MECHANISTIC ASPECTS IN SYNTHESES AND REACTIONS OF DIPIVALOYLMETHYLMERCURY COMPOUNDS*

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Summary

Several mechanistic aspects in the syntheses and reactions of dipivaloylmethylmercury compounds were studied. It was found that mercuric acetate adds to dipivaloylmethane (HDPM) in 75% aqueous ethanol to provide an 80% yield of dipivaloylmethylmercuric acetate (DPMHgOAc). The addition of mercuric acetate to HDPM is postulated to occur via electrophilic attack of $^+$HgOAc on the double bond of the enol tautomer of HDPM to give, after loss of a proton, a C-bonded Hg compound, DPMHgOAc, which can symmetrize in 95% ethanol to afford, after the addition of water, bis(dipivaloylmethyl)mercury (DPM_2Hg). DPMHgOAc undergoes an oxymercuration reaction with styrene in 80% aqueous methanol to yield a product from addition of $^+$HgOAc and $^-OCH_3$ to styrene. Photolysis of DPMHgOAc in chloroform with a Pyrex filter gave a quantitative yield of HDPM and mercurous acetate. Homolytic cleavage of the carbon—mercury bond followed by abstraction of hydrogen from $CHCl_3$ by DPM· and radical dimerization of ·HgOAc provides a rationalization for the observed products. Electrophilic cleavage of $(DPM)_2Hg$ with $HgCl_2$ and $Hg(OAc)_2$ according to the equation: $(DPM)_2Hg + HgX_2 \rightleftharpoons 2\ DPMHgX$ give equilibrium constants (K) which lie toward DPMHgX. Thus when X = Cl, $K = 620 \pm 60$, and when X = OAc, $K = 1.3 \times 10^5 \pm 1 \times 10^4$. Electrophilic cleavage of $(DPM)_2Hg$ with glacial acetic acid gave DPMHgOAc and HDPM in quantitative yield. A discussion of the importance of $\sigma-\pi$ conjugation in properties of dipivaloylmethylmercury compounds will also be presented.
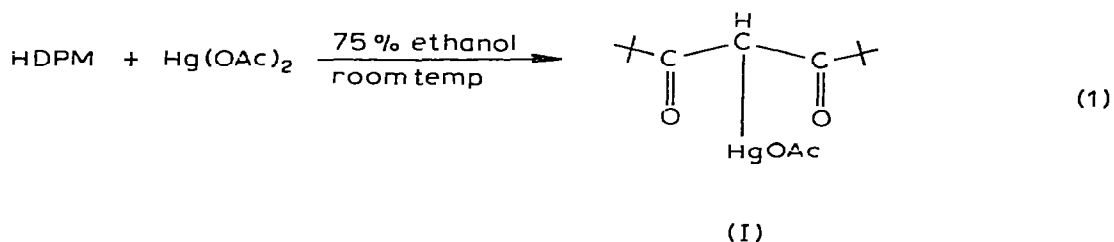

Introduction

Research on metal-β-diketone compounds has been carried out extensively by a number of workers [2a-d]. Interestingly enough, the chemistry of mercury-β-diketone compounds has until recently largely been unexplored with respect to their syntheses, structures, and reactions [2a,d,3a-c]. The most recent and notable work in this exciting area of metal-β-diketone chemistry has been that of Musso and coworkers [2a,4a-c]. Musso's group has reinvestigated the structure of bis(dipivaloylmethyl)mercury (II), and has, for the first time, shown by NMR and single crystal X-ray analysis that the mercury atom is indeed bonded to the central carbon atom of the dipivaloylmethane (HDPM) nucleus and not to the oxygen atoms as was previously assigned by Hammond and coworkers [2d]. Bonati and Minghetti [5] prepared several interesting acetylacetonemercury derivatives and assigned tentative structures to those derivatives.

It became quite apparent that the work reported thus far has only attempted to define the syntheses and structures of these mercury-β-diketone compounds, and that no work had been devoted to the mechanistic aspects of these interesting compounds [1]. In this paper we wish to describe our results concerning the mechanistic implications in the syntheses and reactions of dipivaloylmethylmercury compounds.

