Acetylation produced the **diacetate IIc** with m.p. 113–114°, undepressed upon admixture with a specimen produced according to procedure (a), $[\alpha]^{20}D$ +23.9°.

$\Delta^{7,16}$-Allopregnadiene-3β, 20β (?)-diol (IV).—Produced in 70% yield by lithium aluminum hydride reduction of III[3]; colorless crystals (from ether–hexane), m.p. 145–147°. $[\alpha]^{20}D$ +6.6°, no selective absorption in the ultraviolet.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19. Found: C, 79.36; H, 10.26.

16α,17α-Oxido-Δ^7-allopregnen-3β-ol-20-one (Va).—To a solution of 5.0 g. of $\Delta^{7,16}$-allopregnadien-3β-ol-20-one 3-acetate (III)[3] in 400 cc. of methanol, cooled to 18°, was added dropwise simultaneously from two separatory funnels 10 cc. of 30% hydrogen peroxide and a solution of 2.3 g. of sodium hydroxide in 10 cc. of water and 25 cc. of methanol. After stirring for one hour at room temperature, the mixture was left in the ice-box overnight and then diluted with water. Filtration yielded 4.6 g. of a mixture of free alcohol (Va) and acetate (Vb), which did not show any ultraviolet absorption maximum at 240 mμ. The crude material was saponified by boiling with methanolic potassium bicarbonate solution for one hour and the colorless crystals were recrystallized from acetone–water yielding 4.2 g. (90%) of the alcohol Va with m.p. 124–126°, $[\alpha]^{20}D$ +32.5°.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.38; H, 9.41.

The acetate Vb exhibited m.p. 153–155°, $[\alpha]^{20}D$ +28°; yellow color with tetranitromethane.

Anal. Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 73.94; H, 8.54.

16α,17α-Oxido-$\Delta^{7,9(11)}$-allopregnadien-3β-ol-20-one 3-Acetate (VI).—The mercuric acetate dehydrogenation of the oxide Vb was carried out exactly as described above for Ic and after recrystallization from methanol afforded large prisms of the diene VI with m.p. 153–155°, $[\alpha]^{20}D$ +102°, ultraviolet absorption maxima at 234° mμ (log ε 4.13) and 242 mμ (log ε 4.17). The product gave an orange color with tetranitromethane.

Anal. Calcd. for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.64; H, 8.48.

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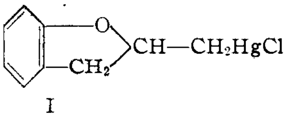
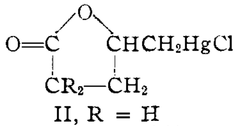
Mercurial Diuretics. V. Stability of Mercury–Olefin Addition Compounds to Hydrochloric Acid

BY R. L. ROWLAND AND E. F. KLUCHESKY

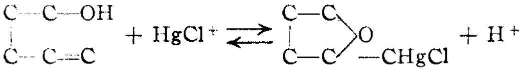
The products obtained by the addition of mercuric salts to olefins in water or alcohol are as a general rule decomposed by mineral acids. Certain exceptions to this rule have been noted: for example, 2-chloromercurimethyl-2,3-dihydrobenzofuran (I) obtained by the mercuration of *o*-allylphenol, exhibits stability to acids which is remarkable when compared with other olefin–mercuric salt addition compounds.[1] Recently the formation of δ-chloromercuri-γ-valerolactones, II, III, by the reaction of allyl acetic acids with mercuric salts, has been reported.[2] The similarity of the structures of I, II and III suggested the study of the stability of II and III toward mineral acid.


I


II, R = H
III, R = C_6H_5

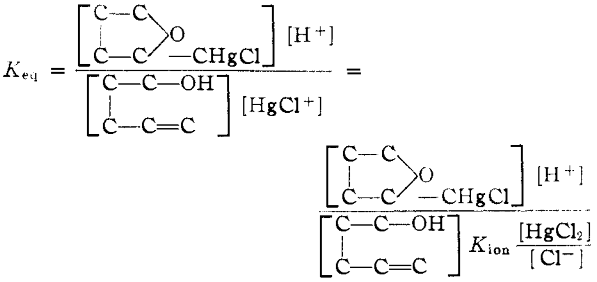
Formation of mercuric chloride from the δ-chloromercuri-γ-valerolactones was studied polarographically. With 0.07 *N* aqueous hydrochloric acid, II was decomposed rapidly while III did not react; III was decomposed, however, by 1 and 6 *N* hydrochloric acid. The pronounced difference in the ease of formation of mercuric chloride from II and from III may be related to stabilization of III by alpha substitution, but it would appear probable that this difference is largely a result of difference in solubility, II being quite soluble in water while III is very insoluble.

