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THE TRANSMISSION POWER OF A BRIDGING MERCURY ATOM

L. S. Golovchenko, S. I. Pombrik,

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A. S. Peregudov, and D. N. Kravtsov

Earlier during investigation of the transmission power of a bridging mercury atom in systems of the $ArHgC_{3}H_{4}F-4$ (I) type by the ¹⁹F NMR method it was established that the transmission of the electronic effects of substituents along the Hg-C_{ar} bonds takes place by an inductive mechanism, and the mercury atom has a lower transmission power than a bridging CH₂ group [1]. However, the quantitative result on the relative effectiveness of the transmission of the electronic effects of the substituents through a mercury bridge can only be regarded as tentative, since the previously obtained data [1] on the chemical shifts of fluorine caused by the substituent for (I) were compared with published data for structurally related compounds of the $ArCH_2C_6H_4F-4$ (II) [2] type, which were determined in solvents similar in nature but not identical. Moreover, the number of compounds in series (I) and (II) with identical Ar groups was small, which (as known) has a significant effect on the quality of the statistical treatment of the experimental results.

In order to obtain quantitative data on the relative conduction of the electronic effects on the substituents by the bridging mercury atom in the present work we synthesized a series of substituted 4-fluorodimethylmethanes with a standard set of variable aromatic radicals (IIa, c-k), where $Ar = 4-Me_2NC_6H_4$ (a), $4-MeOC_6H_4$ (b), $4-MeC_6H_4$ (c), Ph (d), $4-FC_6H_4$ (e), $3-FC_6H_4$ (f), $4-ClC_6H_4$ (g), $3-ClC_6H_4$ (h), $3-CF_3C_6H_4$ (i), $3,4-Cl_2C_6H_3$ (j), $3,4,5-Cl_3H_6H_2$ (k), and we determined the chemical shifts of fluorine (δF) in chlorobenzene (Table 1). In addition, in order to study the effect of the nature of the solvents on the transmission power of mercury we determined the δF values for series (I) and (II) in solvating (pyridine, DMSO) and nonsolvating polar (nitrobenzene, DCE) solvents (Table 1). It should be noted that in the present work, as in [1], the data on the δF values of (I) were obtained during analysis of the PMR spectra of the equilibrium mixtures formed during the reaction of 4-FC_6H_4)_2Hg with Ar_2Hg .

For a quantitative assessment of the relative transmission power of the bridging mercury atom we made a correlation of the data on the δF values in chlorobenzene for (I) in relation to the δF values for the corresponding compounds (II). The tangent of the slope of the obtained straight line (Table 2, No. 1) indicates that the mercury atom has a lower transmission power than the CH₂ group. However, the differences in the effectiveness of the transmission of the electronic effects of the substituents through the -Hg and -CH₂ bridges amounts to \sim 30% and not 50%, as we supposed earlier [1].

Whereas our previously obtained correlation data for systems (I) (Table 2, Nos. 2 and 3) clearly demonstrate the inductive character of the transmission of the electronic effects of the substituents in them, the extremely insignificant differences in the quality of the correlations between δF of (II) and the σ_p^0 or σ_p constants (Table 2, Nos. 4 and 5) indicate that other factors not realized in (I) make a substantial contribution in (II) in addition

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 668-672, March, 1985. Original article submitted December 14, 1983.

