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 ^{19}F 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

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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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TABLE 1. Reaction Conditions and Products for the Reaction of Polybromobenzyl Bromides with Metallic Mercury at 20°C

Starting benzyl bromide	Solvent	Catalyst	Time, h	Products	Yield, %
$C_6Br_5CH_2Br$	DMF	Et_4NBr	3	$(C_6Br_5CH_2)_2Hg$ (I)	~100 [7]
	« *	None	170	$C_6Br_5CH_2HgBr$ (II)	88
	Benzene	«	60	(II)	40 [7]
	«	NaBr. 18-Crown-6	4	(I)	~100
	EtOH	Et_4NBr	4	(I)	~100 [7]
	DMF	Same	4	(I)	~100
	«	NaI	4	(I)	~100
2.3,4,6-$Br_4C_6HCH_2Br$	«	Et_4NBr	10	$(2,3,4,6\text{-}Br_4C_6HCH_2)_2Hg$ (III)	~100
	« *	None	22	2,3,4,6-$Br_4C_6HCH_2HgBr$ (IV)	71
				Starting RBr	25
	« *	«	120	(IV)	~100
2,4,6-$Br_3C_6H_2CH_2Br$	«	Et_4NBr	20	$(2,4,6\text{-}Br_3C_6H_2CH_2)_2Hg$ (V)	76
				2,4,6-$Br_3C_6H_2CH_2HgBr$ (VI)	7
	«	Same	10	(V)	22
				(VI)	39
	« *	None	45	(VI)	98
	Benzene	KBr, 18-Crown-6	36	(V)	80
				(VI)	20
	« *	None	160	Starting RBr	70
				(VI)	27
	«	UV	14	$(2,4,6\text{-}Br_3C_6H_2CH_2)_2$ (VII)	95
	«	UV	4	(VI)	19
				Starting RBr	80
				(VII)	1
2,6-$Br_2C_6H_3CH_2Br$	DMF*	Et_4NBr	70	$(2,6\text{-}Br_2C_6H_3CH_2)_2Hg$ (VIII)	65,3
				2,6-$Br_2C_6H_3CH_2HgBr$ (IX)	29
	« *	None	37	(IX)	95
	Benzene	KBr 18-Crown-6	36	(VIII)	70
				(IX)	30
	« *	None	160	(IX)	10
				Starting RBr	83
	«	UV	14	$(2,6\text{-}Br_2C_6H_3CH_2)_2$	90
	«	UV	4	(IX)	10
				Starting RBr	90
3 5-$Br_2C_6H_3CH_2Br$	DMF*	Et_4NBr	88	$(3,5\text{-}Br_2C_6H_3CH_2)_2Hg$	60
				3,5-$Br_2C_6H_3CH_2HgBr$	8,5
4-$BrC_6H_4CH_2Br$	« *	Same	20	4-$BrC_6H_4CH_2HgBr$ (X)	23
				Starting RBr	5
				4-BrC_6H_4CHO	40,5
	« *, †	«	60	$(4\text{-}BrC_6H_4CH_2)_2Hg$	33
				(X)	12
2-$BrC_6H_4CH_2Br$	« *, †	«	80	$(2\text{-}BrC_6H_4CH_2)_2Hg$	33
				2-$BrC_6H_4CH_2HgBr$	15
				Starting RBr	5
3-$BrC_6H_4CH_2Br$	« *, †	«	30	$(3\text{-}BrC_6H_4CH_2)_2Hg$	34
				3-$BrC_6H_4CH_2HgBr$	34
				Starting RBr	12

*In the dark.

†Under Ar atmosphere.

tion. In the case of mono- and dibromobenzyl bromide an emulsion formed after 1 h, and its dispersity was smaller than in the previous cases; the emulsion formed from monobromobenzyl bromide was unstable. Unsubstituted benzyl bromide, as well as the nitro-, methoxy-, and fluorosubstituted derivatives, did not give emulsions. The course of the reactions was monitored by TLC; the experiments were terminated either upon disappearance of the starting material from the reaction mixture, or when chromatography of the reaction mixture indicated that no further changes were occurring. When the reactions were performed over extended periods of time the agitation was interrupted for 8-10 h periods. These pauses were not included in the total reaction time. Stable emulsions were not disturbed during these intervals. The results obtained using this method are tabulated in Tables 1 and 2.

