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Orthomanganated arenes in synthesis

III *. Transmetallation of orthomanganated aryl ketones by mercuric chloride; synthesis of *ortho*-acyl-substituted aryl-mercury(II) compounds

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Abstract

Mercuric chloride reacts with orthomanganated aryl ketones or esters in refluxing methanol to give the corresponding arylmercury(II) chloride in good yields, with the mercury specifically *ortho* to the ketone function. Thus the manganated acetophenone $2\text{-}CH_3C(\overline{O)C_6H_4Mn}(CO)_4$ gives $2\text{-}CH_3C(O)C_6H_4HgCl$. Similarly prepared from the corresponding ketones were 2-acetyl-5-methoxyphenylmercury(II) chloride, 2-benzoylphenylmercury(II) chloride and 2-acetyl-3-thienylmercury(II) chloride. The 2-carbomethoxy-4,5,6-trimethoxyphenylmercury(II) chloride was also obtained in good yield from the orthomanganated aryl ester. X-ray crystallographic determination of the structure of $2\text{-}CH_3C(O)C_6H_4HgCl$ shows only a very weak interaction between the mercury atom and the acyl oxygen atom.

Introduction

Arylmercury(II) reagents find wide application in organic syntheses because they are easily handled and enter into a wide range of specific reactions [1–3]. The two common routes to arylmercury species are direct mercuration of arenes, and coupling of aryllithium or aryl-Grignard reagents with mercury(II) salts. However these methods do not have unlimited applications. For example, the direct reaction is often not site specific towards substituted arenes and gives mixtures of isomers (or an unwanted isomer) [1], while the alternative cannot be used where there are functional groups on the arene that react with RLi or RMgX. Aryl ketones such as

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* For Part II, see ref. 14.

acetophenone provide a clear illustration of these problems; direct mercuration occurs at the CH_3 group rather than at the aryl ring [4], while the C=O function precludes the alternative approach. For these reasons, in a recent survey of organomercury compounds mercurated aryl ketones are conspicuous by their rarity [1].

We now wish to report a high-yield method for introducing mercury specifically *ortho* to ketone or ester functions by transmetallation of the readily available orthomanganated precursors. The X-ray crystal structure of a typical product 2-acetylphenylmercury(II) chloride (**4**), is also presented.

Experimental

Reactions were performed under a nitrogen atmosphere using standard Schlenk techniques, but subsequent work-up and handling of the mercury derivatives involved no special precautions. NMR spectra were obtained in deuterated acetone solution using a JEOL FX90Q spectrometer, and mass spectra with a Varian CH5 machine. Microanalyses were carried out by the University of Otago microanalytical service. Aryl ketones were commercial samples (Aldrich). Literature procedures were used to synthesise $2\text{-}CH_3C(\overline{O)C_6H_4Mn}(CO)_4$ [5], and $Ph\overline{N{=}NC_6H_4Mn}(CO)_4$ [6] while other orthomanganated ketones and the related ester (**7**) were prepared analogously in good yields using $PhCH_2Mn(CO)_5$ [7].

Preparation of 2-acetylphenylmercury(II) chloride (4). The orthomanganated ketone (**1**) (0.586 g, 2.04 mmol) and $HgCl_2$ (0.554 g, 2.04 mmol) were refluxed for 3 h in methanol (15 ml). After cooling, the white precipitate was collected by filtration, washed with cold methanol, and air-dried to give $2\text{-}CH_3C(O)C_6H_4HgCl$ (**4**) (0.347 g, 48%, m.p. 214.5–216 °C). Found: C, 27.20; H, 2.16%; $M(P^+)$ 356. C_8H_7ClHgO calcd.: C, 27.05; H, 1.99%; $M = 356$. ^1H NMR: δ 7.5–8.4 m, 4H, C_6H_4; 2.86 s, 3H, CH_3.

Preparation of 2-acetyl-5-methoxyphenylmercury(II) chloride (5). This was prepared in a directly analogous manner from **2** in 76% yield on a 0.7 mmol scale, m.p. 223–224 °C. Found: C, 29.86; H, 3.31%; $M(P^+)$386. $C_9H_9ClHgO_2$ calcd.: C, 28.06; H. 2.35%; $M = 386$. ^1H NMR: δ 7.78 d J 8.6 Hz, 1H, H(3); 7.57 d J 2.4 Hz, 1H, H(5); 6.66 dd J 8.6, 2.4 Hz, 1H, H(4); 3.95 s, 3H, OCH_3; 2.53 s, 3H, $C(O)CH_3$.

Preparation of 2-benzoylphenylmercury(II) chloride (6). Similary **3** reacted with $HgCl_2$ in refluxing methanol over 1.5 h to give **6** in 60% yield, m.p. 176–177.5 °C. Found: C, 38.43; H, 2.60. $C_{13}H_9ClHgO$ calcd.: C, 37.42; H, 2.17%. ^1H NMR: δ 7.45–8.02 m.

