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V *. MERCURY(II) DERIVATIVES OF DIETHYL MALONATE, ETHYL ACETOACETATE, ETHYL CYANOACETATE, AND MALONONITRILE

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Summary

Mercury(II) oxide reacts with diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate, but not with malononitrile to give the mercury—carbon bonded derivatives $Hg[CH(COOEt)R]_2$ (R = COOEt, COMe and CN, respectively). Mercury(II) bromide and mercury(II) acetate, as well as mercury(II) chloride, react with diethyl malonate, ethyl acetoacetate, and acetylacetone to yield the *gem*-disubstituted species $(XHg)_2C(COR^1)COR^2$ (X = Cl, Br, MeCOO; R^1, R^2 = Me, OEt): ethyl cyanoacetate and malononitrile react with the chloride and acetate, but not the bromide, of mercury(II), to yield the *gem*-disubstituted species $(XHg)_2C(CN)R$ (X = Cl, MeCOO; R = COOEt, CN).

Introduction

The reaction of mercury(II) oxide with diethyl malonate (diethyl propan-1,3-dioate) yields [1] a compound of composition $Hg[CH(COOC_2H_5)_2]_2$, but of unknown constitution. The mercury(II) derivatives of β-diketones have been shown to exist, both in the solid state [2—5] and in solution [6] in the Hg—C form rather than in the chelated Hg—O form, analogous to the β-diketone complexes of most other metals. By contrast, no mercury(II) derivatives whatever have been reported of the related ligands malononitrile (dicyanomethane), ethyl cyanoacetate, or ethyl acetoacetate (ethyl 3-ketobutanoate). This paper describes such derivatives, together with those of diethyl malonate, all of which are shown to adopt the Hg—C constitution.

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* For Part IV see ref. 14.

Results and discussion

Yellow mercury(II) oxide reacts with diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate, but not with malononitrile, to yield products of composition $Hg[CH(COOEt)R]_2$ (R = COOEt, COMe and CN): this reaction is analogous to the preparation [7] of $Hg[CH(COMe)_2]_2$ described by Hassanein and Hewaidy.

Bonati and Minghetti observed [8] that acetylacetone (pentan-2,4-dione) reacted with aqueous mercury(II) chloride to give the bis(chloromercury) species $(ClHg)_2C(COMe)_2$ [5] but reported that no such reactions occurred with mercury(II) bromide, cyanide, or acetate. This is not wholly correct: although $Hg(CN)_2$ and HgI_2 show no reaction with any of the ligands here considered, $HgBr_2$ and $Hg(OCOMe)_2$ both react like $HgCl_2$ with $CH_2(COR^1)COR^2$ (R^1, R^2 = Me, OEt) to yield $(XHg)_2C(COR^1)COR^2$ (X = Cl, Br, $OCOCH_3$); similarly the ligands RCH_2CN (R = EtOCO, CN) both react with $HgCl_2$ and $Hg(OCOMe)_2$, but not with $HgBr_2$, to yield $(XHg)_2C(CN)R$ (X = Cl, OCOMe).

NMR spectra

In the proton spectra of $Hg[CH(COOEt)R]_2$ (R = COOEt, COMe and CN) the resonances assignable to the central CH proton (at 3.65, 4.07, and 3.97 ppm, respectively) all exhibit satellites due to $^2J(^1\underline{H}C^{199}\underline{Hg})$, indicative of the Hg—C bonded constitution (Table 1): in addition, $Hg[CH(COOEt)_2]_2$ was sufficiently soluble for the observation in its ^{13}C NMR spectrum of ^{199}Hg satellites with $^1J(^{13}\underline{C}^{199}\underline{Hg})$ of 917 Hz. It may be noted that these ^{199}Hg satellites were observed in the proton spectra at 35°C, whereas those in $Hg[CH(COCMe_3)_2]_2$ were observed only at −40°C [6], indicating a much faster rate of ligand exchange in this compound.

