[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE OLEFINS Co., DIVISION OF UNION CARBIDE CORP.]

Organomercury Chemistry. Decomposition of Alkenylmercury Compounds

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The thermal stability of organomercuric acetates, RHgOAc, where R is an alkenyl group, has been investigated. The nature of the products formed and/or the product distribution is dependent upon the position of the double bond and its substitution with regard to the mercury atom. Thermal decomposition of vinyl- or isopropenyl mercuric acetate leads exclusively to the corresponding acetates and metallic mercury, whereas a mixture of products is obtained from allylmercuric and β -substituted vinylmercuric acetates. 3-Butenylmercuric acetates decomposes almost exclusively into acetic acid, butadiene, and metallic mercury. *cis*- and *trans*-1-Propenylmercuric acetates decompose without retention of configuration. A similar dependence of product distribution on the position of the unsaturation is observed in the reaction between mercury dialkenyls and thiophenols.

It has recently been demonstrated¹ that organomercury compounds containing vinyl groups adjacent to a mercury atom undergo reactions that are not observed with organomercury compounds containing aromatic or saturated aliphatic groups. It was therefore of interest to investigate the effect of the double bond in a position other than adjacent to the mercury atom. The thermal decomposition of allyl and 3-butenylmercuric acetates, as well as the reaction of diallylmercury and bis(3-butenyl)mercury with thiophenol was selected for this study. In addition, it was of interest to determine if the decomposition of alkenylmercuric acetate proceeds with retention of configuration. The thermal decomposition of *cis*- and *trans*-1-propenylmercuric acetate was therefore investigated.

DISCUSSION

The effect of unsaturation on the stability of the carbon-mercury bond was demonstrated by heating the organomercuric acetates in acetic acid. The results are summarized in Table I. The stability of alkenylmercuric acetates to the indicated decomposition increases markedly as the unsaturation is removed from the vicinity of the mercury atom. Methyl, phenyl, and cyclopropylmercuric

TABLE I

Decomposition of Alkenylmercuric Acetates in Acetic Acid

$CUCOD + U_{a}$
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CH₃CO₂HgR R	Temp.	Time, Hr.	% Hg Formed ^a	
$\begin{array}{c} CH_2 == CH\\ CH_2 == CHCH_2\\ CH_2 == CHCH_2 CH_2\\ CH_2 == CHCH_2 CH_2\\ CHCH_2 CH_2\\ CHCH_2\\ CHCH_2$	100 120 120	$1.5 \\ 1.0 \\ 4.0$	90 43 4.7	
$C_{6}H_{5}$ Cyclopropyl	150^{b}	4.0	0.0	

^{*a*} The amount of mercury formed is a measure of the stability of the alkenylmercuric acetates. ^{*b*} Sealed tube.

(1) D. J. Foster and E. Tobler, J. Am. Chem. Soc., 83, 851 (1961).

acetate were included to show their stability toward this decomposition reaction.

Only 4.7% of the contained mercury is obtained as the metal when 3-butenylmercuric acetate is heated to 120° in acetic acid for 4 hr. However, heating this compound in the absence of a solvent in the temperature range of $150-200^{\circ}$ results in a complete recovery of mercury as the free metal.

$$\begin{array}{c} CH_2 = CH - CH_2 - CH_2 HgOCOCH_3 \longrightarrow \\ CH_2 = CH - CH = CH_2 + CH_3 CO_2 H + Hg \end{array}$$

Under these conditions, 1.4% of the product is 3-butenylacetate. The major products (greater than 90% yield) are acetic acid and butadiene. Under similar conditions allylmercuric acetate gave a 56% yield of allyl acetate; the remainder of the product was acetic acid, diallyl, and propylene. Vinylmercuric acetate still gave a 95% yield of vinyl acetate under these conditions. This data is summarized in Table II. Two distinct mechanisms are obviously competing in these decompositions. One mechanism predominates in the decomposition of vinylmercuric acetate and isopropenylmercuric acetate while the other predominates in the decomposition of 3-butenylmercuric acetate. The products isolated from the decomposition of allylmercuric acetate indicate that both mechanisms are operating.