The reactions of polybromobenzyl bromides with Hg was found to be strongly dependent on reaction conditions: the solvent, catalysts, presence of oxygen in the air atmosphere, as well as whether the reaction was run in the dark or under irradiation. In the presence of anions with a high affinity for Hg (Br^-, I^-), the main products were symmetrical OMC (see Table 1). Apparently anionic catalysts catalyze not only the oxidative addition of Hg into the C—Br bond, but also the conversion of the initially formed unsymmetrical OMC to the symmetrical derivative.

TABLE 2. Reaction Conditions and Product Composition for the Reaction of Substituted Benzyl Bromides with Metallic Mercury at 20°C

Starting benzyl bromide	Solvent	Catalyst	Time, h	Products	Yield, %
$C_6Cl_5CH_2Br$	DMF *	Et_4NBr	10	$(C_6Cl_5CH_2)_2Hg$	78 [7]
	« *	None	170	$C_6Cl_5CH_2HgBr$ $(C_6Cl_5CH_2)_2$ (XI)	66
	DMF CCl_4, $CHCl_3$, Benzene	UV	60	(XI)	30
$C_6F_5CH_2Br$	DMF *	Et_4NBr	10	$C_6F_5CH_2HgBr$ (XII) $(C_6F_5CH_2)_2Hg$ (XIII) C_6F_5CHO	2 2 Main product
	«*, †	Same	90	(XII) (XIII) Starting RBr	13 29 13
	«*, †	None	90	(XII) (XIII) Starting RBr	6 25 5
$C_6H_5CH_2Br$	« *	Et_4NBr	10	$C_6H_5CH_2HgBr$ (XIV) $(C_6H_5CH_2)_2Hg$ (XV) C_6H_5CHO	1 3,6 Main product
	«*, †	Same	100	(XIV) (XV) Starting RBr	17 12,5 29
	«*, †	None	100	(XIV) (XV) Starting RBr	14 7 40
$4\text{-}NO_2C_6H_4CH_2Br$	«*, †	«	100	$4\text{-}NO_2C_6H_4CH_2HgBr$ $4\text{-}NO_2C_6H_4CH_3$	27 30
$2,4\text{-}(NO_2)_2C_6H_3CH_2Br$	«*, †	«	100	$2,4\text{-}(NO_2)_2C_6H_3CH_3$ Hg_2Br_2	27 42
$4\text{-}CH_3OC_6H_4CH_2Br$	«*, †	Et_4NBr	100	$(4\text{-}CH_3OC_6H_4CH_2)_2$	21

*In the dark.

†Under Ar atmosphere.

In the presence of excess Br^- ions the conversion of the unsymmetrical OMC is strongly shifted in favor of the symmetrical derivative due to complexation of the bromide ions with $HgBr_2$. Another factor influencing the ratio of symmetrical and unsymmetrical OMS is the solubility of the symmetrical compound; this ratio is again shifted in favor of the symmetrical derivative as the solubility of the latter decreases. In the absence of Br^- ions the reactions are substantially slower, and unsymmetrical OMC are obtained. When the reaction is carried out in benzene, the yields are lower than those obtained in DMF; this indicates the catalytic activity of DMF.

In the case of the reactions of monobromobenzyl bromides in DMF in the presence of Br^- ions, substantial amounts of the corresponding bromosubstituted benzaldehydes are obtained if the reactions are carried out in the presence of air, and symmetrical OMC are not formed. This may be attributed to a more rapid rate of oxidation of unsymmetrical OMS in the presence of oxygen in air, compared to the rate of conversion of the unsymmetrical OMC to the symmetrical compound. In this regard it should be noted that solutions of o-, m-, and p-bromobenzyl mercuric bromides in various solvents are unstable in air; their ensuing decomposition can be followed by PMR spectroscopy.

The data in Table 1 indicate that under identical conditions the rate of the reaction is greater for compounds containing increasing numbers of bromine atoms on the benzene ring.

UV irradiation of mixtures of 2,4,6-tribromo- and 2,6-dibromobenzyl bromides with metallic Hg results in the formation of the corresponding dibenzyls; the yield of dibenzyl derivatives increases at the expense of symmetrical OMC as the exposure time increases. Either the organomercury products or the starting benzyl bromides may serve as sources of the dibenzyl derivatives. Because of the possibility of photochemical decomposition the synthesized OMC were stored in light-proof containers.

