$_2$CH=CH$_2$	25°/ 3 days	 (mixed isomers)	60
Me$_3$SiCH$_2$CH=CH$_2$	80°/20 min.	 (mixed isomers)	70
Et$_3$SiH	25°/ 3 days	Et$_3$SiCHFBr	55
Et$_3$SiH	80°/20 min.	Et$_3$SiCHFBr[c]	92

[a] 30 mmol of substrate, 4–5 mmol of PhHgCFBr$_2$ in 10 ml of dry benzene, with stirring under nitrogen. [b] Phenylmercuric bromide was obtained in high yield in each reaction. [c] Was reduced to Et$_3$SiCH$_2$F, n_D^{25} 1.4142, with n-Bu$_3$SnH.

This work establishes firmly that the ease of phenylmercuric halide elimination from phenyl(trihalomethyl)mercurials decreases in the order PhHgI > PhHgBr > PhHgCl (there is no evidence of PhHgF elimination from $PhHgCF_3$ at temperatures as high as 140° [3]). Other factors than the nature of the halogen atom eliminated must be of importance[4], and in this connection, we were surprised to find that phenyl(dibromofluoromethyl)mercury is completely consumed within three days on treatment with an excess of olefinic substrate in benzene solution at room temperature:



In contrast, similar room temperature reactions of $PhHgCBr_3$, $PhHgCClBr_2$ and $PhHgCCl_2Br$ (in which PhHgBr also is eliminated) with olefins require from 15–18 days for completion[2].

The preparation of $PhHgCFBr_2$ was accomplished by reaction of a PhHgCl/MeONa mixture in THF/Et_2O at –25° with $HCFBr_2$. Again, a minimal reaction time and rapid work-up are essential features of this preparation. Best results (yields up to 55% thus far) were obtained when the reaction mixture was evaporated (without heating) and treated with benzene and dilute HCl. The organomercury product then was obtained by adding hexane to the concentrated benzene slurry. $PhHgCFBr_2$ was obtained in analytical purity as white, crystalline solid; it melted (on rapid heating, 10°/min.) at 85–88° and decomposed at 94°*. Examples of its application as a CFBr transfer agent are given in Table 1, and these show that $PhHgCFBr_2$ is an excellent bromofluorocarbene source.

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*Even pure $PhHgCFBr_2$ should be stored at 0°. It is essential that this mercurial be kept scrupulously free of oxygen-containing solvents (such as acetone, THF, alcohols) since even traces of the latter initiate spontaneous, highly exothermic decomposition of the solid mercurial sample. Such solvent-induced decomposition has been observed also in the case of $PhHgCCl_2I$, even with solid samples being stored in the refrigerator.