# PREPARATION AND SPECTRA OF MERCURIBIS ( $\alpha$ -DIAZO KETONES)<sup>1</sup>

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Abstract—Bis ( $\alpha$  - diazophenacyl) mercury (2a), bis ( $\alpha$  - diazo - 2,4,6 - trimethylphenacyl) mercury (2b), bis (1 - diazo - 3,3 - dimethyl - 2 - oxobutyl)mercury (2c), and bis (1 - diazo - 2 - phenylacetonyl) mercury (2d) have been prepared by treatment of the corresponding  $\alpha$ -diazo ketones with mercuric oxide. The solution IR, UV, and 'H NMR spectra of 2a-d and of three other mercuribis ( $\alpha$ -diazo ketones) have been compared with the spectra of the corresponding  $\alpha$ -diazo ketones. The solution the spectra of 2a-d and of three other mercuribis ( $\alpha$ -diazo ketones) have been compared with the spectra of the corresponding  $\alpha$ -diazo ketones. The ''C NMR resonance spectra of 2a and of  $\alpha$ -diazo -  $\alpha$  - methylmercuriacetophenone (9) have been examined for evidence of <sup>199</sup>Hg-C coupling; this was observed in the case of 9 for the Me carbon, but not detected in either case for the diazo carbon; this is attributed to difficulty of detection and/or ligand exchange. The signals of the diazo carbon in these spectra occur at unusually high field; a similar observation was made in the spectra of several  $\alpha$ -diazo ketones, where the chemical shifts were in the range  $\delta$  50-70.

#### INTRODUCTION

Although the mercury derivative 1 of ethyl diazoacetate has long been known<sup>2</sup> mercury derivatives of  $\alpha$ -diazo ketones of type 2 were first described by Yates and Garneau.<sup>3</sup> These were prepared by the reaction of  $\alpha$ -diazo ketones with mercuric oxide. Subsequently, other workers have reported the preparation of compounds of type 2 by this and other routes<sup>4-7</sup> and the preparation of compounds of type 3.<sup>7,8</sup> We report now the details of the original work and a further investigation of bis ( $\alpha$ diazophenacyl) mercury (2a) that was undertaken because of apparent discrepancies between the properties originally reported and those reported<sup>7</sup> for the same compound prepared by a different route.

$$Hg(CN_2CO_2Et)_2$$
  $Hg(CN_2COR)_2$  R'HgCN\_2COR

The mercury derivatives 2a-d of the  $\alpha$ -diazo ketones 4a-d were prepared in high yield by treatment of the latter in petroleum ether with excess yellow mercuric oxide at room temperature (eqn 1), and were purified by recrystallization from organic solvents (Experimental).

$$RCOCHN_{2} \longrightarrow Hg(CN_{2}COR)_{2}$$
(1)  

$$4 \qquad 2$$

$$a; R = Ph \qquad e; R = Me$$

$$b; R = 2,4,6-Me_{3}C_{6}H_{2} \qquad f; R = Et$$

$$c; R = Me_{3}C \qquad g; R = i-Pr$$

$$d; R = Ph CH_{2}$$

That no skeletal change occurs in such reactions was indicated by the observation that the mercury derivatives 2a and 2c were reconverted to their parent diazo

§The CO-stretching bands are broad and could arise from the superimposition of absorption arising from both *trans* and *cis* conformers. ketones, 4a and 4c, respectively, when treated with hydrogen sulfide in aqueous dioxane.

The IR, UV and <sup>1</sup>H NMR (PMR) spectra of compounds 2a-2d are compared in Table 1 with the spectra of the corresponding diazo ketones; also included in Table 1 for comparison are data for the closely related compounds 2e-2g reported by Dominh, Strausz and Gunning.<sup>4</sup> The solution IR spectra of the mercury derivatives resemble those of the parent diazo ketones, showing strong diazo and carbonyl-stretching bands in the 4.8-4.9 and  $6.2-6.3-\mu$ regions, respectively; in the case of each band there is a shift to longer wavelength of  $0.1-0.2 \mu$ . The shift in the position of the diazo band is analogous to that previously observed to be brought about by substitution on the  $\alpha$ -carbon of diazo compounds.<sup>9</sup> In several cases the diazo band in the spectrum of the mercury derivative shows a shoulder, while that in the spectrum of the parent diazo ketone does not. It is possible that this is due to a change in the ratio of trans (5a) and cis (5b) conformers. In the



