(36) D. Ewing, *Org. Magn. Reson.*, **7**, 520 (1975).
(37) A. Bottini, R. Van Etten, and A. Davidson, *J. Org. Chem.*, **30**, 2994 (1965).
(38) C. Kingsbury and C. Cowles, *J. Org. Chem.*, **40**, 1302 (1975).
(39) H. Audier, J. Dupin, and J. Jullian, *Bull. Soc. Chim. Fr.*, 2811 (1966).
(40) The procedure used was similar to that of D. Reynolds and D. Fields in "Heterocyclic Compounds with Three and Four Membered Rings", Part 1, A. Weissberger, Ed., Interscience, London, England, 1964, p 578. The thiiranes in question were reported in *Chem. Abstr.* P115586A, patent to Dunlop Rubber Co.
(41) E. Kohler and M. Chadwell, "Organic Syntheses", Vol. I, Wiley, New York, 1923, p 78.
(42) E. Kohler, *J. Am. Chem. Soc.*, **53**, 205 (1931).
(43) C. Allen and F. Spangler, "Organic Syntheses", Vol. III, Wiley, New York, 1943, p 377.
(44) H. Wassermand and N. Aubrey, *J. Am. Chem. Soc.*, **78**, 1726 (1956).
(45) H. Wasserman and J. Brous, *J. Org. Chem.*, **19**, 515 (1954); C. Stevens, R. Church and V. Traynelis, *Ibid.*, **19**, 522 (1954).
(46) G. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959).
(47) E. Kohler and J. Conant, *J. Am. Chem. Soc.*, **39**, 1404 (1917).
(48) E. Kohler and C. Allen, *J. Am. Chem. Soc.*, **46**, 1530 (1924).
(49) F. Zhurinov and N. Val'fson, *Zh. Org. Khim.*, **3**, 504 (1967).

Novel Decarboxylative Oxidation of α-Hydroxy-β-keto (or -β-imino) Acid Salts of Mercury(II)

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Mercury(II) salts or methylmercuric salts effect oxidative decarboxylation of α-hydroxy-β-keto (or -β-imino)carboxylate anions to convert the hydroxy to keto groups, with concomitant deposition of mercury(0). With certain reactant stoichiometries, mixed hydroxy and keto products are obtained. Dimethylmercury is produced additionally when methylmercuric salts are utilized as oxidant. Possible mechanisms are discussed. These results are important in considering (1) that metals involved in organic reactions may serve dual roles (catalysis and redox) and (2) that the production of biacetyl, which accompanies anaerobic fermentation of sugars to acetoin, probably occurs via an intervening nonenzymatic oxidation of the enolate anion generated upon decarboxylation of acetolactic acid.

Mercury(II) is known to oxidize many classes of organic compounds. The free aqueous ion is a fairly strong oxidant, as shown by the reduction potentials given below:

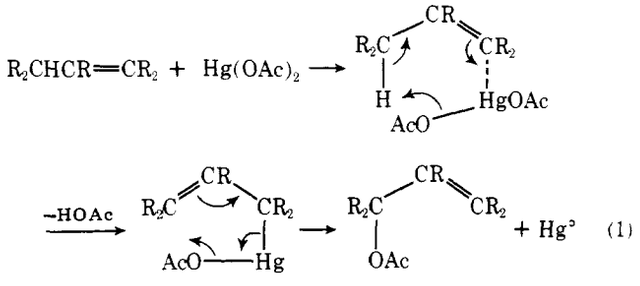
$$Hg^{2+} + 2e^- \rightarrow Hg^\circ \qquad E^\circ_{298} = +0.851\ V$$

$$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+} \qquad E^\circ_{298} = +0.905\ V$$

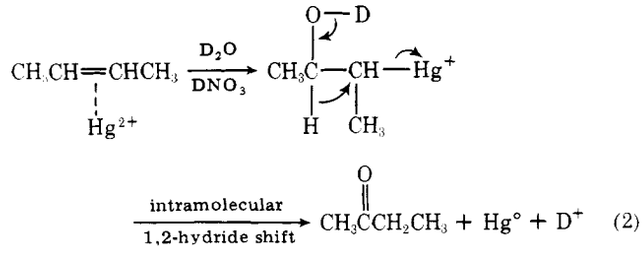
$$Hg_2^{2+} + 2e^- \rightarrow 2Hg^\circ \qquad E^\circ_{298} = +0.796\ V$$

However, as indicated by the reaction mechanisms suggested in the literature (shown below), initial complexation of Hg(II) to a nucleophilic center (>C=C< or a donor lone-pair) is apparently a prerequisite for a kinetically observable redox reaction:

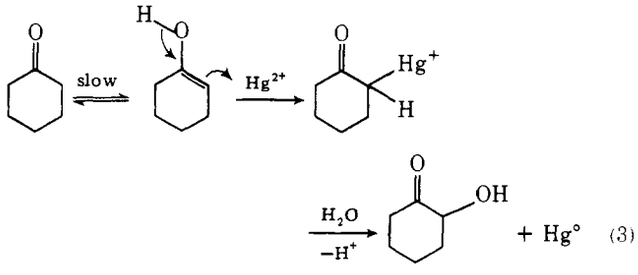
(i) Allylic acetoxylation of olefins (mercuric acetate in hot acetic acid)[1]



