Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE ^{19}F NMR SPECTRA OF SOME FLUOROARYL MERCURIALS AND THE ELECTRONIC EFFECT OF MERCURY SUBSTITUENTS

D. N. KRAVTSOV, B. A. KVASOV, L. S. GOLOVCHENKO AND E. I. FEDIN
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

(Received September 30th, 1971)

SUMMARY

A number of new fluoroaryl mercurials have been prepared, and for the compounds indicated the ^{19}F NMR spectra have been recorded in chloroform, tetrahydrofuran and dimethyl sulphoxide. The values of σ_I and σ_R^0 for mercury substituents have been derived from the fluorine shielding parameters. The dependence of the electronic effect of mercury substituents upon the solvent, the nature of the groups on mercury, steric hindrance and possible intramolecular coordination is discussed.

INTRODUCTION

In a previous communication[1] investigations of the ^{19}F NMR spectra of some bis(fluoroaryl)mercurials and (fluoroaryl)mercury acetates were reported, and it was shown that the electronic effect of mercury substituents is mainly inductive and markedly solvent dependent. Somewhat earlier Petrosyan and Reutov[2], as well as Kitching *et al.*[3], also reported the study of electronic effects in (fluorophenyl)- and (fluorobenzyl)mercurials using fluorine NMR methods, but the spectra of all these authors were, however, recorded using only coordinating solvents such as dioxane and dimethyl sulphoxide. Since all these previous investigations[1-3] were made using only a limited range of mercury substituents, it was thought desirable to obtain additional evidence regarding the factors which determine the electronic effects of such groups.

The present paper reports the results of a more detailed study of the variation of the electronic effect of mercury substituents with the nature of the groups attached to the mercury atom as well as with the solvent, steric hindrance and possible intramolecular coordination. For this purpose some new fluoroaryl mercurials have been synthesized and their ^{19}F NMR spectra recorded in a number of solvents.

RESULTS AND DISCUSSION

The ^{19}F chemical shifts for the fluoroaryl mercurial compounds relative to fluorobenzene in the same solvent are listed in Table 1. The solvents used in the present investigation included chloroform, tetrahydrofuran and dimethyl sulphoxide, DMSO

TABLE 1

^{19}F CHEMICAL SHIFTS OF (FLUOROPHENYL)MERCURY COMPOUNDS RELATIVE TO FLUOROBENZENE (IN PPM)

Compound	Solvent		
	$CHCl_3$	THF	DMSO
$3\text{-}FC_6H_4HgC_6H_5$	−0.5	0.5	0.9
$3\text{-}FC_6H_4HgC{\equiv}CC_6H_5$	−0.9	0.3	0.7
$3\text{-}FC_6H_4HgCF_3$	−2.3	−1.0	−0.3
$3\text{-}FC_6H_4HgCN$	−1.0	0.1	0.7
$3\text{-}FC_6H_4HgCl$	−1.6	−0.6	−0.1
$3\text{-}FC_6H_4HgBr$	−2.5	−0.7	−0.1
$3\text{-}FC_6H_4HgI$	−1.1	−0.8	−0.2
$3\text{-}FC_6H_4HgOCOCH_3$	−2.1	−0.5	−0.1
$3\text{-}FC_6H_4HgOC_6H_5$	−2.2	−0.6	0.1
$3\text{-}FC_6H_4HgNHCOCH_3$	−1.3	0.0	0.2
$3\text{-}FC_6H_4HgSC_6H_5$	−1.6	−0.4	0.1
$3\text{-}FC_6H_4HgSCN$	[a]	−0.8	−0.2
$4\text{-}FC_6H_4HgC_6H_5$	−1.0	0.5	1.1
$4\text{-}FC_6H_4HgC{\equiv}CC_6H_5$	−2.2	−0.2	0.5
$4\text{-}FC_6H_4HgCF_3$	−4.3	−1.1	0.1
$4\text{-}FC_6H_4HgCN$	−4.3	−0.6	0.2
$4\text{-}FC_6H_4HgCl$	−2.8	−0.9	0.1
$4\text{-}FC_6H_4HgBr$	−2.6	−0.7	0.0
$4\text{-}FC_6H_4HgI$	−2.4	−0.8	0.0
$4\text{-}FC_6H_4HgOCOCH_3$	−2.8	−0.5	0.2
$4\text{-}FC_6H_4HgOC_6H_5$	−1.9	−0.4	0.1
$4\text{-}FC_6H_4HgNHCOCH_3$	−2.0	−0.1	0.3
$4\text{-}FC_6H_4HgSC_6H_5$	−2.4	−0.6	0.1
$4\text{-}FC_6H_4HgSCN$	[a]	[a]	0.0

[a] Solubility problems.

being included as a powerful coordinating solvent and THF as one of medium solvating power while chloroform was used as an inert solvent with respect to possible coordination with the mercury atom. On the basis of data for bis(*m*-fluorophenyl)- and bis(*p*-fluorophenyl)mercury[1], chloroform had previously been shown to be similar to solvents such as cyclohexane and carbon tetrachloride in this respect. Unfortunately, the use of the latter solvents, which are usually considered to be the most inert, was in most cases precluded in the present study due to solubility limitations.

