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THE SYNTHESIS AND CHARACTERIZATION OF DIPIVALOYLMETHYLMERCURIC ACETATE

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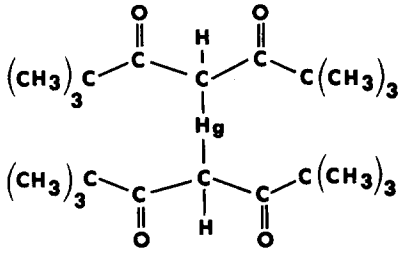
Recently Flatau and Musso[1] characterized the major reaction product of dipivaloylmethane (DPM) and mercuric acetate as the carbon-bonded mercuric compound $\underset{\approx}{1}$.



$\underset{\approx}{1}$

Their main evidence for structure $\underset{\approx}{1}$ was obtained by nuclear magnetic resonance spectroscopy (nmr), which clearly showed a geminal $J_{Hg}{}^{199}$-H coupling of 221 Hz for the major singlet (97%) at 4.86 ppm at -40°. This corrected a structure proposed for the product of DPM and mercuric acetate, where the mercury was thought to be bonded to the oxygen rather than the carbon[2,3]. Flatau and Musso[1], however, pointed out the difficulties in using mercuric salts in the preparation of $\underset{\approx}{1}$ and used bis(hexamethyldisilylamido) mercury for the mercuric-salt-free formation of $\underset{\approx}{1}$.

We would like to report the isolation of a previously unreported compound formed in the reaction of DPM and mercuric acetate and discuss its formation in relation to the mechanism of this reaction.

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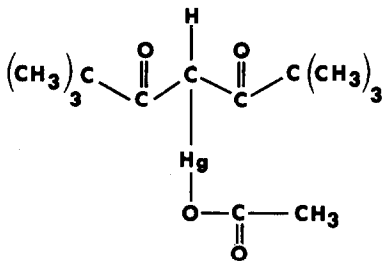
The reaction of DPM and mercuric acetate (2:1) in 75% ethanol for 1 hr gave, after cooling, a single, highly crystalline[4] compound $\underset{\approx}{2}$, mp 179-181°, whose room temperature nmr



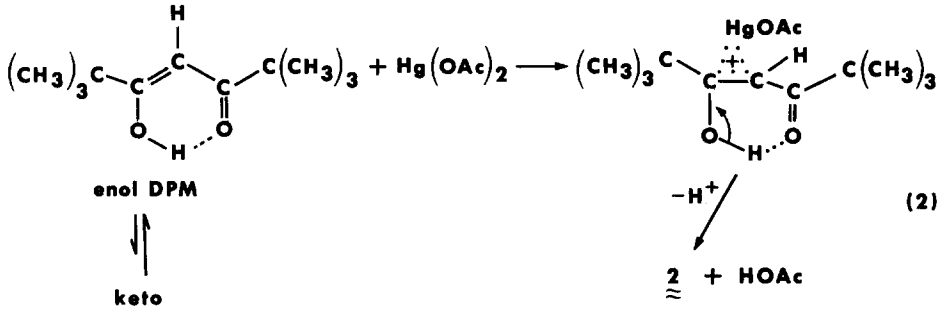
$\underset{\approx}{2}$

spectrum consisted of singlets at 1.22 ppm (18 protons); 2.05 ppm (3 protons); and 5.18 ppm (0.8 proton).[5] The sharp singlet at 5.18 ppm was flanked by the Hg^{199} satellites (intensities of which are about 9% of the total area) indicative of a $J_{Hg^{199}-H}$ coupling of 314 Hz at 31° and 333 Hz at -30°. This is by far the largest geminal Hg^{199}-H coupling we have been able to find in the literature[6,7]. In order to verify this large coupling, we looked at another derivative of $\underset{\approx}{2}$, where the acetate group is replaced by a chloride, $\underset{\approx}{3}$. Compound $\underset{\approx}{3}$ was prepared by Flatau and Musso[1], however, they stated that the $J_{Hg^{199}-H}$ coupling vanished. Apparently they observed the spectrum of $\underset{\approx}{3}$ only at room temperature, where the 12 Hz linewidth of the singlet at 5.16 ppm essentially precludes the observation of the Hg^{199} satellites. However, we find at -30° the singlet at 5.16 ppm has a linewidth of 3 Hz and the two Hg^{199} satellites are quite evident with a coupling of $J_{Hg^{199}-H}$ for $\underset{\approx}{3}$ of 310 Hz. This finding substantiates the large geminal coupling we obtain for $\underset{\approx}{2}$. The infrared spectrum (KBr) of $\underset{\approx}{2}$ showed a strong carbonyl stretch at 1685 cm^{-1}, which is indicative in these systems of a carbon-bonded mercury[1]. The 70 ev mass spectrum of $\underset{\approx}{2}$ gave a molecular ion (Hg^{202}) at m/e 444 with 0.22% relative abundance, and fragment ions at m/e 429 (0.14%) and m/e 387 (0.48%) from loss of methyl and t-butyl respectively[8].