Compound	PhCl	Ру	DMSO	DCE	PhNO₂
(I a) (I b) (Ic) (Id) (Ie) (If) (Ig) (Ih) (Ii) (Ik) (Ila) (IIc) (IId) (IIe) (IIg) (IJh) (IIi)	$\begin{array}{c} 0,30\\ -0,04\\ -0,04\\ -0,16\\ -0,37\\ -0,52\\ -0,44\\ -0,55\\ -0,69\\ -0,78\\ -1,15\\ 4,82\\ 4,26\\ 4,28\\ 4,26\\ 4,28\\ 4,26\\ 3,80\\ 3,49\\ 3,34\\ \end{array}$	$\begin{array}{c} 0,92\\ 1,00\\ 1,00\\ 1,02\\ 1,09\\\\ 1,08\\ 1,05\\ 0,98\\ 0,93\\ 0,83\\ 4,81\\ 4,47\\ 4,33\\ 4,15\\ 3,96\\ 3,83\\ 3,72\\ 3,72\\ \end{array}$	$\begin{array}{c} 0,97\\ -\\ -\\ 1,05\\ 1,05\\ -\\ -\\ -\\ -\\ 1,08\\ 0,98\\ -\\ 4,74\\ 4,28\\ -\\ 4,41\\ 4,28\\ -\\ 4,00\\ 3,88\\ 3,85\\ -\end{array}$	$\begin{array}{c} 0,20\\ -0,03\\ -0,09\\ -0,27\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\$	$\begin{array}{c} 0,43\\ \hline 0,1\\ 0,1\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\$
(11j) (11k)	3,30 2,80	3,53 3,15	3,67	-	_

TABLE 1. The ¹⁹F Chemical Shifts in (I) and (II) in Relation to C_6H_5F in Various Solvents (δ , ppm).

TABLE 2. The Parameters of the Correlation Equations $y = \rho x + 3$

No.	y	x	n	φ±Δρ	s	r	c
1 2 3 4 5 6 7	δF(I) δF(I) δF(I) δF(II) δF(II) δF(II) _{Py} δF(II) _{DMSO}	$\begin{cases} \delta F(II) \\ \sigma_p^{\circ} \\ \sigma_p \\ \sigma_p^{\circ} \\ \sigma_p^{\circ} \\ \delta F(II)_{PhCl} \\ \delta F(II)_{PhCl} \end{cases}$	9 6 5 5 9 8	$\begin{array}{c} 0,69\pm0,09\\ -1.14\pm0.13\\ -0.97\pm0.28\\ -1.34\pm0.50\\ -1.17\pm0.44\\ 0.81\pm0.11\\ 0.64\pm0.11\end{array}$	$\begin{array}{c} 0,064\\ 0,035\\ 0,074\\ 0,098\\ 0,107\\ 0,072\\ 0,067\end{array}$	0,990 0,994 0,974 0,975 0,971 0,991 0,989	$\begin{array}{c} -3,04 \\ -0,20 \\ -0,27 \\ 4,19 \\ 4,12 \\ 0,81 \\ 1,61 \end{array}$

to the inductive effect. In all probability their action is explained by the higher electron conduction in (II). Among these factors it is possible to include the σ , π conjugation of the C-H σ bonds of the bridging group with the π -electron systems of the aromatic rings, expecially as (according to data in [3]) the preferred conformation in compounds of the diarylmethane type is that in which each of the aromatic rings is orthogonal with one C-H bond and parallel to the other. In addition, direct electrostatic interaction through space between the π -electron systems of the substituted and indicator aromatic rings is more likely in compounds of type (II), and this is due to the smaller bond angle at the bridging atom and, accordingly, the shorter distance between the rings in (II) [3] compared with the linear compounds of type (I) [4].

Analysis of the obtained data on the δF values of (I) in various solvents (Table 1) indicates that the transition from chlorobenzene ($E_T = 37.5 \text{ kcal/mole} [5], \pi^* = 0.709 [6]$) to polar coordinating solvents pyridine ($E_T = 40.2 \text{ kcal/mole}, \pi * = 0.867$) and DMSO ($E_T = 45.0$ kcal/mole, π^* = 1.000) leads to the almost complete loss of sensitivity of δF to the effect of the variable substituent – the range of the variations in the δF values ($\Delta \delta F$) in (I) becomes zero. At the same time the transition from chlorobenzene to the polar but not solvating solvents nitrobenzene (E_T = 42 kcal/mole, π * = 1.029) and dichloroethane (E_T = 41.1 kcal/mole, $\pi^* = 0.807$) also leads to a decrease in the electron conduction of (1) but the transmission power "quenching" effect observed here is substantially smaller ($\Delta\delta F_{PhC1}$ = 1.08 ppm, $\Delta \delta F_{C_2H_4Cl_2} = 0.72$, and $\Delta \delta F_{PhNO_2} = 0.57$ ppm). Consequently, the decrease in the transmission power of (I) in polar coordinating solvents takes place as a result of the operation of both dipole-dipole [7] and coordination interactions with the solvent, where the effect of the latter probably predominates. In order to assess quantitatively the relative contribution from the coordination interactions with the solvents to the overall effect of decrease in the transmission power in (I) in polar coordinating solvents we undertook an investigation into the behavior of structurally related diarylmethanes (II) under analogous conditions. During the correlation of δF data for (II) in pyridine and DMSO in relation to

