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ALKYL POLYFLUOROARYL MERCURY COMPOUNDS

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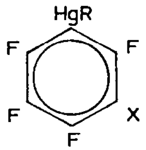
SUMMARY

The preparation of some alkyl(polyfluoroaryl)mercury compounds is described. Ethyl(2,3,4,6-tetrafluorophenyl)mercury, and a small amount of 1,3-bis-(ethylmercuri)-2,4,5,6-tetrafluorobenzene, were obtained from the action of ethylmercuric chloride upon the monolithio derivative of 1,2,3,5-tetrafluorobenzene. 2,4,5,6-Tetrafluoro-1,3-bis-(methylmercuri)benzene was prepared by pyrolysis of di(methylmercuri)tetrafluoroisophthalate, but pyrolysis of pentafluorophenylmercuric heptafluoro-n-butyrate gave only bis-(pentafluorophenyl)mercury. 2,3,5,6-Tetrafluoro-1,4-bis-(heptafluoroisopropylmercuri)benzene was obtained in low yield from heptafluoroisopropylmercuric chloride and 1,4-dilithio-2,3,5,6-tetrafluorobenzene. Reaction between the dilithio derivative of 3,3′-dihydro-octafluorobiphenyl and enthylmercuric chloride gave 3,3′-bis-(ethylmercuri)octafluorobiphenyl.

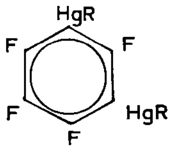
INTRODUCTION

The preparation of some perfluoroaryl- and alkylpentafluorophenyl-mercury compounds has already been described[1,2,3], and their thermal stability and high density has been noted.

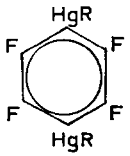
This paper describes the preparation of alkyl(polyfluoroaryl)mercury compounds (I) – (V) and (VII) and the attempted preparation of (VI).



(I) $R = C_2H_5$
$X = H$
(II) $R = C_2H_5$
$X = Br$



(III) $R = C_2H_5$
(IV) $R = CH_3$



(V) $R = i\text{-}C_3F_7$

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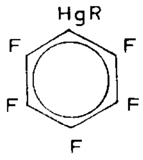
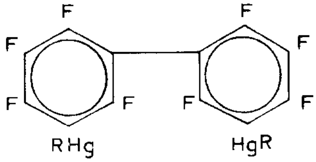


(VI) $R = n\text{-}C_3F_7$



(VII) $R = C_2H_5$

RESULTS AND DISCUSSION

Ethyl(2,3,4,6-tetrafluorophenyl)mercury (I) was prepared in 72–78 % yield by monolithiation of 1,2,3,5-tetrafluorobenzene in ether–hexane solution, followed by treatment with ethylmercuric chloride. Some 1,3-bis-(ethylmercuri)-2,4,5,6-tetrafluorobenzene (III) was isolated in a larger-scale preparation of (I).

Treatment of 1,3-dibromo-2,4,5,6-tetrafluorobenzene with n-butyl-lithium, and subsequent reaction with ethylmercuric chloride, gave only a low yield of impure 3-bromo-2,4,5,6-tetrafluorophenyl-ethylmercury (II).

When (I) in tetrahydrofuran was treated with n-butyl-lithium in hexane a negative Gilman colour test[4] suggested that lithiation of the ring hydrogen had occurred. However, after treatment with ethylmercuric chloride the starting material was recovered in high yield, and none of the desired compound (III) could be isolated.

2,4,5,6-Tetrafluoro-1,3-bis-(methylmercuri)benzene (IV) was prepared by a different route. Connett *et al*[5]. have reported that an alkylmercuric pentafluorobenzoate decomposes on heating, alone or in dry pyridine, to give the corresponding alkyl(pentafluorophenyl)mercury and carbon dioxide. When a pyridine solution of di(methylmercuri)tetrafluoroisophthalate, prepared from disilver tetrafluoroisophthalate and methylmercuric iodide, was heated, compound (IV) was obtained as white crystals in 56 % yield.