In discussing the results for chloroform solutions, the fact that this solvent can form hydrogen bonds to molecules having atoms with lone-pair electrons[4-6] should be taken into account. Indeed, on the basis of the lower electronegativity of mercury compared to that of carbon[7] it may be assumed that the Hg–X bond, with X having an unshared electron pair, will be more polar than the C–X bond. This assumption is strongly supported by the data on the electric dipole moments and NQR spectra of structurally similar compounds. Thus, the dipole moments of benzyl chloride[8] and phenylmercury chloride[9] are 1.85 and 2.99 D, whereas the ^{79}Br NQR frequencies for ethyl bromide[10] and methylmercury bromide[11] are equal to 248.74 and 121.20 MHz respectively. Thus, it may be concluded that hydrogen bonds of the type Hg–X... $CHCl_3$ will be formed more readily than those of type C–X...$CHCl_3$. It is known[12] for example that chloroform forms stronger hydrogen bonds with oxygen and sulphur in the case of organotin and organolead alkoxides and mercaptides than in the case of ethers and thioethers.

As a result of the above interactions, it is possible that the electronic effect of the HgX substituents may be substantially dependent upon the strength of the hydrogen bond formed between chloroform and the group X, and for this reason in all the solvents studied in the present communication the electronic effect of mercury substituents will be modified by the solvent through solvent–metal interaction or through bond formation with the anionic part of the substituent.

From Table 1 it appears that, as far as the solvent effect is concerned, the fluorine chemical shifts for the compounds studied follow the same pattern as in the case of the fluoroaryl mercurials investigated previously[1]. For a given compound, fluorine shielding increases in the order chloroform, THF, DMSO. In chloroform as a solvent the fluorine nucleus is apparently less shielded in all the mercury substituents relative to fluorobenzene, and the same is true for most of the substituents in THF. In DMSO all the mercury substituents in the *p*-position increase the ^{19}F shielding, whereas *m*-substituents either increase, or decrease it, depending on the nature of the group attached to the mercury atom.

The observed solvent dependence of the fluorine chemical shifts is in agreement with the solvent–mercury interactions previously reported. At the same time the reduced shielding capacity of mercury substituents in chloroform may be partly due to the hydrogen bond formation between the solvent and the group on the metal atom mentioned above, *i.e.*:

$$FC_6H_4HgX...CHCl_3$$

Relative to the group attached to the mercury atom, the variation of the ^{19}F chemical shift in a given solvent decreases in the series chloroform, tetrahydrofuran, dimethyl sulphoxide. This suggests that the transmission of electronic interactions through the mercury atom is substantially solvent dependent, decreasing on going from an inert to a coordinating solvent. On the other hand, it seems possible that the large range of observed fluorine chemical shifts in chloroform is also partly due to its differentiating influence on the electronic effect of mercury substituents through hydrogen bond formation.

In the case of chloroform and benzene we have succeeded in demonstrating the influence of specific solvation on the electronic effect of mercury substituents through the use of (4-fluoro-2,6-dimethylphenyl)mercury acetate as a model com-

TABLE 2

^{19}F CHEMICAL SHIFTS RELATIVE TO FLUOROBENZENE AND ^{19}F SCS VALUES FOR THE $HgOCOCH_3$ SUBSTITUENT IN (4-FLUORO-2,6-DIMETHYLPHENYL)MERCURY ACETATE (IN PPM)

Solvent	δ(F)	SCS
$CHCl_3$	0.5	−1.9
C_6H_{12}	1.0	−1.5
CCl_4	0.9	−1.5
C_6H_6	1.7	−0.7
THF	2.2	−0.1
DMSO	2.6	0.5

pound, which also proved to be sufficiently soluble in cyclohexane and carbon tetrachloride for measurements to be made. The ^{19}F chemical shifts relative to fluorobenzene for this compound and the ^{19}F SCS values for the $HgOCOCH_3$ group are given in Table 2. These data show that the SCS values for this latter substituent are the same in cyclohexane and carbon tetrachloride and indicate that as far as the latter solvent is concerned it is essentially inert towards the specific solvation of mercury in the compounds ArHgX.