The three propenylmercuric acetates were prepared and then decomposed. The results are summarized in Table III. Isopropenylmercuric acetate gave isopropenyl acetate in 94.2% yield. Decomposition of the *cis*-isomer of 1-propenylmercuric acetate gave 50% of 1-propenyl acetate while the remainder of the distillable product was acetic acid and propylene. *cis*-trans isomer ratio of the 1-propenyl acetate product was 2. With the *trans* isomer about 40% of the product was 1propenyl acetate and again the *cis/trans* isomer ratio was approximately 2. Acetic acid and propylene again accounted for the remainder of the distillable product. The stability of the 1-propenyl acetates as determined by gas chromatography is indicated in Table IV.

THERMAL DECOMPOSITION OF ALKENYLMERCURIC ACETATES				
CH ₃ CO ₂ HgR —R	Decomposition Temperature	CH ₃ CO ₂ R Formed ^a	Other Products ^b	
CH2=CH-	110-120	95		
CH2=CHCH2-	120-140	56	AcOH, $(CH_2 = CHCH_2)_2$, CH ₂ =CHCH ₃	
$CH_2 = CHCH_2CH_2 - $	150-200	1.4	AcOH, CH_2 =CHCH= CH ₂	

TABLE III

TABLE II THERMAL DECOMPOSITION OF ALKENYLMERCURIC ACETATES

^a In area per cent, by gas chromatography. ^b By gas chromatography and/or mass spectrometry.

INFLUENCE OF SUBSTITUTION AND cis-trans Isomerization					
CH ₂ CO ₂ HgR	Decomposition	CH	I ₃ CO ₂ R Formed]a	Other
-R Temperature	Temperature	% cis-		% trans-	Products ^b
CH ₃					
$CH_2 = C - C$	105-125		94.2		
H H C=C	115-150	33.6		16.8	AcOH, CH2=CHCH3
CH ₃ CH ₃ H C=C	125-150	28.2		12.8	AcOH, CH2==CHCH3
н					

^a In area per cent, by gas chromatography. ^b By gas chromatography and/or mass spectrometry.

			TABLE	IV		
STABILITY	OF	cis-trans	ISOMERS	OF	1-PROPENYL	Acetate

	Per Cent Composition ^a				
	cis i	somer	trans isomer		
Conditions	cis-	trans-	cis-	trans-	
Immediately after distilla- tion	85.4	14.2	6.3	93.7	
ture 3 hr. at 100° 1 hr. at 150°	86.7 86.7 86.9	$12.9 \\ 13.1 \\ 12.9$	$\begin{array}{c} 6.8\\ 6.7\\ 6.4 \end{array}$	93.2 93.2 93.6	

^a In area per cent, by gas chromatography.

The distribution of isomers of 1-propenyl acetate formed during the decomposition of cis- and trans-1-propenylmercuric acetates suggests that either an isomerization prior to decomposition has taken place or more probably the isomers of 1-propenylmercuric acetate decompose through a common intermediate. The data do not allow one to account for the difference in reactivity of isopropenylmercuric acetate¹ and the 1-propenylmercuric acetate.

When thiophenol and divinylmercury² are mixed at room temperature and subsequently warmed on a steam bath for 0.5 hr., a 90% yield of vinyl phenyl sulfide¹ can ultimately be obtained. The reaction proceeds via a vinylmercuric thiophenolate intermediate.¹ A small amount of mercury-bis-thio-

 $(CH_2 = CH)_2 Hg + C_6H_5SH \longrightarrow CH_2 = CH_2 +$

 $CH_2 = CHHgC_6H_5 \longrightarrow Hg + CH_2 = CHSC_6H_5$

phenolate¹ is also formed in this reaction. If diallylmercury³ is substituted for divinylmercury, the yield of allyl phenyl sulfide⁴ is only 30% while the yield of mercury-bis-thiophenolate increases to about 70%. With bis(3-butenyl)mercury almost 90% of the product is mercury-bis-thiophenolate and only 9-10% of 3-butenyl phenyl sulfide is formed. The data is summarized in Table V.

