Reaction of Adducts Ia and Ib with TMVS. Into a glass ampul were placed 1 mole% of benzoyl peroxide, 12.5 mmoles of TMVS, and 1.25 mmoles of adduct Ia or Ib. Test conditions are shown in Table 1, test Nos. 13-16. Composition of the reaction mixture was determined by GLC. Resinification occurred in test No. 15 (140°).

CONCLUSIONS

The homolytic addition of CBr_4 or CCl_2Br_2 to trimethylvinylsilane and the formation of 1:1 adducts is accompanied by stepwise telomerization to compounds with two monomer units in the molecule, of the $CX_2[CH_2CHBrSiMe_3]_2$ type, where X is Cl or Br. Conditions were found that favor the formation of either adducts or telomers.

LITERATURE CITED

1. A. F. Gordon, U. S. Patent 2,715,113 (1955); Chem. Abstr., 50, 7131c (1956).
2. L. Goodman, R. M. Silverstein, and G. W. Gould, J. Org. Chem., 22, 596 (1957).
3. F. G. Yusupov, G. V. Nurtdinova, I. N. Brui, A. N. Nizamova, L. G. Khalilov, G. A. Gailyunas, and V. P. Yur'ev, Zh. Obshch. Khim., 1807 (1981).
4. G. A. Gailyunas, G. V. Nurtdinova, V. P. Yur'ev, G. A. Tolstikov, and S. R. Rafikov, Izv. Akad. Nauk SSSR, Ser. Khim., 914 (1982).
5. T. T. Vasil'eva, L. F. Germanova, V. I. Dostovalova, B. V. Nelyubin, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2759 (1983).
6. V. I. Dostovalov, F. K. Velichko, T. T. Vasil'eva, N. V. Kruglova, and R. Kh. Freidlina, Org. Magn. Reson., 16, 251 (1981).

INFLUENCE OF INTRAMOLECULAR COORDINATION ON THE TRANSMISSABILITY

OF A BRIDGING Hg—N GROUP

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When investigating compounds of the type $ArHg(NPhSO_2)C_6H_4F\text{-}4$ (I) by $^{19}F\text{-}\{^1H\}$ NMR it was established by us that there was a significant reduction in the transmissability (T) of the Hg—N binuclear bridging group (BBG) in a medium of Py and Me_2SO as a result of the approximately similar contributions of the dipolar and intermolecular coordination interactions of the central Hg atom with the solvent [1]. For a more detailed clarification of the role of coordination interactions in the transmission of the electronic influences of substituents (EIS) in bridging systems (I) it seemed of interest to investigate, within the framework of a single method, the influence of intramolecular coordination on the T of the Hg—N BBG. Compounds of type $ArHgN(SO_2Ph)C_6H_3Br\text{-}2\text{-}F\text{-}4$ (II) are convenient models for such an investigation since according to the data of [2] there is an intramolecular coordination bond between the ortho Br atoms and Hg in solution.

With the aim of determining the influence of intramolecular coordination on the character of the electronic effect (EE) of the $PhHgN(SO_2Ph)$ grouping, fluorine chemical shifts (δF) relative to PhF were determined for compounds (I) and (II) (Ar = Ph) and also for their hydrocarbon analogs $ArCH_2N(SO_2Ph)C_6H_4F\text{-}4$ (III) (Ar = Ph) and $ArCH_2N(SO_2Ph)C_6H_3Br\text{-}2\text{-}F\text{-}4$ (IV) (Ar = Ph) in PhCl. In addition, chemical shifts caused by substituents (CSCS) were determined [3] in systems (II) and (IV) relative to $BrC_6H_4F\text{-}3$. Analysis of the data of Table 1 showed that on going from (III) to (IV) a reduction was observed in the CSCS for the $PhCH_2N(SO_2Ph)$ grouping and there was a corresponding reduction in its electron donating effect. This is entirely according to the rules since the introduction of a bulky Br atom into system (III) must lead to a reduction in the population of the conformation in which the C—N bond is coplanar with the aromatic ring as a result of the van der Waals interactions of Br with the hydrogen atoms of the CH_2 group. This consequently leads to a reduction of $P_\pi\text{-}P_\pi$ conju-