Results and discussion

### Synthesis of dipivaloylmethylmercuric acetate (I)

The synthetic procedure that has been successfully used involves the reaction of mercuric acetate or chloride with the corresponding β-diketone [2a,2d,4c]. Musso and Flatau [4a,c] have also successfully used bis(hexamethyldisilylamido)mercury to prepare II and bis(diacetylmethyl)mercury. We wish to elaborate on our results with mercuric acetate and HDPM [1]. The reaction of a 1/1 or 2/1 mole ratio of HDPM with mercuric acetate in 75% ethanol gave a crystalline compound (eqn. 1) in 80% yield. The NMR spectrum in

$$\text{HDPM} \quad + \quad \text{Hg(OAc)}_2 \quad \xrightarrow[\text{room temp}]{75\% \text{ ethanol}} \quad \text{(structure I)} \tag{1}$$

(I)

chloroform-d was quite definitive for the assigned structure I, with singlets at 1.22 ppm (18 protons); 2.05 ppm (3 protons); and 5.18 ppm (0.8 protons). The sharp singlet [6]* at 5.18 ppm was flanked by ^{199}Hg satellites (intensities

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* Musso [4a] states that the half-width of the methine proton is dependent on the method of preparation, with particular concern on trace mercury salts being present. While we feel Musso's point is well taken, we also wish to point out that linebroadening of the methine proton can also result when dynamic equilibria are present, i.e., mercury keto—enol tautomerization [6].

of each are about 9% of the total area) indicative of a $J(^{199}Hg-H)$ coupling of 314 Hz at 31°. The $J(^{199}Hg-H)$ for I was also temperature dependent, and we found that by lowering the temperature to $-30°$ (CDCl$_3$) the coupling increased to 330 Hz. This occurred without any chemical shift or lineshape effect on the methine proton, and we strongly feel that this increase in $J(^{199}Hg-H)$ coupling is due to a conformational effect of the mercury atom in relation to the carbonyl groups. Since $\sigma-\pi$ conjugation [7a-f] has been shown to be important in spectroscopic and chemical properties of carbon—metal compounds, we feel that lowering the temperature might maximize the interaction of the mercury—carbon σ-bond electrons with the π-orbitals of the carbonyl group, i.e. increase $\sigma-\pi$ conjugation and thus be reflected in the geminal $J(^{199}Hg-H)$ coupling in I. This might be due to an increase in the s character of the C—H orbital in I as the carbon—mercury electrons maximize their overlap of the π-electrons of the carbonyl groups upon lowering the temperature. A direct relationship to this type of coupling increase can be found in $^{13}C-H$ couplings as well as H—C—^{199}Hg and $^{13}C-^{199}Hg$ couplings which also increase as the s character of the carbon—hydrogen [8a-c] or carbon—mercury [8d,e] bond increases. The fact that $\sigma-\pi$ conjugation is important in mercury-β-diketone compounds is further substantiated by the single crystal X-ray analyses of I [9] and II [4c]. It is clearly shown that the mercury—carbon bond in 1, as well as in II, in a static situation, is orthogonal to the nodal plane of the carbonyl groups of the dipivaloylmethane nucleus. Thus overlap of the mercury—carbon σ-bond electrons with the π-orbitals of the carbonyl groups is maximized, i.e., the dihedral angle, θ, between the carbon—mercury bond and π-orbitals of the carbonyl group is close to zero [10a,b].
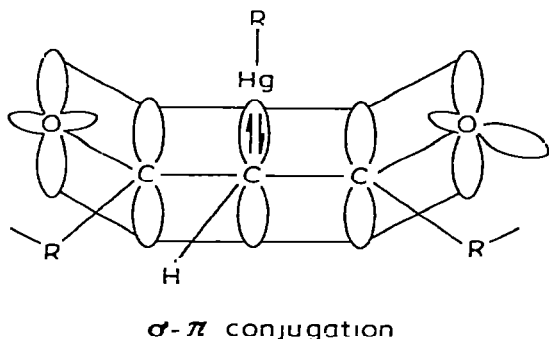
$\sigma-\pi$ conjugation