TABLE V

REACTION OF MERCURY DIALKENYLS WITH THIOPHENOL

R_2Hg	Relative Product Distribution (in $\%$) ^a				
R—	PhSR	(PhS) ₂ Hg			
CH2=CH-	90	10			
CH2=CHCH2-	30	70			
$CH_2 = CHCH_2CH_2 = $	10	90			

^a Based on isolated products.

EXPERIMENTAL

Allylmercuric acetate. A mixture of 25.80 g. of allylmercuric iodide⁵ (0.07 mole), 11.69 g. of silver acetate (0.07 mole), and 250 ml. of tetrahydrofuran were shaken for 20 hr.

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(4) D. S. Tarbell and M. A. McCall, J. Am. Chem. Soc., 74, 48 (1952).

(5) F. C. Whitmore, Organic Compounds of Mercury, The Chemical Catalog Company, Inc., New York, 1921, p. 122.

⁽²⁾ B. Bartocha, F. E. Brinckman, H. D. Kaesz, and F. G. A. Stone, *Proc. Chem. Soc.*, 116 (1958); G. F. Reynolds, R. E. Dessy, and H. H. Jaffé, *J. Org. Chem.*, 23, 1217 (1958).

To 2.44 g. of diallylmercury³ (8.63 mmoles) was added 0.53 g. of acetic acid (8.63 mmoles) in 10 ml. of heptane at room temperature. The flask was connected to a gas collecting apparatus. The mixture was then refluxed until gas evolution had ceased. The produced gas was analyzed in a mass spectrometer and found to be propylene of 99.6 mole % purity. On cooling to room temperature, white crystals precipitated from the reaction mixture. The crystalline solid (40% yield), allylmercuric acetate, melting at 78-79° proved to be identical with the product obtained from allylmercuric iodide and silver acetate.

Anal. Calculated for C5H8HgO2: C, 20.00; H, 2.67. Found: C, 20.17; H, 2.72.

Bis(3-butenyl)mercury. 1. 3-Butenol (1-buten-4-ol). To a stirred solution of vinylmagnesium bromide, prepared from 337 g. of vinylbromide (3.15 moles) and 73 g. of magnesium (3g.-atoms) in 1 l. of tetrahydrofuran, was added dropwise at 50° a solution of 132 g. of ethylene oxide (3 moles) in 300 ml. of tetrahydrofuran. After all the ethylene oxide had been added, the mixture was stirred at 50° for 1 hr. The reaction mixture was then hydrolyzed with dilute hydrochloric acid. The upper layer was decanted and the lower layer was extracted five times with ether. The combined organic layers were dried over night, filtered, and distilled. 3-Butenol, (146 g., 73.7%) b.p. $112-114^\circ$, n_D^{20} 1.4234, was obtained.

2. 1-Chloro-3-butene. 3-Butenol (146 g, 2.00 moles) was converted to 1-chloro-3-butene according to Juvala.⁶ Yield: 111 g. (61%) 1-chloro-3-butene, b.p. 75-75.8°, $n_{\rm D}^{20}$ 1.4240. (lit.⁶ b.p. 75°, n_{D}^{20} 1.4233).

3. Bis(3-butenyl)mercury. To a solution of 3-butenylmagnesium chloride, prepared from 111 g. of 1-chloro-3-butene (1.23 moles) and 29.8 g. of magnesium in 400 ml. of tetrahydrofuran, was added dropwise at 50° with stirring a solution of 135.8 g. of mercuric chloride (0.50 mole) in tetrahydrofuran. After stirring for 2 hr. at 60° , the reaction mix-ture was hydrolyzed with water at $0-5^{\circ}$. When some white, gummy solids separated, the water addition was stopped and the organic layer was decanted. After drying, the product was distilled to give 89.5 g (60%) bis(3-butenyl)mercury, b.p. 88-89° at 4 mm., d^{20} 1.863, n_D^{20} 1.5383.

