

the latter had been oxidized. In a second experiment, 50 mmoles of adduct in a solvent mixture of methyl chloride (70 ml.) and methylene chloride (30 ml.) was treated with 6.5 g. of freshly distilled dimethyl sulfide. Oxidation was rapid. After 1 hr. at -50° the solvent was carefully removed. The amount of sulfoxide (66 mmoles) and sulfone (3.6 mmoles) in the residue was determined by gas phase chromatography.³³ This represented a total of 73 milliatoms of oxygen placed upon the sulfide substrate.

When excess dimethyl sulfoxide was added to 50 mmoles of adduct in a separate experiment, little reaction appeared to occur at -40° . The mixture was held at -30 to -40° for 24 hr. Workup and determination of sulfone as in the previous case indicated that only 59 mmoles of sulfoxide had been oxidized. Isolation of the sulfone by quenching the residue mixture in ether yielded 5.3 g. (55 mmoles) of fairly good quality dimethyl sulfone, m.p. $103-106^{\circ}$, lit.³⁴ m.p. 109.5° .

Ozone Oxidation of Phosphines. (a) **Tributylphosphine.**—Ozone (69 mmoles) was absorbed from a standardized ozone-oxygen stream on a cold -70° column of silica gel.¹³ The column was then swept with dry nitrogen and slowly warmed over about 4 hr. The gas stream was added to a solution of 20.2 g. (100 mmoles) of tributylphosphine in 100 ml. of dry methylene chloride. Reaction was complete before the column was swept free of ozone. Sweeping was continued with the off-gas going into potassium iodide traps. Of the 69 mmoles of ozone delivered 55.2 were consumed in oxidation of the phosphine. Tributylphosphine oxide, 20.0 g. (92%), b.p. $123-125^{\circ}$ (1 m.m.), m.p. $61-63^{\circ}$, lit.²⁹ b.p. 300° , was isolated by removal of solvent and distillation of residue.

(b) **Triphenylphosphine.**—Oxygen-free ozone¹³ (42 mmoles) was swept by a nitrogen stream into a solution of

(33) We thank Dr. E. M. Emery and Mr. A. Bybell for these measurements.

(34) L. Ruzicka, M. W. Goldberg and H. Meister, *Helv. Chim. Acta*, **23**, 560 (1940).

13.1 g. (50 mmoles) of triphenylphosphine in 90 ml. of methylene chloride at -65° . When oxidation was complete, excess ozone in the solution and on the silica gel column was swept into potassium iodide traps. The total ozone consumed oxidizing the phosphine was 32.3 mmoles. Removal of solvent gave 13.8 g. (99%) of good quality triphenylphosphine oxide, m.p. $153-155^{\circ}$, lit.²⁹ m.p. 153° .

Ozone Oxidation of Dialkyl Sulfides.—The following experiments, though lacking in precise quantitative detail, illustrate clearly the pronounced effect of high substrate concentration upon ozone proportion.

(a) **Diethyl Sulfide.**—To 18 g. (200 mmoles) of diethyl sulfide in 50 ml. of methylene chloride at -60° was added a standardized ozone-oxygen mixture until 72.8 mmoles of ozone had been absorbed. Solvent was removed from the mixture and the residue carefully fractionated. In all, a total of approximately 11.2 g. (105 mmoles), b.p. $66-75^{\circ}$ (4 mm.), lit.³⁵ b.p. $83-85^{\circ}$ (12 mm.), of diethyl sulfoxide along with 6.0 g. (49 mmoles) of diethyl sulfone, m.p. $67-72^{\circ}$, lit.³⁶ m.p. 72° , was obtained. This represents a total of roughly 203 milliatoms of oxygen placed upon sulfur by approximately 73 mmoles of ozone.

(b) **Dibutyl Sulfide.**—Ozone (74.3 mmoles) was added to 29.3 g. (200 mmoles) of dibutyl sulfide at $0-5^{\circ}$ without solvent. Toward the end of the addition some solid began to separate. No ozone passed through the reaction vessel into the potassium iodide traps. Without isolation of products (presumably sulfoxide and sulfone as in the case of diethyl sulfide) the crude mixture was subjected to elemental analysis. The values obtained were C, 59.25; H, 11.35; S, 19.18. By difference the oxygen content was determined as approximately 10.0%. From this and the weight of sample (32.6 g.) it was calculated that approximately 202 milliatoms of oxygen had been introduced into the substrate under these conditions.

(35) D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2939 (1941).

(36) A. E. Wood and E. G. Travis, *ibid.*, **50**, 1227 (1928).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE OLEFINS CO., DIVISION OF UNION CARBIDE CORP., SOUTH CHARLESTON, W. VA.]