case of several diazo ketones of type 4 it has been found that the cis conformer largely predominates;<sup>10</sup> an increase in the relative amount of the trans conformer in the mercury derivatives could result in the observation of diazo bands originating from both conformers. Such an increase could result from steric interaction between the R group and the mercury atom in the cis conformer and from coordination of the mercury with the carbonyl O atom in the *trans* conformer.<sup>11</sup> The shift of the CO-stretching bands to longer wavelength can be attributed to the electropositivity of mercury relative to hydrogen and to coordination of the type referred to above.§ One further relationship of the IR spectra of the mercury derivatives with those of the parent diazo ketones is of interest: the strong bands in the latter in the  $7.35-7.5-\mu$  region<sup>9</sup> are replaced by medium to strong bands in the 7.6-7.8- $\mu$  region.

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Table 1. Spectra of mercuribis( $\alpha$ -diazo ketones) 2a-g and their parent  $\alpha$ -diazo ketones 4a-g

	$\lambda_{max}^{CHCl_3}, \mu$		λ EtOH	nm (e)°	δ <sup>CDCI</sup> 3, ppm <sup>b</sup>		
	2	4	2	4	2	4	
a	4·80°	4.73	241 (20,900)	251 (11,200)		5-92 (1H)	
	4.84		304 (18,200)	297 (12,300)	~7.55*	7·62 (5H) <sup>4</sup>	
	6.27	6.19					
b	4.82	4.76	242 (19,500)°	240 (10,200)	2.28 (01)	2·30 (9H)	
	6.27	6.20	278 (18,600)	276 (10,200)	2.32		
						5·40(1H)	
					6·87 (2H)	6·92 (2H)	
с	4·80°	4.75	254 (11,000)	251 (8900)	1-26	1·15 (9H)	
	4.87		284 (10,500)	265 (8100)°		5-46 (1H)	
	6.29	6.14					
d	4.81	4.74	253 (11,000)	251 (10,5000)	3-66 (2H)	3-60 (2H)	
	4.84°		293 (10,500)	273 (7800)°	_	5·11 (1H)	
	6-26	6-14	•		~7·23 (5H)d	7.26 (5H)d	
e	4.81	4.76	252 (14,100)	250 (9100)	2-28	2-10 (3H)	
	4·88°		278 (15,500)	273 (9800)		5-40 (1H)	
	6-23	6.06	378 (115)	350 (23)			
f	4.88	4.75	248 (13,800)	246 (8500)	1-13 (3H)*	1-13 (3H)*	
	6-25	6.06	285 (11,500)	275 (7800)	2.55 (2H)*	2.35 (2H)*	
				352 (23)		5-30 (1H)	
gʻ	4·76°	4.74	248 (12,600)	250 (7200)	1·10 (6H)'	1·13 (6H)'	
9	4-89		272 (10,000)	272 (6200)	2.86 (1H)	2.50 (1H)	
	6-21	6.06	/	354 (27)		5-30 (1H)	

"Only high intensity maxima were recorded for a-d. <sup>b</sup> Singlets unless otherwise specified. <sup>c</sup> Shoulder. <sup>d</sup> Multiplet. <sup>c</sup> The data for e-g are from Ref. 4, except for the IR spectrum of 2e. Professor O. P. Strausz has informed us that the IR spectrum for 2e reported in Ref. 4 was recorded in a KBr matrix. <sup>c</sup> Corrected values kindly provided by Professor O. P. Strausz. \* Triplet.<sup>h</sup> Quartet. <sup>c</sup> Doublet. <sup>c</sup> Heptet.