The influence of reaction time on the course of the reaction and on the product ratio was studied for the case of 2,4,6-tribromobenzyl bromide in DMF in the presence of Et_4Br. After 10 h the main product was the unsymmetrical OMC, whereas after 20 h the main product was the symmetrical organomercury compound. It is reasonable to assume, therefore, that in the reaction of benzyl bromides with metallic Hg the initial products are unsymmetrical OMC, and that these are converted to the symmetrical derivatives upon interaction with Br^- ions.

The results in Table 1 indicate that optimum reaction conditions for the synthesis of bromosubstituted benzyl mercury compounds involve the use of the DMF—Br^- system in the dark and with the exclusion of air.

In order to compare the reactions of bromosubstituted benzyl bromides with reactions of compounds containing other substituents the product composition for the reactions of pentafluoro-, pentachloro-, p-nitro-, 2,4-dinitro-, p-methoxy-, and unsubstituted benzyl bromides with metallic Hg was measured (see Table 2). Reaction of pentachlorobenzyl bromide in DMF in the presence of Br^- ions proceeds smoothly to give bis(pentachlorobenzyl)mercury [7]. In the absence of Br^- ions the reaction in DMF is slower, and a mixture of unsymmetrical OMC and decachlorodibenzyl is obtained; when the process is carried out in benzene in the dark no reaction is observed after 600 h.

The reaction of pentafluorobenzyl bromide in the presence of air gives very low yields of OMC; the main product is pentafluorobenzaldehyde. When oxygen is excluded from the reaction mixture by purging with argon pentafluorobenzaldehyde is not produced. Qualitatively similar results were obtained for the reaction of unsubstituted benzyl bromide.

In the absence of Br^- ions and air p-nitrobenzyl bromide reacts with Hg to give the unsymmetrical OMC and p-nitrotoluene; 2,4-dinitrobenzyl bromide, on the other hand, gives 2,4-dinitrotoluene and $HgBr_2$. Reaction of p-methoxybenzyl bromide produces 4,4'-dimethoxydibenzyl. Use of 2,3,5-tribromobenzylidene dibromide as the substrate gives a compound in which two Hg atoms have been added simultaneously across the two C-Br bonds of the geminal dibromide, according to the following equation:

$$2,3,5\text{-}Br_3C_6H_2CHBr_2 + 2Hg \rightarrow 2,3,5\text{-}Br_3C_6H_2CH(HgBr)_2 \quad (\text{Yield } 54\%)$$

The results presented in Tables 1 and 2 demonstrate that the product composition is strongly dependent on the structure of the organic substrate, even when all other reaction conditions are identical. With the exception of monobromobenzyl bromide, bromosubstituted benzyl bromides react most smoothly in this general reaction.

EXPERIMENTAL

The starting substituted benzyl bromides were obtained from the corresponding toluenes via side chain bromination in dry CCl_4 according to the method described in the literature. Physical constants for the synthesized compounds agreed with the literature data, and structures were confirmed by PMR spectroscopy (HMDS as internal standard). Chromatographic separation and isolation of the OMC were carried out on columns protected from light; in the case of monobromosubstituted OMC the procedure was performed under an argon atmosphere.

Bis(2,3,4,6-tetrabromobenzyl)mercury. A mixture of 300 mg (0.62 mmole) of 2,3,4,6-tetrabromobenzyl bromide and 5 h of Hg in 5 ml of a saturated solution of Et_4NBR in DMF was agitated in sealed ampoule in the dark. After 1 h a precipitate appeared. After 10 h the precipitate was removed by filtration, washed with ethyl acetate, and dried. Bis(2,3,4,6-tetrabromobenzyl)mercury was obtained (314 mg, 100%), mp 224-225°C. Found: C 16.84; H 0.73; Br 61.97; Hg 19.73%. $C_{14}H_6Br_8Hg$. Calculated: C 16.58; H 0.60; Br 63.04; Hg 19.76%.