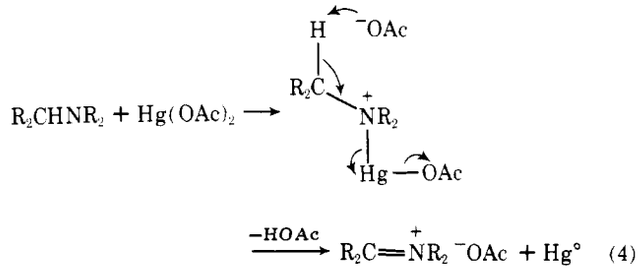
(ii) Oxidation of olefins to ketones (mercuric nitrate in warm aqueous nitric acid)[2,3]



(iii) α-Hydroxylation of ketones (mercuric perchlorate in aqueous perchloric acid)[4]



(iv) Oxidation of tertiary amines (mercuric acetate in hot aqueous acetic acid)[5]



The above transformations likely entail *two-electron* redox reactions and the experimentally observed production of Hg(I), as of an apparent one-electron reduction, is attributable to the mercury(II) oxidant reacting with the initial Hg° product to form mercury(I) compounds:

$$Hg^\circ + HgX_2 \rightarrow Hg_2X_2 \qquad (5)$$

Reported herein is the novel finding that mercury(II) effects an oxidative decarboxylation of α-hydroxy-β-keto (or -β-imino)carboxylate anions (the conjugate acids of which are not isolable,[6,7] vide infra). The following stoichiometries have been demonstrated:

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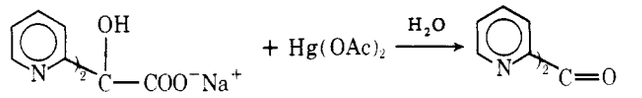
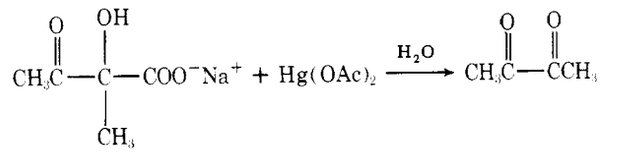
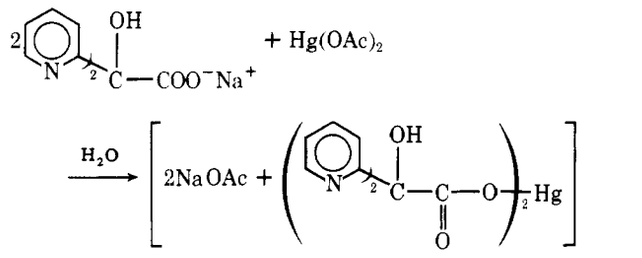


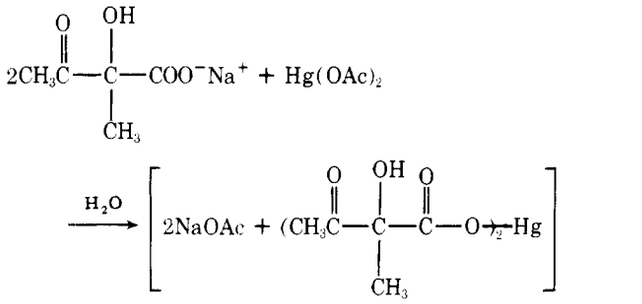
+ Hg° + CO_2 (+ HOAc + NaOAc) (6)



+ Hg° + CO_2 (+ HOAc + NaOAc) (7)



+ $2CO_2$ + Hg° (8)

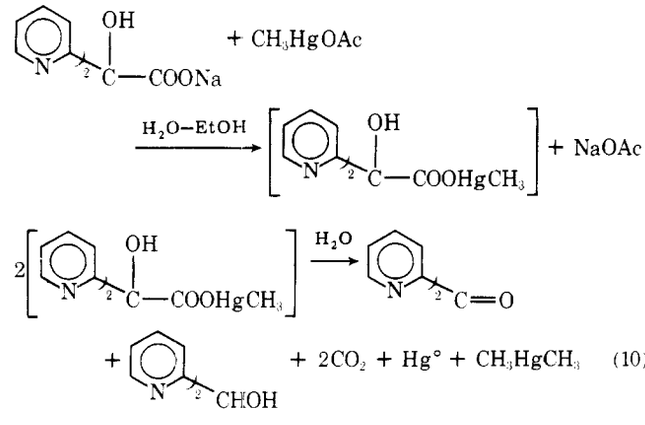


(9)

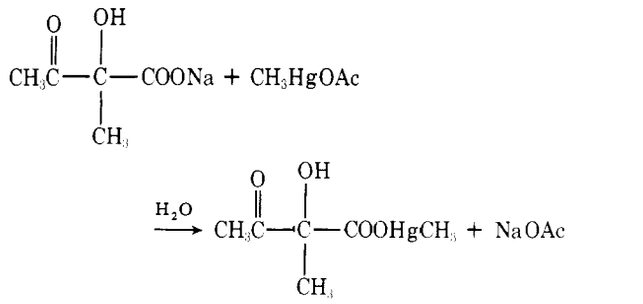
In attempting to isolate the methylmercuric(II) salt of di-2-pyridylhydroxyacetic acid, a white precipitate formed in cold aqueous ethanol, but upon warming the solution to room temperature evolution of carbon dioxide occurred with concomitant deposition of Hg° (eq 10 represents the experimentally observed stoichiometry, including formation of $(CH_3)_2Hg$).

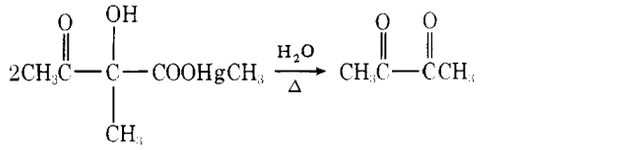
The methylmercury(II) salt of acetolactic acid[7] was found to decompose only slowly in hot water (eq 11).