Anal. Calculated for C₈H₁₄Hg: C, 30.91; H, 4.54; Hg, 64.5. Found: C, 30.72; H, 4.38; Hg, 64.8.

3-Butenylmercuric acetate. A solution of 6.37 g. of mercuric acetate (0.02 mole) in ethanol-tetrahydrofuran was filtered into a solution of 6.22 g. of bis(3-butenylmercury (0.02 mole) in 30 ml. of ethanol. After 2 hr., the solvents were evaporated in vacuo, leaving a viscous residue which solidified on cooling in an ice bath. After recrystallization from pentane and drying at 1 mm., the white needles melted at 40-41° (yield, 5.26 g, 88%).

Anal. Calculated for C6H10HgO2: C, 24.12; H, 3.37. Found: C, 24.25; H, 3.42.

3-Butenylacetate was obtained from 3-butenol and acetic acid in the presence of concentrated sulfuric acid. b.p. 124-126°, n²⁰_D 1.4115 (lit.⁷ b.p. 124-126°).

cis- and trans-1-Propenylacetate. 1-Propenylacetate, boiling 104-106°, $n_{\rm D}^{20}$ 1.4122 was obtained in a 12% yield from propionaldehyde according to the method of Curtin and Hurwitz.⁸ According to vapor phase chromatography, this material consisted of 1.1% propionaldehyde, 52.5% cis-, and 46.2% trans-1-propenylacetate. Distillation on a Podbielniak spinning band column of 65 theoretical plates yielded the cis-isomer in 85.4% purity (b.p. 101°, $n_{\rm D}^{20}$ 1.4130) and the trans isomer in 93.7% purity (b.p. 103°, $n_{\rm D}^{20}$ 1.4140). These isomers were used as reference compounds in the analysis of the decomposition products formed from the corresponding propenylmercuric acetates.

cis- and trans-1-Bromopropene.9 Commercial 1-bromopropene with the composition: 2-bromopropene, 19.8%, cis-1-bromopropene, 57.7%, and trans-1-bromopropene, 22.4%(by vaporphase chromatography), was distilled on a Podbielniak spinning band column (65 plates). The distillation cuts were stabilized with mercury metal¹⁰ and stored under refrigeration. The cis-isomer, b.p. 56°, (lit.¹¹ b.p. 57°) was obtained in 92.7% purity and the trans isomer, b.p. 61°, (lit.¹¹ b.p. 62.5-63°) in 85.7% purity (by vapor phase chromatography).

cis-1-Propenylmercuric bromide. cis-1-Propenylmercuric bromide was obtained in 77% yield from cis-1-propenyllithium¹¹ and mercuric bromide, m.p. 63-64° (lit.¹¹ m.p. 60-62°).

trans-1-Propenylmercuric chloride. Prepared from trans-1propenylithium¹¹ and mercuric chloride in 80% yield, m.p. 127-128° (lit.¹¹ m.p. 124-125°).

cis-1-Propenylmercuric acetate. A solution of 40.3 g. of cis-1-propenylmercuric bromide (0.125 mole) in 100 ml. of tetrahydrofuran was added to a suspension of 20.9 g. of silver acetate (0.125 mole) in 200 ml. of tetrahydrofuran. The mixture was shaken in the dark for 15 hours, filtered, the solvent taken off the filtrate in vacuo to give 31.8 g (85%) of a white solid, melting 74-78°. After two recrystallizations from hexane, the m.p. was 75-78°.

Anal. Calculated for C5H3HgO2: C, 20.00; H, 2.67. Found: C, 19.87; H, 2.75.

trans-1-Propenylmercuric acetate was prepared in 82%yield from trans-1-propenylmercuric chloride and silver acetate as described above. The crude product was recrystallized from hexane-benzene, m.p. 109-110°.

Anal. Calculated for C₅H₈HgO₂: C, 20.00; H, 2.67. Found: C, 19.92; H, 2.78.