2,3,5,6-Tetrafluoro-1,4-bis-(heptafluoroisopropylmercuri)benzene (V) was obtained by the reaction of heptafluoroisopropylmercuric chloride[6] with the dilithio derivative of 1,4-dibromo-2,3,5,6-tetrafluorobenzene, in only 9 % yield. This low yield is surprising because the 1,4-dilithio derivative is known to be formed in high yield[7], and alkylmercuric chlorides generally react readily with polyfluoroaryl-lithium compounds. It is possible that the perfluoroalkyl group in heptafluoroisopropylmercuric chloride reduces the susceptibility of the mercury–chlorine bond to attack by the aryl-lithium.

A polyfluorobiphenyl compound substituted with two alkylmercuri groups was prepared by lithiation of 3,3′-dihydro-octafluorobiphenyl (in tetrahydrofuran–hexane solution) followed by addition of ethylmercuric chloride. 3,3′-Bis-(ethylmercuri)octafluorobiphenyl (VII) was isolated in 39 % yield as a viscous, dense, high-boiling liquid, which was purified by distillation in high vacuum.

An attempted preparation of pentafluorophenyl(heptafluoro-n-propyl)mercury (VI) by pyrolysis of pentafluorophenylmercuric heptafluoro-n-butyrate (prepared from silver heptafluoro-n-butyrate and pentafluorophenylmercuric bromide) failed, but instead bis-(pentafluorophenyl)mercury was obtained in almost quantitative yield. As little gas evolution was noted during the pyrolysis and no other organic material was recovered, it seems likely that mercury di(heptafluoro-n-butyrate) was formed but was lost in the aqueous work up.

EXPERIMENTAL

All reactions involving n-butyl-lithium were carried out under dry N_2. Infrared spectra were recorded on a Perkin–Elmer model 337 grating infrared spectrophotometer. Melting points are uncorrected.

Ethyl(2,3,4,6-tetrafluorophenyl)mercury (I) (nc)

n-Butyl-lithium in hexane (18.4 ml, 0.05 mole) was added to a solution of 1,2,3,5-tetrafluorobenzene (7.5 g, 0.05 mole) in dry ether (100 ml) at −70°. A solution of ethylmercuric chloride (13.3 g, 0.05 mole) in tetrahydrofuran (100 ml) was then added at −65° and the mixture was stirred at −70° for 2 h, at −40° for 3 h and then left to warm to room temperature overnight. Water (200 ml) and 6 *N* HCl (5 ml) were added, and the product was isolated by ether extraction. After being shaken with 1 *N* NaOH solution (20 ml) to remove ethylmercuric chloride, the ether layer was separated off, dried ($MgSO_4$) and distilled, giving ethyl(2,3,4,6-tetrafluorophenyl)mercury (I) (13.7 g, 72 % yield), b.p. 73–75°/0.5 mm, m.p. 6°, d_4^{25} 2.43 g/ml. (Found: C, 25.2; H, 1.5; F, 20.0; Hg, 52.4. $C_8H_6F_4Hg$ requires: C, 25.4; H, 1.6; F, 20.1; Hg 52.9%).

1,3-Bis-(ethylmercuri)-2,4,5,6-tetrafluorobenzene (III) (nc)

(a) In a second preparation of (I), carried out as described above, 1,2,3,5-tetrafluorobenzene (75 g, 0.5 mole) was treated with n-butyl-lithium (0.5 mole) and ethylmercuric chloride (133 g, 0.5 mole). Ethyl(2,3,4,6-tetrafluorophenyl)mercury (106 g) and a white residue (36 g) were obtained. A sample of the residue was recrystallised three times from light petroleum (boiling range 40–60°) and then sublimed, (110°/0.05 mm) giving 1,3-bis-(ethylmercuri)-2,4,5,6-tetrafluorobenzene (III) as white needles, m.p. 75–76°. (Found: C, 20.1; H, 1.6; Hg, 65.2. $C_{10}H_{10}F_4Hg_2$ requires: C, 19.8; H, 1.6; Hg 66.1%).