The UV spectra of the mercury derivatives also resemble the UV spectra of the parent diazo ketones in showing two high intensity maxima in the region 240-300 nm. In general the lower wavelength maximum is little shifted;† the longer wavelength maximum also shows little change in position in some cases but in others shows small bathochromic shifts. As expected in terms of the postulated structural relationship, the molecular extinction coefficients of these maxima in the spectra of the mercuri diazo ketones are in general approximately twice those of the maxima in the diazo ketones; compounds 2c and 2d are exceptional in this respect, but the discrepancies can be attributed to overlap of the maxima in the spectra of 4c and 4d.  $\alpha$ -Diazo ketones also show weak maxima in the region 356-400 nm. This region was not investigated in the present work; however, the results of Dominh, Strausz and Gunning<sup>4</sup> demonstrate that such a maximum is also present in the spectrum of the mercury derivative 2e, showing a bathochromic shift of ca 30 nm. Analogous absorption presumably occurs in the spectra of the other mercury derivatives, but may be obscured by overlap with the tail of a high intensity band.

The PMR spectra of the mercury derivatives also closely resemble the spectra of the parent diazo ketones, except for the absence of the one-proton signals in the  $\delta$ 5-6 region of the latter spectra, arising from the diazomethyl (COCHN<sub>2</sub>) protons.

It has tacitly been assumed in the previous discussion that mercury is bonded to carbon in these diazomercurials, as depicted in 5, rather than to oxygen as in 6 or to nitrogen as in 7. This view is based on the close similarity



of the IR and UV spectra of the mercury derivatives with those of the diazo ketones themselves; it is considered that bonding of the mercury as in 6 or 7 would lead to very much greater changes in these spectra. Since all these spectra were recorded in solution, this conclusion applies only to the solution and not the solid state. It is of interest to note that Allmann *et al.*<sup>12</sup> have recently demonstrated that bis(dipivaloylmethyl)mercury (8) exists in the crystalline state with the mercury bound to the central C atom of the keto form; the molecules are associated in pairs with coordination of the mercury atom of each member of the pair with two of the dione oxygen atoms of the other member. PMR spectroscopy showed that in solution in deuterochloroform the compound exists largely as 8 with a small amount of a tautomer with an O-Hg bond.



In an attempt to obtain additional evidence regarding the bonding in the mercury derivatives of the diazo ketones, we examined the <sup>13</sup>C NMR (CMR) spectrum of **2a** (Table 2). In addition to signals in the  $\delta$  126–140 region attributable to the aromatic carbon atoms, the spectrum of **2a** in DMSO-d<sub>6</sub> showed a singlet at  $\delta$  192.7 assigned to the

<sup>&</sup>lt;sup>†</sup>Compound 2a is exceptional in showing a significant hypsochromic shift; this may be due to overlap with the tail of a yet lower wavelength maximum.

´δ, ppm <sup>b</sup>								
Assignment	2 <b>8</b> °	9	42	<b>4</b> ±°	4c*	1	0 <b>a</b>	1 <b>0</b> b
sp <sup>3</sup> -C		11.0"			27.1			26.6
•					42.6			28.4
								31-3
								44.5
$C = N_2$	<b>78</b> ·3	93-1	53-9	54.0	51-9	7:	2.4	68-9
Phenyl C	126-4	126-6	126-3	126-8		126-0	128-9	
-	128-5	128-6	128-3	128.7		126-8	131-6	
	131-3	131-2	132-4	132-8		127.7	137-9	
	140-2	140-4	136-3	136-4		128-4		
C = 0	192·7	194-9	186-1	185-9	201-4	18	8-1	199-4

Table 2. CMR spectra of mercuri( $\alpha$ -diazo ketones) 2a and 9 and  $\alpha$ -diazo ketones 4a, 4c, 10a and 10b<sup> $\alpha$ </sup>

<sup>6</sup> Spectra are proton-decoupled unless otherwise specified <sup>6</sup> Chemical shift downfield from tetramethylsilane in deuterochloroform, unless otherwise specified. <sup>6</sup> In DMSO- $d_6$ . <sup>4</sup> In undecoupled spectrum: 27·1 (q, J = 127 Hz), 42·6 (s), 51·9 (d, J = 198 Hz), 201·4 (s). <sup>e</sup> With satellites due to <sup>199</sup> Hg-C coupling; J = 1116 Hz. <sup>7</sup> In undecoupled spectrum, appears as d,  $J = 201 \cdot 5$  Hz.

carbonyl carbon atoms, and a singlet at  $\delta$  78.3 assigned to the diazo carbon atoms. We had hoped to observed satellites of this last signal resulting from <sup>1</sup>J coupling with <sup>199</sup>Hg, which is present in 17% natural abundance, and to correlate the magnitude of the coupling constant with other <sup>13</sup>C-<sup>199</sup>Hg coupling constants observed by Weigert and Roberts.<sup>13</sup> However, no coupling could be detected.

