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Preliminary communication

VERY FACILE DECARBOXYLATION SYNTHESSES OF POLYMETHOXY-
 PHENYLMERCURY COMPOUNDS

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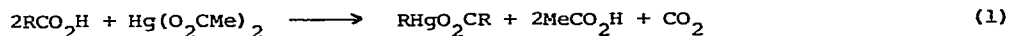
Summary

The mercurials RHgO_2CR [$\text{R} = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$, $2,3,4\text{-(MeO)}_3\text{C}_6\text{H}_2$, or $2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_2$], RHgO_2CMe and R_2Hg [$\text{R} = 2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_2$] have been obtained in good yield from decarboxylation reactions between mercuric acetate and the corresponding polymethoxybenzoic acids in aqueous methanol at room temperature.

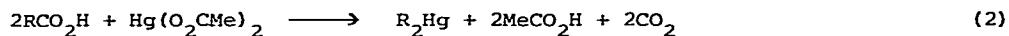
The formation of organomercurials from mercuric carboxylates (or mercuric salts and carboxylic acids) by decarboxylation reactions requires either heating or radical initiation (by peroxides, U.V. irradiation, or anodic oxidation) [1-4]. We now report that some polymethoxyphenylmercurials can be prepared by reaction between mercuric acetate and the appropriate polymethoxybenzoic acids at room temperature. This behaviour is surprising since non-initiated decarboxylation (*ipso* mercuration) is normally facilitated by electron withdrawing substituents [5,6]. In addition, these substituents suppress competition from mercuration [1,6], which, by contrast, should be favoured by the methoxy groups of the present substrates. The synthesis of organometallics by decarboxylation at room temperature without radical initiation is unusual and hitherto has been restricted to compounds with electron-withdrawing organic groups, e.g. formation of $\text{trans-RhC}_6\text{F}_5(\text{CO})(\text{PPh}_3)_2$ [7] and $(\text{CF}_3)_2\text{CHAg}$ [8] from corresponding carboxylates on dissolution in pyridine.

Reaction of mercuric acetate with 2,6-dimethoxy-, 2,3,4-trimethoxy- or 2,4,6-trimethoxy-benzoic acid (mole ratio 1:2) in aqueous methanol at room temperature did not result in precipitation of the corresponding mercuric carboxylate (the normal

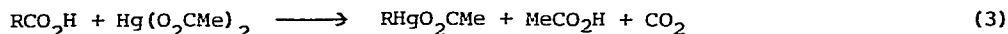
outcome of similar reactions, e.g. [6]), but carbon dioxide was evolved and the polymethoxyphenylmercuric polymethoxybenzoate was deposited [eq. (1): R = 2,6-(MeO)₂C₆H₃, 2,3,4- or 2,4,6-(MeO)₃C₆H₂].



Yields of 55-90% were obtained after reaction times of 15-90 minutes. An increase in reaction time from 15 min to 120 min for R = 2,4,6-(MeO)₃C₆H₂ resulted in formation of bis(2,4,6-trimethoxyphenyl)mercury in high yield.



Use of a 1:1 reaction stoichiometry for R = 2,4,6-(MeO)₃C₆H₂ resulted in precipitation of 2,4,6-trimethoxyphenylmercuric acetate,



but a mixture of RHgO₂CMe and RHgO₂CR derivatives was obtained when R = 2,3,4-(MeO)₃C₆H₂ and only the RHgO₂CR species when R = 2,6-(MeO)₂C₆H₃.

All products were identified by microanalysis and by ¹H n.m.r. spectra, which showed mercury-proton coupling of appropriate magnitude [9] for the number of organic groups directly bound to mercury and two different polymethoxyphenyl groups in the case of RHgO₂CR derivatives. These compounds gave R₂Hg⁺ as the highest mass ions in their mass spectra, but the presence of the carboxyl group was clearly evident from broad ν_{asym} (CO₂) absorption at ca. 1600 cm⁻¹ in their infrared spectra. Parent ions were observed for R₂Hg and RHgO₂CMe [R = 2,4,6-(MeO)₃C₆H₂]. Identification of RHgO₂CR derivatives was further confirmed by conversion into the corresponding polymethoxyphenylmercuric chlorides on treatment with aqueous sodium chloride [R = 2,3,4- or 2,4,6-(MeO)₃C₆H₂] or hydrochloric acid [R = 2,6-(MeO)₂C₆H₃]. In the latter case, a high yield of 2,6-dimethoxybenzoic acid was also obtained. The organomercuric chlorides were identified by microanalysis, parent ions in their mass spectra, ¹H n.m.r. spectroscopy, and ν(Hg-Cl) absorption at 340-315 cm⁻¹ in their far infrared spectra.

Other polymethoxybenzoic acids examined at this stage do not undergo specific decarboxylation with mercuric acetate at room temperature. Thus 2,3-dimethoxybenzoic acid gave the mercuric carboxylate (as does 4-methoxybenzoic acid [10]), whilst there was no reaction with 3,4-dimethoxy- and 3,4,5-trimethoxybenzoic acids.

Similar yields of 2,6-dimethoxyphenylmercuric 2,6-dimethoxybenzoate were obtained in the light or dark, and under nitrogen, oxygen, or a mixture of nitric oxide and nitrogen, hence free radical decarboxylation can be ruled out. The substituent effects suggest that carbon dioxide elimination occurs by classical electrophilic aromatic substitution, a mechanism rarely encountered in

decarboxylation syntheses of organometallics. (It has been proposed for decarboxylation during mercuriation of monomethoxybenzoic acids in molten mercuric trifluoroacetate [10]). Thermal decarboxylations usually proceed by electrophilic attack of the metal on a carbon atom which develops considerable carbanionic character in the transition state, as indicated by the effect of electron withdrawing groups on the reactions [5-7]. In the present reactions, it is of particular interest that the strong electron donating substituents lead to specific *ipso* attack with no competition from mercuriation [eq. (1) - (3)].

Acknowledgement:

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