Vaporphase chromatography (Beckman GC-2 gas chromatograph). All the liquid decomposition products from the alkenylmercuric acetates were separated on a 3.3-m column containing 60:40 Silicone 550-Carbowax 4000 on Chromosorb W (30-60) at 95° and a He pressure of 55 p.s.i. The isomeric 1-bromopropenes were separated on a 4-m. column containing 33:33:33 propylene carbonate-ethylene carbonate-dibutyl phthalate at 50° and a helium pressure of 54 p.s.i.

Infrared spectra. The infrared spectra were dermined in carbon disulfide and carbon tetrachloride using sodium chloride optics. Following are the principal wave lengths in microns.

Allylmercuric acetate: 3.27, 3.38, 3.43, 6.16, 7.03, 7.33, 7.66, 8.42, 8.90, 9.59, 9.91, 10.83, 11.14, 12.91, 14.70.

Bis(3-butenyl)mercury: 3.27, 3.43, 3.52, 6.11, 6.92, 7.05, 7.63, 7.75, 8.03, 8.42, 9.60, 10.11, 11.05, 13.85.

S-Butenylmercuric acetate: 3.27, 3.43, 3.52, 6.16, 7.01, 7.33,

7.64, 8.02, 8.47, 8.66, 9.57, 9.92, 10.12, 10.95, 14.02. cis-1-Propenylacetate: 3.26, 3.41, 3.49, 5.67, 5.97, 6.92, 7.20, 7.30, 7.37, 8.2, 8.93, 9.11, 9.57, 10.13, 10.79, 11.01, 13.52.

trans-1-Propenylacetate: 3.26, 3.31, 3.39, 5.67, 5.94, 6.95,

7.29, 7.67, 7.80, 8.2, 8.90, 9.11, 9.58, 10.02, 10.79, 11.07. cis-1-Propenylmercuric bromide: 3.36, 6.20, 6.93, 7.24,

7.62, 8.35, 9.60, 10.35, 10.83, 15.0. trans-1-Propenylmercuric chloride: 3.34, 3.40, 3.45, 3.52,

6.95, 7.30, 8.27, 9.41, 10.36. cis-1-Propenylmercuric acetate: 3.37, 3.41, 6.13, 6.95,

7.33, 7.69, 8.33, 9.56, 9.91, 10.33, 10.84, 14.42, 14.88.

trans-1-Propenylmercuric acetate: 3.33, 3.40, 3.50, 6.12, 6.95, 7.31, 7.68, 8.24, 9.92, 10.34, 10.83, 14.36.

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(10) L. F. Hatch and K. E. Harwell, J. Am. Chem. Soc., 77, 1682 (1955).

(11) A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1174 (1959).

⁽⁶⁾ A. Juvala, Ber., 63B, 1989 (1930).

⁽⁷⁾ A. Juvala et al., Ber., 61, 1773 (1928).

⁽⁸⁾ D. Y. Curtin and M. J. Hurwitz, J. Am. Chem. Soc., 74, 5381 (1952).

Reaction of diallylmercury with thiophenol. To 5.66 g. of diallylmercury³ (0.02 mole) was added dropwise at room temperature 2.20 g. of thiophenol (0.02 mole). After the exothermic reaction had subsided, the mixture was heated on a steam bath for 0.5 hr. The solid, grey reaction mixture was extracted with an excess of hot acetone, leaving 1.14 g (28.5%) of metallic mercury. On cooling, white needles separated from the acetone solution, 2.76 g. (66%). After recrystallization, the mercury-bis-thiophenolate mellet at 154-155° (lit.¹ m.p. 155-156°). Distillation of the acetone mother liquor yielded 0.84 g (28%) allyl phenyl sulfide, b.p. 47-48° at 0.3 mm, n_D^{20} 1.5755 (lit.⁴ b.p. 59-60° at 1.5 mm, n_D^{20} 1.5760). The infrared spectrum was identical with the one published by Tarbell and McCall.⁴

Reaction of bis(3-butenyl)mercury with thiophenol. Equimolar amounts of bis(3-butenyl)mercury and thiophenol treated under identical conditions as described above, gave 80% mercury-bis-thiophenolate, m.p. 153.5-154°. and 9% 3-butenyl phenyl sulfide. The infrared spectrum of the latter was identical with the one obtained from an authentic sample.