It is well known that β-keto acids[8] and 2-pyridylacetic acids[9]

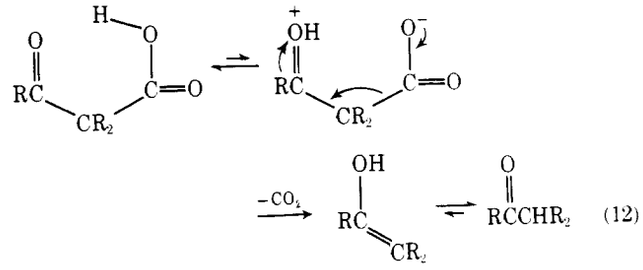


+ $2CO_2$ + Hg° + CH_3HgCH_3 (10)

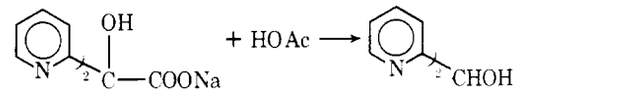




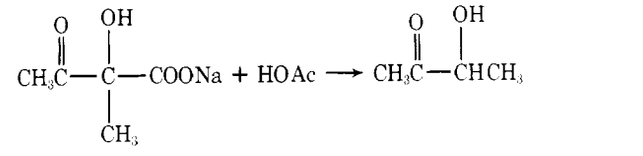
+ $CH_3C(=O)CHCH_3$ + $2CO_2$ + Hg° + CH_3HgCH_3 (11)



(see also ref 6 concerning di-2-pyridylhydroxyacetic acid) undergo slow spontaneous decarboxylation (eq 12). Therefore, it is expected that the mole of acetic acid generated in eq 6 and 7 would cause decarboxylation of a second mole of substrate if the latter were present in excess of the mercury(II) oxidant. This was verified by the observation that each of the sodium salts when mixed with an equivalent of acetic acid underwent rapid decarboxylation as shown in eq 13 and 14. The observed stoichiometries 8 and 9 are evidently then mere composites of eq 6 and 7 with eq 13 and 14, respectively.



+ NaOAc + CO_2 (13)



+ NaOAc + CO_2 (14)

In reaction 10, dimethylmercury is one of the products, which is surprising considering that alkylmercuric cations are weak oxidizing agents. The process by which organomercuric salts are converted to diorganomercurials, termed "symmetrization", represents the unfavorable direction of an equilibrium regarded as bimolecular electrophilic substitution:[10]

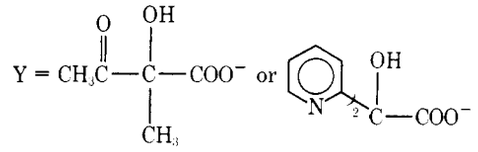
$$2RHg^+(L)_n \underset{n=0,1,2}{\rightleftharpoons} R_2Hg + Hg^{2+}(L)_{2n} \quad (15)$$

In order to achieve "symmetrization", the equilibrium is displaced to the right by removal of the Hg^{2+} product, usually via formation of an especially stable complex with strong li-

gands (L) (e.g., HgI_4^{2-} or $HgX_2 \cdot 2NH_3$).[11] Although R_2Hg is readily obtained in this way when R is aryl or β-unsaturated alkyl, simple alkylmercuric salts are usually resistant to such conversion.[12] However, methylmercuric salts have been reported to symmetrize slowly (with such ligands as thiocyanate[13] or phosphines[14]), and it is therefore reasonable to interpret eq 10 and 11 in terms of the slow, low-level equilibrium production of a mercury(II) complex (eq 16) which is removed in this case via the redox eq 8 and 9, respectively.[15]

Exclusive of their biasing effect on the *equilibrium*, strong ligands promote the *rate* of symmetrization processes as well.[16] The overall transformation shown in eq 10 proceeds much faster to completion than that in eq 11 probably because the rate limiting step is symmetrization in each case—pyridine