The role of $\sigma-\pi$ conjugation in carbon-bonded mercury compounds such as I, II, and IV can be compared to allylic mercurials. It has been shown by Bach et al. [7e,f] that a substituent such as a mercury atom on a carbon that is allylic to a carbon—carbon double bond is sufficiently polarized to create a significant role for $\sigma-\pi$ conjugation. Since the mercury atom in our example is allylic to a carbonyl group, and carbonyl groups themselves are more polarized in the ground state than a carbon—carbon double bond, we feel that the mercury—carbon σ-electrons would be more polarized in the ground state of compounds such as I, II and IV and thus $\sigma-\pi$ conjugation plays a more significant role in these compounds than in the ground state of allylic mercurials. This is further verified by the infrared spectra of I, as well as for II and IV, which

shows carbonyl stretching vibration between 1650 and 1690 cm^{-1}. The fact that the mercury atom bonds to carbon rather than oxygen in HDPM is conceivably a consequence of the mechanism of addition. Unlike other metals that have been shown to bond to the oxygens of β-diketones, the Hg^{2+} ion has the ability of adding to carbon—carbon double bonds. Since numerous examples of electrophilic additions by mercuric ions have been cited [11a,b], it seems reasonable to postulate that the electrophile, $^+$HgOAc, could add to the double bond of the enol tautomer of HDPM and then the loss of a proton gives compound I (eqn. 2).

$$\text{(2)}$$
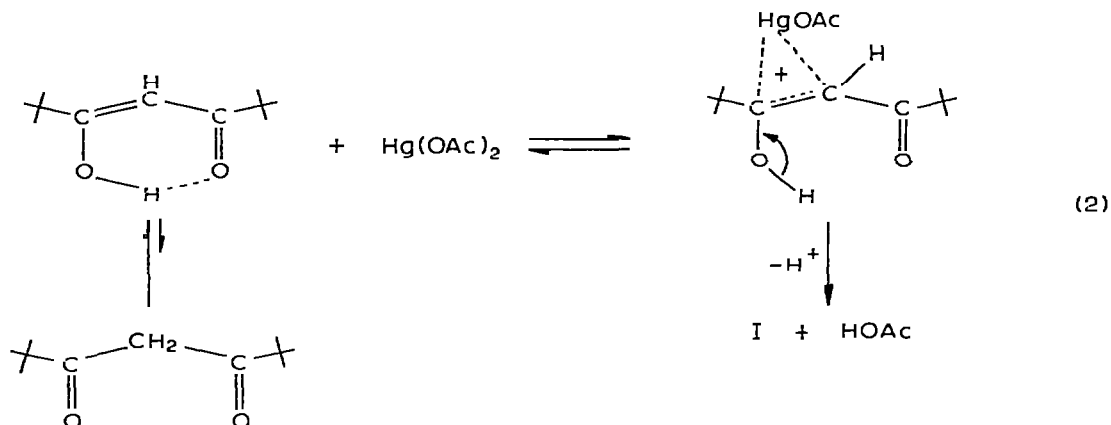
Although S_E1' or S_E2' reaction mechanisms can be postulated, we feel that the recent work by Olah [12] and Bach [13a,b] give credence to mercurinium ions as viable intermediates. The formation of the mercurinium ion by reaction with the enol form of HDPM followed by loss of a proton to form compound I provides a driving force for carbon—mercury formation and the added stabilization of σ—π conjugation.

Reactions of I
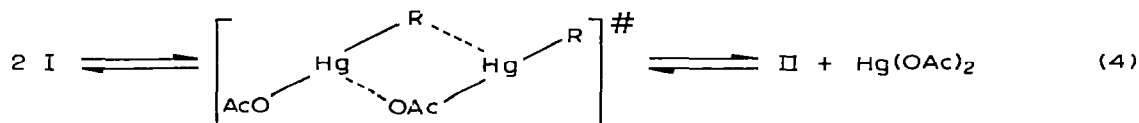*A. Symmetrization.* The reaction of HDPM and mercuric acetate was further studied, and it was found that by allowing this reaction (eqn. 2) to proceed for 24 h in 95% ethanol (instead of 1 h in 75% ethanol) that compound II was formed exclusively after addition of water to the reaction mixture (eqn. 3) in 70% yield. A dynamic nuclear magnetic resonance study (DNMR) on com-
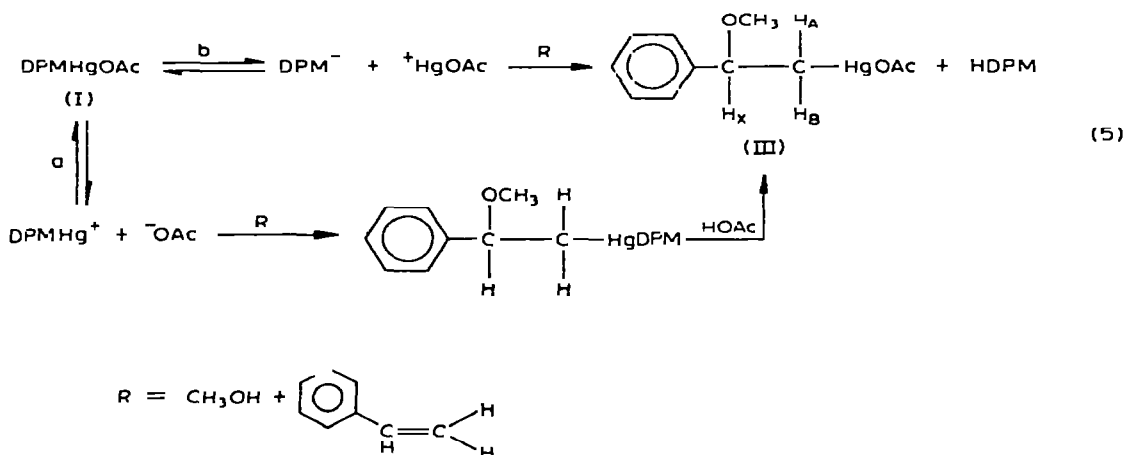