2,3,4,6-Tetrabromobenzyl Mercuric Bromide. A mixture of 200 mg (0.41 mmole) of 2,3,4,6-tetrabromobenzyl bromide and 5 g of Hg in 1 ml of dry DMF was agitated in a sealed ampoule in the dark. After 22 h the white precipitate which had formed was removed by filtration, washed with ether, and dried. The mother liquor was precipitated with distilled water and separated on a column (silica gel L 40/100 μ; the eluent for the isolation of the starting bromide was CCl_4—hexane (2:1), this was followed by $CHCl_3$—hexane (2:1)). 2,3,4,6-Tetrabromobenzyl mercuric bromide was obtained (200 mg, 71%), mp 204-206°C. Found: C 14.21; H 0.74; Br 58.03; Hg 25.63. $C_7H_3Br_5Hg$. Calculated: C 12.24; H 0.41; Br 58.14; Hg 29.18%. Starting bromide (50 mg, 25%) was also isolated.

Reaction of 2,4,6-Tribromobenzyl Bromide with Mercury. a) A mixture of 300 mg (0.73 mmole) of 2,4,6-tribromobenzyl bromide and 5 g of Hg in 5 ml of a dry, saturated DMF solution of Et_4NBr was agitated in the dark in a sealed ampoule. A precipitate began to appear after 40 min. After 10 h the reaction mixture was poured into water, and the resulting precipitate was removed by filtration and dried. Chromatography on a silica gel L (40/100 μ) column (eluent CCl_4–hexane (2:1)) gave bis(2,4,6-tribromobenzyl)mercury (70 mg, 22%), mp 180-181°C, and 2,4,6-tribromobenzyl mercuric bromide (170 mg, 39%), mp 206-207°C.

Bis(2,4,6-tribromobenzyl)mercury. Found: C 20.63; H 1.19; Br 55.47; Hg 22.36%. $C_{14}H_8Br_6Hg$. Calculated: C 19.63; H 0.94; Br 56.025; Hg 23.45%. PMR spectrum ($CDCl_3$, 100 MHz, δ, ppm): 3.06 s (2H), 8.04 s (2H). Exposure to sunlight gave a metallic Hg deposit after 4 h.

2,4,6-Tribromobenzyl Mercuric Bromide. Found: C 14.81; H 1.01; Br 50.79; Hg 30.97%. $C_7H_4Br_4Hg$. Calculated C 13.82; H 0.66; Br 52.55; Hg 32.96%.

b) A mixture of 500 mg (1.2 mmole) of 2,4,6-tribromobenzyl bromide and and 5 g Hg in 7 ml of a saturated solution of Et_4NBr in DMF was agitated in a sealed ampoule in the dark. After 20 h the reaction mixture was poured into water, and the resulting precipitate was removed by filtration and dried. Column chromatography gave 400 g (76%) of bis(2,4,6-tribromobenzyl)mercury, mp 181°C, and 50 mg (7%) of 2,4,6-tribromobenzyl mercuric bromide, mp 207°C.

c) A mixture of 30 mg (0.074 mmole) of 2,4,6-tribromobenzyl bromide and 5 g Hg in 1 ml of dry benzene containing 9 mg (0.074 mmole) KBr and 19 mg (0.074 mmole) 18-crown-6 in a sealed ampoule was agitated in the dark. After 36 h the products were isolated by column chromatography (CCl_4 eluent); 30 mg (80%) bis(2,4,6-tribromobenzyl)mercury and 9 mg (20%) 2,4,6-tribromobenzyl mercuric bromide were obtained.

d) A mixture of 30 mg (0.074 mmole) of 2,4,6-tribromobenzyl bromide and 5 g Hg in 1 ml dry DMF was agitated in a sealed ampoule in the dark. After 45 h the only product present in the reaction mixture was 2,4,6-tribromobenzyl mercuric bromide (20 mg, ∿100%), which was obtained via precipitation with water.

e) A mixture of 30 mg (0.074 mmole) of 2,4,6-tribromobenzyl bromide and 5 g Hg in 1 ml dry benzene was agitated in a sealed glass ampoule under UV irradiation with a SDRT-400 lamp. After 1.5 h a bright precipitate appeared; this material darkened after 4 h, and after 14 h only one product, 2,4,6-hexabromodibenzyl, mp 219°C, was present in the reaction mixture.

f) A mixture of 50 mg (0.12 mmole) of 2,4,6-tribromobenzyl bromide and 5 g Hg in 1 ml dry benzene in a sealed glass ampoule was agitated under irradiation with a mercury SDRT-400 lamp. After 4 h the reaction mixture consisted of 80% of the starting bromide, 19% 2,4,6-tribromobenzyl mercuric bromide, and 1% of hexabromodibenzyl. The products were isolated by chromatography on Silpearl plates with CCl_4 eluent.

g) A mixture of 30 mg (0.074 mmole) of 2,4,6-tribromobenzyl bromide and 5 g Hg in 1 ml of dry benzene was agitated in a sealed glass ampoule in the dark. After 160 h the reaction mixture consisted of 70% of the starting benzyl bromide and 27% of 2,4,6-tribromobenzyl mercuric bromide. The products were separated by chromatography on Silpearl plates with CCl_4 eluent.