In contrast, changing the solvent from cyclohexane to chloroform leads to a decrease in the fluorine shielding in (4-fluoro-2,6-dimethylphenyl)mercury acetate, indicating hydrogen bonding with the anionic part of the molecule. On the other hand, the ^{19}F SCS value for the $HgOCOCH_3$ substituent increases on passing from cyclohexane to benzene, suggesting a decrease in the electron-accepting ability of the substituent due to coordination of the solvent molecules with the mercury atom. For the same reason, it may be supposed that the levelling effect of coordinating solvents upon the electron-withdrawing power of mercury substituents is due to the fact that the solvent partly compensates electron withdrawal from the metal atom by donating a lone electron pair into a vacant mercury orbital.

In order to obtain a more detailed understanding of the electronic effects of mercury substituents it is more appropriate to use σ_I and σ_R^0 constants derived from the ^{19}F shielding parameters[13,14] rather than the fluorine chemical shifts relative to fluorobenzene. The values of σ_I and σ_R^0 are listed in Table 3. The data obtained show that for most mercury substituents studied σ_R^0 values are close to zero. This indicates that the conjugation of mercury with the aromatic ring is rather weak regardless of the group on the metal atom, the electronic effect of mercury substituents being mainly inductive. The σ_R^0 values are substantially greater than zero only for substituents such as HgCN and $HgCF_3$ in chloroform, which may be attributed to the strong electron-attracting properties of the CN and CF_3 groups. For groups where σ_R^0 differs from zero, the value of this constant decreases progressively on passing from chloroform to DMSO. This is due to the fact that coordinating solvents inhibit mesomeric interaction between mercury and the aromatic ring and thus block the

TABLE 3

INDUCTIVE AND RESONANCE PARAMETERS OF MERCURY SUBSTITUENTS

Substituent	Solvent					
	$CHCl_3$	THF	DMSO	$CHCl_3$	THF	DMSO
HgC_6H_5	0.16	0.01	−0.03	0.01	0.00	−0.01
$HgC{\equiv}CC_6H_5$	0.21	0.04	−0.02	0.04	0.02	0.01
$HgCF_3$	0.41	0.22	0.13	0.07	0.00	−0.01
HgCN	0.23	0.07	0.00	0.11	0.02	0.02
HgCl	0.31	0.17	0.10	0.04	0.01	−0.01
HgBr	0.44	0.18	0.10	0.00	0.00	0.00
HgI	0.24	0.20	0.11	0.04	0.00	−0.01
$HgOCOCH_3$	0.38	0.16	0.09	0.02	0.00	0.00
$HgOC_6H_5$	0.39	0.17	0.07	0.00	0.00	0.00
$HgNHCOCH_3$	0.26	0.08	0.06	0.03	0.00	0.00
$HgSC_6H_5$	0.31	0.14	0.07	0.03	0.01	0.00
HgSCN		0.20	0.11			0.00

vacant 6*p* orbitals of the mercury atom. On transfer to such a strongly coordinating solvent as DMSO the σ_R^0 values may even change sign, suggesting a weak mesomeric electron-releasing effect, probably due to the mercury 5*d* electrons.

In contrast to mesomeric interaction, the inductive effect of mercury substituents can be quite large. Comparison of the σ_I values in different solvents reveals that the inductive effect of mercury substituents varies from relatively strongly electron attracting to weakly electron releasing, depending on the solvent and on the nature of the group on mercury. It is noteworthy that the values of σ_I in chloroform for many mercury substituents approximate to, and in some cases even exceed, those for the corresponding groups on the metal atom. This may be also explained in terms of the enhancing of the electron-attracting capacity of mercury substituents through hydrogen bond formation.

Although small values of σ_R^0 indicate largely inductive interaction of mercury substituents with the aromatic ring, it has not been possible to correlate the ^{19}F chemical shifts for *m*- and *p*-fluorophenyl mercurials with the σ_I values for the groups bonded to mercury as derived from fluorine shielding parameters[13]. Only a general trend is observed (Figs. 1 and 2). The observed lack of correlation can be partly accounted for in terms of the above discussed solvent effects and may be associated with the fact that the solvent susceptibility of the electronic effect of mercury substituents (measured as a first approximation as the change in the fluorine chemical shift on transfer from chloroform to DMSO) is substantially dependent on the nature of the group on mercury. Thus, in the case of (*p*-fluorophenyl)mercury cyanide, the change in the ^{19}F chemical shift on passing from chloroform to DMSO amounts to 4.5 ppm, whereas with phenyl(*p*-fluorophenyl)mercury it is only equal to 2.6 ppm. In this connection it is interesting to note that the solvent susceptibility of the electronic effects of HgCN and $HgCF_3$ groups is markedly greater than that of all the substituents investigated by Taft *et al.*[13,14]. As a result of different solvent susceptibilities, the electronic effects of various mercury substituents may change to a