TABLE 1. Values of δF and CSCS* in PhCl in Relation to PhF and BrC₆H₄F-3, ppm

Compound	Substituent	δF	CSCS
$PhHgN(SO_2Ph)C_6H_4F$-4	$PhHgN(SO_2Ph)$	4,36	4,46
$PhHgN(SO_2Ph)C_6H_3Br$-2-F-4	$PhHgN(SO_2Ph)$	1,56	3,77
$PhCH_2N(SO_2Ph)C_6H_4F$-4	$PhCH_2N(SO_2Ph)$	0,13	0,13
$PhCH_2N(SO_2Ph)C_6H_3Br$-2-F-4	$PhCH_2N(SO_2Ph)$	-2,89	-0,68
BrC_6H_4F-3	H	-2,21	-2,21

*Chemical shift of fluorine caused by the appropriate substituent determined as fluorine chemical shifts relative to the substituted fluorobenzene not containing the given substituent.

TABLE 2. δF for (I) and (II) in PhCl, ppm

Compound	δF	Compound	δF	Compound	δF	Compound	δF
(IIa)	1,82	(Ia)	4,79	(IVa)	-2,29	(IIIa)	0,51
(IIb)	1,57	(Ib)	4,50	(IVb)	-2,66	(IIIb)	0,24
(IIc)	1,56	(Ic)	4,36	(IVc)	-2,89	(IIIc)	0,13
(IId)	1,28	(Id)	3,97	(IVd)	-3,29	(IIId)	-0,27
(IIe)	1,28	(Ie)	3,96	(IVe)	-3,13	(IIIe)	-0,23
(IIf)	0,89	(If)	3,37	(IVf)	-3,67	(IIIf)	-0,67
(IIg)	—	(Ig)	3,12	(IVg)	-3,87	(IIIg)	-0,89

gation of the unshared electron pair of nitrogen with the π-electron system. As follows from Table 1 a similar effect, but to a lesser extent, was also observed for the $PhHgN(SO_2Ph)$ grouping on going from (I) to (II). A smaller change in the electron donating effect of the $PhHgN(SO_2Ph)$ group under the influence of the ortho Br atom may be caused by the difference in conformation behavior of the considered group and $PhCH_2N(SO_2Ph)$ as in the case of the MeS and PhHgS groupings in [4, 5] and/or intramolecular coordination of the organomercury grouping with o-Br. Since there is no information at the present time on the conformation of compounds (I) and (II) in solution then in order to assess the relative contribution of intramolecular coordination to the change of EE of the $PhHgN(SO_2Ph)$ grouping we proposed carrying out later a similar investigation on systems of type $PhHgN(SO_2Ph)C_6H_3$-Me-2-F-4.

With the aim of studying the influence of intramolecular coordination on the T of Hg—N BBG we synthesized two series of model compounds (IIa-g) and (IVa-g), where Ar = $4-Me_2NC_6H_4$ (a), $4-MeC_6H_4$ (b), Ph (c), $4-ClC_6H_4$ (d), $3-FC_6H_4$ (e), $3,5-Cl_2C_6H_3$ (f), and $3,4,5-Cl_3H_6H_2$ (g) for which δF was determined in PhCl from PhF (Table 2). Statistical treatment of the δF values for (II) and (IV) was carried out for a quantitative assessment of the relative T of Hg—N and CH₂—N BBG in the o-Br-substituted systems (II) and (IV) and also for the corresponding data of (I) from [6] and (III) from [1] (Table 3). On comparing values of δF for (II) relative to δF for the corresponding (I) a straight line was obtained the slope of which was markedly less than unity. Consequently, within the framework of the approach used it may be asserted with a 95% level of confidence probability that the introduction of Br into the ortho position relative to N of the fluorobenzene ring of (I) led to an appreciable reduction in the effectiveness of transfer of the EIS through the Hg—N BBG. On the contrary, the size of the coefficient ρ for the dependence of δF values for (III) relative to (IV) is close to unity, and this indicates that a similar operation in the case of hydrocarbon analogs is not reflected in practice on the T of the CH₂—N BBG. In accordance with the fact that systems (II) and (IV) are structural analogs to a first approximation, the reduction in T of the Hg—N BBG on going from (I) to (II) may apparently be explained by the presence in (II) of intramolecular coordination interactions with the participation of vacant 6p orbitals of the bridging Hg atom.