None of the $(XHg)_2CR^1R^2$ species is very soluble in any solvent, but all the chloro and acetato complexes were sufficiently soluble in acetone-d_6 for ^1H NMR investigation: none showed any resonance assignable to the central CH_x unit, indicative of geminal disubstitution on the central carbon, as found in the solid state for $(ClHg)_2C(COMe)_2$ [5]. The poor solubility, coupled with the rather low thermal stability in solution, has precluded the recording of ^{13}C NMR spectra for any of these species except $(ClHg)_2C(COOEt)CN$: the rate of data

TABLE 1

NMR DATA

Compound	$\delta(\underline{C}Hg)$ [a]	$\delta(\underline{H}CHg)$ [a]	$^1J(^{13}\underline{C}^{199}\underline{Hg})$/Hz	$^2J(^1\underline{H}C^{199}\underline{Hg})$/Hz
$Hg[CH(COOEt)_2]_2$ [b]	53.5	3.65	917	226
$Hg[CH(COMe)COOEt]_2$	n.o.	4.07	n.o.	234
$Hg[CH(COOEt)CN]_2$	n.o.	3.97	n.o.	216
$Hg[CH(COCMe_3)_2]_2$ [c]	n.o.	4.86	n.o.	221
$(ClHg)_2C(COOEt)CN$ [d]	31.4	—	852	—

[a] Chemical shifts in ppm from Me_4Si. [b] Other ^{13}C shifts: $\delta(CH_3)$, 14.3; $\delta(\underline{C}H_2)$, 60.5; $\delta(\underline{C}O)$, 169.9 ppm. [c] Recorded at −40°C [6]. [d] Other ^{13}C shifts: $\delta(\underline{C}H_3)$, 14.2; $\delta(\underline{C}H_2)$, 62.3; $\delta(\underline{C}N)$, 121.6; $\delta(\underline{C}O)$ 167.7 ppm.

acquisition is generally inadequate in comparison with the rate of sample decomposition. In the ^{13}C spectrum of $(ClHg)_2C(COOEt)CN$, the central carbon resonance (δ, 31.4 ppm) exhibits a triplet satellite having $^1J(^{13}\underline{C}^{199}\underline{Hg})$ of 852 Hz, indicative of direct Hg—C bonds.

Infrared spectra

Oxygen-bonded chelated β-diketones almost invariably exhibit [9,10] two or three bands in the range 1500—1600 cm^{-1}, but none in the range 1600—1800 cm^{-1}: in contrast, we observe that $Hg[CH(COMe)_2]_2$ exhibits bands assignable to ν(CO) at 1694 and 1640 cm^{-1}, but no bands in the range 1500—1600 cm^{-1}. Consequently the frequencies of the carbonyl bands can be used as a diagnostic of constitution: in Table 2 are listed the observed ν(CO) frequencies. In compounds of the type $Hg[CHR^1R^2]_2^2$, $(ClHg)_2CR^1R^2$ and $(BrHg)CR^1R^2$ (R^1, R^2 = CN, COOEt, COMe), there is no absorption in the region characteristic of chelated β-diketo ligands, 1500—1600 cm^{-1}: only in certain of the acetato complexes do bands appear below 1600 cm^{-1}. Similarly in all complexes of $CH_2(CN)_2$ and $NCCH_2COOEt$, ν(CN) appears at ca. 2200 cm^{-1}, typical of an uncomplexed cyano group [11,12], The infrared spectra demonstrate that, with the possible exception of $(MeCOOHg)_2C(COOEt)CN$, all mercury(II) complexes of type $(XHg)_2CR^1R^2$ adopt Hg—C bonded constitutions.

Mass spectra

The mass spectrum of each of the mercurials $Hg[CHR^1R^2]_2$ contains a molecular ion. Of the $(XHg)_2CR^1R^2$ species only $(ClHg)_2C(COOEt)_2$, $(BrHg)_2C(COOEt)_2$ and $(BrHg)_2C(COMe)COOEt$ exhibit molecular ions: the mass spectrum of each of the remaining species of this type, but not of those containing molecular ions, contains the ion Hg_2^+. The rearrangement ion CH_3Hg^+ occurs in

TABLE 2

DIAGNOSTIC CARBONYL STRETCHING FREQUENCIES (cm^{-1})