Reaction of 2,6-Dibromobenzyl Bromide with Mercury. a) A mixture of 1.8 g (5.47 mmole) of 2,6-dibromobenzyl bromide and 5 g Hg in 5 ml of a saturated DMF solution of Et_4NBr was agitated in a sealed ampoule in the dark. After 70 h the reaction mixture was poured into water, and the resulting precipitate was removed by filtration, dried, and applied to a silica gel L (40/100 μ) column with CCl_4 eluent. The isolated products were 1.15 g (65%) of bis(2,6-dibromobenzyl)mercury, mp 166-167°C, and 0.85 g (29%) of 2,6-dibromobenzyl mercuric bromide, mp 175-176°C.

Bis(2,6-dibromobenzyl)mercury. Found: C 24.24; H 1.54; Br 45.85; Hg 23.86%. $C_{14}H_{10}Br_4Hg$. Calculated: C 24.08; H 1.45; Br 45.77; Hg 29.71%. PMR spectrum (DMSO-d_6, 100 MHz, δ, ppm): 3.10 s (4H), 7.68-7.83 m (6H).

2,6-Dibromobenzyl Mercuric Bromide. Found: C 16.44; H 1.09, Br 45.08; Hg 37.67%. $C_7H_5Br_3Hg$. Calculated: C 15.88; H 0.95; Br 45.29; Hg 37.88%. PMR spectrum (DMSO-d_6, 100 MHz, δ, ppm): 3.40 s (2H), 7.81-7.89 m 3H.

b) A mixture of 30 mg (0.09 mmole) of 2,6-dibromobenzyl bromide and 5 g Hg in 1 ml of dry benzene containing 10 mg (0.09 mmole) KBr and 24 mg (0.09 mmole) 18-crown-6 was agitated in a sealed ampoule in the dark. After 36 h the products were separated by column chromatography (CCl_4 eluent) to give 20 mg (70%) bis(2,6-dibromobenzyl)mercury and 15 mg (30%) 2,6-dibromobenzyl mercuric bromide.

c) A mixture of 30 mg (0.09 mmole) of 2,6-dibromobenzyl bromide and 5 g Hg in 1 ml dry benzene was agitated in a sealed glass ampoule under UV irradiation. After 1.5 h the solution became turbid, and after 14 h a small amount of a dark solid had precipitated. The main product in the reaction mixture was 2,2',6,6'-tetrabromodibenzyl.

d) A mixture of 50 mg (0.15 mmole) 2,6-dibromobenzyl bromide and 5 g Hg in 1 ml dry benzene was agitated in a sealed glass ampoule under UV irradiation. After 4 h the reaction mixture was separated by chromatography (Silpearl, CCl_4 eluent) to give 45 mg (90%) of the starting benzyl bromide and 10 mg (10%) of 2,6-dibromobenzyl mercuric bromide.

e) A mixture of 30 mg (0.09 mmole) of 2,6-dibromobenzyl bromide and 5 h Hg in 1 ml of dry DMF was agitated in a sealed glass ampoule in the dark. After 37 h chromatography on a Silpearl plate with CCl_4 eluent gave 46 mg (95%) of 2,6-dibromobenzyl mercuric bromide.

f) A mixture of 30 mg (0.09 mmole) of 2,6-dibromobenzyl bromide and 5 g Hg in 1 ml of dry benzene was agitated in a sealed glass ampoule in the dark. After 160 h separation of the reaction mixture gave 25 mg (83%) of the starting benzyl bromide and 5 mg (10%) of 2,6-dibromobenzyl mercuric bromide. Product isolation was carried out on Silpearl plates with CCl_4 eluent.