(b) Ethyl(2,3,4,6-tetrafluorophenyl)mercury (9.5 g, 0.025 mole) in dry tetrahydrofuran (75 ml) at −70° was treated with an n-hexane solution of n-butyl-lithium (9.2 ml, 0.025 mole). A subsequent Gilman colour test[4] was negative, showing the absence of butyl-lithium. A solution of ethyl mercuric chloride (6.65 g, 0.025 mole) in dry tetrahydrofuran (100 ml) was added to the reaction

mixture at −20°. After working up as above, the starting material was recovered in quantitative yield.

2,4,5,6-Tetrafluoro-1,3-bis-(methylmercuri)benzene (IV) (nc)

(a) Disilver 2,4,5,6-tetrafluoroisophthalate

A mixture of freshly-prepared silver oxide (0.1 mole) and 2,4,5,6-tetrafluoroisophthalic acid (23.8 g, 0.1 mole) in water (4 l) was stirred at 100° for 2 h in a dark room. The resulting clear solution was filtered and evaporated to dryness at reduced pressure in subdued light to give a white residue (39.0 g, 86% yield) of disilver 2,4,5,6-tetrafluoroisophthalate. (Found: Ag, 45.4. $C_8Ag_2F_4O_4$ requires: Ag, 47.8%).

(b) Di(methylmercuri)-2,4,5,6-tetrafluoroisophthalate (nc)

A mixture of disilver tetrafluoroisophthalate (39.0 g, 0.086 mole) and methylmercuric iodide[9] (59.0 g, 0.172 mole) in methanol (3 l) was boiled under reflux with stirring for 5 h. After filtering off the silver iodide and evaporating the filtrate, there remained a residue (52.9 g) which after crystallisation from n-butanol gave the title compound (36.5 g, 64% yield), m.p. 174° (decomp.). Two further crystallisations of a small quantity from n-butanol gave an analytical sample of di(methylmercuri)- 2,4,5,6-tetrafluoroisophthalate, m.p. 187° (decomp.). (Found: C, 18.2; H, 0.8; Hg, 59.4. $C_{10}H_6F_4Hg_2O_4$ requires C, 18.0; H, 0.9; Hg, 60.1%).

(c) 2,4,5,6-Tetrafluoro-1,3-bis-(methylmercuri)benzene (IV) (nc)

A mixture of di(methylmercuri)-2,4,5,6-tetrafluoroisophthalate (28.0 g, 0.042 mole) and dry pyridine (140 ml) was maintained at 100° for 1.5 h. A vigorous effervescence was observed. The mixture was poured on to ice, and the precipitate was filtered off and extracted repeatedly with boiling light petroleum (boiling range 60–80°). Evaporation of the combined extracts gave a yellow product (13.5 g, 56% yield) which, after two crystallisations from light petroleum (boiling range 60–80°), was sublimed (at 110°/0.05 mm) to give 2,4,5,6-tetrafluoro-1,3-bis-(methylmercuri)benzene (IV), m.p. 135.5–136°. (Found: C, 16.3; H, 0.9; Hg, 68.5; F, 13.1. $C_8H_6F_4Hg_2$ requires C, 16.6; H, 1.0; Hg, 69.3; F, 13.3%).

2,3,5,6-Tetrafluoro-1,4-bis-(heptafluoroisopropylmercuri)benzene (V) (nc)

A solution of n-butyl-lithium in hexane (14.0 ml, 0.038 mole) was added drop-wise to a solution of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (5.8 g, 0.019 mole) in tetrahydrofuran (75 ml) stirred at −70°. A solution of heptafluoroisopropylmercuric chloride[6] (15.5 g, 0.038 mole) in tetrahydrofuran (50 ml) was then added over 0.3 h, maintaining the reaction mixture at −70° during the addition, then at −40° for 3.5 h before allowing it to warm to room temperature. Hydrochloric acid (0.3 *N*, 100 ml) was added and the solvents were removed at reduced pressure. Ether extraction of the resulting aqueous suspension, followed by evaporation of the combined dried extracts, afforded a brown sticky residue (8.5 g). Sublimation at 100°/10 mm gave 2.8 g of perfluoroisopropylmercuric chloride. Further sublimation at 150°/0.05 mm gave (V) (1.9 g, 9% yield), m.p. *ca.* 142°.

