804. (*Trifluoromethyl*)*phenylmercurials.*

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The preparation and characterization of the isomeric (trifluoromethyl)-phenylmercuric hydroxides and the isomeric bis(trifluoromethylphenyl)-mercurials are described. Equilibrium constants for the ionization of the (trifluoromethyl)phenylmercuric hydroxides, and solubility products for the corresponding chlorides, bromides, and iodides, in aqueous solution, have been determined potentiometrically. The results are discussed in terms of the electronic effect of the trifluoromethyl group.

IN a general investigation into the electronic effect of trifluoromethyl groups on the properties of metal atoms in organometallic compounds the isomeric (trifluoromethyl)-phenylmercurials and (trifluoromethyl)phenylmercuric chlorides and hydroxides were prepared and characterized. The properties of these compounds reflect the extent to which the inductive effect of a trifluoromethyl group is modified by the presence of, and its position on, the benzene nucleus.

EXPERIMENTAL

Preparation of (*Trifluoromethyl*)*phenylmercuric Compounds.*—The synthesis of the compounds reported here proceeded from the isomeric (trifluoromethyl)iodobenzenes. (Trifluoromethyl)phenylmercuric chloride was prepared from mercuric chloride and (trifluoromethyl)-phenyl-lithium, the latter being obtained by halogen–metal exchange[1] with n-butyl-lithium. In a typical preparation a solution of *p*-(trifluoromethyl)iodobenzene (12 g.) in anhydrous ether (20 ml.) was added with stirring during 20 min. to butyl-lithium (3 g.) in ether (50 ml.) at −25°.[2] After 2 hours' stirring at −25° the yield of *p*-(trifluoromethyl)phenyl-lithium was determined by titration with standard acid. Mercuric chloride (1 mol.) in anhydrous ether (100 ml.) was then added during 30 min. at −35° and the mixture was stirred for an additional 2 hr. while it was allowed to attain ambient temperature. All operations were conducted in a dry nitrogen atmosphere. The solvent was removed *in vacuo* and the residue purified by repeated sublimation *in vacuo* at 80—100°. The *arylmercuric chlorides* prepared are listed in Table 1. Mercury was determined electrolytically,[3] and chlorine gravimetrically as silver chloride. It was difficult to decompose the mercurials completely before electrolysis without volatilizing some of the sample, which accounts for the low results for the more volatile compounds.

TABLE 1.

Characterization and analytical data for the isomeric (trifluoromethyl)phenylmercuric chlorides and bis(trifluoromethyl)phenylmercurials.

Compound	Yield * (%)	M. p.	Found † *M*	Cl (%)	Hg (%)
o-$\mathrm{CF_3{\cdot}C_6H_4{\cdot}HgCl}$	60	135—137°	380·6	9·7	51·9
m-$\mathrm{CF_3{\cdot}C_6H_4{\cdot}HgCl}$	70	180—182	383·9	9·8	50·5
p-$\mathrm{CF_3{\cdot}C_6H_4{\cdot}HgCl}$	45	242—243	384·3	9·1	50·8
o-$\mathrm{(CF_3{\cdot}C_6H_4)_2Hg}$	56	133—135	479·6	—	37·9
m-$\mathrm{(CF_3{\cdot}C_6H_4)_2Hg}$	60	165—167	480·2	—	38·2
p-$\mathrm{(CF_3{\cdot}C_6H_4)_2Hg}$	45	130—132	500·2	—	38·3

* Based on (trifluoromethyl)iodobenzene. † $\mathrm{C_7H_4ClF_3Hg}$ requires M, 382; Cl, 9·3; Hg, 52·6%. $\mathrm{C_{14}H_8F_6Hg}$ requires *M*, 491; Hg, 40·9%.

Attempts were made to prepare (trifluoromethyl)phenyl-lithium derivatives directly from (trifluoromethyl)iodobenzene and lithium in boiling ether. The *ortho*- and *para*-isomers did

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[1] Pierce, McBee, and Judd, *J. Amer. Chem. Soc.*, 1954, **76**, 474.

[2] Gilman, Bell, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499.