Reaction of 3,5-Dibromobenzyl Bromide with Mercury. A mixture of 1.3 g (3.95 mmole) of 3,5-dibromobenzyl bromide and 5 g Hg in 5 ml of a saturated DMF solution of Et_4NBr was agitated in a sealed ampoule in the dark. After 88 h of agitation the mixture was poured into water, and the resulting solid was removed by filtration, dried, and purified by column chromatography (CCl_4 eluent). The isolated products were 0.82 g (60%) bis(3,5-dibromobenzyl)mercury, mp 163°C, and 0.17 g (8.5%) 3,5-dibromobenzyl mercuric bromide, mp 159°C.

Bis(3,5-dibromobenzyl)mercury. Found: C 24.08; H 1.46; Br 45.94; Hg 28.47%. ($C_{14}H_{10}Br_4$-Hg. Calculated: C 24.08; H 1.45; Br 45.77; Hg 29.71%. PMR spectrum ($CDCl_3$, 60 MHz, δ, ppm): 2.9 s (4H), 7.55-7.68 m (6H).

3,5-Dibromobenzyl Mercuric Bromide. Found: C 16.27; H 1.10; Br 45.43; Hg 37.40%. $C_7H_5Br_3Hg$. Calculated: C 15.88; H 0.95; Br 45.29; Hg 37.80. PMR spectrum (DMSO-d_6, 100 MHz, δ, ppm): 3.16 s (2H), 7.56-7.93 m (3H).

Reaction of p-Bromobenzyl Bromide with Mercury. a) A mixture of 5 g (20 mmole) p-bromobenzyl bromide and 5 g Hg in 5 ml of a saturated DMF solution of Et_4NBr was agitated in a sealed ampoule in the dark (the reaction mixture was not purged with Ar). After 20 h of agitation the reaction mixture consisted of the starting benzyl bromide, p-bromobenzaldehyde, and p-bromobenzyl mercuric bromide. The reaction mixture was poured into water, and the resulting precipitate was subjected to column chromatography ($CHCl_3$—hexane (2:1) eluent). The following products were obtained: 0.3 g (6%) p-bromobenzyl bromide, 1.5 g (40.5%) p-bromobenzaldehyde, and 2.07 g (23%) p-bromobenzyl mercuric bromide, mp 161°C (from CCl_4).

p-Bromobenzyl Mercuric Bromide. Found: C 18.71; H 1.40; Br 35.40; Hg 44.13%. $C_7H_6Br_2Hg$. Calculated: C 18.66; H 1.35; Br 35.48; Hg 44.51%. PMR spectrum (acetone-d_6, 100 MHz, δ, ppm): 2.9 s (2HO, 6.83-7.05 m A_2B_2 (4H).

b) A mixture of 1 g (4 mmole) of p-bromobenzyl bromide and 5 g Hg in 2.5 ml of a saturated solution of Et_4NBr in dry DMF was agitated in a sealed ampoule in the dark (the reaction mixture had been purged with Ar). After several hours an abundant white precipitate appeared. After 60 h of agitation the reaction mixture consisted of the starting benzyl bromide, bis(p-bromobenzyl)mercury, and p-bromobenzyl mercuric bromide. The precipitate was filtered, washed with ether, and dried. The main constituent of the precipitate was bis(p-bromobenzyl)mercury contaminated with a small amount of the starting material as well as p-bromobenzyl mercuric bromide. The precipitate and mother liquor (after precipitation with water) were separated by column chromatography (silica gel L, 40/100 μ; for the starting material the eluent was CCl_4—hexane (2:1), for bis(P-bromobenzyl)mercury the eluent was $CHCl_3$—hexane (2:1), and the final eluent was $CHCl_3$). The isolated product yields were 0.05 g (5%) p-bromobenzyl bromide, 0.34 g (33%) bis(p-bromobenzyl)mercury, mp 168°C (dec), and 0.2 g (12%) p-bromobenzyl mercuric bromide, mp 161°C.

Bis(p-bromobenzyl)mercury. Found: C 31.75; H 2.46; Br 29.62; Hg 36.02%. $C_{14}H_{12}BrHg$. Calculated: C 31.11; H 2.24; Br 29.56; Hg 37.09%. PMR spectrum ($CDCl_3$, 100 MHz, δ, ppm): 2.8 s (4H), 7.30-7.80 m A_2B_2 (8H).