$$\text{(3)}$$

(II)
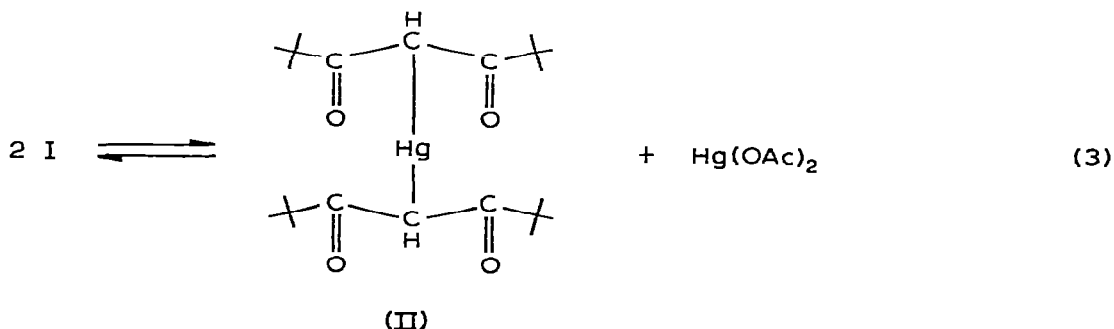
pound I in chloroform-d (50 to $-40°$) and 95% ethanol-d_6 (30 to $-100°$) showed no line shape or chemical shift change for the methine proton, confirming that in solution the equilibrium in eqn. 3 lies far toward I. This is further confirmed by reaction of II with mercuric acetate (see electrophilic cleavage section). Compound I undergoes the symmetrization reaction only after water is added, causing the equilibrium to shift to the more insoluble compound II.

The mechanism for symmetrization of organomercurials has been thoroughly discussed by Jensen and Rickborn [14] and one logical mechanism for eqn. 3 that can be written has a four centered transition state as in eqn. 4.
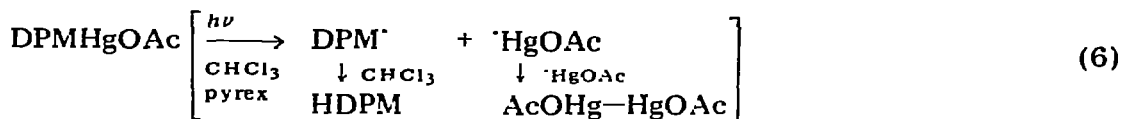
$$2 \ I \ \rightleftharpoons \ \left[\begin{array}{c} \text{AcO} \diagdown \text{Hg} \diagup \overset{\displaystyle R}{\diagdown} \text{Hg} \diagup \overset{\displaystyle R}{} \\ \diagdown \text{OAc} \diagup \end{array} \right]^{\#} \ \rightleftharpoons \ \text{II} \ + \ Hg(OAc)_2 \qquad (4)$$

B. Oxymercuration. Since numerous examples of oxymercuration reactions have been reported in the literature [11b], it was of interest to treat I with an olefin in an aqueous alcohol solvent. Thus reaction of II and styrene in 75% methanol provides compound III in quantitative yield (eqn. 5). The mechanism (eqn. 5) could either occur by pathway a or pathway b.