Consequently, when generalizing the obtained data and the results of [1, 7] it may be asserted that the T of Hg-containing BBG of the Hg—X type (X = N, S) depends appreciably on the participation of the Hg atom in the inter- and intramolecular coordination interactions. Thus, as shown by comparison of the T of Hg—N and Hg—S BBG under conditions of forming intermolecular coordination bonds, the greater the coordination interaction, the lower the T of the BBG.

TABLE 3. Parameters of the Correlation Equation $y = \rho x + c$

x	y	n	$\rho \pm \Delta\rho$	S	r	c
$\delta F(I)$	$\delta F(II)$	6	0,64±0,07	0,030	0,996	−1,27
$\delta F(IV)$	$\delta F(III)$	7	1,10±0,11	0,071	0,993	−2,92

TABLE 4. Constants of Investigated Compounds

Com-pound	Empirical formula	Yield, %	mp, °C	Found/Calc., %		
				C	H	N
(IIa)	$C_{20}H_{18}BrFHgN_2SO_2$	92	150—151 (methanol)	$\frac{37,00}{36,96}$	$\frac{2,85}{2,80}$	$\frac{4,25}{4,31}$
(IIb)	$C_{19}H_{15}BrFHgNSO_2$	96	78—80 (methanol)	$\frac{36,33}{36,75}$	$\frac{2,75}{2,44}$	—
(IIc)	$C_{18}H_{13}BrFHgNSO_2$	95	101—102 (methanol)	$\frac{35,58}{35,62}$	$\frac{2,18}{2,16}$	$\frac{2,00}{2,31}$
(IId)	$C_{18}H_{12}BrClFHgNSO_2$	90	71—72 (methanol)	$\frac{33,65}{33,71}$	$\frac{2,07}{1,89}$	$\frac{2,03}{2,19}$
(IIe)	$C_{18}H_{12}BrF_2HgNSO_2$	89	165—166 (methanol)	$\frac{34,59}{34,60}$	$\frac{2,04}{1,94}$	$\frac{2,19}{2,24}$
(IIf)	$C_{18}H_{11}BrCl_2FHgNSO_2$	88	217—218 (methanol)	$\frac{32,16}{31,99}$	$\frac{1,58}{1,64}$	$\frac{2,06}{2,07}$
(IIg)	$C_{18}H_{10}BrCl_3FHgNSO_2$	91	226 (methanol)	$\frac{29,99}{30,44}$	$\frac{1,52}{1,42}$	$\frac{1,78}{1,97}$
(IVa)	$C_{21}H_{20}BrFN_2SO_2$	71	110—111 (hexane)	$\frac{54,91}{54,43}$	$\frac{4,53}{4,36}$	—
(IVb)	$C_{20}H_{17}BrFNSO_2$	61	81 (hexane)	$\frac{55,02}{55,30}$	$\frac{3,84}{3,95}$	—
(IVc)	$C_{19}H_{15}BrFNSO_2$	48	80—81 (pet. ether)	$\frac{54,30}{54,29}$	$\frac{3,80}{3,60}$	$\frac{3,26}{3,33}$
(IVd)	$C_{19}H_{14}BrClFNSO_2$	64	107—108 (pet. ether)	$\frac{50,21}{50,17}$	$\frac{3,09}{3,11}$	$\frac{3,38}{3,08}$
(IVe)	$C_{19}H_{14}BrF_2NSO_2$	70	87—88 (hexane)	$\frac{52,01}{52,06}$	$\frac{3,17}{3,23}$	$\frac{3,09}{3,20}$
(IVf)	$C_{19}H_{13}BrCl_2FNSO_2$	69	98—99 (hexane)	$\frac{46,49}{46,65}$	$\frac{2,45}{2,68}$	$\frac{2,85}{2,86}$
(IVg)	$C_{19}H_{12}BrCl_3FNSO_2$	51	175—176 (hexane)	$\frac{43,58}{43,58}$	$\frac{2,30}{2,32}$	$\frac{2,92}{2,68}$
(V)	$C_{15}H_{14}BrFN_2$	93	87—89 (ethanol)	$\frac{56,03}{55,08}$	$\frac{4,50}{4,40}$	$\frac{8,86}{8,72}$
(VI)	$C_{15}H_{16}BrFN_2$	68	106—107 (pet. ether)	$\frac{56,19}{55,73}$	$\frac{4,81}{5,00}$	$\frac{8,80}{8,67}$