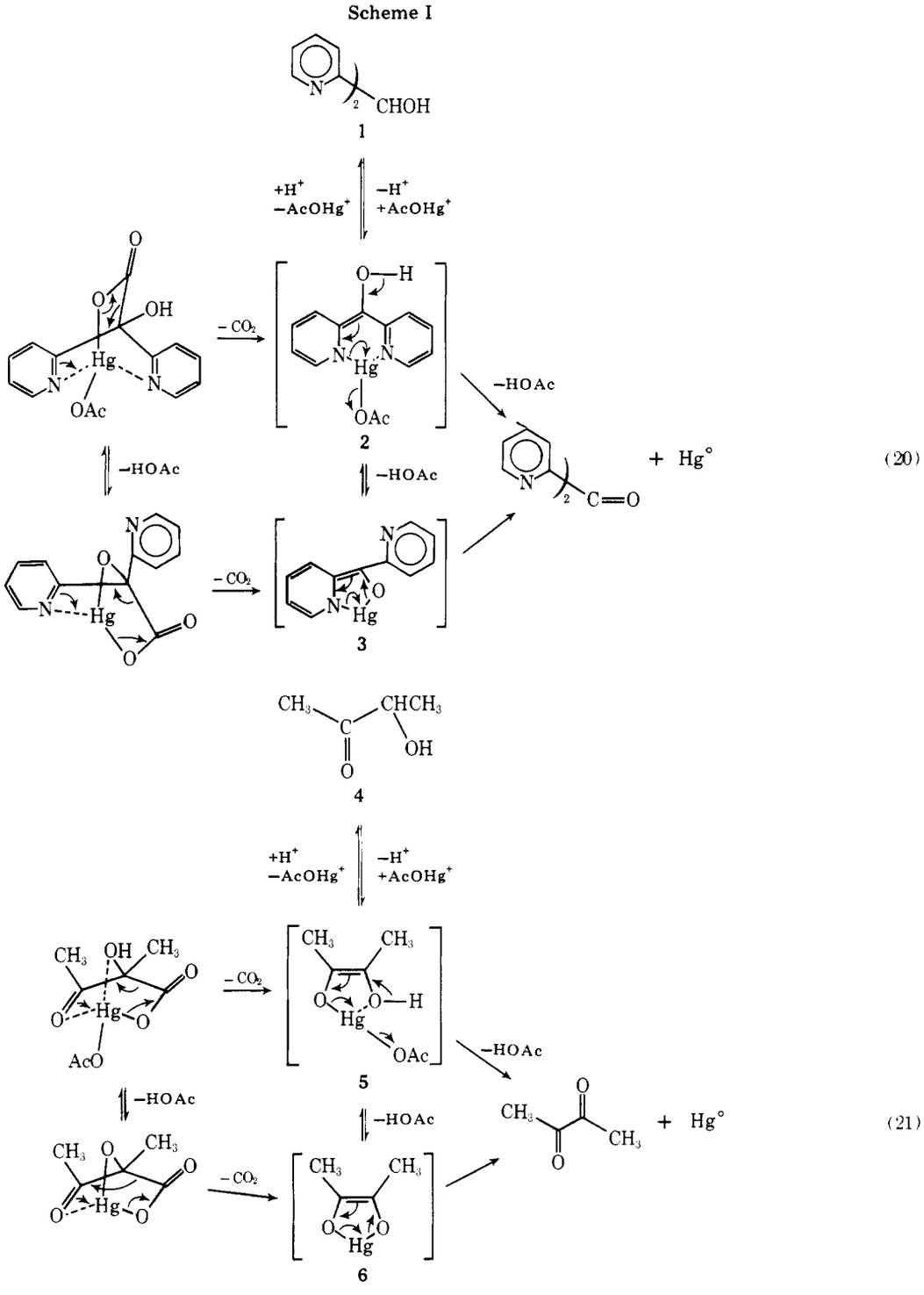
$$2NaY + 2CH_3HgOAc \longrightarrow [2NaOAc + 2CH_3HgY] \rightleftharpoons CH_3HgCH_3 + HgY_2 \quad (16)$$



is a much better mercury ligand than is carbonyl[17] and thus is likely a much better catalyst for symmetrization.

The requirement of the β-keto or β-imino group for reaction is appreciated in view of the inertness of mercuric benzilate

Scheme I



to undergo oxidative decarboxylation (β >C=C< instead of β >C=O:: or β >C=N–):

$$Ph_2C(OH)COO^- + Hg^{2+} \rightarrow \text{no reaction} \quad (17)$$

This inertness is especially noteworthy since benzilate is oxidatively decarboxylated by strong *single*-electron oxidants (Ce^{IV},[18] Mn^{III},[19] V^V,[20] and Cr^{VI} [21]). The latter reactants are believed to proceed via intermediate formation of a "benzylic" radical (ox = high oxidation and red = reduced states):

$$Ph_2C(OH)COOM^{ox} \rightarrow Ph_2\dot{C}OH + CO_2 + M^{red} \quad (18)$$

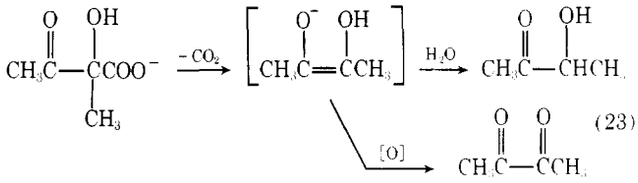
$$Ph_2\dot{C}OH + M^{ox} \rightarrow Ph_2C{=}O + H^+ + M^{red} \quad (19)$$

A mechanism for eq 6 and 7 that is consistent with the above results and information is a mercury(II)-catalyzed decarboxylation followed immediately by *two*-electron (inner-sphere) redox (Scheme I). Chelation of the β-keto (or β-imino) group to mercury provides an electron sink for the decarboxylation. The loss of acetic acid could presumably occur prior to redox or concurrent with redox. Intermediates **2** and **5** are the metal enolates (conjugate bases) of the β-keto (or β-imino) alcohols **1** and **4**. Additional experiments demonstrated that these alcohols are resistant to oxidation by mercury(II). Thus, once formed, the enolates **2** and **5** must decompose to products, preclusive of the establishment of the **1**–**2** and **4**–**5** (protonation) equilibria. Independent generation of the enolate **5** by adding $Hg(OAc)_2$ to a premixture of acetoin (**4**) with one equivalent of NaOH led to the deposition of Hg°. Although the similar experiment performed with di-2-pyridylmethanol (**1**) does not produce Hg°,[22] this is apparently due to the failure therein in generating the enolate **2**; it was shown that the "benzylic" proton of **1** did not exchange in D_2O with up to two added equivalents of NaOH.

Although it would be unusual, concerted decarboxylation redox cannot be eliminated here. That the enolate from **4** (and presumably from **1** also, if it could be independently formed) can reduce mercury(II) does not guarantee that it is an intermediate along the title reaction pathway.