Because of the considerations referred to earlier, we do not interpret this failure as due to a remote relationship between the mercury and the diazo C atoms, but suggest two alternative explanations. One is that decomposition of the sample and the relatively long relaxation time of the diazo C atoms combine to make acquisition time for a sufficiently strong spectrum prohibitive.<sup>†</sup> A second is that ligand exchange is taking place at mercury sufficiently rapidly to wash out the coupling. Ligand exchange has been observed between the mercury derivative of acetaldehyde,  $Hg(CH_2CHO)_2$ , and diphenylmercury,  $Hg(C_6H_3)_2$ , in pyridine; however, in this case it is not sufficiently fast to wash out Hg-H coupling. <sup>14</sup>‡

In order to investigate this matter further, the CMR spectrum of ( $\alpha$ -diazophenacyl)methylmercury (9) was examined. This compound, originally prepared by Lorberth *et al.*<sup>7</sup> via the methylmercury derivative of hexamethyldisilazane, was prepared by a route patterned after a method of Skell and Valenty<sup>8</sup> using methylmercuric ethoxide. It was chosen because it was expected to have a greater solubility than 2a in solvents less polar than DMSO and because it is known that the Me-Hg bond is not subject to rapid exchange, and thus if comparable intensities could be achieved in the CMR spectrum for the methyl and diazo carbon signals, the satellites should also be of comparable intensity. In the event, an acceptable spectrum of 9 was obtained in deuterochloroform (Table 2), in which the coupling of mercury to the methyl carbon

MeHgCN <sub>2</sub> COC <sub>6</sub> H <sub>5</sub>	RCOCN <sub>2</sub> R		
9	10a, $R = C_6 H_5$		
	$100. K = Me_{1}C$		

<sup>&</sup>lt;sup>†</sup>The best spectrum of 2a was obtained on a 500 mg sample dissolved in 2 ml of DMSO- $d_e$ , using 1-6 sec/pulse of acquisition time plus delay and 32,000 pulses; this involved *ca.* 14 hr of instrument time, and resulted in some decomposition of the sample leading to the appearance of mercury.

atom is visible (J = 1116 Hz), but the corresponding satellite peaks are very small and those of the diazo C atom, which gives a peak only 37% of the height of the methyl C atom peak, would be unobservable if present.

The unusually high field position of the diazo C signal in the CMR spectrum of 2a led us to examine the CMR spectra of the parent diazo ketone 4a and three other  $\alpha$ -diazo ketones 4c, 10a, and 10b (Table 2). These spectra each showed a singlet in the region  $\delta$  185–200, characteristic of the carbon of a highly conjugated CO group, and a singlet at  $\delta$  50-70, assigned to the diazo C atom. The signals of the diazo C atoms occur at remarkably high field for sp<sup>2</sup> C atoms. A similar observation has recently been made for the diazo C atoms of diazohydrocarbons and interpreted in terms of the high electron density on these atoms resulting from major contributions of canonical forms of type 11 to the resonance hybrids.<sup>16</sup> Even more closely analogous to the case of the  $\alpha$ -diazo ketones is methyl  $\alpha$ -diazoacetate, which was found to have its diazo carbon signal at  $\delta$  46·3.<sup>16</sup> Interestingly, the diazo signals in a series of dimethyl aryldiazomethanephosphonates (12) come at much lower field— $\delta$  118–136 ( $\delta$  127.5 for  $\mathbf{X} = \mathbf{H}$ ).<sup>16</sup>



