

Preliminary communication

PERMERCURATED ARENES

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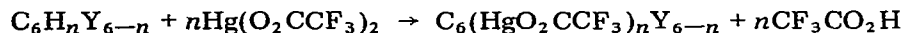
(Received January 17th, 1974)

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 permercured 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], tri-carbonyl(η -cyclobutadienyl)iron [11], and acetanilide [12], have been permercured. We are undertaking a detailed investigation of per- and poly-mercurated compounds, and now report the synthesis and properties of several permercured arenes. As mercury substituents may be displaced by a range of electrophiles [13], permercured 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 permercured arene (Table 1) rapidly formed (< 5 mins).

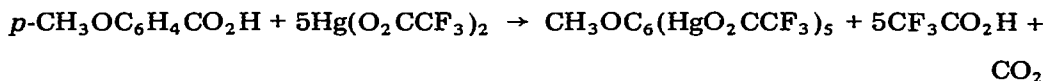


Preparation of hexakis(trifluoroacetatomercuri)benzene required use of a large excess of mercuric trifluoroacetate, as otherwise the pentamercurated derivative was obtained. The difficulty in introducing the sixth mercury atom is probably steric in origin. Attempted permercuration of anisic acid was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

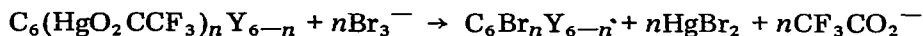
TABLE 1
PREPARATION AND CLEAVAGE OF POLYMERCURATED ARENES

Reactant (10 mmol)	Hg(O ₂ CCF ₃) ₂ (mmol)	Temp. (°C)	Polymercurated arene	Cleavage conditions	Product	Recrystallization solvent	Yield ^a (%)
C ₆ H ₅ CO ₂ Na ^δ	70	180	C ₆ (HgO ₂ CCF ₃) ₅ CO ₂ Na	c	C ₆ Br ₂ CO ₂ H	toluene	60
C ₆ H ₅ NO ₂	70	240	C ₆ (HgO ₂ CCF ₃) ₅ NO ₂	c	C ₆ Br ₂ NO ₂	ethanol	64
C ₆ H ₅ CONH ₂	70	200	C ₆ (HgO ₂ CCF ₃) ₅ CONH ₂	c	C ₆ Br ₂ CONH ₂	ethanol	56
C ₆ H ₅ HgCl	150	200	C ₆ (HgO ₂ CCF ₃) ₆	d	C ₆ Br ₆	toluene	60
C ₆ H ₅ HgCl	70	180	C ₆ H(HgO ₂ CCF ₃) ₇	e	C ₆ HBr ₂	acetic acid	70
p-CH ₃ OC ₆ H ₄ CO ₂ H	70	180	CH ₃ OC ₆ (HgO ₂ CCF ₃) ₅	d	C ₆ Br ₂ OCH ₃	ethanol	70

^a Analytically pure products; identification confirmed by mass spectrometry. Crude C₆Br₂CO₂H and C₆Br₂H contained impurities of 2,3,5,6-Br₄C₆HCO₂H and C₆Br₄ respectively. ^b Benzole acid can be used, but purification is more difficult. ^c Polymercurated arene stirred with KBr and Br₂ (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 Br₂ (each 150 mmol) in water (pH 7.0). ^e Stirred for 1 h at room temperature with KBr and Br₂ (each 70 mmol) in aqueous methanol.



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).



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

Acknowledgement

We are grateful to the Australian Research Grants Committee for support.

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- 13 See e.g. L.G. Makarova, *Organometal. Reactions*, 1 (1970) 119.

*Analytical data are an unsatisfactory basis for identification, e.g. tetra-, penta-, and per-mercurated benzenes have similar analytical composition: $\text{C}_6\text{H}_2(\text{HgO}_2\text{CCF}_3)_4$ calcd.: C, 12.7; F, 17.2; Hg, 60.4%; $\text{C}_6\text{H}(\text{HgO}_2\text{CCF}_3)_5$ calcd.: C, 11.7; F, 17.4; Hg, 61.1%; $\text{C}_6(\text{HgO}_2\text{CCF}_3)_6$ calcd.: C, 11.1; F, 17.5; Hg, 61.6%.