$$ \text{(5)} $$

DPMHgOAc $\underset{b}{\rightleftharpoons}$ DPM$^-$ + $^+$HgOAc $\xrightarrow{R}$ (III)

(I)

a ↓↑

DPMHg$^+$ + $^-$OAc $\xrightarrow{R}$

R = CH$_3$OH + styrene

Compound III can be readily characterized by its NMR spectrum, which notably gave an ABX spectrum with the $J(^{199}Hg-H)$ couplings verifying the position of the mercury atom. Compound III was also conventionally prepared via reaction of mercuric acetate with styrene in 75% methanol to provide unequivocal proof that indeed it was the same compound isolated as in eqn. 5. It is noteworthy to mention that II did not react with styrene under similar conditions, and this result would seem to indicate that pathway a (eqn. 5) is preferred over pathway b.

C. Photolysis. Compound I ($\lambda_{max}^{CHCl_3}$ 275 nm, ϵ 2500) was photolyzed in chloroform (1%) using a 200 W Hanovia lamp with a pyrex filter. The photolysis of I is complete in minutes with mercurous acetate precipitating out of chloroform and HDPM being the only volatile compound formed as shown by gas—liquid chromatographic analysis of the photochemical reaction solution. This result is strictly typical of what occurs when R—Hg—X compounds are

photolyzed [15], with homolytic cleavage of the carbon—mercury bond usually being the primary photoprocess (eqn. 6). Thus the dipivaloylmethane

$$DPMHgOAc \begin{bmatrix} \xrightarrow{h\nu} & DPM^{\cdot} & + & ^{\cdot}HgOAc \\ \text{CHCl}_3 & \downarrow \text{CHCl}_3 & & \downarrow ^{\cdot}\text{HgOAc} \\ \text{pyrex} & HDPM & & AcOHg-HgOAc \end{bmatrix} \qquad (6)$$

radical abstracts hydrogen from chloroform, while the monomercuric acetate radical dimerizes to give mercurous acetate.

Electrophilic cleavage reactions of bis(dipivaloylmethyl)mercury (II)

The electrophilic cleavage reactions of II with mercuric chloride and mercuric acetate were studied via NMR spectroscopy to ascertain the equilibrium constants (K) for eqn. 7. The reaction of II with HgCl$_2$ (1/1 mole ratio) was

$$(DPM)_2Hg + HgX_2 \xrightarrow{\ K\ } 2DPMHgX$$
$$\text{(I) X} = \text{OAc} \qquad (7)$$
$$\text{(IV) X} = \text{Cl}$$
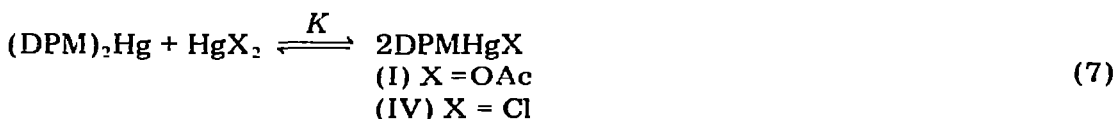
followed by NMR spectroscopy for 48 h, after which the ratio of II to IV did not change. This equilibrium was measured at slow exchange rates, on the NMR time scale, at −30° where both signals for II and IV were sharp and the ^{199}Hg satellites were readily observed. The major signal at 5.16 ppm was assigned to IV ($J(^{199}$Hg—H) 310 Hz) and that at 4.89 ppm to II ($J(^{199}$Hg—H) 220 Hz) [4a,c]. The equilibrium constant (K) for eqn. 7 was found to be 620 ± 60 with the assumption that the HgCl$_2$ concentration was equal to that of II after the areas of II to IV were normalized. The equilibrium constant, K = 620 ± 60 for X = Cl, repre-

$$K = \frac{[DPMHgX]^2}{[(DPM)_2Hg][HgX_2]}$$

sents a free energy difference of $-\Delta G^{\circ}$ = 3.0 ± 0.3 kcal/mole between II and IV. Equilibrium for the reaction of II and Hg(OAc)$_2$ was attained instanteneously as expected for the more electrophilic reagent Hg(OAc)$_2$ and gave a constant (K) at −30°, of $1.3 \times 10^5 \pm 1 \times 10^3$, which gives a free energy difference between I and II of $-\Delta G^{\circ}$ = 5.8 ± 0.6 kcal/mole.