[3] Vernon, *Analyt. Chem.*, 1961, **33**, 1435.

not react; the *meta*-isomer reacted very slowly. These observations are consistent with the highly electronegative character of the trifluoromethyl group.[4]

(Trifluoromethyl)phenylmercuric hydroxides were prepared by the action of moist silver oxide on the chlorides. An aqueous suspension of freshly prepared silver oxide, free from alkali, was shaken with a solution of the (trifluoromethyl)phenylmercuric chloride in 95% ethanol for 18 hr., the slurry then diluted with an equal volume of distilled water, the ethanol removed by distillation, and the unchanged silver oxide and silver chloride were removed by filtration. The filtrate was concentrated and the (trifluoromethyl)phenylmercuric hydroxide which separated on cooling was recrystallized from water (yield, 40—60%). *p*-(Trifluoromethyl)phenylmercuric hydroxide melted at 115—118°, resolidified, and remelted at 180—200°. The *meta*-isomer melted at 207—210°. The *ortho*-isomer melted first at 128—129° and then at 200—210° after resolidifying. The equivalent weights, determined by potentiometric titration with standard acid, were 359·8, 359·1, and 360·1 for *o*-, *m*-, and *p*-compounds, respectively ($CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH$ requires 362·6); the molecular weight of *p*-$CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH$ was determined in camphor as 362·5.

Preparation of Bis(trifluoromethyl)phenylmercurials.—The isomeric bis(trifluoromethyl)phenylmercurials were prepared in anhydrous ether by allowing the corresponding (trifluoromethyl)phenyl-lithium derivatives to react with mercuric chloride (0·5 mol.), by the procedure described for (trifluoromethyl)phenylmercuric chloride. It was important to establish the correct stoicheiometry since an excess of mercuric chloride led to a mixture of the desired product and the corresponding (trifluoromethyl)phenylmercuric chloride which was difficult to separate.

Apparatus.—The apparatus and the method used to determine the ionization constants and the solubility products of the (trifluoromethyl)phenylmercuric hydroxides and halides have been reported previously.[5,6] Infrared spectra were obtained with a Beckman IR-7 recording spectrophotometer, and a Varian model DP-60 high-resolution spectrometer was used to determine nuclear magnetic resonance spectra.

DISCUSSION

The nature of the products obtained by reaction of the (trifluoromethyl)phenylmercuric chlorides with silver oxide depends upon the manner in which they are isolated and purified. Crystallization of the product from ethanol–water yields a compound which is water-soluble and exhibits the free and " bound " O–H infrared absorption bands at 3200—3600 cm.$^{-1}$, the properties that would be expected for $CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH$. A deuteriochloroform solution of the compound has a proton nuclear magnetic resonance spectrum which is consistent with that formulation (aromatic protons at 7·3 p.p.m. and a hydroxyl proton at 5·1 p.p.m. below tetramethylsilane as external reference), as are the equivalent weight and molecular weight. If the hydroxide is sublimed or recrystallized from chloroform, the product is insoluble in water and has a higher and wider melting range and a markedly higher molecular weight in camphor (in the range 683—730). The O–H stretching bands are absent from the infrared spectrum of this substance, and the hydroxyl proton resonance absorption is absent from its nuclear magnetic resonance spectrum (CCl_3D), suggesting the formation of bis(trifluoromethyl)phenylmercuric oxide. Solidification and remelting at higher temperatures of the *o*- and *p*-(trifluoromethyl)-mercuric hydroxide support the suggestion that the hydroxides are dehydrated readily to the oxides.

Dilute aqueous solutions of (trifluoromethyl)phenylmercuric hydroxides were titrated potentiometrically with perchloric and hydrohalogen acid. The results were treated as described previously,[5] to afford ionization constants for the equilibria. $CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH \rightleftharpoons CF_3{\cdot}C_6H_4{\cdot}Hg^+ + OH^-$ and $CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}X \rightleftharpoons CF_3{\cdot}C_6H_4{\cdot}Hg^+ + X^-$ (X = Cl, Br, or I). As in the titration of perfluoroalkylmercuric hydroxides with perchloric acid, addition of potassium chloride (1—2 g.) to the solution before the equivalence point had

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[4] Lagowski, *Quart. Rev.*, 1959, **13**, 233.

[5] Powell and Lagowski, *J.*, 1962, 2047.