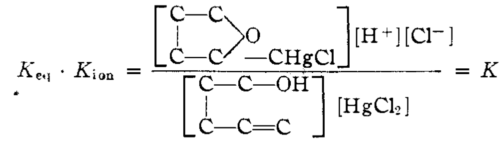
Since our study of the rate of decomposition of III in 1 *N* acid apparently measured the rate of solution of III, attention was directed to the equilibria involved in the acid decomposition of II and III. On the basis of the mechanism resulting from the study of Lucas, Hepner and Winstein,[3] the reaction under consideration would be



Since

$$K_{ion} = \frac{[HgCl^+]\,[Cl^-]}{[HgCl_2]}$$





The value of *K* has been determined previously for the reaction of ethylene with mercuric chloride in water.[4]

Although decomposition of 0.0001 mole of II by 100 ml. of 0.07 *N* hydrochloric acid was essentially complete, only 50% decomposition occurred with 0.01 *N* acid (note Table I). Accordingly, the value of *K* for the reaction of allylacetic acid with mercuric chloride in water was calculated to be 0.19.[5] When the equilibrium was approached by reaction of allylacetic acid with mercuric chloride in an aqueous solution which was originally 0.01 *M* in both reactants, the equilibrium concentration of mercuric chloride was determined polarographically to be 0.0019 *M;* on the basis of this observation, the value of *K* was 0.15.

No mercuric chloride was detected after agitation of III and 0.07 *N* hydrochloric acid for 312 hours.

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[1] R. Adams, F. L. Roman and W. N. Sperry, THIS JOURNAL, **44**, 1781 (1922).

[2] R. L. Rowland, W. L. Perry and H. L. Friedman, *ibid.*, **73**, 1040 (1951).

[3] H. J. Lucas, F. R. Hepner and S. J. Winstein, *ibid.*, **61**, 3102 (1939); J. Chatt, *Chem. Revs.*, **48**, 37 (1951).

[4] J. Sand and F. Breest, *Z. physik. Chem.*, **59**, 424 (1907).

[5] In this and subsequent calculations, the value of $HgCl_2$ was corrected for the formation of $HgCl_3^-$ and $HgCl_4^=$ utilizing the constants $[HgCl_3^-]/[HgCl_2][Cl^-] = 7$ and $[HgCl_4^=]/[HgCl_2][Cl^-]^2 = 70$, determined by B. Lindgren, A. Jonsson and L. G. Sillen, *Acta Chem. Scand.*, **1**, 479 (1947).

Table I

Decomposition of Mercurials by Aqueous Hydrochloric Acid

	Compound		Acid		Time,	Decomp.,
	mg.	mmole	ml.	N	hr.	%
	37	0.10	100	0.01	230	16
	37	.10	100	.07	4	3
					7	7
					24	20
					66	50
					188	76
					316	90
I	370	1.0	100	.07	168	11
II	66.8	0.20	200	.01	0.5	51
					24	48
II	33.4	.10	100	.07	0.5	85
					1	100
III	48.7	.10	100	.07	312	0
III	120	.25	10	1.0	24	18
					136	63
					312	68
III	120	.25	10	6.0	16	90

Decomposition of 0.00025 mole of III by 10 ml. of 6 N hydrochloric acid was close to 100% within 16 hours. With 1 N hydrochloric acid decomposition was relatively slow and equilibrium appeared to have been reached after 312 hours. Because of difficulty in determining the solubility of III and of allyldiphenylacetic acid in water, an equilibrium constant was not calculated for this reaction.