Elemental analysis provided the following results for $\underset{\approx}{2}$. Calc. for $C_{13}H_{22}O_4Hg$: C, 35.25; H, 5.01; Hg, 45.3; Found: C, 35.2; H, 5.01; Hg, 45.6. We have also independently synthesized $\underset{\approx}{2}$ by reacting $\underset{\approx}{1}$ with glacial acetic acid (eq. 1)[9].

$$\underset{\approx}{1} + \text{HOAc} \xrightarrow[24\ \text{hr}]{25°} \underset{\approx}{2} + \text{DPM} \qquad (1)$$

The interesting fact that mercury differs from other metals[10], in that it is bonded to carbon instead of oxygen, can be rationalized by the following mechanism (eq. 2).



(2)

Numerous examples of electrophilic additions to olefins by mercuric ions have been cited[11,12]. Since DPM exists as an equilibrium between the enol and keto forms (the enol/keto ratio (K) depends on solvent: CD_3OD, 1.26 immediately after mixing (decreases to 0.08 after 30 hours); $CDCl_3$, 15; CCl_4, 83, as measured by nmr), it would seem reasonable that addition to the enol form of DPM by the electrophile ⊕HgOAc followed by loss of proton (eq. 2) gives $\underset{\approx}{2}$[13]. It is evident from our results that the reaction of $\underset{\approx}{2}$ with enol DPM to form $\underset{\approx}{1}$ is a slower reaction, and we have verified by nmr ($CDCl_3$) that addition of mercuric acetate to a mixture of DPM and $\underset{\approx}{2}$ causes the disappearance of the DPM signal (enol C = $\underline{\text{CH}}$–) at 5.75 ppm, with a corresponding increase for the signal of $\underset{\approx}{2}$ at 5.18 ppm. We have also found that by increasing the reaction time of DPM and mercuric acetate from 1 hr to 24 hr that $\underset{\approx}{1}$ is formed exclusively.

We hope to report on other reactions of $\underset{\approx}{2}$ and also our results on the reaction of mercuric acetate with other β-diketones.

REFERENCES

1. K. Flatau and H. Musso, Angew. Chem. Internat. Edit. 9, 379 (1970).
2. D. C. Nonhebel, J. Chem. Soc., 738 (1963).
3. G. S. Hammond, D. C. Nonhebel, and C. H. S. Wu, Inorgan. Chem., 2, 73 (1963).
4. A single crystal X-ray analysis of 2 is underway. K. J. Palmer, R. Wong and R. H. Fish. Unpublished results.
5. Repeated integrations of 2 at 31° and -10° with freshly prepared samples gave less than one proton (0.8 proton with the CH_3 of the acetate group taken at 3.00 protons) for the singlet at 5.18 ppm. We feel that any of the compound with -HgOAc on oxygen would be seen at 5.75 ppm if it were present[1]. However, no absorption in that region of the nmr spectrum was evident either at 31° or -30°. We have at this time no explanation for this loss of proton area.
6. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, N.Y., 1966, P. 1079.
7. R. M. Babb and P. D. Gardner, Chem. Comm., 1678 (1968).
8. The detailed mass spectral work on compound 2 and others will be reported. W. F. Haddon and R. H. Fish, unpublished results.
9. F. R. Jensen and B. Richborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill Book Company, New York, N.Y., 1968, Chap. 3 and references therein.
10. B. Bock, K. Flatau, H. Junge, M. Kuhr, and H. Musso, Angew. Chem. Internat. Edit. 10, 225 (1971) and references therein.
11. J. Chatt, Chem. Rev., 48, 7 (1951).
12. T. G. Traylor and A. W. Baker, J. Am. Chem. Soc., 85, 2746 (1963).
13. Equation 2 has some analogy to the addition of mercuric acetate to 1-butene or 2-butene, where allylic mercurials are formed by addition of +HgOAc to the double bond followed by loss of proton. The mechanism for this reaction could be $S_E i'$ or $S_E 2'$ or as we prefer through a mercurinium ion intermediate. See Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, Tetrahedron Lett. 3719 (1965).