EXPERIMENTAL

The $^{19}F\text{-}\{^1H\}$ NMR spectra were obtained on a Tesla BS-497 (94.075 MHz) instrument at 25°C for 0.2 or 0.05 M solutions. The solvents used for measuring δF were purified by standard procedures and were distilled in a stream of dry argon. Errors in the determination of δF did not exceed ±0.01 ppm.

Arylmercury derivatives of 4'-fluoro-2'-bromobenzenesulfonanilide with aryl groups 4-$ME_2NC_6H_4$ and Ph (Ia, c) were obtained by the interaction of the corresponding arylmercury hydroxides with 4'-fluoro-2'-bromobenzenesulfonanilide and the remaining arylmercury derivatives of 4'-fluoro-2'-bromobenzenesulfonanilide (Ib, d-f) by the reaction of arylmercury acetates with the sodium derivative of 4'-fluoro-2'-bromobenzenesulfonanilide.

The N-benzyl-N-benzenesulfo-4'-fluoro-2'-bromoanilides (IV) were obtained in the following manner. Compound (IVa) was obtained by reduction of the corresponding benzazomethine and subsequent treatment with $PhSO_2Cl$ and (IIIb-g) by alkylation of the sodium derivative of 4'-fluoro-2'-bromobenzenesulfoanilide with the appropriate substituted benzyl chloride. The starting materials were identical by melting and boiling point with those described previously. The purity of products was checked by NMR and mass spectra. Constants and analytical data of products are given in Table 4. Typical examples of the synthesis of the studied compounds are given below.

N-(4-Dimethylaminophenylmercury)-4'=fluoro-2'-bromobenzenesulfonanilide (IIa). A filtered hot solution of 4-dimethylaminophenylmercury hydroxide (1.69 g: 5 mmoles) in methanol (50 ml) was added to a hot solution of 4-fluoro-2-bromobenzenesulfonanilide (1.65 g: 5 mmoles) in methanol (20 ml). After removal of the solvent a colorless crystalline substance (3.0 g: 92%) was obtained which had mp 150-151°C after recrystallization from methanol.

N-(3,5-Dichlorophenylmercury)-4'-fluoro-2'-bromobenzenesulfonanilide (IIe). A mixture of solutions of benzenesulfon-4-fluoro-2-bromoanilide (0.85 g: 2.5 mmoles) in hot methanol (20 ml) and NaOH (0.1 g: 2.5 mmoles) in distilled water (2 ml) was poured with stirring into a solution of 3,5-dichlorophenylmercury acetate (0.98 g: 2.5 mmoles) in hot methanol (50 ml). The mixture was heated to boiling (10-15 min), filtered, and left overnight. The precipitated crystals were filtered off. The solution was evaporated, washed with water, and dried. After recrystallization from methanol, product (1.5 g: 88%) with mp 217-218°C was obtained.