The percentages of decomposition of 2-chloromercurimethyl-2,3-dihydrobenzofuran (I), determined after vigorous shaking with hydrochloric acid appear in Table I. From these studies and a solubility of I in water at room temperature of *ca.* 0.0001 M, values of K for the reaction of mercuric chloride and *o*-allylphenol were found to lie in a range from 0.4 to 1.0. The value of 1.0 calculated from the 90% decomposition of 0.0001 mole of I by 0.07 N hydrochloric acid is the least reliable; in this case a variation of 5% in the measurement of mercuric chloride could lower the value of K to 0.45. When the equilibrium was approached from the opposite direction by the reaction of 0.0001 M mercuric chloride with 0.0001 M *o*-allylphenol in 0.001 N hydrochloric acid, the reaction was 87% complete; the value of K as determined by this experiment was 0.55.

The rate of reaction of I with acid, similar to the rate of reaction of III with acid, would appear to be limited by the rate of solution of I.

Polarographic study of the decomposition in alcoholic solution was not possible by the technique which we attempted which involved dilution with water prior to analysis. The equilibria were indicated, however, by the yields of I and III produced in ethyl alcohol by reaction of mercuric chloride with *o*-allylphenol and with allyldiphenylacetic acid.

Although the results of this investigation suggest a study of the rate of reaction of mercuric chloride with allylacetic acid and with *o*-allylphenol, as well as a more complete study of the decomposition by mineral acid of olefin–mercury addition compounds, we are unable at the present time to devote further attention to these problems.

Experimental

Mercuric ion was determined polarographically using the standard addition technique[6] at zero potential with a saturated calomel anode. The analyses gave high results which were corrected by a factor determined using known concentrations of mercuric chloride. Although the inherent error may be relatively large, this method appeared suitable for the purpose of this investigation. Prior to study of their decomposition the mercurials were crystallized to constant melting point as previously described.[1,2]

Equilibria in Alcohol.—Polarographic study of the reaction of III with hydrochloric acid in ethyl alcohol was hindered, presumably owing to the shifting of the reaction by the addition of aqueous hydrochloric acid prior to the polarographic determination. Thus addition of 3.1 ml. of 2.2 N ethanolic hydrogen chloride to a boiling mixture of ethyl alcohol and 0.22 g. of III followed by dilution with ethyl alcohol to a volume of 100 ml. resulted in complete solution of III. No precipitation occurred upon cooling to room temperature although the solubility of III in ethyl alcohol is only *ca.* 0.5 mg./ml. In contrast to this indication of decomposition of 75% or more, polarographic analysis after dilution with aqueous acid showed no mercuric chloride present. Moreover, from concentration at room temperature of a mixture of 1.0 g. of III, 125 ml. of boiling methyl alcohol and 0.5 ml. of concentrated hydrochloric acid, was isolated 0.2 g. (40%) of a solid melting at 142–143° which did not depress the melting point of allyldiphenylacetic acid.

By reaction of a solution of 1.26 g. of allyldiphenylacetic acid in 20 ml. of ethyl alcohol with a solution of 1.36 g. of mercuric chloride in 20 ml. of ethyl alcohol, a precipitate of III was obtained which weighed 0.89 g. Allowing for the solubility of the mercurial, the mercuration proceeded to the extent of 37%.

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[6] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 251–252, 257.

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The Heat of Formation of Aluminum Borohydride[1,2]

By Richard M. Rulon and L. S. Mason

The present investigation is a continuation[3,4] of studies of the thermochemical and thermodynamic properties of certain metallo-borohydrides and related compounds. The reactions of aluminum borohydride with a number of substances were examined in order to select reactions which would be most suitable for determinations of the changes of heat content for the reactions in a bomb calorimeter. The heat of formation of the aluminum borohydride could then be calculated from the heats of reaction and the known heats of formation of all other reactants and products. The direct hydrolysis of liquid aluminum borohydride with liquid water in the bomb produced dark colored residues, strong odors and variation in the extent of completion of the reaction. The reaction of the liquid with oxygen in a combustion bomb offered similar complications. Aluminum borohydride vapor reacted with chlorine and with hydrogen chloride to give white products and apparently

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[1] This report is part of a thesis presented by Richard M. Rulon to the Faculty of the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

[2] The Office of Naval Research supported the major part of this work.

[3] W. D. Davis, L. S. Mason and G. Stegeman, This Journal, **71**, 2775 (1949).

[4] Joe Smisko and L. S. Mason, *ibid.*, **72**, 3679 (1950).