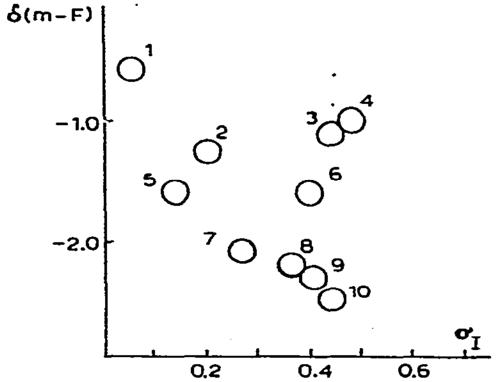

Fig. 1. A plot of the ^{19}F chemical shifts for (*m*-fluorophenyl)mercury compounds in $CHCl_3$ *vs.* the inductive parameters of the groups on mercury: 1 C_6H_5, 2 CH_3CONH, 3 I, 4 CN, 5 C_6H_5S, 6 Cl, 7 CH_3COO, 8 C_6H_5O, 9 CF_3, 10 Br.

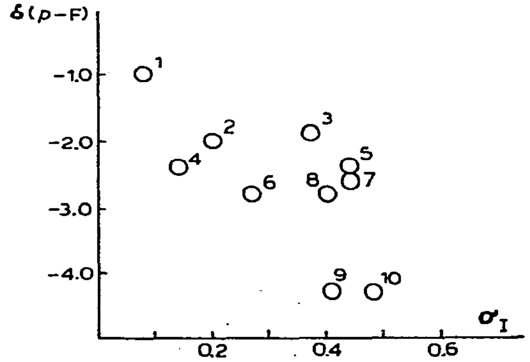

Fig. 2. A plot of the ^{19}F chemical shifts for (*p*-fluorophenyl)mercury compounds in $CHCl_3$ *vs.* the inductive parameters of the groups on mercury: 1 C_6H_5, 2 CH_3CONH, 3 C_6H_5O, 4 C_6H_5S, 5 I, 6 CH_3COO, 7 Br, 8 Cl, 9 CF_3, 10 CN.

different extent on transfer from a sufficiently inert solvent to a solvent coordinating to mercury or forming hydrogen bonds with the anionic part of the substituent.

Another possible explanation for the lack of correlation between the fluorine chemical shifts in the mercurials investigated and the inductive parameters of the groups on mercury atom involves the specificity of electronic interactions across the Hg–X bond as compared with those across the C–X bond. Thus in the case of the mercury–halogen bond, for example, the possibility of p_π–p_π and d_π–d_π conjugation should be taken into account:

Further studies concerning the above problems may show which of the factors mentioned plays a major role in the dependence of the electronic effect of mercury substituents on the nature of the groups attached to mercury.

Finally, the influence of CH_3 groups and bromo substituents in the ortho-position on the electronic effect of mercury substituents and its solvent susceptibility will be considered. Comparison of the data listed in Tables 1, 2 and 4 shows that the introduction of methyl groups in positions 2 and 6 relative to the metallic substituents has apparently no influence on the electronic effect of the axially symmetric substituent HgBr, but that it decreases the electron-withdrawing power of unsymmetrical mercury substituents. Thus, the electronic effect of axially symmetric mercury substituents seems to be as insensitive to steric influences as that of other groups of similar geometry[15]. The decrease in the electron-attracting properties of axially unsymmetrical mercury substituents may be due to an additional polarization of the Hg–C bond caused by the mutual repulsion between the *o*-methyl groups and the substituent on the mercury atom. The difference between axially symmetric and axially unsymmetrical mercury substituents may also involve the solvent susceptibility of their electronic effects. With the HgBr substituent, the introduction of *o*-methyl groups does not substantially affect this but a decrease is observed for $HgOCOCH_3$ and $HgSC_6H_5$ substituents. The most pronounced decrease in the coordinating ability of mercury is observed with bis(4-fluoro-2,6-dimethylphenyl)mercury. Nevertheless, even in this compound the metal atom can be solvated by strongly coordinating solvents. The observed reduction of the solvent susceptibility of