Preparation of 2-carbomethoxy-4,5,6-trimethoxyphenylmercury(II) chloride (8). The ester **7** (0.509 g, 1.3 mmol) and $HgCl_2$ (1.3 mmol) were refluxed in methanol for 1h. The product was collected by filtering, washed with cold methanol and dried to give **8** 0.539 g, 90%, m.p. 190–194 °C. Found: C, 28.54; H, 2.91. $C_{11}H_{13}ClHgO_5$ calcd.: C, 28.64; H, 2.84%. ^1H NMR: δ 7.72 s, 1H, H(3); 4.06 s, 9H, OCH_3; 2.94 s, 3H, ester CH_3.

Preparation of 2-acetylthienylmercury(II) chloride (10). The reaction of $2\text{-}CH_3C(\overline{O)C_4H_2S\text{-}3\text{-}Mn}(CO)_4$ (**9**) (0.398 g, 1.36 mmol) with $HgCl_2$ in refluxing MeOH (15 ml) for 2.5 h gave **10**, 76%, m.p. 204.5–206 °C. Found: C, 20.16; H, 1.53%, $M(P^+)$ 362. $C_6H_5ClHgOS$ calcd.: C, 19.95; H, 1.40%, $M = 362$. ^1H NMR: δ 8.14 d J 4.7 Hz, 1H, H(5); 7.55 d J 4.7 Hz, 1H, H(4); 2.74 s, 3H, CH_3.

Preparation of 2-phenylazophenylmercury(II) chloride. $HgCl_2$ (0.255 g, 0.94 mmol) and $PhN{=}NCC_6H_4Mn(CO)_4$ (0.321 g, 0.92 mmol) were refluxed in methanol for 3 h. Filtration yielded some product (0.046 g). After evaporation of the filtrate, chromatography of the residue on silica (1/9 ether/petroleum spirit) gave unchanged orthomanganated azobenzene (0.077 g, 24%) and further product. Combined yield of $2\text{-}PhN{=}NC_6H_4HgCl$ was 0.248 g, 65%, as light-orange crystals, m.p. 200–202° C (lit. [8] 200–202°, 202–204° C). Longer reaction times (12 h) resulted in consumption of all the starting material but gave lower overall yields.

X-ray structure of $2\text{-}CH_3C(O)C_6H_4HgCl$ *(4)*

Needle-shaped crystals were obtained from chloroform. Preliminary precession photography showed orthorhombic symmetry. Intensity data were obtained on a Nicolet XRD P3 diffractometer using monochromated Mo-K_α X-rays.

Table 1

Final positional parameters for $CH_3C(O)C_6H_4HgCl$

Atom	*x*	*y*	*z*
Hg	0.9955(1)	0.1462(1)	0.0820(1)
Cl	1.0111(7)	0.3620(3)	0.0507(2)
C(1)	1.008(3)	−0.045(1)	0.1127(8)
C(2)	1.180(2)	−0.124(1)	0.0711(8)
C(3)	1.186(3)	−0.255(1)	0.0864(9)
C(4)	1.011(3)	−0.305(1)	0.1467(9)
C(5)	0.826(3)	−0.229(1)	0.1854(9)
C(6)	0.827(3)	−0.098(1)	0.1666(8)
C(7)	0.625(3)	−0.018(1)	0.211(1)
C(8)	0.459(3)	−0.072(1)	0.286(1)
O(1)	0.600(2)	0.092(1)	0.1907(7)

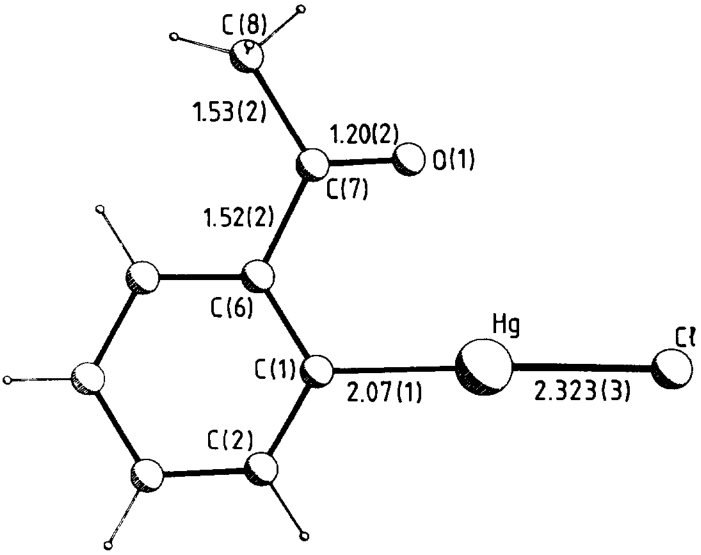

Fig. 1. The structure of $CH_3C(O)C_6H_4HgCl$ showing main bond lengths. All aromatic C–C bonds 1.39 ± 0.02 Å, Hg...O 2.712(10). Bond angle C(1)–Hg–Cl 175.9(4)°, all other bond angles 120 ± 3°.