The present case features a metal which serves as a catalyst for decarboxylation of a substrate to an intermediate and then as a reactant in subsequent oxidation of that intermediate. Dual roles of metals in organic reactions have been reported previously, but may be a common and synthetically useful phenomenon.

Of further interest is that the title reaction occurs under physiological conditions (pH ~7 and ambient temperature) with biologically important compounds: Two pertinent substrates, acetolactate (see eq 7, 9, 11, 14, and 21) and the homologous α-aceto-α-hydroxybutyrate, are crucial intermediates in the biosynthesis of valine and isoleucine, respectively.[23] Acetolactate is also a major intermediate in the anaerobic fermentation of sugars, formed by the condensation of "active" acetaldehyde with pyruvate.[24] Subsequent enzymatic decarboxylation leads to acetoin and varying amounts of biacetyl (eq 22). That the biacetyl is formed *during* decarboxylation is shown by the inability of cell-free enzymes to oxidize acetoin to biacetyl.[25] Apparently, biacetyl formation is dependent only on the reducing potential of the fermentation medium.[26] Many bacterial, plant, or animal tissues can condense "active" acetaldehyde with acetaldehyde directly, forming acetoin uncontaminated by biacetyl (eq 22).[27] In general, those cell-free extracts which do not form biacetyl also do not decarboxylate acetolactate.[28] Our results demonstrate that biacetyl formation may be the result of diversion from the normal pathway leading to acetoin via oxidation of the precursor enolate anion:



(23)

Experimental Section

General. All reactions involving mercury compounds were carried out with protection from light. Methylmercuric nitrate and acetate were obtained by treating methylmercuric iodide (from CH_3MgI and $HgBr_2$) with silver nitrate and acetate, respectively. The nitrate was purified by recrystallization from methanol and the acetate from carbon tetrachloride.

NMR spectra were recorded using a Varian T-60 spectrometer and sample resonances are reported with respect to internal solvent references: $CHCl_3$ at δ 7.38 and CH_2Cl_2 at δ 5.34.

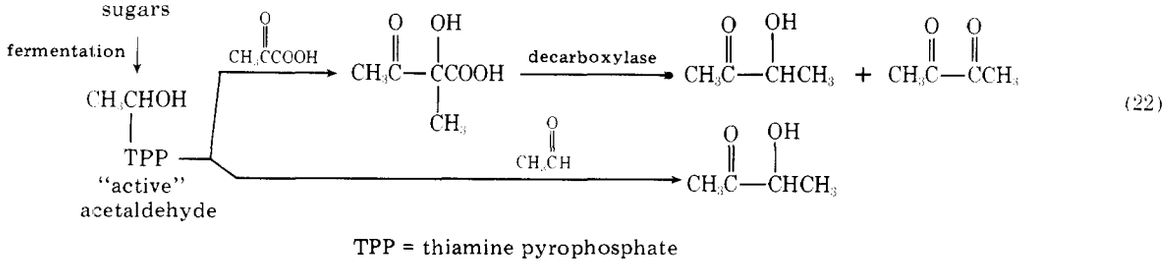
Unless indicated otherwise, all experiments were performed at ambient temperature (about 22 °C).

Reactions of Sodium Di-2-pyridylhydroxyacetate (7) (see ref 6). (A) With CH_3HgOAc or CH_3HgNO_3. Mercurial (1 mmol) and 1.1 mmol of **7** were stirred together in 1.5 mL of D_2O and 1.5 mL of $CDCl_3$. At low temperature the fluffy white solid formed persisted, but blackening occurred within a couple minutes at room temperature. After being stirred overnight the black particulate mercury had collected into a small metallic drop. This was collected by filtration, washed with a little ether, and weighed, yield 85–95% theoretical (0.5 mmol, see eq 10). NMR spectra were obtained for the two layers of the filtrate. The spectrum of the $CDCl_3$ layer indicated the presence of dipyridyl ketone (by comparison to a spectrum obtained on commercially available material) and dimethylmercury (singlet at δ 0.27 with characteristic (J = 103 Hz) ^1H–^{199}Hg satellites).

(B) With 1 Equiv of Mercuric Acetate. Mercuric acetate (1 mmol) and 1.03 mmol of **7** were stirred into 2 mL of D_2O and 2 mL of CH_2Cl_2. Immediate blackening occurred concomitant with evolution of a gas. After several hours the mixture was filtered. The NMR spectrum of the CH_2Cl_2 layer showed only dipyridyl ketone (H_5 doublet at δ 8.69).

(C) With 0.5 Equiv of Mercuric Acetate (or Sulfate). The mercury salt (1 mmol) and 2.1 mmol of **7** were stirred together in 2 mL of D_2O and 2 mL of CH_2Cl_2. Immediate blackening occurred (with gas evolution). After several hours a ball of mercury formed which was collected by filtration, yield 90–95% theoretical (1 mmol, see eq 8). NMR of the CH_2Cl_2 layer showed the presence of two substituted pyridine compounds (H_5 doublets at δ 8.69 and 8.51). Bubbling oxygen through the solution overnight caused nearly complete disappearance of the upfield doublet and resolution of the entire pattern of pyridine resonances to that of dipyridyl ketone. This is consistent with initial equimolar production of dipyridylmethanol.

(d) With 1 Equiv of HOAc. Acetic acid (2 mmol) and 2 mmol of **7** were stirred together into 2 mL of D_2O and 3 mL of CH_2Cl_2. Immediate effervescence and warming occurred. After stirring for several hours, the NMR spectrum of the CH_2Cl_2 layer showed the presence of a (single) substituted pyridine (only one H_5 doublet at δ 8.51; the methine hydrogen appears at δ 5.97). Superimposing this spectrum



(22)

TPP = thiamine pyrophosphate

on the spectrum from the previous experiment (3) showed complete matching of all resonances not belonging to dipyridyl ketone.