The reaction of II with glacial acetic acid was also studied and was found to give I and HDPM quantitatively, after stirring II in glacial acetic acid for 24 h at room temperature (eqn. 8).

$$II + HOAc \left[\xrightarrow[\text{room temp.}]{24 \text{ h}}\right] I + HDPM \qquad (8)$$

Although we cannot define the exact mechanism in the electrophilic cleavage reactions of II, we can reasonably be assured that mercuric salts i.e., mercuric acetate and chloride, attacks the carbon—mercury bond giving I and IV [14]. However, the result with II and glacial acetic is complicated by the fact that the HDPM, which is formed in the reaction, can also undergo a proton keto—enol tautomerization. Thus the site of protonation cannot be ascertained.

Conclusions

It was our intent in this paper to elucidate several mechanistic aspects in the reactions and syntheses of dipivaloylmethylmercury compounds. We found that carbon-bonded mercury β-diketone derivatives of HDPM are stabilized by $\sigma—\pi$ conjugation and that they behave, in their reactivity, in a similar fashion as other organomercury derivatives [14].

Experimental

Proton NMR spectra were recorded on a Varian HR 100 with internal field frequency lock and equipped with a variable temperature probe and a 1024 channel signal averager. The infrared spectra were recorded on a Cary—White 90 instrument. The photolysis apparatus was equipped with a Hanovia 200 W high pressure mercury lamp. Gas—liquid chromatography analyses were performed on an F & M 800 instrument with 6′ × 0.25″ SE 30 on chromosorb W columns. The ultraviolet spectra were obtained on a Cary 15 UV spectrophotometer.

Preparation of I

In a flask was placed 3.19 g (0.01 mole) mercuric acetate and 1.84 g (0.01 mole) dipivaloylmethane in 50 ml of 75% ethanol. The reaction mixture was stirred for 1 h and then placed in a refrigerator to yield 3.5 g (80%) of long clear crystals which were filtered and dried under vacuum. The m.p. 179-181° of the crystals was sometimes complete and other times a partial melting was observed at 179-181° with further melting at 209-211°. This was investigated by Musso and Flatau [4b,c] and it was found that two different crystal modifications of I existed which were long rods m.p. 179-181 and cubes 209-211°. The NMR spectrum in chloroform-d at 31° consisted of singlets at 1.22 (18 H) $(CH_3)_3C$; 2.05 (3 H) CH_3C; and 5.18 ppm (0.8 H) C—H. The sharp signal at 5.18 ppm was flanked by ^{199}Hg satellites indicating a $J(^{199}Hg—H)$ coupling of 314 Hz at 31°. The infrared spectrum showed a strong C=O stretch at 1685 (KBr) and 1719 cm^{-1} (CHCl$_3$). The UV spectra had λ_{max} 275 nm (ϵ = 2768) in 95% ethanol and 275 nm (ϵ 1235) in CHCl$_3$. (Anal. found: C, 35.2; H, 5.01, Hg, 45.6. $C_{13}H_{22}O_4Hg$ calcd.: C, 35.25; H, 5.01; Hg, 45.3%.)

Variable temperature NMR experiment of I

In a clean NMR tube was placed 8 mg of I dissolved in 0.5 ml of 95% ethanol-d_6 (~2% solution). The proton spectrum was recorded at various temperatures from +31 to —90°. A methanol NMR thermometer with a Varian calibration curve was used to establish the temperatures to ± 2°. We observed one signal that is sharp to 0° and then broadens slightly to —60° (half-band width 4 Hz) and is quite broad at —90° (half-band width 12 Hz). The chemical shift does not change appreciably over this entire temperature range with a value of 5.20 ppm at 31°.

Preparation of II

In a flask was placed 1.84 g (0.01 mole) dipivaloylmethane and 1.53 g (0.05 mole) mercuric acetate in 50 ml of 95% ethanol. The reaction mixture, which

was homogeneous, was stirred for 24 h after which 25 ml of water was added and immediately a white precipitate formed which was filtered and dried to yield 2.0 g (70% of II; m.p. 196-198° (lit. 4c 195-197°). The mass and NMR as well as infrared spectra were consistent with values reported by Musso et al. [4c].

