

## Non Carbenoid Alkylidene Transfer from Monohalogenoalkylmercury(II) Compounds to Amines; Synthesis of Bis-(4-aminophenyl)alkanes

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**Summary** Monohalogenoalkylmercury(II) compounds react with aromatic amines to give bis-(4-aminophenyl)alkanes in high yields; alkylidene insertion reactions in the N-H bond are not observed.

THE ability of polyhalogenomethylmercury(II) compounds to transfer halogenocarbene to suitable organic substrates has been extensively investigated by Seyferth and his co-workers.<sup>1,2</sup> However, monohalogenoalkylmercurials have received little attention, and only reactions in which CH<sub>2</sub> is transferred from -HgCH<sub>2</sub>Hal to olefins to give cyclopropanes<sup>3</sup> are known.

We have found that monohalogenoalkylmercurials derived from organomercury(II) halides and diazoalkanes<sup>4</sup> react with aliphatic and aromatic amines to yield mercury(0), and products of a different nature depending on the structure of the reactants. The reactions of the mercurials (1) with the aromatic amines (2) in a molar ratio of 1:4 gave the bis-(4-aminophenyl)alkanes (3) in high yields (reaction 1; Table). Reactions were continued until no further mercury(0) precipitation was noticeable. Products were recovered from the reaction mixture by extraction in basic media, isolated by distillation under reduced pressure,

and then purified by recrystallization (solids) or column chromatography (oils).† Reactions proceeded rapidly (20–30 min) at room temperature when primary or secondary amines were used but longer reaction times (2 h) and higher temperatures (100–125 °C) were necessary for tertiary aromatic amines. The reaction rate appears to be governed mainly by the co-ordination ability of the amine nitrogen owing to both steric effects and differences in basicity. The enhancement of the amine basicity greatly accelerates the reaction since aliphatic amines react, in general, much faster than do aromatic amines with equal numbers of substituents on the nitrogen (see Table).

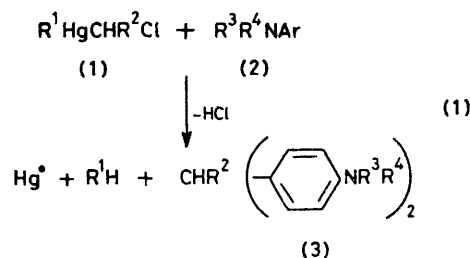


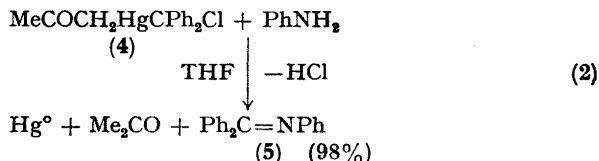
TABLE. Reaction of the monohalogenomercury(II) compounds (1)<sup>a</sup> with the aromatic amines (2) to give the diamines (3)<sup>b</sup> (reaction 1).

(1)		(2)			Temp./°C	Time	% Yield of (3)	M.p. (T/°C) of (3)
R <sup>1</sup>	R <sub>2</sub>	R <sup>3</sup>	R <sup>4</sup>	Ar				
CHOCH <sub>2</sub>	H	H	H	Ph	20	20 min	88	91–92 <sup>c</sup>
MeCOCH <sub>2</sub>	H	H	H	2,6-xyllyl	20	30 min	74	114–115
MeCOCH <sub>2</sub>	H	Me	Me	Ph	125	2 h	78	90–91 <sup>d</sup>
MeO <sub>2</sub> CCH <sub>2</sub>	H	H	Ph	Ph	70	1 h	43	112–113 <sup>e</sup>
MeCOCH <sub>2</sub>	Et	Me	Me	Ph	125	3 h	69	Oil

<sup>a</sup> Ref. 4. <sup>b</sup> All reactions were performed in the absence of solvent. <sup>c</sup> Lit. (Beilstein, vol. 13, Band 2, p. 111) m.p. 92–93 °C. <sup>d</sup> Product is (3,5-Me<sub>2</sub>-4-NH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>; lit. (ref. as in c) m.p. 91–92 °C. <sup>e</sup> Lit. (Beilstein, vol. 13, Band 1, p. 73) m.p. 113 °C.