Recently Lorberth *et al.*,<sup>7</sup> have reported the preparation of the  $\alpha$ -diazoacetophenone mercury derivative **2a** by a route [eqn (2)] different from that originally used.<sup>3</sup> The

$$2C_{6}H_{3}COCHN_{2} + [(Me_{3}Si)_{2}N]_{2}Hg \rightarrow (C_{6}H_{3}COCN_{2})_{2}Hg$$

$$4g \qquad 2g \qquad + 2(Me_{3}Si)_{2}NH \qquad (2)$$

melting point and spectroscopic data reported<sup>7</sup> for this product were sufficiently at variance with those earlier reported for  $2a^3$  that we considered it advisable to repeat both preparations and make a direct comparison between the product from each synthesis. This comparison has now established unequivocally that the products are identical. The discrepancy in previously reported melting points stems from the extraordinarily great sensitivity of the m.p. to the rate of heating, resulting from the fact that considerable thermal decomposition takes place below the m.p. Comparison of spectroscopic data was originally

<sup>‡</sup>In the present case exchange might be catalyzed by mercury formed by decomposition of the sample.<sup>15</sup>

clouded by lack of knowledge of the media used for the recording of the spectra of the product prepared via equ (2). We have now found that the very significant differences in the IR spectra reported for the two products relate to very real differences between the spectrum of 2a in solution in deuterochloroform and its solid state spectrum in a Nujol mull. In the former spectrum the CO-stretching peak appears at  $6.27 \mu$ , presumably superimposed on benzenoid absorption, accompanied by a weaker peak at  $6.38 \mu$ ; in the latter a strong peak appears at 6.42  $\mu$  accompanied by a weaker peak at 6.31  $\mu$ . Insofar as the identity of the two products is concerned, this was readily established by spectroscopic comparison of each sample in each of the two states. However, the solid state spectrum of 2a raises the interesting question as to whether it exists in a different tautomeric modification in the crystalline state than it does in solution. The strong band at  $6.42 \mu$  must arise largely from the mercury diazoacetyl system itself since we have observed similar band systems in the solid state IR spectra of compound 2d, where the phenyl ring is not conjugated with the carbonyl group, and of the mercuri bis( $\alpha$ -diazo ketone) 13,<sup>†</sup> which contains no Ph group. The long wavelength of this band suggests that these mercury derivatives may exist in the solid state as enol derivatives of type 6; however, definitive evidence must await X-ray crystallographic studies.



One other aspect of the report<sup>7</sup> on the properties of 2a prepared by the route of eqn (2) was particularly noteworthy. The mass spectrum of the sample showed no molecular ion peak but contained a strong peak at m/e 246 (rel. abund. ~75%) that was assigned to the doubly charged molecular ion, ( $M^{2+}$ . However, examination of the published spectrum establishes that the isotopic satellite pattern is not consistent with this interpretation and that the ion giving rise to this peak must be singly charged. The mass spectra of the samples of 2a prepared by us by either route failed to show this peak, and it must now be attributed to an impurity in the earlier sample.

## EXPERIMENTAL

M.ps were taken on a Fisher-Johns hot stage apparatus unless otherwise specified and are uncorrected.<sup>‡</sup> Spectroscopic data are given in Tables 1 and 2.

 $\alpha$ -Diazo ketones. The  $\alpha$ -diazo ketones 4a,4c, and 4d were prepared by treatment of the corresponding acyl chlorides with diazomethane by standard procedures. The  $\alpha$ -diazo ketones 4b, 10a and 10b were prepared by oxidation of the monohydrazones of the corresponding  $\alpha$ -diones with active manganese dioxide.<sup>18</sup>

### Mercuribis(a-diazo ketones)

General procedure. Finely ground yellow mercuric oxide (5.76 g, 0.026 mol) was added to a soln of the  $\alpha$ -diazo ketone (0.026 mole) in light petroleum ether (b.p. 40-60°; 500 ml). The mixture was stirred in the dark at room temp for 4 hr. The solid material was

<sup>†</sup>This compound was prepared from the corresponding  $\alpha$ -diazo ketone by the routes of both Eq 1 and 2; it was very unstable thermally and was not characterized by elemental analysis.

 $\pm$ See discussion spection for comment on the unreliability of m.ps of the mercuribis( $\alpha$ -diazo ketones).