Ligand, LH_2	$(LH)_2Hg$	$L(HgCl)_2$	$L(HgBr)_2$	$L(HgOCOMe)_2$	$(LH)_2Cd$
$(NC)_2CH_2$	—	[a] —	—	1586m 1570s [b]	—
$NC(EtOCO)CH_2$	1743s 1650s [c]	1706s [d]	—	1654s 1618m 1586s [e]	—
$(EtOCO)_2CH_2$	1730vs 1684vs	1730s 1716s	1729m 1714s	1688vs 1665m 1639s	—
$MeCO(EtOCO)CH_2$	1726s 1705s 1678vs	1710s 1683vs	1701m 1648vs	1679vs 1610m	1650s 1631s 1550s 1522ms
$(MeCO)_2CH_2$	1694vs 1640s	1695vs 1645s	1683s 1633m	1694s 1664s 1639vs	1618s 1559m 1515vs

[a] ν(CN) 2200 cm^{-1}. [b] ν(CN) 2208 cm^{-1}. [c] ν(CN) 2205 cm^{-1}. [d] ν(CN) 2228 cm^{-1}. [e] ν(CN) 2204 cm^{-1}.

the spectra of $(ClHg)_2C(COMe)_2$, $(MeCOOHg)_2C(COOEt)_2$ and $(MeCOOHg)_2C(COMe)_2$: none of the spectra provides evidence of constitution.

Analogous derivatives of cadmium(II)

Acetylacetone [7] and ethyl acetoacetate both react with cadmium(II) oxide to give products of composition $Cd[CH(COMe)_2]_2$, which is polymeric in the solid state [13], and $Cd[CH(COMe)COOEt]_2$, respectively: no conditions were found under which this oxide would react with diethyl malonate, ethyl cyanoacetate or malononitrile.

In the infrared spectrum of $Cd[CH(COMe)COOEt]_2$, which is insoluble in most solvents, absorptions occur at 1650(s), 1631(s), 1550(s) and 1522(ms) cm^{-1}, but with no absorption in the range 1650—1800 cm^{-1}. A carbon-bonded structure if thereby ruled out: the spectrum is consistent with either a chelated oxygen-bonded constitution, or an enolate containing an uncomplexed carbonyl group. It is possibly significant that cadmium(II) oxide did not react to form a complex with diethyl malonate or with ethyl cyanoacetate: either constitution would require the participation of a carboxyl group in enol formation. Similarly, although both mercury(II) oxide and cadmium(II) oxide react with 5,5-dimethylcyclohexan-1,3-dione (LH_2) to form derivatives $(LH)_2M$ ($M = Hg, Cd$) which are respectively carbon-bonded and enol oxygen-bonded, zinc oxide forms no such derivative as the steric properties of the ligand prevent chelation.

Experimental

Preparation of $Hg[CH(COOEt)_2]_2$. Yellow mercury(II) oxide (10 g) and diethyl malonate (10 g) were stirred together at room temperature during 1 week. The mixture was extracted with 10 × 100 cm^{-3} $CHCl_3$: the combined extracts were dried and reduced to small volume: addition of anhydrous diethyl ether precipitated the product (12.5 g, 77%). (Found: C, 32.2; H, 4.3. $C_{14}H_{22}HgO_8$ calcd.: C, 32.4; H, 4.3%.)

Preparation of $Hg[CH(COMe)COOEt]_2$. Yellow mercury(II) oxide (11 g) and ethyl acetoacetate (13 g) were stirred at room temperature during 18 h. The product was purified by repeated decantation using anhydrous petroleum ether (b.p. 40—60°C), and dried in vacuo (yield: 18.0 g, 78%). (Found: C, 30.9; H, 3.8. $C_{12}H_{18}HgO_6$ calcd.: C, 31.4; H, 3.9%.)

Preparation of $Hg[CH(COOEt)CN]_2$. Yellow mercury(II) oxide (4.4 g) and ethyl cyanoacetate (19 g) were stirred at room temperature during 60 h. After repeated decantation with petroluem ether, the product was isolated by centrifugation and dried in vacuo (yield: 7.1 g; 80%). (Found: C, 28.1; H, 2.5; N, 6.3. $C_{10}H_{10}HgN_2O_4$ calcd.: C, 28.4; H, 2.4; N, 6.6%.)