Com-	Formula	Yi el d,	bp. °C	bp, °C (p, mm	^{n²⁰D}	Found / calculated,	
pound	•	70		Hg)		C	н
(II ^a)	4- (CH ₃) 2NC ₆ H ₄ CH ₂ C ₆ H ₄ F-4	5	32-33 (pet. ether)	-		<u>78,24</u> 78,57	<u>6,67</u> 7,03
(IIb)	$4\text{-}\mathrm{CH}_{3}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CH}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{F}\text{-}4$	32	_	135(6)	1,5569	<u>83,83</u> 83,96	$\tfrac{6,32}{6,54}$
(1Id)	C ₆ H ₅ CH ₂ C ₆ H ₄ F-4	66		123 (9)	1,5571	83,53 83,84	$\tfrac{6,05}{5,95}$
(11g)	4-ClC ₆ H ₄ CH ₂ C ₆ H ₄ F-4	28	-	142— 143 (2)	1,5680	70,51 70,75	$\frac{4,31}{4,56}$
(IIh)	$3-ClC_6H_4CH_2C_6H_4F-4$	37	-	195(1)	1,5691	$\frac{70,55}{70,75}$	$\frac{4,64}{4,56}$
(IIi)	$3-CF_{3}C_{6}H_{4}CH_{2}C_{6}H_{4}F-4$	51	-	140– 141 (15)	1,5025	$\tfrac{66,14}{65,62}$	$\frac{4,02}{4,72}$
(IIj)	3,4,5-Cl ₃ C ₆ H ₂ CH ₂ C ₆ H ₄ F-4	27	61-62 (pentane)	-	-	<u>54,27</u> 53,95	<u>2,80</u> 2,78
	3-ClC ₆ H ₄ CH (OH) C ₆ H ₄ F-4	38	_	173– 175 (2–3)	1,5808	$\tfrac{66,40}{65,96}$	4,53 4,25
	3-CF ₃ C ₆ H ₄ CH (OH) C ₆ H ₄ F-4	63	-	141– 142(1)	1,5154	$\begin{array}{r} \underline{61,84}\\ \hline 62,22 \end{array}$	$\frac{3,58}{3,73}$
	3,4,5-Cl ₃ C ₆ H ₂ CH (OH) C ₆ H ₄ F-4	36	71-72 (pentane)	_	-	$\frac{50,94}{51,09}$	$\frac{2,62}{2,63}$

TABLE 3. The Physical Constants and Analytical Data of 4-Fluorophenylarylcarbinols and 4-Fluorophenylarylmethanes

the corresponding δF values of (II) in chlorobenzene (Table 2, Nos. 5 and 6) we obtained straight lines, the tangents of the slopes of which indicated that the loss of transmission power in (II) on account of dipole-dipole interactions amounts to 20% in pyridine and 40% in DMSO. Consequently, it can be concluded to a first approximation that the coordination interactions in (I) in fact make a more substantial contribution, amounting to $\sim 80\%$ in pyridine and 60% in DMSO.