Crystal data: C_8H_7ClHgO, M 355.10, orthorhombic, space group $P2_12_12_1$, a 5.346(1), b 10.543(3), c 14.743(2) Å, U 831.0 Å^3. D_c 2.84 g cm^{-1} for $Z = 4$. $F(000)$ 640, $\mu(\text{Mo-}K_\alpha)$ 187 cm^{-1}, T −150 °C. Intensity data in the range $5° < 2\theta < 55°$ were collected using a θ–2θ scan technique. Absorption corrections were applied based on a series of azimuthal scans. A total of 1140 unique reflexions were collected and those 1023 for which $I > 2\sigma(I)$ were used in all calculations.

The position of the mercury atom was located by Patterson methods, and all other non-hydrogen atoms were found routinely in subsequent difference maps. In the final cycles of full-matrix least-squares refinement the mercury and chlorine atoms were assigned anisotropic temperature factors, other atoms were treated isotropically, and hydrogen atoms were included in their calculated positions. The refinement converged at $R = 0.044$, $R_w = 0.053$ where $w = [\sigma^2(F) + 0.008F^2]^{-1}$. Refinement with inverted coordinates gave $R = 0.046$, $R_w = 0.055$, which suggests that the original solution represents the true absolute configuration. Calculations were performed using SHELX-76 [9]. The final positional parameters are given in Table 1, while bond length and angle data are given in Fig. 1, which illustrates the structure.

Results and discussion

The manganese tetracarbonyl group is readily displaced from various orthomanganated phenyl ketones **1**–**3** by treatment with $HgCl_2$ to give the corresponding phenylmercury(II) chlorides **4**–**6** (Scheme 1). The reaction is not restricted to benzenoid aromatics since the analogous mercurated acetylthiophene **10** is generated similarly. The orthomanganated ester **7** also reacts with $HgCl_2$ to give the corresponding 2-carbomethoxy-4,5,6-trimethoxyphenylmercury(II) chloride (**8**). Methanol is the solvent of choice for these reactions since the products are generally insoluble and precipitate out from the otherwise homogeneous solution as the reaction proceeds, making work-up particularly straightforward. Transmetallation is site-specific, with no trace of other isomers being detected and yields range from good to excellent.

For reasons discussed in the Introduction, arylmercury reagents incorporating ketone functions are rare and all the examples reported above are, to the best of our knowledge, new compounds *. They are white, crystalline, air-stable species and were readily characterised by microanalysis and by NMR and mass spectroscopy (see Experimental).

Our main interest is in O-donor ligands but to test the generality of the reaction we have briefly examined the reaction of orthomanganated azobenzene [6] with mercuric chloride. Again displacement of the manganese was observed for $Ph\overline{N{=}NC_6H_4}Mn(CO)_4$ to give the corresponding orthomercurated azobenzene in 65% yield but the reaction was noticeably more sluggish than that for the O-donor substrates. The mercurated azobenzene can be prepared directly in moderate yields with reasonable isomeric purity [8] so the route reported here offers no real advantage.