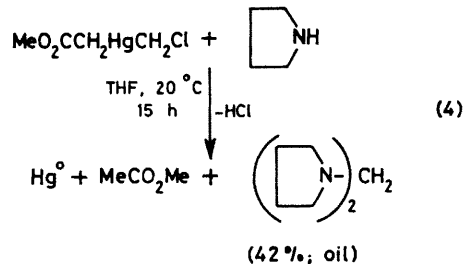
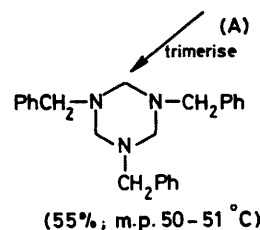
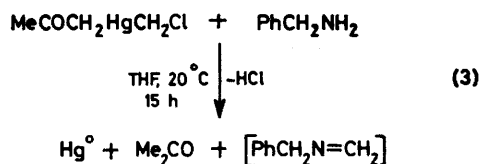
† Satisfactory C, H, and N analyses and i.r. and n.m.r. spectra were obtained for new compounds.

The reaction of compound (4) derived from diphenyldiazomethane and generated *in situ* with aniline in tetrahydrofuran (THF) for 1 h at 20 °C gave the Schiff base (5) (m.p. 111–112 °C)<sup>5</sup> almost quantitatively (reaction 2). We attribute the different course of this reaction compared to reaction (1) to steric factors.



Reactions (20 °C; 15 h) of the monohalogenomercurials [e.g. (1; R<sup>1</sup> = MeCOCH<sub>2</sub>, R<sup>2</sup> = H)] with primary aliphatic amines (e.g. benzylamine) afforded hexahydrotriazine derivatives (reaction 3), whereas secondary aliphatic amines (e.g. pyrrolidine) and the mercurials [e.g. (1; R<sup>1</sup> = MeO<sub>2</sub>CCH<sub>2</sub>, R<sup>2</sup> = H)] afforded diamines (reaction 4). These reactions are extremely exothermic (explosive without solvent) and must be carried out in dilute solution e.g., THF, by dropping the amine on to the mercurial. The formation of the triazine derivative can be explained in terms of an unstable imine intermediate (A) by analogy with reaction (2).

When halogenoalkylmercurials behave as divalent carbon transfer reagents to amines *via* a free carbene or a carbenoid path, the mercury remains in the oxidation state II throughout the process, and almost exclusively insertion products into the N–H<sup>6</sup> or the N–C<sup>7</sup> (tertiary amines) bond are observed. However, in the reactions described herein, the mercury is always nearly quantitatively reduced to the elemental state and products derived from alkylidene



insertion are never generated, at least, to a noticeable extent. These facts clearly show that monohalogenoalkylmercury(II) compounds do not react with amines *via* a carbene-type mechanism as do their polyhalogenoalkyl analogues.

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<sup>1</sup> D. Seyferth, *Pure Appl. Chem.*, 1970, **23**, 391; *Accounts Chem. Res.*, 1972, **5**, 65.

<sup>2</sup> R. C. Larock, *Angew. Chem. Internat. Edn.*, 1978, **17**, 27; A. J. Bloodworth in 'The Chemistry of Mercury,' ed. C. A. McAuliffe, MacMillan, London, 1977, p. 238.

<sup>3</sup> D. Seyferth and C. K. Haas, *J. Organometallic Chem.*, 1972, **39**, C41; R. Scheffeld and U. Michel, *Angew. Chem. Internat. Edn.* 1972, **11**, 231.

<sup>4</sup> J. Barluenga, P. J. Campos, M. A. Roy, J. C. García-Martin, and G. Asensio, submitted for publication.

<sup>5</sup> G. Reddelien, *Ber.*, 1913, **46**, 2172, 2718, gives m.p. 113 °C.

<sup>6</sup> W. E. Parham, and J. R. Potoski, *Tetrahedron Letters*, 1966, 2311.

<sup>7</sup> D. Seyferth, M. E. Gordon, and R. Damrauer, *J. Org. Chem.*, 1967, **32**, 469.