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Preliminary communication

PERMERCURATED ARENES

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Summary

Permercuration of sodium benzoate, nitrobenzene, benzamide, and benzene, and pentamercuration of benzene have been achieved by heating the appropriate arenes or monomercurated arenes with mercuric trifluoroacetate, while anisic acid gave permercurated anisole; the products react with tribromide ions to give the corresponding polybromobenzenes.

Since the electronic effect of mercury in a benzene ring is weak [1—4] and the size of mercury (Van der Waals radius [5], 150 pm; cf. Br [6], 195 pm) is not exceptionally large, there appears to be no insuperable barrier to complete mercuration (permercuration) of aromatic compounds. However, few aromatic species, viz. furan [7], pyrrole [7, 8], thiophene [9], 1,3-thiazole [10], tricarbonyl(η-cyclobutadienyl)iron [11], and acetanilide [12], have been permercurated. We are undertaking a detailed investigation of per- and polymercurated compounds, and now report the synthesis and properties of several permercurated arenes. As mercury substituents may be displaced by a range of electrophiles [13], permercurated substrates are potentially of considerable use in organic synthesis as a source of polysubstituted aromatic compounds.

Fusion of mercuric trifluoroacetate (prepared *in situ* from mercuric oxide and trifluoroacetic acid) with sodium benzoate, nitrobenzene, benzamide, or phenylmercuric chloride caused vigorous evolution of trifluoroacetic acid, and an infusible residue of the corresponding permercurated arene (Table 1) rapidly formed (< 5 mins).

$$C_6H_nY_{6-n} + n Hg(O_2CCF_3)_2 \rightarrow C_6(HgO_2CCF_3)_nY_{6-n} + n CF_3CO_2H$$

Preparation of hexakis(trifluoroacetatomercuri)benzene required use of a large excess of mercuric trifluoroacetate, as otherwise the pentamercurated derivative was obtained. The difficulty in introducing the sixth mercury atom is probably steric in origin. Attempted permercuration of anisic acid was accompanied by decarboxylation, and pentakis(trifluoroacetatomercuri)anisole was formed (cf. $C_6H_5CO_2Na$ or $C_6H_5CO_2H$, Table 1).

TABLE 1

PREPARATION AND CLEAVAGE OF POLYMERCURATED ARENES

Reactant (10 mmol)	$Hg(O_2CCF_3)_2$ (mmol)	Temp. (°C)	Polymercurated arene	Cleavage conditions	Product	Recrystallization solvent	Yield [a] (%)
$C_6H_5CO_2Na$ [b]	70	180	$C_6(HgO_2CCF_3)_5CO_2Na$	[c]	$C_6Br_5CO_2H$	toluene	60
$C_6H_5NO_2$	70	240	$C_6(HgO_2CCF_3)_5NO_2$	[c]	$C_6Br_5NO_2$	ethanol	64
$C_6H_5CONH_2$	70	200	$C_6(HgO_2CCF_3)_5CONH_2$	[c]	$C_6Br_5CONH_2$	ethanol	56
C_6H_5HgCl	150	200	$C_6(HgO_2CCF_3)_6$	[d]	C_6Br_6	toluene	60
C_6H_5HgCl	70	180	$C_6H(HgO_2CCF_3)_5$	[e]	C_6HBr_5	acetic acid	70
p-$CH_3OC_6H_4CO_2H$	70	180	$CH_3OC_6(HgO_2CCF_3)_5$	[d]	$C_6Br_5OCH_3$	ethanol	70

[a] Analytically pure products; identification confirmed by mass spectrometry. Crude $C_6Br_5CO_2H$ and C_6Br_5H contained impurities of 2,3,5,6-$Br_4C_6HCO_2H$ and C_6Br_6 respectively. [b] Benzoic acid can be used, but purification is more difficult. [c] Polymercurated arene stirred with KBr and Br_2 (each 60 mmol) in water (pH adjusted to 7.0) or aqueous methanol for 1 h at room temperature. [d] Stirred for 24 h at room temperature with KBr and Br_2 (each 150 mmol) in water (pH 7.0). [e] Stirred for 1 h at room temperature with KBr and Br_2 (each 70 mmol) in aqueous methanol.

$$p\text{-}CH_3OC_6H_4CO_2H + 5Hg(O_2CCF_3)_2 \rightarrow CH_3OC_6(HgO_2CCF_3)_5 + 5CF_3CO_2H + CO_2$$

The polymercurated arenes were identified* by cleavage with tribromide ions under mild conditions to give the corresponding polybromoarenes, which, after recrystallization, were obtained analytically pure in good yield (Table 1).

$$C_6(HgO_2CCF_3)_nY_{6-n} + nBr_3^- \rightarrow C_6Br_nY_{6-n} + nHgBr_2 + nCF_3CO_2^-$$

These results confirm that polymercurated aromatics are likely to be of value in organic synthesis.

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*Analytical data are an unsatisfactory basis for identification, e.g. tetra-, penta-, and per-mercurated benzenes have similar analytical composition: $C_6H_2(HgO_2CCF_3)_4$ calcd.: C, 12.7; F, 17.2; Hg, 60.4%; $C_6H(HgO_2CCF_3)_5$ calcd.: C, 11.7; F, 17.4; Hg, 61.1%; $C_6(HgO_2CCF_3)_6$ calcd.: C, 11.1; F, 17.5; Hg, 61.6%.