The reaction of o-bromobenzyl bromide with mercury and the product separation were carried out in a similar manner to that described above for p-bromobenzyl bromide in an argon atmosphere. Isolated product yields were 0.02 g (5%) o-bromobenzyl bromide, 0.33 g (33%) bis(o-bromobenzyl)mercury, mp 111-112°C, and 0.25 g (15%) o-bromobenzyl mercuric bromide, mp 124°C.

Bis(o-bromobenzyl)mercury. Found: C 31.85; H 2.38; Br 29.99 Hg 35.91%. $C_{14}H_{12}Br_2Hg$. Calculated: C 31.11; H 2.24; Br 29.56; Hg 37.09%. PMR spectrum ($CDCl_3$, 100 MHz, δ, ppm): 2.8 s (4H), 7.15-7.91 m (8H).

o-Bromobenzyl Mercuric Bromide. Found: C 18.83; H 1.35; Br 35.48; Hg 44.25%. $C_7H_6Br_2Hg$. Calculated: C 18.66; H 1.35; Br 35.48; Hg 44.51%. PMR spectrum (acetone-d_6, 100 MHz, δ, ppm): 2.9 s (2H), 6.66-7.38 m (4H).

The reaction of m-bromobenzyl bromide with mercury and the product separation were carried out in a similar manner to that described above for p-bromobenzyl bromide. Isolated product yields were 0.061 g (12%) m-bromobenzyl bromide, 0.13 g (34%) bis(m-bromobenzyl)-mercury, mp 83°C, and 0.30 g (34%) m-bromobenzyl mercuric bromide, mp 132°C.

Bis(m-bromobenzyl)mercury. Found: C 31.18; H 2.23; Br 29.69; Hg 36.44%. $C_{14}H_{12}Br_2Hg$. Calculated: C 31.11; H 2.24; Br 29.56; Hg 37.09%. PMR spectrum ($CDCl_3$, 100 MHz, δ, ppm): 2.73 s (4H), 7.15-7.45 m (8H).

m-Bromobenzyl Mercuric Bromide. Found: C 19.54; H 1.43; Br 36.78; Hg 41.82%. $C_7H_6Br_2Hg$. Calculated: C 13.66; H 1.35; Br 35.48; Hg 44.51%. PMR spectrum (acetone-d_6, 60 MHz, δ, ppm): 2.9 s (2H), 6.85-7.12 m (4H).

Pentachlorobenzyl Mercuric Bromide. A mixture of 0.4 g (1.16 mmole) pentachlorobenzyl bromide and 5 g Hg in 6 ml of a saturated solution of Et_4NBr in dry DMF was agitated in a sealed ampoule in the dark. After 2 h a copious white precipitate formed. The reaction was carried out over 170 h. At this time no starting material remained in the reaction mixture. The precipitate was removed by filtration, washed with ether, and dried. The precipitate consisted of 0.27 g of pure pentachlorobenzyl mercuric bromide. Column chromatography of the mother liquor (the DMF solution contained pentachlorobenzyl mercuric bromide contaminated with a small amount of impurities) on silica gel L (40/100 µ) with $CHCl_3$—hexane (2:1) eluent yielded an additional 0.15 g of pentachlorobenzyl mercuric bromide, giving a total yield of 0.42 g (66%), mp 220-222°C. Found: C 22.36; H 0.78; halogen 50.05; Hg 23.47%. $C_7H_2Cl_5BrHg$. Calculated: C 15.46; H 0.37; halogen 47.29; Hg 36.89%. The reactions of pentafluorobenzyl bromide and benzyl bromide with mercury and the corresponding product isolation procedures were carried out in a manner similar to that described above. The results of these reactions are presented in Table 2.

Reaction of p-Nitrobenzyl Bromide with Mercury. A mixture of 420 mg (1.94 mmole) of p-nitrobenzyl bromide and 5 g Hg in 1 ml of dry DMF under an Ar atmosphere was agitated in a sealed ampoule in the dark. After 100 h the reaction mixture (a DMF solution) was subjected to column chromatography ($CHCl_3$ eluent). The isolated product yields were 75 mg (30%) p-nitrotoluene and 200 mg (27%) p-nitrobenzyl mercuric bromide, mp 183°C (see [8]).

PMR spectrum (DMSO-d_6, 60 MHz, δ, ppm): 3.30 s (2H), 7.61-8.38 m A_2B_2 (4H).