§Taken in a sealed, evacuated capillary in a Thomas Hooser apparatus.

collected by gravity filtration and was extracted several times with chloroform (400 ml total). Evaporation of the solvent from the combined extracts under reduced pressure gave the mercuribis( $\alpha$ diazo ketone) as a yellow solid, which was purified by crystallization. Evaporation of the original petroleum ether filtrate gave unconsumed  $\alpha$ -diazo ketone (yields are not corrected for this).

Bis ( $\alpha$ -diazophenacyl)mercury (2a), yield 76%; yellow crystals from dichloromethane; m.p. 148-149.5° (dec at 126-128°); m.p. 131-132° (dec) (evacuated, sealed capillary in bath preheated to 128-129°). (Found: C, 39.51; H, 2.20; N, 11.39. Calcd for C<sub>16</sub>H<sub>10</sub>HgN<sub>4</sub>O<sub>2</sub>: C, 39.13; H, 2.05; N, 11.39%).

Bis ( $\alpha$ -diazo - 2,4,6 - trimethyl (phenacyl) mercury (2b), yield 80%; yellow crystals from NOAc: m.p. 138–139.5° (dec). (Found: C, 45.95; H, 3.99; N, 9.35. Calcd for C<sub>22</sub>H<sub>22</sub>HgN<sub>4</sub>O<sub>2</sub>: C, 45.94; H, 3.85; N, 9.74%).

Bis(1 - diazo - 3,3 - dimethyl - 2 - oxobutyl)mercury (2c), yield 81%; yellow crystals from CCL<sub>1</sub>; m.p. 130–131° (dec). (Found: C, 32·15; H, 4·03; N, 12·54. Calcd for  $C_{12}H_{16}HgN_4O_2$ : C, 31·94; H, 4·02; N, 12·43%).

Bis (1 - diazo - 2 - phenylacetonyl)mercury (2d), yield 53%; yellow crystals from benzene; m.p. 116-5-118° (dec). (Found: C, 41.68; H, 2.78; N, 10.83. Calcd for C<sub>18</sub>H<sub>14</sub>HgN<sub>4</sub>O<sub>2</sub>:C, 41.67; H, 2.72; N, 10.80%).

#### Reaction of 2n with hydrogen sulfide

 $H_2S$  was bubbled through a soln of 2a (109 mg) in aqueous dioxane (20 ml). A black ppt was formed. This was removed by filtration and the filtrate was extracted with ether. The ethereal extract was washed with water dried over MgSO<sub>4</sub> and evaporated to give yellow crystals (56 mg, 87%), m.p. 35-40°, identified as a 4a by IR and PMR spectroscopy.

Similar treatment of 2c gave 4c.

## $(\alpha$ -Diazophenacyl)methylmercury (9)

A soln of methylmercuric ethoxide in EtOH was prepared from methylmercuric chloride (3.94 g, 15.7 mmol) in EtOH (60 ml) and ethanolic KOEt [from 0.615 g (15.7 mmol) of K and 10 ml of EtOH] by the method of Valenty and Skell.<sup>6</sup> This was cooled under N<sub>2</sub> to 0° and  $\alpha$ -diazoacetophenone (2.30 g, 15.7 mmol) in EtOH (15 ml) was added dropwise with stirring. After an additional 15 min of stirring, the EtOH was removed on the rotary evaporator, and the residue was crystallized from CCl<sub>4</sub> to give 9 (3.34 g; 58%). Recrystallization from the same solvent gave fine, very pale yellow needles, m.p. 104–105° (dec)§ (it.<sup>7</sup> m.p. 97–100°);  $\lambda_{max}^{excl}$ 4.90, 6-30, 6-41  $\mu$ ;  $\lambda_{max}^{NUOL}$  4.84, 6-32 (m), 6-46  $\mu$ ; <sup>H</sup> $\delta$ (CDCl<sub>3</sub>) 0.87 (s with <sup>199</sup>Hg coupling satellites, J = 154 Hz, 3 H), 7-55 (m, 5 H); H $\delta$ (DMSO-d<sub>6</sub>) 0.55 (s with <sup>199</sup>Hg coupling satellites, J = 163 Hz, 3 H), 7-58 (m, 5 H); m/e 362.

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