TABLE 4

^{19}F CHEMICAL SHIFTS RELATIVE TO FLUOROBENZENE AND ^{19}F SCS VALUES FOR MERCURY SUBSTITUENTS (IN PPM)

Compound	Solvent					
	$CHCl_3$		THF		DMSO	
	δ(F)	SCS	δ(F)	SCS	δ(F)	SCS
4-F-2,6-$(CH_3)_2C_6H_2HgBr$	−0.1	−2.5	1.7	−0.6	2.3	0.2
4-F-2,6-$(CH_3)_2C_6H_2HgSC_6H_5$	0.8	−1.6	2.0	−0.3	2.6	0.5
[4-F-2,6-$(CH_3)_2C_6H_2]_2Hg$	1.7	−0.7	2.6	0.3	2.8	0.9
4-F-2,6-$Br_2C_6H_2HgCl$	−6.1	−1.7	−4.0	0.6	−3.6	1.2

electronic effect may be assumed to result from the free rotation of the two axially unsymmetrical groups on mercury, thus hindering the approach of the solvent molecule to the metal atom.

The introduction of two *o*-bromo substituents lowers the electron-accepting capacity of the HgCl group, without affecting the solvent susceptibility of its electronic effect. The first observation may be associated either with an increase in the electron-withdrawing power of the aromatic ring, or with an increased flow of electron density from the metallic substituent to the halogen atoms. On the other hand, when the strong electron-attracting properties of the *ortho*-bromo substituents[16], the equivalence of the van der Waals radii of the bromine atoms and the methyl groups[17], together with the results obtained for (4-fluoro-2,6-dimethylphenyl)mercury bromide are considered, it may be that the absence of a change in solvent susceptibility of the electronic effect of the HgCl substituent on the introduction of *ortho* halogen groups is due to intramolecular coordination between the mercury substituent and the bromine atoms.

EXPERIMENTAL

General comments

The ^{19}F NMR spectra were recorded using Hitachi H-60 and Hitachi–Perkin–Elmer R-20 spectrometers operating at 56.4 MHz. All the measurements were taken at 34° using diluted solutions with concentration not greater than 0.2 *M*. Fluorine chemical shifts relative to internal fluorobenzene were obtained using the substitution method[18]. The spectra of the compounds with low solubilities were obtained employing a spectrum accumulator[1]. The accuracy of the data was not less than 0.1 ppm. The ^{19}F SCS values for mercury substituents were calculated using the data for the fluorine chemical shifts in 3,5-dimethylfluorobenzene and 3,5-dibromofluorobenzene relative to fluorobenzene in the corresponding solvents.

Most of the *m*- and *p*-fluoroaryl mercurials were prepared from the corresponding acetates and hydroxides by interaction with the appropriate acids or salts. Fluorophenyl(trifluoromethyl)mercury compounds were synthesized by decarboxylation of the trifluoroacetates. (Fluorophenyl)phenyl mercurials were obtained by arylation of the (fluorophenyl)mercury acetates with phenylboronic acid. (4-Fluoro-2,6-dimethylphenyl)- and (4-fluoro-2,6-dibromophenyl)mercury compounds were prepared starting from 4-fluoro-2,6-dimethylbromobenzene and 4-fluoro-2,6-dibromoaniline, respectively. 3,5-Dimethylfluorobenzene and 3,5-dibromofluorobenzene were synthesized using procedures previously reported[15,19].

Analytical results and melting points relating to new compounds are given in Table 5. The preparations of some fluoroaryl mercurials described below are illustrative of the experimental procedures used in the present investigation.

(m-Fluorophenyl)mercury iodide

To a solution of 1.77 g (5 mmole) of (*m*-fluorophenyl)mercury acetate[1] in 20 ml of hot ethanol was added a solution of 0.84 g (5 mmole) of potassium iodide in 5 ml of water. After cooling to room temperature the resulting white solid was filtered, washed with water and dried. Recrystallization from benzene gave colourless crystals. Yield 2.0 g (95%).