Organomercury Chemistry. A Novel Synthesis of Vinyl Esters, Vinyl Ethers and Vinyl Thioethers¹

BY DONALD J. FOSTER AND ERICH TOBLER

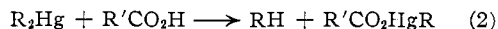
RECEIVED OCTOBER 5, 1960

Organomercury compounds containing vinyl or substituted vinyl groups adjacent to a mercury atom undergo reactions that are not observed in the absence of the unsaturation. Divinylmercury reacts with organic acids to form the corresponding vinyl ester and metallic mercury. The reaction goes through a vinylmercuric ester intermediate that can be isolated if desired. Phenols and thiophenols react with divinylmercury to form aryl vinyl ethers or thioethers rather than nuclear mercurated products. Even alkyl thiols react with unsaturated organomercury compounds to yield the corresponding alkyl thioethers.

Introduction

The reaction of organomercury compounds of the general formula R_2Hg , where R is alkyl, aryl or aralkyl, with a variety of reagents has been studied quite extensively. Thus inorganic²⁻⁴ and organic⁵⁻⁹ acids cleave organomercury compounds and

form a hydrocarbon, RH, and an organomercuric ester, $RHgX$ or $R'CO_2HgR$, according to eq. 1 and 2.



While the rate of cleavage varies considerably with the substituent R, the product is always a hydrocarbon and a mercuric ester. The reaction of organomercury compounds with phenols is described in a series of papers by Koton.¹⁰⁻¹⁴ Dialkyl- and diarylmercury compounds react with phenols to

(10) M. M. Koton and T. M. Zorina, *J. Gen. Chem. USSR*, **17**, 1220 (1947).

(11) M. M. Koton, *ibid.*, **19**, 730 (1949).

(12) M. M. Koton and V. F. Martynova, *ibid.*, **24**, 2177 (1954).

(13) M. M. Koton and V. F. Martynova, *ibid.*, **25**, 705 (1955).

(14) M. M. Koton and V. F. Martynova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1063 (1955).

(1) Presented at the 138th Meeting of The American Chemical Society, New York, N. Y., Sept., 1960.

(2) C. S. Marvel and H. D. Calvery, *J. Am. Chem. Soc.*, **45**, 820 (1923).

(3) M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

(4) R. E. Dessy, G. F. Reynolds and Jin-Young Kim, *ibid.*, **81**, 2683 (1959).

(5) M. M. Koton, *J. Gen. Chem., USSR*, **9**, 912 (1939).

(6) A. H. Corwin and M. A. Naylor, *J. Am. Chem. Soc.*, **69**, 1004 (1947).

(7) I. A. Chernov, *J. Gen. Chem., USSR*, **22**, 113 (1952).

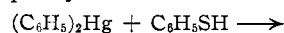
(8) S. Winstein, T. G. Traynor and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741, 3747 (1955).

(9) F. Nerdel and S. Makower, *Naturwiss.*, **45**, 490 (1958).

yield mono-, di- and trimercurated products depending upon the reaction conditions



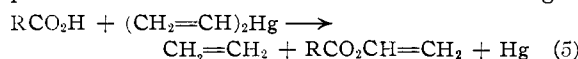
Koton¹⁵ also reported the reaction of diphenylmercury with thiophenol. The products isolated were benzene, mercuri-bis-thiophenolate and diphenyl disulfide.



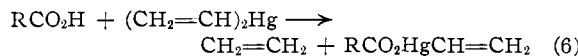
We have found that divinylmercury¹⁶ and substituted vinylmercury compounds react with these reagents but the vinylmercuric products are capable of undergoing further reaction, not previously observed, to give a convenient and novel method for the preparation of vinyl esters, vinyl ethers and vinyl thioethers. The reaction of divinylmercury with these reagents is discussed under separate headings.

Discussion

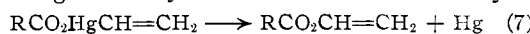
Carboxylic Acids.—Warming an aromatic or aliphatic carboxylic acid with divinylmercury either alone or in the presence of a solvent results in the formation of ethylene, a vinyl ester and metallic mercury. The reaction is usually over 50% complete in less than five minutes if the two reagents



are mixed in the absence of a solvent and warmed on a steam-bath. Prolonging the reaction time leads to essentially complete recovery of the mercury. If the reaction is carried out in an inert solvent to lengthen the reaction time, it is possible to isolate the vinylmercuric ester intermediate as the major product in most cases. The first and rapid step in the reaction is the evolution of ethylene and the formation of a vinylmercuric ester. Vinylmercuric esters are crystalline solids and for the most part



sharp melting with a fair degree of stability at an ambient temperature. On heating, they decompose to give a vinyl ester and metallic mercury.



