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Preliminary communication

Preparation and characterization of ethyl 3-(bromomercuri)perfluorobutanoate

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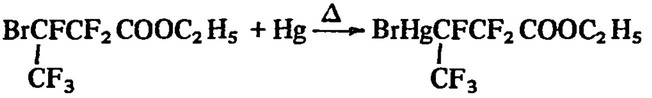
A variety of perfluoroalkyl iodides has been coupled via C—I as the reactive center[1] and has also been converted to the corresponding mercuric iodide by reacting the iodide with mercury[2]. However, only recently the successful coupling of perfluoroalkyl bromides via C—Br as the reactive center has been reported[3]. No direct formation of a perfluoroalkylmercuric bromide from the reaction of a perfluoroalkyl bromide with mercury has yet been described. The perfluoroalkylmercuric bromides recorded were obtained indirectly as shown in eqn.1.[2]

$$R_fI \xrightarrow{Hg} R_fHgI \xrightarrow{AgOH} R_fHgOH \xrightarrow{HBr\,(aq.)} R_fHgBr \qquad (1)$$

$(R_f = CF_3 \text{ and } C_2F_5)$

A perfluoroalkylmercuric halide containing a functional group on the organic portion of the molecule has not been documented. We now wish to report that when ethyl 3-bromoperfluorobutanoate (I)[4] was treated with an excess of mercury in a sealed tube at *ca.* 180° or under a vigorous reflux while shaking or stirring, a novel and potentially useful intermediate, ethyl 3-(bromomercuri)perfluorobutanoate (II), b.p. 83—84° (0.7 mm), n_D^{25} 1.4615, was formed in 50—60% yield based on the unrecovered starting material (eqn.2)[*].



$$\underset{\displaystyle CF_3}{BrCF}CF_2COOC_2H_5 + Hg \xrightarrow{\Delta} BrHg\underset{\displaystyle CF_3}{CF}CF_2COOC_2H_5 \qquad (2)$$

(I) (II)

The bromide II could be distilled and analyzed for purity by gas chromatography without any noticeable decomposition.

The elemental analysis is in agreement with the formula $BrC_6H_5F_6O_2Hg$ (Found: C, 14.72; H, 1.18; Br, 16.1. Calcd.: C, 14.31, H, 1.00; Br, 15.87.) The infrared and proton resonance spectra confirm the presence of a carbethoxy function, and the ^{19}F resonance spectrum is consistent with the assigned structure II. The spectrum is comprised of signals

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[*] In the presence of ultraviolet irradiation, the diester, $C_2H_5OOCCF_2CF(CF_3)(CF_3)CFCF_2COOC_2H_5$, was formed as a major product at 25°[3].

centered at δ +68.99 (3F), +110.26 (1F), +113.58 (1F), and +188.54 ppm (1F) relative to CCl_3F. When II was heated at 120° with an excess of bromine, the original ester I and mercuric bromide were formed, and the isolated yields were greater than 85%. This regeneration of the original ester I does not only support the assigned structure II but also suggests that other derivatives of 3-substituted perfluorobutanoate, which would otherwise be difficult to prepare, could be obtained by the use of II.

REFERENCES

1 (*a*) M. Hauptschein, M. Braid and F.E. Lawlor, *J. Amer. Chem. Soc.*, 79 (1957) 6248; (*b*) W.T. Miller, E. Bergman and A.H. Fainberg, *ibid.*, 79 (1957) 4159; (*c*) R.D. Chambers, W.K.R. Musgrave and J. Savory, *J. Chem. Soc.*, (1962) 1995.
2 (*a*) H.J. Emeléus and R.N. Haszeldine, *J. Chem. Soc.*, (1949) 2948; (*b*) J. Banus, H.J. Emeléus and R.N. Haszeldine, *ibid.*, (1950) 3041; (*c*) H.J. Emeléus and J.J. Lagowski, *ibid.*, (1959) 1497.
3 Y.K. Kim and O.R. Pierce, *J. Org. Chem.*, 33 (1968) 442.
4 Y.K. Kim, *J. Org. Chem.*, 32 (1967) 3673.

J. Organometal. Chem., 19 (1969) P11–P12