N-(4-N,N-Dimethylaminobenzyl)-4'-fluoro-2'-bromoaniline (IVa). A solution of 4-(N,N-dimethylaminophenyl)-(4'-fluoro-2'-bromo)azomethine (5.2 g: 16 mmoles) in abs. ether (100 ml) was added dropwise with stirring to a suspension of $LiAlH_4$ (0.76 g: 20 mmoles) in abs. ether (20 ml). At the end of evolution of hydrogen the mixture was boiled for 1 h, cooled, decomposed with ethyl acetate, diluted with water (50 ml), extracted with ether, and dried over Na_2SO_4. The solvent was removed in vacuum. After recrystallization of the residue from petroleum ether a bright-yellow crystalline product was obtained having mp 106-107°C.

N-(3,4,5-Trichlorobenzyl)-N-benzenesulfon-(4'-fluoro-2'-bromo)anilide (IVg). A solution of 3,4,5-trichlorobenzyl chloride (3 g: 13 mmoles) in ethanol (50 ml) was added to a mixture of solutions of 4'-fluoro-2'-bromobenzenesulfonanilide (3 g: 9 mmoles) in ethanol (50 ml) and KOH (0.6 g: 11 mmoles) in distilled water (2 ml). The mixture was boiled under reflux for 3 h and left overnight. The mixture was diluted with distilled water (200 ml), extracted with ether, dried over Na_2SO_4, and the ether distilled off. Bright-yellow product (2.4 g: 51%) of mp 175-176°C was obtained after recrystallization from pentane-petroleum ether.

4-(N,N-Dimethylaminophenyl)-N-(4'-fluoro-2'-bromo)azomethine. A solution of 4-fluoro-2-bromoaniline (3.6 g: 20 mmoles) in ethanol (50 ml) was added with stirring to a solution of p-dimethylaminobenzaldehyde (2.98 g: 20 mmoles) in ethanol (50 ml). The mixture was heated for 15 min. After removal of the solvent a bright-yellow product (6 g: 93%) was obtained which had mp 87-89°C after recrystallization from ethanol.

4-N',N'-Dimethylaminobenzyl-N-benzenesulfon-(4'-fluoro-2'-bromo)anilide. A solution of benzenesulfonyl chloride (1 g: 5.7 mmoles) in acetone (5 ml) was added with stirring to a solution of N-(4-N,N-dimethylaminobenzyl)-4'-fluoro-2'-bromoaniline (1.6 g: 5 mmoles) in a mixture of acetone (7 ml) and pyridine (2 ml); the mixture was heated to boiling, left overnight, then poured into distilled water (100 ml); the solid was filtered off, washed with water, and dried. After recrystallization from hexane the colorless product (1.65 g: 71%) having mp 110-111°C was obtained.

CONCLUSIONS

On investigation the $^{19}F-\{^1H\}$ NMR spectra of two series of model compounds of type $ArQN(SO_2Ph)C_6H_3Br-2-F-4$ (Q = Hg, CH_2) it was established that participation of the Hg bridging atom in intramolecular coordination interactions with the ortho Br atom led to a reduction in the transmissability of the binuclear Hg—N bridging groupings.

LITERATURE CITED

1. S. I. Pombrik, E. V. Polunkin, A. S. Peregudov, É. I. Fedin, and D. N. Kravtsov, Izv. Akad. Nauk SSSR, Ser. Khim., 1289 (1982).
2. A. S. Peregudov, D. N. Kravtsov, and L. A. Fedorov, J. Organomet. Chem., 71, 347 (1974).

3. L. Goodman and R. W. Taft, J. Am. Chem. Soc., 86, 4385 (1965).
4. D. N. Kravtsov, B. A. Krasov, L. S. Golovchenko (Golousheuko), E. M. Rokhlina (Rohlina), and E. I. Fedin, J. Organomet. Chem., 39, 107 (1972).
5. L. G. Kuz'mina, N. G. Bokii, Yu. T. Struchkov, D. N. Kravtsov, and E. M. Rokhlina, Zh. Strukt. Khim., 15, 491 (1974).
6. A. N. Nesmeyanov, S. I. Pombrik, E. V. Polunkin, A. S. Golovchenko, D. N. Kravtsov, and É. I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim., 763 (1981).
7. S. I. Pombrik. L. S. Golovchenko, A. S. Peregudov, É. I Fedin, and D. N. Kravtsov, Izv. Akad. Nauk SSSR, Ser. Khim., 803 (1983).