Preparation of $Hg[CH(COOCH_2)_2CMe_2]_2$. Yellow mercury(II) oxide (4.3 g) and 5,5-dimethylcyclohexan-1,3-dione (5.6 g) were stirred together at room temperature in aqueous acetone (100 cm^3) during 4 days. The white solid was washed by repeated decantation using chloroform, filtered, and dried (7.4 g, 76%). (Found: C, 39.8; H, 4.9. $C_{16}H_{22}HgO_4$ calcd.: C, 40.1; H, 4.6%); ν(CO), 1680m, 1644s cm^{-1}.

Preparation of $Cd[CH(COCH_2)_2CMe_2]_2$. Cadmium(II) oxide (2.6 g) and 5,5-dimethylcyclohexan-1,3-dione (5.6 g) were stirred together at room tempera-

TABLE 3

MICROANALYTICAL DATA FOR $(XHg)_2CR_1R_2$

X	R^1	R^2	Found (%)			Calculated (%)		
			C	H	N	C	H	N
Cl	CN	CN	6.9	0.05	5.4	6.7	0.0	5.2
Cl	CN	COOEt	10.3	0.9	2.4	10.3	0.9	2.4
Cl	COOEt	COOEt	13.0	1.7	0.0	13.3	1.6	0.0
Cl	COMe	COOEt	12.3	1.5	0.0	12.0	1.3	0.0
Cl	COMe	COMe	10.1	1.2	0.0	10.5	1.1	0.0
Br	COOEt	COOEt	11.7	1.3	0.0	11.7	1.4	0.0
Br	COMe	COOEt	10.3	1.5	0.0	10.5	1.2	0.0
Br	COMe	COMe	9.4	1.1	0.0	9.1	0.9	0.0
MeCOO	CN	CN	14.5	1.0	5.5	14.4	1.0	4.8
MeCOO	CN	COOEt	17.9	1.7	3.0	17.2	1.8	2.2
MeCOO	COOEt	COOEt	19.7	2.3	0.0	19.5	2.4	0.0
MeCOO	COMe	COOEt	18.1	2.3	0.0	18.6	2.2	0.0
MeCOO	COMe	COMe	17.8	1.9	0.0	17.5	2.0	0.0

ture in aqueous acetone (100 cm^3) during 3 days. The mixture was filtered and the residue washed with water (2 × 50 cm^3): the combined filtrate and washings were evaporated to yield a colourless oil. Addition of anhydrous ether precipitated a white solid which was collected by filtration, washed, and dried (7.1 g, 91%). (Found: C, 49.4; H, 5.7, $C_{16}H_{22}CdO_4$ calcd.: C, 49.2; H, 5.7%); ν(CO), 1690w, 1629m, 1512s cm^{-1}.

Reactions of $CH_2R^1R^2$ (R^1, R^2 = CN, COOEt, COMe) with HgX_2. (i) X = Cl, OCOMe: Equimolar quantities of $CH_2R^1R^2$ and HgX_2 were stirred overnight in aqueous solution: the product was filtered off, washed with water and dried in vacuo.

(ii) X = Br: Equimolar quantities of $CH_2R^1R^2$ and $HgBr_2$ in ethanol solutions were mixed and set aside at room temperature during 1 week. The product was filtered off, washed with water and dried.

(iii) X = I, CN: No reaction was found for X = CN in aqueous solution, or for X = I in ethanol solution.

Microanalytical data for $(XHg)_2CR^1R^2$ are in Table 3.

Preparation of $Cd[CH(COMe)COOEt]_2$. Cadmium(II) oxide (2.0 g) and ethyl acetoacetate (1.3 g) were stirred together at room temperature during 1 week. Repeated washing with petroleum ether and acetone gave the product. (Found: C, 39.1; H, 4.6. $C_{12}H_{18}CdO_8$ calcd.: C, 38.9; H, 4.9%.)

No reactions were observed between (i) CdO and $CH_2(COOEt)_2$, $NCCH_2COOEt$ or $CH_2(CN)_2$, either at room temperature or on reflux in toluene, (ii) HgO and $CH_2(CN)_2$, either at room temperature or on reflux in toluene, and (iii) $CdCl_2$ and $CH_2(COMe)_2$, $CH_2(COMe)COOEt$, $CH_2(COOEt)_2$, $NCCH_2COOEt$ or $CH_2(CN)_2$ in water at room temperature, (iv) ZnO and $CH_2(COOCH_2)_2CMe_2$ in aqueous acetone at room temperature or at reflux.

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