Reaction of 2,4-Dinitrobenzyl Bromide with Mercury. A mixture of 430 mg (1.65 mmole) of 2,4-dinitrobenzyl bromide and 5 h Hg in 1 ml of dry DMF under an Ar atmosphere was agitated in a sealed ampoule in the dark. The reaction mixture turned red, and after several days a bright precipitate appeared. After 100 h of mechanical agitation the precipitate was removed by filtration, washed with ether, and dried. The precipitate consisted only of **HgBr. The** mother liquor was subjected to column chromatography on silica gel L (40/100 µ) with $CHCl_3$ eluent. The isolated product yields were 81 mg (27%) of 2,4-dinitrotoluene, mp 69°C (see [6]), and 0.20 g (42%) of Hg_2Br_2, mp 360°C (dec) (see [9]).

Reaction of p-Methoxybenzylbromide with Mercury. A mixture of 1.4 g (6.97 mmole) p-methoxybenzyl bromide and 5 g Hg in 1 ml of a saturated solution of Et_4NBr in dry DMF under an Ar atmosphere was agitated in a sealed ampoule in the dark. After 100 h the reaction mixture (solution in DMF) was subjected to column chromatography with $CHCl_3$ eluent. The isolated product yield was 0.18 g (21%) of 4,4'-dimethoxydibenzyl. Mass spectrum: M^+ 242. PMR spectrum (CCl_4, 60 MHz, δ, ppm): 2.53 s (4H), 3.95 s (6H), 6.87-7.43 m (8H).

Reaction of 2,3,5-Tribromobenzylidene Dibromide with Mercury. A mixture of 0.7 g (1.6 mmole) of 2,3,5-tribromobenzylidene dibromide and 5 g Hg in 3 ml of a saturated solution of Et_4NBr in DMF was agitated in a sealed ampoule in the dark. After 20 h the reaction mixture was poured into water, and the resulting white precipitate was removed by filtration and purified by column chromatography on silica gel L (40/100 μ) with $CHCl_3$—hexane (2:1) eluent. The isolated product yields were 0.3 g of the starting dibromide and 0.70 g (54%) α,α'-bis-(bromomercury)2,3,5-tribromotoluene, which decomposed at 240°C without melting. Found: C 11.57; Br 41.07; Hg 44.86; H 0.58%. $C_7H_3Br_5Hg_2$. Calculated: C 9.47; Br 45.00; Hg 45.17; H 0.37%. PMR spectrum (DMSO-d_6, 100 MHz, δ, ppm): 3.86 s (1H), 8.27 s (1H).

CONCLUSIONS

1. The reactions of pentafluoro-, pentachloro-, polybromo-, nitro-, and p-methoxy-substituted benzyl bromides with metallic mercury, leading to the synthesis of benzyl mercury compounds, have been investigated. The ease of the reaction increases as the number of bromine atoms on the benzene ring increases. Optimum reaction conditions have been recommended; these involve use of DMF as solvent in the presence of Br^- ion catalysts.

2. The oxidative addition reaction of Hg (into the C—Br bond) is accompanied in many cases by side products of radical origin (dibenzyls, toluenes, benzaldehydes). The smoothest reactions were encountered with polybromo- and polychlorobenzyl bromide substrates.

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1,2-ADDITION OF $PhCH(SnMe_3)CO_2Et$ TO α,β-UNSATURATED ALDEHYDES

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Regioselective addition of organometallic compounds to α,β-unsaturated carbonyl compounds is an important reaction for C—C bond formation. The direction of this reaction depends both on the structure of the reagents and on the experimental conditions [1]. In particular, at low temperature, lithium enolates of esters undergo addition to α,β-unsaturated aldehydes at the carbonyl group [2]. However, this reaction, important for synthesis, proceeds only with the carbonyl compounds that do not polymerize during the reaction [3]. There is no polymerization of carbonyl compounds in reactions involving organotin compounds. Several of such reactions now known always proceed as 1,2 addition. Thus, for example, α-stannylated ketones react with cinnamaldehyde and mesityl oxide [4]. Similarly, $Et_2Sn \cdot CH_2CO_2Et$ undergoes addition to cinnamaldehyde in the presence of halide ions [5]. However, the latter reaction cannot be carried out with acrolein and crotonaldehyde because they polymerize in the presence of halide ions.

In the present paper, to study reactions of addition to α,β-unsaturated aldehydes, we chose the stannylated ester $PhCH(SnME_3)CO_2Et$, which is active even in the absence of halide

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