[6] Waugh, Walton, and Laswick, *J., Phys. Chem.*, 1955, **59**, 395.

been reached was necessary to obtain the characteristic break in the titration curve. At the concentrations employed ($0{\cdot}1$—10×10^{-4}M) only *o*- and *m*-(trifluoromethyl)phenylmercuric chloride remained in solution. Precipitation of the bromides and iodides of these isomers and the *p*-(trifluoromethyl)phenylmercuric halides began immediately on addition of hydrohalogen acid. If precipitation occurred, the solubility products of the halides were calculated from the expression $\log K_{sp} = (E - E^\circ)/0{\cdot}05915 + pK_w + \log K_B + \log [CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH]$, where K_{sp} = the solubility product constant for the equilibrium $CF_3{\cdot}C_6H_4{\cdot}HgX(solid) \rightleftharpoons CF_3{\cdot}C_6H_4{\cdot}Hg^+ + X^-$ (X = Cl, Br, or I), K_B = the ionization constant of the base, and the other symbols have their usual significance.

TABLE 2.

Ionization constants and solubility products at 25°.

	K_i		K_{sp}		
Cation	OH^-	Cl^-	Cl^-	Br^-	I^-
p-$CF_3{\cdot}C_6H_4{\cdot}Hg$	$8{\cdot}3 \times 10^{-11}$	—	$1{\cdot}2 \times 10^{-10}$	$1{\cdot}0 \times 10^{-12}$	$7{\cdot}7 \times 10^{-16}$
o-$CF_3{\cdot}C_6H_4{\cdot}Hg$	$9{\cdot}1 \times 10^{-11}$	$4{\cdot}6 \times 10^{-6}$	$2{\cdot}6 \times 10^{-10}$	$6{\cdot}3 \times 10^{-12}$	$3{\cdot}5 \times 10^{-15}$
m-$CF_3{\cdot}C_6H_4{\cdot}Hg$	$1{\cdot}2 \times 10^{-10}$	$6{\cdot}0 \times 10^{-6}$	$4{\cdot}8 \times 10^{-10}$	$8{\cdot}3 \times 10^{-12}$	$3{\cdot}9 \times 10^{-15}$
$C_6H_5{\cdot}Hg$ [6]	1×10^{-10}	—	$5{\cdot}0 \times 10^{-10}$	$1{\cdot}8 \times 10^{-12}$	$1{\cdot}0 \times 10^{-15}$

In the derivation of this expression the concentrations of halide and hydroxide ions are assumed to be negligible [5] and no attempt was made to apply activity corrections. The ionization constants and solubility products obtained for the (trifluoromethyl)phenylmercuric hydroxides and halides at 25° are summarized in Table 2 (average values each from 4—5 titrations).

The ionization constants of the isomeric (trifluoromethyl)phenylmercuric hydroxides are consistent with the relatively high effective electronegativities which have been suggested for perfluoroalkyl groups.[4] The electronic density about the mercury atom in the *o*- and *p*-(trifluoromethyl)phenylmercuric hydroxides is decreased with respect to that in phenylmercuric hydroxide as a result of the inductive effect of the trifluoromethyl group, and this is reflected in the smaller value of their ionization constants. The deactivating effect of a trifluoromethyl group is less effectively transmitted through the benzene nucleus to the mercury atom when the trifluoromethyl group is in the *meta*- than when it is in the *ortho*- or *para*-position, and, indeed, the value of the ionization constant for *m*-$CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH$ is essentially the same as that for phenylmercuric hydroxide. The decrease of the ionization constants for *o*- and *p*-$CF_3{\cdot}C_6H_4{\cdot}Hg{\cdot}OH$, when compared with that of phenylmercuric hydroxide, is less than that for $CF_3{\cdot}Hg{\cdot}OH$ ($1{\cdot}7 \times 10^{-11}$) [5] compared with that of $CH_3{\cdot}Hg{\cdot}OH$ ($3{\cdot}1 \times 10^{-10}$),[6] indicating that the inductive effect of a trifluoromethyl group is diminished when it acts through a benzene nucleus. Unfortunately, similar comparisons for the (trifluoromethyl)phenylmercuric halides are not possible since the ionization constants of a complete series could not be obtained.

Although the inductive effect of a trifluoromethyl group on the mercury atom is decreased when it acts through a benzene nucleus, oscillometric titrations indicate that complex compounds of the types $(CF_3{\cdot}C_6H_4)_2HgL$ and $(CF_3{\cdot}C_6H_4)_2HgL_2$ (L = ligand) can be formed in benzene solution with a variety of ligands.[7] Since phenylmercuric hydroxide and *m*-(trifluoromethyl)phenylmercuric hydroxide have similar ionization constants, it is not surprising that the former undergoes complex formation under the same conditions as the latter.[7]

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[7] Powell, Maung, and Lagowski, *J.*, 1963, 2787.