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Preliminary communication

ORGANOMERCURY DERIVATIVES OF DIBENZOYLMETHANE

R.J. BERTINO and G.B. DEACON
Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia)
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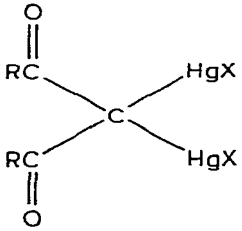
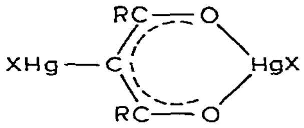
Summary

From reaction of dibenzoylmethane or its monosodium salt with suitable monoorganomercurials or mercuric acetate, the dimercurated complexes $XHgC(COPh)_2HgX$ ($X = C_6F_5, p\text{-}HC_6F_4$, Ph, or $MeCO_2$) and the adducts $HC(COPh)(COHPh)\cdot 2C_6F_5HgY$ (Y = Cl or Br) have been prepared. In the complexes, dibenzoylmethane is chelated through oxygen to one mercury atom and is carbon-bonded to the other, whilst in the adducts the enolic form of dibenzoylmethane is possibly weakly coordinated to two mercury atoms..

There have been a number of studies of the reactions of β-diketones with mercuric salts [1-6], but only one study of interactions with organomercury derivatives [7]. Mercuration of dibenzoylmethane with arylmercuric hydroxides was reported to give I (R = Ph; X = Ph or $p\text{-}Me_2NC_6H_4$), the structural proposal being based solely on reactions of the compounds. As part of a detailed study of organomercury complexes of β-diketones, we now report that dimercurated derivatives of dibenzoylmethane, including the known [7] phenylmercuri derivative, have the novel structure II and not I. Adducts of dibenzoylmethane, $HC(COPh)(COHPh)\cdot 2C_6F_5HgY$ (Y = Cl or Br), have also been prepared.



(I)



(II)

The complexes, $XHgC(COPh)_2HgX$ ($X = C_6F_5$ or p-HC_6F_4)*, were precipitated on reaction of the monosodium salt of dibenzoylmethane with the appropriate polyfluorophenylmercuric chlorides in methanol, and the corresponding acetatomercuri complex ($X = MeCO_2$) was obtained by mercuration of dibenzoylmethane with mercuric acetate.

$$Na[HC(COPh)_2] + 2XHgCl \longrightarrow XHgC(COPh)_2HgX + NaCl + HCl$$
$$HC(COPh)(COHPh) + 2HgX_2 \longrightarrow XHgC(COPh)_2HgX + 2HX$$

Carbon—oxygen stretching frequencies of these complexes and the known $PhHgC(COPh)_2HgPh$ (Table 1) are as expected [8] for chelated dibenzoylmethane, indicative of structure II ($X = C_6F_5$, p-HC_6F_4, Ph, or $MeCO_2$), and are well below free carbonyl frequencies of substituted dibenzoylmethanes with the diketone structure (Table 1), thereby excluding I. The possibility that the complexes have structure I and that the ν(CO) frequencies are lowered to the values of Table 1 due to intermolecular carbonyl—mercury interactions can be ruled out, since available evidence shows such interactions are weak. For example, crystal structures of bis(dipivaloylmethyl)mercury [1] and dipivaloylmethylmercuric acetate [3] show only very weak intermolecular carbonyl—mercury bonds, and the compounds have ketonic carbonyl frequencies.

TABLE 1

CARBON—OXYGEN STRETCHING FREQUENCIES FOR DERIVATIVES OF DIBENZOYLMETHANE

X	Y	ν(CO)
$XHgC(COPh)_2HgX$		
C_6F_5		1553s
p-HC_6F_4		1549s (br)
Ph		1545s (br)
$MeCO_2$		1568s
$XYC(COPh)_2$		
Me	H	1684, 1661vs (br
$MeCO_2Hg$ [a]	Me	1660s, 1635s

[a] Prepared by the reaction of the sodium salt of dibenzoylmethylmethane with mercuric acetate in methanol.

Crystallization from a solution containing equimolar amounts of dibenzoylmethane and pentafluorophenylmercuric chloride or bromide in hexane yields the adducts, $HC(COPh)(COHPh)\cdot 2C_6F_5HgY$ ($Y = Cl$ or Br). X-ray powder photography showed that the solid adducts were not mixtures of the reactants, though complete dissociation occurs in solution. Infrared data are consistent with a structure in which the enolic form of dibenzoylmethane is very weakly coordinated to two mercury atoms.

Acknowledgement

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*All new compounds were obtained analytically pure.

References

1 R. Allmann, K. Flatau and H. Musso, Chem. Ber., 105 (1972) 3067.
2 F. Bonati and G. Minghetti, J. Organometal. Chem., 22 (1970) 5.
3 R.H. Fish, R.E. Lundin and W.F. Haddon, Tetrahedron Letters, (1972) 921; R. Allmann and H. Musso, Chem. Ber., 106 (1973) 3001.
4 G.S. Hammond, D.C. Nonhebel and C.S. Wu, Inorg. Chem., 2 (1963) 73; D.C. Nonhebel, J. Chem. Soc., (1963) 738.
5 G.B. Marini-Bettoli and L. Paolini, Gazz. Chim. Ital., 75 (1945) 78; L. Paolini, Gazz. Chim. Ital., 89 (1959) 2171.
6 G.T. Morgan and H.W. Moss, J. Chem. Soc., 105 (1914) 189; M. Hassanein and I.F. Hewaidy, Z. Anorg. Allgem. Chem., 373 (1970) 80.
7 A.N. Nesmeyanov and D.N. Kratsov, Bull. Acad. Sci. USSR, (1962) 398.
8 R.D. Hancock and D.A. Thornton, Inorg. Nucl. Chem. Lett., 3 (1967) 423; J. Molec. Struct., 4 (1969) 377.