TABLE 5

ANALYTICAL DATA AND MELTING POINTS FOR (FLUOROARYL)MERCURY COMPOUNDS

Compound	M.p. (°C)	Analysis (%)			
		Found		Calcd.	
		C	H	C	H
3-$FC_6H_4HgC{\equiv}CC_6H_5$	114–115	42.47	2.13	42.42	2.29
3-$FC_6H_4HgCF_3$	93–94	23.68	1.34	23.05	1.10
3-FC_6H_4HgCN	179–180	26.13	1.27	26.16	1.24
3-FC_6H_4HgOH	193–195	23.35	1.53	23.07	1.60
3-FC_6H_4HgI	217–218	16.86	1.10	17.06	0.94
3-$FC_6H_4HgOC_6H_5$	142–143	37.34	2.42	37.11	2.31
3-$FC_6H_4HgNHCOCH_3$	150–151	27.20	2.43	27.19	2.20
3-$FC_6H_4HgSC_6H_5$	102–103	35.57	2.34	35.64	2.22
3-FC_6H_4HgSCN	179–180	23.84	1.20	23.79	1.13
4-$FC_6H_4HgC{\equiv}CC_6H_5$	131–132	42.66	2.23	42.42	2.29
4-$FC_6H_4HgCF_3$	100–101	23.02	1.39	23.05	1.10
4-FC_6H_4HgCN	216–217	25.90	1.18	26.16	1.24
4-FC_6H_4HgOH	180–181	23.61	1.65	23.07	1.60
4-FC_6H_4HgI	281–282	16.95	0.92	17.06	0.94
4-$FC_6H_4HgOC_6H_5$	148–149	37.64	2.47	37.11	2.31
4-$FC_6H_4HgNHCOCH_3$	162–163	27.07	2.38	27.19	2.20
4-$FC_6H_4HgSC_6H_5$	124–125	35.56	2.35	35.64	2.22
4-FC_6H_4HgSCN	238–239	24.02	1.39	23.79	1.13
4-F-2,6-$(CH_3)_2C_6H_2HgBr$	225–226	23.96	2.00	23.82	1.98
4-F-2,6-$(CH_3)_2C_6H_2HgOCOCH_3$	116–117	31.57	2.77	31.41	2.87
4-F-2,6-$(CH_3)_2C_6H_2HgSC_6H_5$	108–109	38.94	2.93	38.88	3.00
[4-F-2,6-$(CH_3)_2C_6H_2]_2Hg$	231–232	43.47	3.57	43.04	3.58
4-F-2,6-$Br_2C_6H_2HgCl$	194–196	14.99	0.46	14.75	0.40

(*m*-Fluorophenyl)mercury hydroxide

A solution of 1.2 g (30 mmole) of sodium hydroxide in 10 ml of water was added to a solution of 3.54 g (10 mmole) of (*m*-fluorophenyl)mercury acetate in 50 ml of boiling ethanol. The reaction mixture was diluted with 300 ml of water and cooled. The resulting precipitate was filtered, washed several times with water and recrystallized from aqueous ethanol. 2.0 g (64 %) of white solid was obtained.

(*m*-Fluorophenyl)mercury thiophenoxide

To a solution of 2.48 g (7 mmole) of (*m*-fluorophenyl)mercury acetate in 30 ml of hot ethanol was added 0.28 g (7 mmole) of NaOH in 1 ml of H_2O and then 0.77 g (7 mmole) of thiophenol. The reaction mixture was cooled and diluted with 200 ml of water. The white precipitate formed was filtered, washed with water and dried. Crystallization from ethanol afforded white crystals. Yield 2.25 g (80 %).

(*m*-Fluorophenyl)(phenylethynyl)mercury

To a solution of 1.56 g (5 mmole) of (*m*-fluorophenyl)mercury hydroxide in 10 ml of hot ethanol was added a solution of 0.2 g (5 mmole) of NaOH in 1 ml of H_2O followed by 0.5 g (5 mmole) of phenylacetylene. The reaction mixture was heated to reflux and then cooled. The solvent was removed in vacuum and the resulting residue treated with water, filtered and dried. Recrystallization from aqueous ethanol gave colourless crystals. Yield 1.9 g (91 %).

N-[(m-Fluorophenyl)mercury]acetamide

A solution of 0.3 g (5 mmole) of acetamide in 2 ml of methanol was added to a hot solution of 1.56 g (5 mmole) of (*m*-fluorophenyl)mercury hydroxide in 20 ml of the same solvent. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from benzene yielding 1.32 g (75 %) of white crystals.

Phenyl(p-fluorophenyl)mercury

To a solution of 3.54 g (10 mmole) of (*p*-fluorophenyl)mercury acetate in 50 ml of boiling ethanol was added a hot solution of 1.2 g (10 mmole) of phenylboronic acid and 1.2 g (30 mmole) of NaOH in 30 ml of water. A white precipitate of the product formed immediately. The reaction mixture was cooled, filtered, and the solid washed with water and dried. Crystallization from light petroleum/cyclohexane afforded white crystals with m.p. 114–116°. Lit.^{20} m.p. 115–116°. Yield 1.7 g (46 %).