Photolysis of I

Compound I (1.0 g) ($\lambda_{max}^{CHCl_3}$ 275 nm (ϵ = 1.235) was dissolved in 125 ml of chloroform and the solution was placed in a 125 ml pyrex photolysis flask equipped with a quartz immersion well and a 200 W Hanovia lamp with a pyrex filter. Infrared spectroscopy was used to monitor the reaction and specifically the C=O stretch at 1719 cm^{-1}. This band at 1719 cm^{-1} disappeared after ~10 min and a new band at 1600 cm^{-1} appeared. The formation of a white precipitate occurred immediately after the lamp was turned on and this was removed by filtration and identified as mercurous acetate by Raman spectroscopy. The Hg—Hg bond stretch at 267 cm^{-1} is well defined for mercurous compounds [16]. The mass spectrum was also consistent with $Hg_2(OAc)_2$ and also small amounts of ClHgHgOAc and Hg_2Cl_2 were evident. The chloroform photolysate was analyzed by GLC 6" × 1/8" SE 30 on Chromosorb W to give, in addition to chloroform, one peak with the same retention time as dipivaloylmethane. Distillation gave a pure sample of dipivaloylmethane identical to a known sample by infrared, NMR, and mass spectra.

Oxymercuration reaction of II with styrene

In a flask, covered with aluminum foil, was placed 0.424 g (0.96 mmole) of I and 0.104 g (0.96 mmole) of styrene in 80% aqueous methanol. The reaction mixture was stirred overnight and then the methanol and water were removed on a rotary evaporator at room temperature. The residue was further pumped on under vacuum overnight. The white solid m.p. 57-61° was recrystallized from ether-skelly F to give small white needles m.p. 58.7-59.1°. The NMR spectrum of III (CCl$_3$D) gave the following signals: C_6H_5, 7.35 ppm (singlet); H_X—C, 4.56 ppm (triplet, $J(H_X—H_A)$; $J(H_X—H_B)$ 5.5 Hz, $J(^{199}Hg—H_\beta)$ 264 Hz): CH$_3$OC≤ 3.26 ppm (singlet: H_A—C—H_B, 2.38 ppm (2 quartets, J_{AB} 12 Hz; J_{AX}, J_{BX} 5.5 Hz, $J(^{199}Hg—H_\alpha)$ 212 Hz); CH$_3$C(O)O 2.05 ppm (singlet). Ratio of areas 5/1/3/2/3.

Compound III was also prepared by reaction of mercuric acetate and styrene (1/1) in 80% methanol to give a compound similar in its NMR spectrum and mixed m.p. as described above. (Anal. found: C, 33.5; H, 3.64; Hg, 51.0. $C_{11}H_{14}HgO_3$ calcd.: C, 33.45; H, 3.58; Hg, 50.78%.)

Electrophilic cleavage reaction of II with mercuric chloride, mercuric acetate, and glacial acetic acid

$HgCl_2$. In a clean dry NMR tube was placed 11.1 mg II and 5.35 mg mercuricchloride (1/1 mole ratio) which were then dissolved in 0.5 ml of chloroform-*d* with tetramethylsilane as the internal standard. The NMR tube was kept at room temperature and at various intervals the NMR spectrum was recorded at −30°. After 72 h there was no change in the ratio of the signal of IV at 5.19 ppm and II at 4.98 ppm.

The areas of the signal for II and IV were integrated and that for II was divided by 0.5 in order to normalize the areas of II and IV. The mercuric chlo-

ride concentration was assumed to be equal to that of II. The equilibrium constant (620 ± 60) was calculated using the equation in the text. Compound IV can be prepared by the procedure described by Musso et al. [4c].

Hg(OAc)₂. A similar procedure as described above was used except that 11.8 mg of II was treated with 6.6 mg of $Hg(OAc)_2$ (1/1 mole ratio). The equilibrium was attained extremely rapidly (~10 min) and the NMR spectrum recorded after 10 min did not change in an hour. The equilibrium constant was calculated similarly as for $HgCl_2$ and was found to be $1.3 \times 10^5 \pm 1 \times 10^4$.

HOAc. In a flask was placed 9.74 mg of II dissolved in 20 ml of glacial acetic acid. The reaction mixture was stirred for 24 h at room temperature and the solvent removed on a rotary evaporator. The residue was analyzed by GLC to show the presence of HDPM (SE 30 on chromosorb W at 50°). The residue was recrystallized from 95% ethanol to give white needles whose m.p., IR and NMR spectra were identical to compound I.

Acknowledgements

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