Pyrolysis of Mercuric Bromo-4-methoxybenzoates – Unexpected, High Yield Synthesis of Bis(2,5-dibromo-4-methoxyphenyl)mercury

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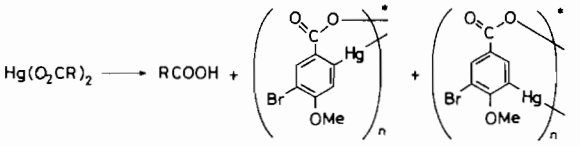
The two principal reactions observed on thermal decomposition of mercuric arenecarboxylates are mercuration of the aromatic ring and decarboxylation (ipso-mercuration) [1]. In general the latter is favored by electron-withdrawing substituents in the organic group since these both deactivate the ring towards mercuration (electrophilic aromatic substitution [2]) and facilitate decarboxylation by an S_Ei mechanism with carbanionic character in the transition state. The conditions also affect the balance between the decomposition paths. Thus, heating mercuric 2,6-dihalogenobenzoates under vacuum gives mainly 3-mercurated-2,6-dihalogenobenzoate groups and the 2,6-dihalogenobenzoic acid due to mercuration, by contrast with the occurrence of decarboxylation in boiling pyridine or dimethyl sulphoxide [3]. As part of a continuing study of the factors favoring each path we have examined pyrolysis of four mercuric bromo-4-methoxybenzoates under vacuum and report that the 2,5-dibromo-4-methoxybenzoate undergoes smooth decarboxylation whereas *ortho* mercuration would be expected on the basis of the current understanding [1] of these decompositions.

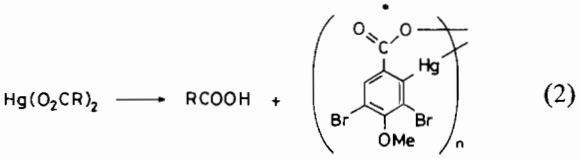
From mercuration of 4-methoxybenzoic acid under varying conditions and bromodemercuration of the mercuration products, 3-bromo-4-methoxy-2,5-dibromo-4-methoxy-, 3,5-dibromo-4-methoxy- and 2,3,5-tribromo-4-methoxy-benzoic acids have been prepared [4]. Their mercuric salts are readily prepared from mercuric acetate and the carboxylic acids in boiling methanol or aqueous methanol, and were obtained analytically pure except for the 2,3,5-tribromo-4-methoxybenzoate which contained a small amount of the decarboxylation product, bis(2,3,5-tribromo-4-methoxyphenyl)mercury.

On heating mercuric 3-bromo-4-methoxybenzoate under vacuum (190 °C, 6 h or 220 °C, 40 min), 3-bromo-4-methoxybenzoic acid was slowly evolved and an involatile mercuration product was obtained. Bromodemercuration of the latter with tribromide ions gave a mixture of 2,5-dibromo- and 3,5-dibromo-4-methoxybenzoic acids (4:1) (and a trace of 2,3,5-tribromo-4-methoxybenzoic acid). This is indicative of predominant *ortho* mercuration and some *meta* mercuration on thermal decomposition (reaction (1), R = 3-Br-4-$MeOC_6H_3$).



(1)

Similarly, mercuric 3,5-dibromo-4-methoxybenzoate at 225 °C for 4 h under vacuum gave 3,5-dibromo-4-methoxybenzoic acid and 2-mercurio-3,5-dibromo-4-methoxybenzoate (reaction (2), R = 3,5-Br_2-4-$MeOC_6H_2$).



(2)

The identity of the latter was established by formation of 2,3,5-tribromo-4-methoxybenzoic acid on bromodemercuration. Blank reactions established that 3-bromo-4-methoxy-, 2,5-dibromo-4-methoxy- and 3,5-dibromo-4-methoxy-benzoic acids are not significantly brominated under the bromodemercuration conditions.

By contrast with these examples of mercuration (predominantly *ortho* in the case of reaction (1)), heating mercuric 2,5-dibromo-4-methoxy-benzoate under vacuum (220 °C, 1 h) resulted in smooth decarboxylation, and gave bis(2,5-dibromo-4-methoxyphenyl)mercury as a sublimate in near quantitative yield (reaction (3), R = 2,5-Br_2-4-$MeOC_6H_2$).

$$Hg(O_2CR)_2 \longrightarrow R_2Hg + 2CO_2 \quad (3)$$

Crystallization from toluene/petroleum ether gave analytically pure crystals, m.p. 290 °C. Identification was supported by a parent ion in the mass spectrum and by the ^1H NMR spectrum (in $(CD_3)_2SO$): 3.85, s, 6H, OMe; 7.30, s, with satellites $^4J_{Hg,H3}$ 36Hz, 2H, H3; 7.76, s, with satellites $^3J_{Hg,H6}$ 116Hz, 2H, H6. The coupling constants are characteristic of those expected for mercury coupled to the *meta* and *ortho* protons, respectively, of a diarylmercurial [5, 6]. Bromodemercuration gave 2,4,5-tribromoanisole as the sole product.

The surprising nature of reaction (3) was further illustrated when decomposition of mercuric 2,3,5-tribromo-4-methoxybenzoate under vacuum (at 200

*Drawn as polymers rather than in the cyclic anhydride form because of the preference of mercury for linear two coordination.

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°C, 20 min or 180 °C, 3 h) gave some 2,3,5-tribromo-4-methoxybenzoic acid and a mixture of decarboxylation and mercuration products. These were shown by cleavage with tribromide and triiodide ions and hydrogen bromide to contain bis(2,3,5-tribromo-4-methoxyphenyl)mercury, 6-mercurated-2,3,5-tribromo-4-methoxybenzoate groups and 2,3,6-tribromo-4,5-dimercurioanisole.

At this stage, a mechanistic rationalization for reaction (3) cannot be given. The failure of the 2,3,5-tribromo-4-methoxybenzoate to undergo decarboxylation regiospecifically [by contrast with (3)] rules out an S_Ei mechanism where the transition state has some carbanionic character, as this is promoted by increasing the number of inductively electron-withdrawing substituents [1]. Although multiple methoxy substituents in the organic group can promote facile decarboxylation by a different mechanism, classical electrophilic aromatic ipso-substitution [7, 8], it is apparent that one methoxy group cannot have this effect (reactions (1) and (2), see also pyrolysis of mercuric 4-methoxybenzoate [8, 9]). Radical decarboxylation, well known as a route to monoorganomercurials [*cf.* reaction (3)] by irradiation or peroxide induced decomposition of mercuric carboxylates in organic solvents [1], cannot be conclusively ruled out but is perhaps inconsistent with the very clean nature of reaction (3) and with substituent effects normally observed for radical decarboxylation of mercuric arenecarboxylates [10].

Acknowledgement

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