REACTIONS OF PERALKYL ORGANOTIN AND ORGANOMERCURY COMPOUNDS

WITH DI- AND TRIARYLMETHYL SALTS
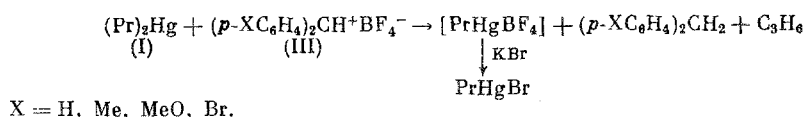
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The reaction of peralkyltin and peralkylmercury compounds with ionic triarylmethyl salts results exclusively in β-elimination with the formation of triarylmethane, olefin, and the dealkylation product of the organometallic compound (OMC) [1, 2]. A study of the reactions of organotin and organomercury compounds with diphenylmethyl salts has shown that the course of these reactions differs in many cases from that of the analogous reactions with triaryl-methyl salts [3]. When a secondary or tertiary β-H atom is present in these OMC, they react with diphenylmethyl fluoroborate exclusively by β-elimination. When, however, a primary β-hydrogen atom is present as in Et_2Hg or Et_4Sn, in addition to β-elimination alkyldemetalla-tion (substitution) takes place with the formation of compounds such as Ph_2CHEt [3]. The ratio of the products of the substitution and β-elimination reactions with R_2Hg and R_4Sn is the same for any given radical R, and is independent of the solvent [3].

We here examine the effects of the stability of the di- and triarylmethyl cations (pK_R^+) and steric factors on the ratios of the competing reactions (substitution and β-elimination). For this purpose, an examination was carried out of the products of the reaction of dipropyl-mercury (I) and tetraethyltin (II) with diarylmethyl fluoroborates ($p\text{-}XC_6H_4)_2CH^+BF_4^-$ (IIIa-e), where X = MeO (a), Me (b), H (c), Cl (d), and Br (e), and with triarylmethyl fluorocar-borates ($p\text{-}XC_6H_4)_3C^+BF_4^-$ (IVa-b), where X = H (a) and NO_2 (b). The stabilities of the di- and triarylmethyl cations varied within quite wide limits, but the volume of the reacting species (the steric factor) remained sensibly constant for (III), and increased in the case of (IV).

The reactions were carried out under standard conditions, as described in [3], at ∿20°C. Compounds (IIIa-e) and (IVb) were obtained directly from the reaction mixtures of the appro-priate di- or triarylmethyl halides with $AgBF_4$. The solvents used were CH_2Cl_2 and acetoni-trile. The reactions of (I) with (III) were normally complete within 1 day, but those of (II) with (III) or (IVb) required considerably longer. This is in accordance with earlier reports [1, 2] that peralkyl organotin compounds react much more slowly than the correspond-ing mercury compounds in reactions of this type. Reactions with (II) were therefore inter-rupted after 1 week. In all cases, the compounds were analyzed as described in [3].

The reactions of (I) with (III), either in CH_2Cl_2 or acetonitrile, resulted in exclusive β-elimination, irrespective of the stability of the cation

$$(Pr)_2Hg + (p\text{-}XC_6H_4)_2CH^+BF_4^- \rightarrow [PrHgBF_4] + (p\text{-}XC_6H_4)_2CH_2 + C_3H_6$$
$$\text{(I)} \qquad\qquad \text{(III)} \qquad\qquad\qquad \downarrow KBr$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad PrHgBr$$

X = H, Me, MeO, Br.

No substitution product was observed in any instance. The yields of the principal com-pounds, isolated from the reactions between (I) and (III), are given in Table 1. When MeCN