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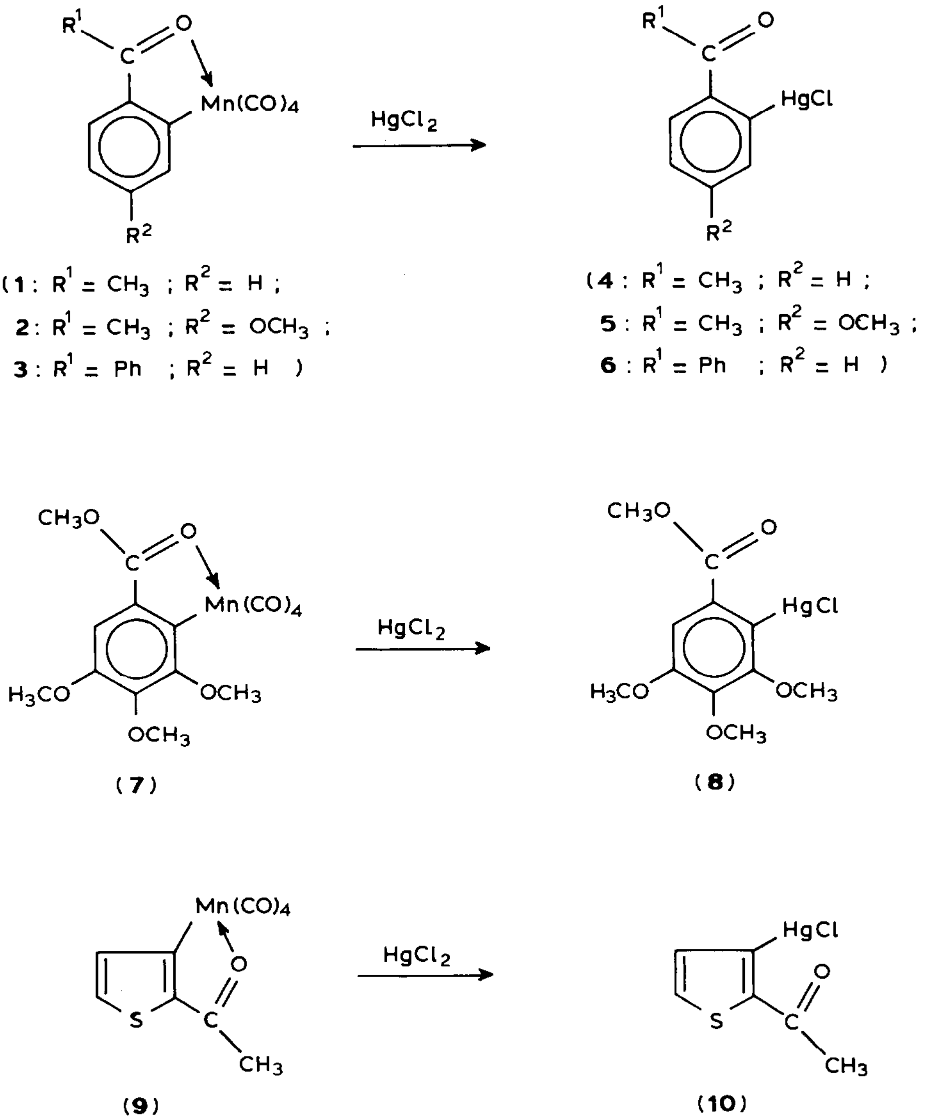
* A brief report suggests direct mercuration of benzophenone gives mixtures of isomers [10] while 2-substituted thiophenes mercurate preferentially at the 5-position [1].



(1 : $R^1 = CH_3$; $R^2 = H$;
2 : $R^1 = CH_3$; $R^2 = OCH_3$;
3 : $R^1 = Ph$; $R^2 = H$)

(4 : $R^1 = CH_3$; $R^2 = H$;
5 : $R^1 = CH_3$; $R^2 = OCH_3$;
6 : $R^1 = Ph$; $R^2 = H$)

(7)

(8)

(9)

(10)

Scheme 1

Cleavage of transition metal–carbon bonds by mercuric salts is well known [1–3,11] but previous studies have often been more concerned with the mechanisms of such reactions rather than with their use in synthesis. In fact the reverse, the alkylation of transition metals (including manganese [12]) by organomercury compounds has been more widely used in preparations. An extensive range of aryl ketones can be orthometallated in high yields under mild conditions by $PhCH_2Mn(CO)_5$ [5,7], and since the transmetallation with mercury(II) seems to be generally applicable, mercurated arylketones can now be regarded as being routinely available. The expense of manganese carbonyl will be a disadvantage but it is a necessary reagent since cheaper metal carbonyl compounds (such as $PhCH_2Co(CO)_4$ or $PhCH_2Fe(CO)_2(\eta\text{-}C_5H_5)$) cannot orthometallate aryl ketones [7].

Although the NMR data strongly indicated that the mercurated products had the mercury *ortho* to the carbonyl group, the X-ray structure of one example, **4**, was determined to prove this unambigously. The degree of intramolecular O...Hg interaction was also of interest.

The structure is illustrated in Fig. 1, and confirms that it is the *ortho* isomer that is formed. The crystal contains individual molecules, with the shortest intermolecular Hg...Cl and Hg...O distances being 3.25 and 3.65 Å, respectively. The molecule is essentially planar although the acetyl group is slightly twisted so that the oxygen atom is 0.17 Å above the mean plane and C(8) is 0.16 Å below it. The acetyl group has adopted an orientation in which the oxygen atom is directed towards the mercury atom with a Hg...O distance of 2.71 Å. This is well within the sum of the Van der Waal's radii (ca. 2.9–3.1 Å) although longer than an Hg–O covalent bond (2.01–2.16 Å) [2]. Such distances indicate secondary coordination [2], but the interaction in the present example must be weak since the Cl–Hg–C(1) angle is only 4° from linear, and the C=O bond length does not differ from that in free acetophenone [13]. There does not appear to be any previous X-ray structural determination of a phenylmercury(II) chloride for comparison (from the Cambridge Crystallographic Data Centre File, January 1987), but the Hg–C(1) and Hg–Cl distances are in the range expected [2,3].

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