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Preliminary communication

Phenyl (1-bromo-1,2,2,2-tetrafluoroethyl)mercury: a useful tetrafluoroethylidene source

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SUMMARY

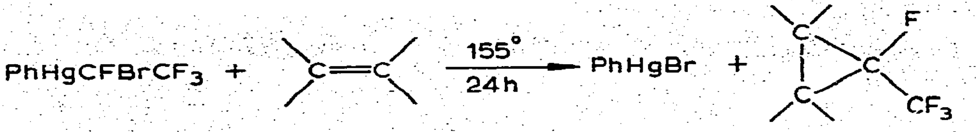
The reaction of phenylmercuric chloride, 1-bromo-1,2,2,2-tetrafluoroethane and methanolic sodium methoxide in THF at –35° gave $PhHgCFBrCF_3$ in good yield. Thermolysis of this mercurial at 155° for 24 h in the presence of olefins gave *gem*-fluoro(trifluoromethyl)cyclopropanes, while its reaction with triethylsilane produced $Et_3SiCHFCF_3$.

In continuation of our studies concerning organomercurials as reagents for the generation of fluorinated carbenes ($C_6H_5HgCF_3$ [1], $C_6H_5CCl_2F$ [2], $C_6H_5HgCBr_2F$ [3], $C_6H_5HgCFClCO_2Et$ [4], and $C_6H_5HgCClBrCF_3$ [5]), we report here concerning $C_6H_5HgCFBrCF_3$, a compound whose thermolysis results in the extrusion of tetrafluoroethylidene, CF_3CF.

Although there were indications that pyrolysis of $C_2F_5SiF_3$ (at 180° [6]) and of $C_2F_5PF_4$ (at 240° [7]) results in the generation of CF_3CF, neither of these compounds can be considered a useful preparative divalent carbon transfer reagent. Organomercurials which were potential CF_3CF sources, $(CF_3CFBr)_2Hg$ [8], $(CF_3CFCl)_2Hg$ [9], and $CF_3CFClHgCl$ [10], had been prepared by addition of mercuric fluoride to bromotrifluoroethylene and chlorotrifluoroethylene, but these had not been examined for divalent carbon transfer reactivity. Since bis(polyfluoroalkyl)mercury compounds are volatile and their vapors toxic[11], we chose to direct our studies to mercurials of type $C_6H_5HgCFXCF_3$.

The preparation of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury was accomplished in good yields (~ 65%) by the reaction shown in eqn.(1). This mercurial, m.p. 120–122° (from hexane), (found: C, 20.95; H, 1.21; Br, 17.61. $C_8H_5BrF_4Hg$ calcd.: C, 20.99; H, 1.10; Br, 17.46%) proved to be an excellent source of tetrafluoroethylidene, as indicated by its reactions with several olefins (eqn.2) and with triethylsilane (eqn.3). Results are summarized in Table 1.

$$PhHgCl + CF_3CHFBr + NaOMe\ (in\ MeOH) \xrightarrow{THF,\ -35^\circ} PhHgCFBrCF_3 + NaCl + MeOH \quad (1)$$

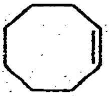
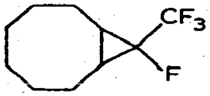
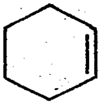
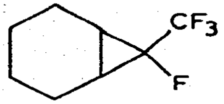
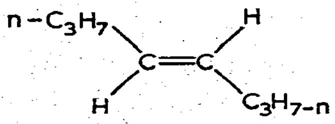
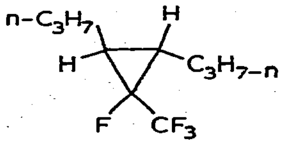
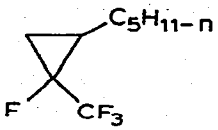
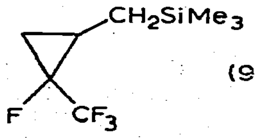


(2)

$$PhHgCFBrCF_3 + Et_3SiH \xrightarrow[24\,h]{155^\circ} PhHgBr + Et_3SiCHFCF_3 \quad (3)$$

TABLE 1

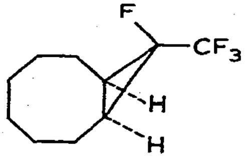
REACTIONS[a] OF PHENYL(1-BROMO-1,2,2,2-TETRAFLUOROETHYL)MERCURY

Carbenophile	*Product (% yield)*	*Isomer ratio*	*C_6H_5HgB (% yield)*
	 (98)	3.4	96
	 (87)	3.6	87
	 (80)		92
n-$C_5H_{11}CH{=}CH_2$[b]	 (70)	1.9	80
$Me_3SiCH_2CH{=}CH_2$[c]	 (93)	1.8	99
Et_3SiH	$Et_3SiCHFCF_3$ (53)		61

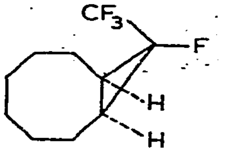
[a] Reactions at 155° for 24 h in a sealed tube, carbenophile to mercurial ratio of 3, benzene diluent, unless otherwise noted. [b] 72 h reaction time. [c] OLefin (10 ml) used as solvent.

Compared with the related $C_6H_5HgCClBrCF_3$, a source of CF_3CCl whose transfer reactions required reaction times of about 5 days at around 140°[5], phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury was rather more reactive. Nevertheless, higher reaction temperatures than those used in the case of the $C_6H_5HgCCl_nBr_{3-n}$ reagents[12] were required, and it was found convenient to carry out these $C_6H_5HgCFBrCF_3$ reactions in sealed tubes at 155° for 24 h. In most cases benzene was used as diluent. In these reactions it was found important to ensure the absence of air by thorough degassing of the reaction mixtures. In those cases where the formation of two cyclopropane isomers was expected, both were observed, with one predominating (Table 1).

It would appear that the isomer which is preferred is the less hindered one with the CF_3 group *anti* with respect to the one or two alkyl substituents. Thus in the case of the product derived from cyclooctene, compound A was the major isomer formed, and B was the minor product. These assignments are based on the ^{19}F NMR spectra of the isomers. In the spectrum of A, the CF_3 group was seen as a doublet ($J(FF)$ 8 Hz) at −84.1 ppm relative to hexafluorobenzene and the *syn* F substituent as a triplet of quartets ($J(HF)_{trans}$ about 5 Hz) at +67.8 ppm. The ^{19}F NMR spectrum of B showed the CF_3 group as a doublet ($J(FF)$ 8 Hz) at −92.5 ppm and the *anti* F substituent as a triplet of quartets ($J(HF)_{cis}$ about 23 Hz) at +23.2 ppm.



(A)



(B)

Continuing studies are aimed at delineating the divalent carbon transfer chemistry of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury. Addition of CF_3CF thus generated to other multiple linkages and its insertions into other single bonds are under investigation.

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