To the D_2O–CH_2Cl_2 mixture (evidently containing dipyridylmethanol) was added 1 mmol of $Hg(OAc)_2$. The resulting solution remained clear and homogeneous (two layers) for several days. NMR spectra of the respective layers indicated that dipyridylmethanol is extracted into the aqueous layer (presumably via complexing to mercuric ion).

In another experiment, 2 mmol each of 7 and HOAc were stirred into a little H_2O/CH_2Cl_2. The CH_2Cl_2 layer was separated off, washed with D_2O, and added to 0.4 mL of D_2O and this mixture was concentrated in vacuo to about 0.4 mL. Solid NaOH (2 mmol) was added and stirred to solution. NMR spectra taken the next day indicated that about 26% oxidation of the alcohol to the ketone had occurred (based on integration of the pyridine H_5 doublets), but no integrational discrepancy for the methine hydrogen (δ 5.97) (i.e., no deuterium exchange) could be seen for the remaining (74%) alcohol.

Synthesis of Ethyl 2-Methyl-3-oxobutanoate. Sodium ethoxide (0.5 mol) was stirred into 300 mL of absolute ethanol under nitrogen. Ethyl acetoacetate (MCB) (0.5 mol) was added and the resulting solution was stirred for 15 min and then brought to reflux. Methyl iodide (0.55 mol), freshly distilled from P_2O_5, in 30 mL of absolute ethanol was added dropwise to the mechanically stirred solution. After addition was complete, the mixture was stirred at reflux for several hours. The mixture was cooled to 0 °C and suction filtered (to remove NaI). The filtrate was concentrated by rotary evaporation. Vacuum distillation of the residue afforded a constant boiling fraction at 53 °C and 5 mm Hg.

Synthesis of Ethyl 2-Acetoxy-2-methyl-3-oxobutanoate (8). The lead tetraacetate method of Krampitz (see ref 7) was used without modification. Vacuum distillation afforded a constant boiling fraction at 75 °C and 0.2 mm Hg.

Reactions of Sodium Acetolactate (9) (see ref 7). (A) With CH_3HgOAc. (CH_3HgNO_3 was actually used but standard solutions of the anion 9 contain 1 equiv of acetate ion.) Methylmercuric nitrate (2.52 mmol) was added to a solution of 2.52 mmol of sodium acetolactate (generated from 2.52 mmol of 8 and 15.7 mL of 0.321 M NaOH) and the resulting clear homogenate was stirred for 24 h at room temperature. A small ball of mercury had deposited at this time. Approximately 0.4 mL of volatiles was collected by slow fractional distillation at 1 atm. The distillate consisted of two layers. The upper layer proved to be EtOH (by NMR), generated from the saponification of 8. NMR of the lower (yellow) layer (diluted with a little CH_2Cl_2) showed a singlet at δ 2.26 (consistent with biacetyl, vide infra) and a singlet at δ 0.27 (consistent with dimethylmercury; ^1H–^{199}Hg satellites, J = 103 Hz). The mercury droplet obtained from the cooled distillation pot corresponded to 83% of the theoretical yield (1.26 mmol, see eq 11).

(B) With 1 Equiv of $Hg(OAc)_2$. Mercuric acetate (1.26 mmol) was added to a solution of 1.26 mmol of sodium acetolactate (from 8 and aqueous NaOH) and stirred overnight. At that time a small ball of mercury was present. A few drops of a yellow oil (bp 75 °C) was collected by slow fractional distillation. It possessed the characteristic odor of biacetyl and NMR showed the expected singlet at δ 2.26 (as well as resonances due to EtOH from saponification of 8).

(C) With 0.5 Equiv of $Hg(OAc)_2$. Mercuric acetate (0.68 mmol) was added to a solution of 1.36 mmol of sodium acetolactate (from 8 and aqueous NaOH) and stirred for 24 h. A few drops of volatiles were collected by fractional distillation and shown to be (NMR) mainly biacetyl (δ 2.26, and having characteristic odor) and ethanol. The distillation pot was cooled and filtered to remove the mercury ball (yield 0.52 mmol, 76% of theoretical, see eq 9). The filtrate was saturated with KOAc and extracted several times with ether. The ether extract was added to 0.5 mL of D_2O and the mixture was rotovapped to remove ether. NMR of the residue displayed a singlet at δ 2.20 and a doublet at δ1.33 with equal integration and was identical with the NMR spectrum of commercial acetoin (85% in water). The methine quartet was obscured in both cases by the water peak.

(D) With 1 Equiv of HOAc. Acetic acid (2.1 mmol) was added to a solution of 2.2 mmol of sodium acetolactate (from 8 and aqueous NaOH) and stirred for 30 min. The aqueous layer was saturated with NaCl and extracted several times with ether. Rotary evaporation left a residue which displayed an NMR spectrum identical with that of commercial acetoin (85% in water) (as well as resonances due to ethanol).

Reaction of the Enolate Anion of Acetoin with $Hg(OAc)_2$. Commercial acetoin (5 mmol, 0.5183 g of 85% aqueous solution) and 5 mmol of NaOH were stirred to homogeneity in 2 mL of H_2O. Mercuric acetate (5 mmol) dissolved in 2 mL of H_2O was added. Immediate blackening occurred (with transient appearance of yellow HgO). Stirring for 20 h left a clear solution, possessing the strong characteristic odor of biacetyl, and a ball of mercury.