Crystallisation from light petroleum (boiling range 60–80°) gave an analytical sample m.p. 158–160°. (Found: C, 16.9; F, 38.2, Hg, 43.0. $C_{12}F_{18}Hg_2$ requires C, 16.2; F, 38.5; Hg, 45.3%).

3,3′-Bis-(ethylmercuri)-2,2′,4,4′,5,5′,6,6′-octafluorobiphenyl (VII) (nc)

To a solution of 3,3′-dihydro-octafluorobiphenyl (14.91 g, 0.05 mole) in tetrahydrofuran (125 ml) at —76° was added a solution of n-butyl-lithium in hexane (37 ml, 0.1 mole) over 0.5 h. The resulting suspension was stirred at —76° for 1.5 h and then a solution of ethylmercuric chloride (26.5 g, 0.1 mole) in tetrahydrofuran (200 ml) was added over 0.75 h. The grey suspension was stirred at —70° for a further 2 h and allowed to warm to 0°. Water (200 ml) was then added, and the organic layer was separated off and combined with ether extracts of the aqueous phase. Distillation gave a fraction (5.4 g) b.p. 130–138°/0.15 mm and a residue (22.5 g). Further distillation of the residue afforded 3,3′-bis-(ethylmercuri)-2,2′,4,4′,5,5′,6,6′-octafluorobiphenyl (VII) (14.7 g, 39% yield), boiling range 165–168°/9–25 $\times$ 10^{-4} mm as a clear viscous liquid. (Found: C, 26.7; H, 1.3; F, 19.6; Hg 51.1. $C_{16}H_{10}F_8Hg_2$ requires C, 25.5; H, 1.3; F, 20.1; Hg 53.1%).

Thin layer chromatography of this product (on silica gel GF 254 with repeated elution by n-hexane) resolved the material into one major component and a minor, faster eluting, impurity. The thermal decomposition temperature, T_D (the temperature at which there is 0.84 mm min^{-1} increase of vapour pressure in a nitrogen atmosphere[8]) measured in glass, was 180°.

Attempted preparation of pentafluorophenyl(heptafluoro-n-propyl)mercury (VI)

(a) Pentafluorophenylmercuric heptafluoro-n-butyrate

Silver heptafluoro-n-butyrate (3.30 g, 0.01 mole) was suspended in stirred dry methanol (100 ml) and a solution of pentafluorophenylmercuric bromide[2] (4.60 g, 0.01 mole) in dry methanol (100 ml) was added. Silver bromide precipitated out fairly rapidly. The mixture was boiled for 5 h under nitrogen, the silver bromide (1.93 g, 100% yield) being then filtered off. The filtrate was evaporated to dryness *in vacuo* giving a yellow residue of the crude mercuric salt (4.1 g, 71% yield). Attempts to purify the salt by crystallisation and sublimation were not successful. The infrared spectrum was, however, consistent with the structure of the title compound.

(b) Pentafluorophenyl(heptafluoro-n-propyl)mercury (VI)

Crude pentafluorophenylmercuric heptafluoro-n-butyrate (3.16 g, 0.005 mole) was dried at 70°/0.1 mm for 2 h, then heated in dry re-distilled pyridine (20 ml) at 100° for 0.75 h and at 130° for 0.5 h. Little evolution of carbon dioxide occurred. The hot solution was filtered to remove a small amount of grey precipitate and the filtrate was added to ice-cold water (300 ml). The resulting white precipitate (1.39 g) was filtered off and recrystallised three times from light petroleum (boiling range 60–80°) giving white needles (0.42 g), m.p. 141–141.5°. The infrared spectrum of this material was identical to that of bis-(pentafluorophenyl)mercury, m.p. 140–145°. (Found: F, 34.9; Hg 37.7. Calc. for $C_{12}F_{10}Hg$: F, 35.5; Hg 37.6%).

In a second preparation carried out on the same scale, pentafluorophenylmercuric heptafluoro-n-butyrate (0.005 mole) was heated in dry pyridine at 100° for 1 h rising to 120° over a further 2 h. The only material obtained was bis-(pentafluorophenyl)mercury (2.7 g, 0.005 mole), m.p. 138–139.5°, the latter being undepressed on admixture with authentic material.

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