(m-Fluorophenyl)(trifluoromethyl)mercury

To a solution of 1.56 g (5 mmole) of (*m*-fluorophenyl)mercury hydroxide in 30 ml of ethanol was added 0.57 g (5 mmole) of trifluoroacetic acid in 2 ml of the same solvent. The solvent was removed in vacuum, the resulting solid dissolved in 10 ml of dimethoxyethane and the solution heated at 60–70° until the evolution of CO_2 ceased. The solvent was removed under reduced pressure and the glassy residue treated with water. The product formed was filtered, washed with water and dried. Crystallization from cyclohexane gave 1.0 g (55 %) of colourless crystals.

4-Nitro-2,6-dimethylbromobenzene

A solution of 22.4 g (0.135 mole) of 4-nitro-2,6-dimethylaniline^{21} in a mixture of 60 ml concentrated sulphuric acid and 185 ml H_2O was diazotized at 0–5° by dropwise addition of a solution of 9.5 g (0.135 mole) of $NaNO_2$ in 15 ml H_2O. After the addition was completed, the reaction mixture was stirred for 2 h at the same temperature and was left overnight in a refrigerator. The filtered diazo solution was added dropwise to a boiling solution of 26 g of CuBr in 100 ml of 48 % HBr. The precipitate formed was separated and steam distilled yielding 19.6 g (63 %) of pale yellow crystals with m.p. 101–102° after crystallization from ethanol. Lit.^{22} m.p. 102–103°. Reduction of the nitro compound with iron turnings and hydrochloric acid in ethanol^{21} afforded 4-bromo-3,5-dimethylaniline in 75 % yield.

4-Fluoro-2,6-dimethylbromobenzene

A solution of 10 g (0.05 mole) of 4-bromo-3,5-dimethylaniline in a mixture of 20 ml of concentrated hydrochloric acid and 20 ml H_2O was diazotized at 0–5° by addition of 3.5 g (0.05 mole) $NaNO_2$ in 5 ml H_2O. After stirring for 1 h, the resulting diazo solution was filtered and added to a solution of 5 g (0.08 mole) H_3BO_3 in 15 ml of 40 % hydrofluoric acid. The precipitate formed was filtered, washed with little cold water, methanol, ether and dried. 7.7 g (52 %) of diazonium tetrafluoroborate was obtained which was decomposed. The resulting oil was steam distilled, extracted with ether, the ethereal solution dried over $CaCl_2$, the solvent removed, and the residue fractionated under reduced pressure yielding 2.9 g (55%) of a colourless oil with b.p. 114°/60 mm, n_D^{25} 1.5308. Lit.[15] n_D^{25} 1.5293.

(4-Fluoro-2,6-dimethylphenyl)mercury bromide

To a solution of (4-fluoro-2,6-dimethylphenyl)magnesium bromide, prepared from 5.1 g (2.5 mmole) of 4-fluoro-2,6-dimethylbromobenzene and 0.72 g of magnesium in 50 ml of ether, was added in portions 9.0 g (2.5 mmole) of mercuric bromide with constant stirring. After the addition was completed, the reaction mixture was refluxed for 3 h, cooled to room temperature and hydrolyzed with 50 ml of 2% HBr solution. The resulting solid was filtered, washed with hot water and dried. Yield 7.2 g (72%). Recrystallization from aqueous dimethylformamide gave colourless crystals.

(4-Fluoro-2,6-dimethylphenyl)mercury acetate

To a hot solution of 4.03 g (1 mmole) of (4-fluoro-2,6-dimethylphenyl)mercury bromide in 20 ml of DMF was added a solution of 1.66 g (1 mmole) of silver acetate in 50 ml of 5% acetic acid. The precipitate of AgCl was filtered and the filtrate was diluted with 500 ml of water and cooled. The resulting solid was filtered, washed with water and dried. Crystallization from aqueous ethanol afforded white crystals. Yield 3.1 g (81%).

Bis(4-fluoro-2,6-dimethylphenyl)mercury

A mixture of 2.0 g (0.5 mmole) of (4-fluoro-2,6-dimethylphenyl)mercury bromide and 2.0 g of copper powder in 20 ml of pyridine was stirred at reflux under nitrogen for 6 h and then left overnight. The copper was filtered and washed twice with 10 ml of pyridine. The filtrate was evaporated to dryness and the residue was treated with 20 ml of 10% NH_4OH. The resulting solid was filtered, washed with water and dried. Yield 0.62 g (55%). Recrystallization from cyclohexane gave colourless crystals.