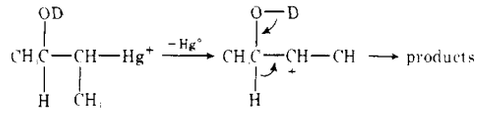
Attempted Reaction of Sodium Benzilate with $Hg(OAc)_2$. Sodium benzilate was prepared by mixing equimolar quantities of benzilic acid and NaOH in methanol and evaporating, in vacuo, to dryness. The salt was purified by precipitation from methylene chloride/petroleum ether. Mercuric acetate (0.5 mmol) and sodium benzilate (1.05 mmol) were stirred into 2 mL of D_2O plus 2 mL of CH_2Cl_2. No visible reaction occurred for several days. NMR spectra obtained for each layer indicated that mercuric benzilate is partitioned into the organic layer.

Acknowledgment. Grateful acknowledgment is made to the National Institutes of Health (GM-15373) and the National Science Foundation (GP-33669) for support of this work.

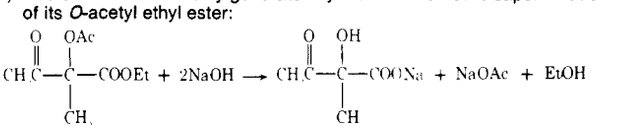
Registry No.—Sodium di-2-pyridylhydroxyacetate, 67761-52-8; ethyl 2-acetoxy-2-methyl-3-oxobutanoate, 25409-39-6; sodium acetolactate, 67761-53-9; ethyl 2-methyl-3-oxobutanoate, 609-14-3; methylmercuric acetate, 108-07-6; methylmercuric nitrate, 2374-27-8; mercuric acetate, 1600-27-7; acetic acid, 64-19-7; acetoin, 513-86-0; sodium benzilate, 13154-93-3; ethyl acetoacetate, 141-97-9; methyl iodide, 74-88-4.

References and Notes

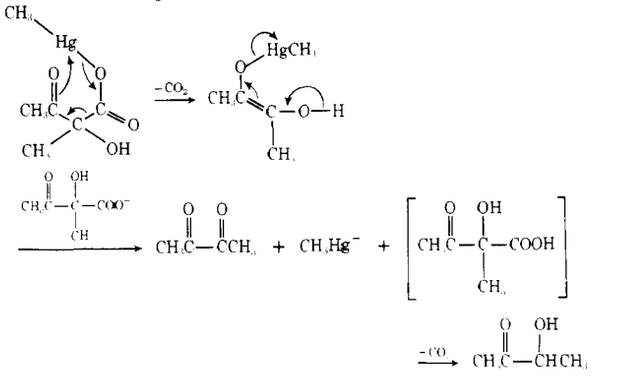
(1) (a) R. L. Augustine, "Oxidation", Vol. I, Marcel Dekker, New York, N.Y., 1969, p 24; (b) B. C. Fielding and H. L. Roberts, *J. Chem. Soc. A*, 1627 (1966).
(2) (a) T. Iwayanagi, M. Matsuo, and Y. Saito, *J. Organomet. Chem.*, **135**, 1 (1977); (b) M. Matsuo and Y. Saito, *J. Org. Chem.*, **37**, 3350 (1972).
(3) The decomposition of the alkylmercury cation probably occurs in two steps:

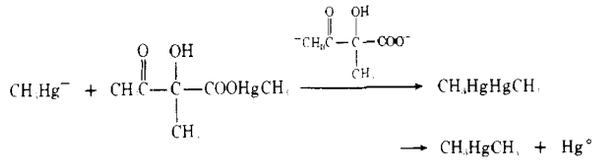


F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961); *ibid.*, **85**, 363 (1963).
(4) J. S. Littler, *J. Chem. Soc.*, 827 (1962).
(5) See p 102, ref 1a.
(6) Sodium di-2-pyridylhydroxyacetate was prepared according to J. Klosa, *J. Prakt. Chem.*, **282**, 335 (1960). It was reported therein that neutralization in water yielded di-2-pyridylmethanol.
(7) Acetolactate was freshly generated by the stoichiometric saponification of its *O*-acetyl ethyl ester:



L. O. Krampitz, *Arch. Biochem.*, **17**, 81 (1948).
(8) R. G. Button and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 557 (1973).
(9) W. von E. Doering and V. Z. Pasternak, *J. Am. Chem. Soc.*, **72**, 143 (1950).
(10) (a) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, N.Y., 1968, p 120; (b) L. G. Makarova in "Methods of Elemento-Organic Chemistry", Vol. 4, A. N. Nesmeyanov and K. A. Kocheshkov, Eds., North-Holland Publishing Co., Amsterdam, 1967, p 302; (c) Y. Halpern and N. Garti, *J. Organomet. Chem.*, **92**, 291 (1975).
(11) (a) G. B. Deacon, *J. Organomet. Chem.*, **12**, 389 (1968); (b) see ref 10a, pp 121 and 123.
(12) See ref 10a, p 121.
(13) J. Relf, R. P. Cooney, and H. F. Henneike, *J. Organomet. Chem.*, **39**, 75 (1972).
(14) G. E. Coates and A. Lauder, *J. Chem. Soc.*, 1857 (1965).
(15) In analogy to the known Mg-induced process (cf. ref 10a, p 141), one can also write a direct two-electron reduction-induced symmetrization for the present case, e.g.,





However, this is considered to be an unlikely prospect in the aqueous environment.