EXPERIMENTAL

The ¹⁹F - {¹H} NMR spectra were obtained on an RYa-2309 spectrometer at 84.56 MHz and 25°C for dilute solutions (0.2 M). The experimental error in the measurement of δ F was not greater than ±0.01 ppm. The solvents were purified by standard procedures. The substituted aryl-4-fluorophenylmethanes (II) were synthesized by the reduction of aryl-4-fluorophenyl-carbinols with a saturated solution of hydrogen iodide in acetic acid. The carbinols were obtained by the reaction of 4-fluorobenzaldehyde with the corresponding arylmagnesium bromides. The ¹⁹F chemical shifts (in hexane) of the compounds (II) synthesized in the present work agreed with published data [2] with an accuracy of ±0.03 ppm. The constants and analytical data for the previously undescribed compounds and those having different physical characteristics from the published values are given in Table 3. A typical example of the synthesis of the compounds investigated in the present work is given below.

3-Trifluoromethyl-4-fluorodiphenylcarbinol. To an ether solution of 3-trifluoromethylphenylmagnesium bromide (obtained from 11.25 g (0.05 mole) of 3-trifluoromethylbromobenzene and 1.2 g of magnesium) we added with stirring (0-5°C) an ether solution of 4-fluorobenzaldehyde. The mixture was stirred at \sim 25°C for 1 h and was then decomposed with a saturated aqueous solution of ammonium chloride. The ether layer was separated and dried with sodium sulfate. After removal of the solvent and vacuum distillation of the residue we obtained 11 g of a colorless viscous liquid; bp 141-142°C (1 mm Hg). All the operations were carried out in an inert atmosphere.

4-Fluorodiphenylmethane. A hot solution of 11.5 g (0.06 mmole) of 4-fluorodiphenylcarbinol in 40 ml of acetic acid was added cautiously to 210 ml of acetic acid saturated with hydrogen iodide. The mixture was heated to boiling and added to an aqueous solution of sodium sulfite. The oil which separated was extracted with ether, washed with a saturated solution of alkali and with water, and dried over sodium sulfate. After removal of the solvent and twofold distillation we obtained 3.4 g of a colorless liquid boiling at 123-124°C (9 mm Hg).

CONCLUSIONS

1. It was established by the ¹⁹F NMR method that the bridging mercury atom in compounds of the $ArHgC_6H_4F-4$ and $ArCH_2C_6H_4F-4$ type transmits the electronic effects of substituents less effectively than the CH_2 group.

2. The decrease in the transmission power of the mercury atom in polar coordinating solvents results mainly from coordination interactions.

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A STUDY OF REACTION CONDITIONS FOR THE REACTION OF POLYBROMOBENZYL BROMIDES AND OTHER BENZYL BROMIDES WITH METALLIC MERCURY

K. B. Butin, A. A. Ivkina, UDC 541,124:542.91:547.539.3:546.49 and O. A. Reutov

One of the simplest methods for the synthesis of organomercury compounds (OMC) involves the direct reaction of organic halides with elemental mercury. Both organic iodides and bromides undergo this reaction; the yield of final products is strongly dependent on the nature of the organic radical and the reaction conditions [1]

$$R - X + Hg \rightarrow R - Hg - X \tag{1}$$

Although the detailed mechanism for reaction (1) is unknown, it apparently involves a radical process [1], although not necessarily a chain reaction (cf. reviews [2-4]). The heterogeneous reaction depicted in (1) is facilitated by efficient dispersion of the metallic Hg, UV irradiation, and also by the addition of anionic catalysts with a high affinity for mercury [5, 6].

In the preceding communication [7] we described the synthesis of pentabromo- and pentachlorobenzylic mercury derivatives according to reaction (1) under bromide ion-catalysis. In the present study we investigate the reaction of tetra-, tri-, di-, and monosubstituted benzyl bromides with elemental Hg; for comparison, the reactions of benzyl bromides containing various other substituents have also been studied.

The reactions were carried out under mechanical agitation (100-120 oscillations per min) using 5 g of metallic Hg in 5 ml (or 1 ml) of a solution of the benzyl bromide contained in a standard ampul (10 ml volume). The surface area of the dispersed mercury particles was neither measured not standardized.

In the case of reactions of tri-, tetra-, and pentabromobenzyl bromides of $C_6Cl_5CH_2Br$, a stable gray emulsion formed approximately 10-15 min after the onset of mechanical agita-

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