(4-Fluoro-2,6-dibromophenyl)mercury chloride

A suspension of 8.1 g (3 mmole) of 4-fluoro-2,6-dibromoaniline[19] in 50 ml of hydrochloric acid 1/1 was diazotized at 0° with a solution of 2.1 g (3 mmole) $NaNO_2$ in 10 ml of H_2O. After stirring for 3 h at 5°, the resulting diazo solution was filtered and added dropwise to a solution of 8.1 g (3 mmole) of mercuric chloride in 16 ml of hydrochloric acid 1/1. A precipitate of the double diazonium salt separated immediately. After standing for 1 h, it was filtered, washed with ethanol and dried. The double salt obtained was added portion-wise with vigorous stirring to a suspension of 2.4 g of copper powder in 60 ml of acetone at −5°. After the decomposition of the salt was completed, the solvent was removed in vacuum. The oily residue was treated with 100 ml of 10% hydrochloric acid, filtered, washed with water, light petroleum and dried. The solid obtained was recrystallized from benzene. Yield 2.1 g (14%).

ACKNOWLEDGEMENTS

The authors are indebted to Prof. A. N. Nesmeyanov for his interest in this study.

REFERENCES

1 D. N. KRAVTSOV, B. A. KVASOV, E. I. FEDIN, B. A. FAINGOR AND L. S. GOLOVCHENKO, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 979.
2 V. S. PETROSYAN AND O. A. REUTOV, *Dokl. Akad. Nauk SSSR*, 180 (1968) 876.
3 W. KITCHING, W. ADCOCK AND B. F. HEGARTY, *Aust. J. Chem.*, 21 (1968) 2411.
4 L. W. REEVES AND W. G. SCHNEIDER, *Can. J. Chem.*, 35 (1957) 251.
5 G. J. KORINEK AND W. G. SCHNEIDER, *Can. J. Chem.*, 35 (1957) 1157.
6 K. B. WHETZEL AND R. E. KAGARISE, *Spectrochim. Acta*, 18 (1962) 329.
7 H. O. PRITCHARD AND H. A. SKINNER, *Chem. Rev.*, 55 (1955) 745.
8 A. PARTS, *Z. Phys. Chem.*, B12 (1931) 323.
9 J. C. SIPOS, H. SAWATZKY AND G. F. WRIGHT, *J. Amer. Chem. Soc.*, 77 (1955) 2759.
10 S. KOJIMA, K. TSUKADA, S. OGAWA AND A. SHIMAUCHI, *J. Chem. Phys.*, 21 (1953) 1415.
11 A. N. NESMEYANOV, O. YU. OKHLOBYSTIN, E. V. BRYUKHOVA, V. I. BREGADZE, D. N. KRAVTSOV, B. A. FAINGOR, L. S. GOLOVCHENKO AND G. K. SEMIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 1928.
12 E. W. ABEL, D. A. ARMITAGE AND D. B. BRADY, *Trans. Faraday Soc.*, 62 (1966) 3459.
13 R. W. TAFT, E. PRICE, I. R. FOX, I. C. LEWIS, K. K. ANDERSEN AND G. I. DAVIS, *J. Amer. Chem. Soc.*, 85 (1963) 709.
14 R. W. TAFT, E. PRICE, I. R. FOX, I. C. LEWIS, K. K. ANDERSEN AND G. I. DAVIS, *J. Amer. Chem. Soc.*, 85 (1963) 3146.
15 M. J. S. DEWAR AND Y. TAKEUCHI, *J. Amer. Chem. Soc.*, 89 (1967) 390.
16 M. T. TRIBBLE AND J. G. TRAYNHAM, *J. Amer. Chem. Soc.*, 91 (1969) 379.
17 R. L. AVOYAN, YU. T. STRUCHKOV AND V. G. DASHEVSKY, *Zh. Strukt. Khim.*, 7 (1966) 289.
18 A. N. NESMEYANOV, D. N. KRAVTSOV, E. I. FEDIN, B. A. KVASOV, V. M. PACHEVSKAYA AND L. S. GOLOVCHENKO, *Dokl. Akad. Nauk SSSR*, 183 (1968) 1098.
19 A. PAVLATH AND G. OLAH, *Acta Chim. Acad. Sci. Hung.*, 10 (1956) 227.
20 M. S. KHARASH, H. PINES AND J. H. LEVINE, *J. Org. Chem.*, 3 (1938) 347.
21 B. M. WEPSTER, *Recl. Trav. Chim. Pays-Bas*, 73 (1954) 809.
22 W. C. SPITZER AND C. W. WHELAND, *J. Amer. Chem. Soc.*, 62 (1940) 2995.