(16) See ref 10a, p 125. This statement holds when such ligands are present in excess over the satisfaction of mercury(II) coordination.
(17) I. P. Beletskaya, K. P. Butin, A. N. Ryabtsev, and O. A. Reutov, *J. Organomet. Chem.*, **59**, 1 (1973).
(18) (a) S. K. Misra and R. C. Mehrotra, *J. Indian Chem. Soc.*, **44**, 927 (1967); (b) V. K. Grover and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **31**, 1403 (1969).
(19) K. K. Sengupta, D. K. Khemrui, and D. C. Mukherjee, *J. Indian Chem. Soc.*, **52**, 467 (1975).
(20) W. A. Waters and J. S. Littler in "Oxidation in Organic Chemistry: Part A", K. B. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 207.
(21) J. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1192 (1964).
(22) A yellow precipitate, presumably HgO, was initially produced, and no further transformation occurred.
(23) A. L. Lehninger, "Biochemistry", Worth Publishers, New York, N.Y., 1970, p 550.
(24) H. J. Strecker and S. Ochoa, *J. Biol. Chem.*, **209**, 313 (1954).
(25) (a) A. D. Portno, *J. Inst. Brewing*, **72**, 458 (1966); (b) H. Suomalainen and P. Ronkainen, *Nature (London)*, **220**, 792 (1968).
(26) T. Inoue, K. Masuyama, Y. Yamamoto, and K. Okada, *Rep. Res. Lab. Kirin Brew. Co.*, 17 (1968).
(27) E. Juni, *J. Biol. Chem.*, **195**, 727 (1952).
(28) (a) L. F. Chuang and E. B. Collins, *J. Bacteriol.*, **95**, 2083 (1968); (b) E. Juni, *J. Biol. Chem.*, **195**, 715 (1952).

Radical Isomerization and Hydrogen–Deuterium Exchange in Reactions of Silver *p-tert*-Butylbenzoate

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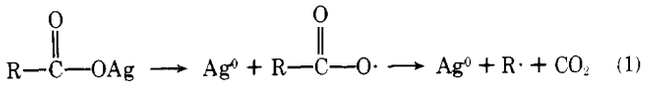
Silver *p-tert*-butylbenzoate decomposes at 300 °C to products that retain the *tert*-butyl group intact. Among these products are five isomeric di-*tert*-butylbiphenyls, evidently resulting by isomerization of the first-formed *p-tert*-butylphenyl radical. With labeled benzophenone and benzene, the silver salt gives products in which much protium–deuterium exchange has occurred. The photolyzed silver salt arylates 1,2,4-trichlorobenzene; thermal decomposition in benzonitrile yields triphenyltriazine in addition to the radical arylation product.

We discovered that silver carboxylates decompose at 200–400 °C according to eq 1. We have described the formation and reactions of mono- and polyradicals from silver arenecarboxylates in a previous publication.[1] More recently, we wished to find if a thermally labile group such as *tert*-butyl could survive the elevated temperatures at which silver salts decompose. Accordingly, we pyrolyzed 8.55 g (30 mmol) of silver *p-tert*-butylbenzoate (294 °C dec) at 300 °C under nitrogen and obtained 4.2 g of a distillate composed of the products listed in Table I. All products apparently retained the *tert*-butylphenyl group intact.



(1)

In addition to demonstrating the survival of the *tert*-butyl groups at the pyrolysis temperature, analyses of the products presented two other points of interest.

The presence in a single spectrum of *tert*-butylbenzene and of biphenyl, terphenyl, and quaterphenyl with a *tert*-butyl group on each ring offered a clear illustration of the effect of molecular size on a favored decomposition in the mass spectrum. All *tert*-butylarenes have a marked tendency to lose CH_3 under electron impact. In a small molecule such as *tert*-butylbenzene, the intensity ratio of $[M^+ - CH_3]/[M^+]$ in 70 eV spectra usually is about 4 or 5:1. With increase of molecular size, this ratio tends to drop, presumably because of the increased number of degrees of freedom. The ratios are shown in Table II.

Directly coupled gas chromatography/mass spectrometry revealed the presence of five isomeric di-*tert*-butylbiphenyls, whose partial spectra are shown in Table III. The high intensity at m/z 195 for $(M - CH_3 - C_4H_8)^+$ ions in isomers **1** and **2** suggested that these contained two and one *tert*-butyl groups, respectively, ortho to the second ring and that isomers **3, 4,** and **5** contained no *tert*-butyl group ortho to the second ring. The absence of ortho substitutions in **3, 4,** and **5** was confirmed by synthesis of authentic 3,3′- and 4,4′-di-*tert*-butylbiphenyl and of a mixture containing known amounts of the 3,3′, 3,4′, and 4,4′ isomers; this allows firm identification by retention time of isomers **3, 4,** and **5,** respectively, as the 3,3′-, 3,4′-, and 4,4′-di-*tert*-butylbiphenyls. The relative amount of each isomer formed from silver *tert*-butylbenzoate, as determined by gas chromatography, is shown in Table IV.

One might expect 3,4′-di-*tert*-butylbiphenyl to be the

Table I. Products from Silver *p-tert*-Butylbenzoate at 300 °C

product	relative concentration[a]
tert-butylbenzene	38.6
tert-butylbenzoic acid	4.5
di-*tert*-butylbiphenyl	30.1
di-*tert*-butylbenzocoumarin	2.2
tri-*tert*-butylterphenyl	5.6
tetra-*tert*-butylquaterphenyl	0.7

[a] Percent of total ions in the low-voltage (7.5 eV nominal) mass spectrum.

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