3-Butenyl phenyl sulfide was prepared in 70% yield from potassium thiophenolate and 1-chloro-3-butene in ethanol according to Ipatieff et al.,¹² b.p. 85.5-86.5° at 1.5 mm, n_D^{20} 1.5645. Anal. Calc. for $C_{10}H_{12}S$: C, 73.12; H, 7.36; S, 19.46. Found: C, 73.24; H, 7.25; S, 19.30. Major infrared absorption bands: 3.25, 3.41, 6.10, 6.75, 6.95, 7.82, 8.20, 9.18, 9.38, 9.77, 10.12, 10.95, 13.59, and 14.51 μ .

A small amount of 1,4-bis(phenylmercapto)butane,¹³ m.p. 85-86°, was formed as a by-product in this reaction.

S-Butenyl phenyl sulfone was obtained in 60% yield by oxidizing 3-butenyl phenyl sulfide with hydrogen peroxide according to Pomerantz and Connor,¹⁴ b.p. 120-122° at 0.3 mm, n_D^{20} 1.5404. Anal. Calculated for C₁₀H₁₂O₂S: C, 61.19; H, 6.16; S, 16.34.

Anal. Calculated for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.00; H, 6.13; S, 15.99. The infrared spectrum of the compound exhibits the two characteristic $-SO_2$ -absorptions at 7.55 and 8.68 μ .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Mechanistic Aspects of the Reaction of Di-*n*-butyltin Dihydride with Acetic Acid¹

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When di-n-butyltin dihydride and di-n-butyltin diacetate are mixed, a reaction occurs leading to an equilibrium mixture of these two compounds and di-n-butylacetoxytin hydride.² This same equilibrium mixture, along with one mole of hydrogen, is formed when one mole of di-n-butyltin dihydride is allowed to react with one mole of acetic acid. When the equilibrium mixture is allowed to stand, hydrogen is involved and 1,1,2,2-tetra-n-butyl-1,2-diacetoxyditin is formed. It reacts with acetic acid to produce di-n-butyltin diacetate.

In a previous investigation³ it was found that di-*n*-butyltin dihydride reacts with acetic acid to give either of two products as shown in Equations 1 and 2.

⁽²⁾ For the purpose of this paper, the new tin hydride species, showing Sn—H absorption at 1880 cm.⁻¹, is assumed to be di-*n*-butylacetoxytin hydride. This is the simplest structure consistent with its analysis and properties, and the one which involves the least structural change. Other species which would have the same empirical formula include polar species such as $Bu_2Sn^{++} Bu_2Sn(OAc)_2H_2^{--}$, and bridged structures such as



(3)(a) A. K. Sawyer and H. G. Kuivila, J. Org. Chem., in press. (b) A. K. Sawyer and H. G. Kuivila, J. Am. Chem. Soc., 82, 5958 (1960).

1,1,2,2-Tetra-*n*-butyl-1,2-diacetoxyditin is the main product when the acid-hydride ratio is 1.0, and di-*n*-butyltin diacetate is the major product when the acid-hydride ratio is 2.0. With diphenyltin dihydride, on the other hand, irrespective of whether the acid-hydride ratio is 1.0 or 2.0, the main product is 1,1,2,2-tetraphenyl-1,2-diacetoxyditin. Parallel behavior is observed when other carboxylic acids are allowed to react with these hydrides. It appeared to be of interest to examine the reactions involving di-*n*-butyltin dihydride and acetic acid in detail in order to gain some understanding regarding their mechanisms.

A starting point was provided by the discovery that 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin could be prepared by the reaction of di-*n*-butyltin dihydride with di-*n*-butyltin diacetate as shown in Equation 3. (It was also observed that the analogous reaction could be carried out with di-*n*-

⁽¹⁾ Support of this work by Metal and Thermit Corporation is gratefully acknowledged.