The rate of formation of the vinylmercuric esters and their stability is related to the dissociation constant and the concentration of the carboxylic acid. A similar effect of the acid strength on the rate of cleavage of a vinyl group from organotin compounds has been reported.¹⁷ Some of the acids investigated, reaction conditions and the products formed are summarized in Table I. The three chloroacetic acids begin to react with divinylmercury even at room temperature, while weaker acids such as acetic and benzoic require heating to obtain a measurable rate. While vinylmercuric chloroacetate is reasonably stable and can be isolated, vinylmercuric dichloroacetate begins to decompose almost immediately, and is best identified spectroscopically.

(15) M. M. Koton, E. P. Moskvina and F. S. Florinskii, *J. Gen. Chem. USSR*, **20**, 2093 (1950).

(16) G. F. Reynolds, R. E. Dessy and H. H. Jaffé, *J. Org. Chem.*, **23**, 1217 (1958).

(17) A. Saitow, E. G. Rochow and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).

TABLE I
DIVINYLMERCURY AND ACIDS

| Acid | Dissocn. const. $\frac{K_1}{K_2}$ | Solvent | Reacn. time, hr. Hg formed ^a | Products | M.p., °C. | B.p., °C. (mm.) | | Elemental analyses, % | | | | | |
|---|-----------------------------------|---------|---|--|-------------|--------------------|-----------------------------|-----------------------|-------|--------------------|-------|------|--------------------|
| | | | | | | Obsd. | Lit. | Calculated | Found | C | H | Hg | |
| Cl ₃ CCO ₂ H | 1.8×10^{-5} | None | 0.08 | C ₆ H ₅ CO ₂ HgCH=CH ₂ | 92-93 | 71-73 | 72.5 ^b | 16.75 | 2.09 | 70.0 | 16.43 | 1.9 | 69.7 |
| ClCH ₂ CO ₂ H | 1.4×10^{-1} | None | 0.5 | C ₆ H ₅ CO ₂ CH=CH ₂ | 67-69 | 41-46(20) | 37-38(16) ^{b,c} | 14.90 | 1.56 | 62.4 | 14.73 | 1.4 | 61.9 |
| Cl ₂ CHCO ₂ H | 5×10^{-2} | None | 0.08 | [Cl ₂ CHCO ₂ HgCH=CH ₂] | <i>d</i> | 46-48(15) | 51(20) ^b | 9.13 | 1.13 | 13.5 ^f | 8.89 | 1.12 | 13.37 ^f |
| Cl ₃ CCO ₂ H | 2×10^{-1} | None | 1.0 | Cl ₂ CHCO ₂ CH=CH ₂ | 184-185 | 38-40(5) | 67-68(42) ^f | 20.07 | 2.01 | 67.0 | 19.92 | 2.13 | 66.8 |
| CH ₂ =CHCO ₂ H | 5.6×10^{-3} | None | 0.08 | Polymer | 83-84 | 90-92 | 94 ^b | 31.00 | 2.29 | 57.4 | 30.91 | 2.27 | 57.2 |
| C ₆ H ₅ CO ₂ H | 6.3×10^{-3} | None | 0.08 | CH ₂ =CHCO ₂ HgCH=CH ₂ | 68-69 | 57-59(1) | 74(3) ^b | 15.87 | 1.98 | 10.58 ^e | 15.63 | 2.02 | 10.32 ^e |
| CH ₃ CO ₂ H | 4.7×10^{-4} | EtOH | 3.0 | CH ₃ COSHgCH=CH ₂ | 154.0-154.5 | 122-123 | 121 ^b | 20.04 | 2.36 | | 20.57 | 2.25 | |
| <i>p</i> -Cl ₃ C ₆ H ₄ SO ₃ H | 3.9×10^{-5} | EtOH | 0.3 | <i>p</i> -Cl ₃ C ₆ H ₄ SO ₃ CH=CH ₂ | 138-139.5 | 100-105(0.3) | 106-107.5(0.3) ^g | | | | | | |
| HO ₂ C(CH ₂) ₂ CO ₂ H | 5.3×10^{-5} | Xylene | 1.0 | (CH ₂) ₂ (CO ₂ H)CH=CH ₂ | <i>d</i> | 76-78(0.5) | 105-106(4) ^h | | | | | | |
| <i>m</i> -C ₆ H ₄ (CO ₂ H) ₂ | 2.9×10^{-4} | Toluene | 2.0 | <i>m</i> -C ₆ H ₄ (CO ₂ HgCH=CH ₂) ₂ | 60-61 | 59-60 ⁱ | | 66.04 | 4.63 | | 65.63 | 4.72 | |

^a The percentage mercury is a measure of the ester formation from the vinylmercuric ester. ^b See ref. 25, pp. 327, 370, 373, 378, 383. ^c *Org. Syntheses*, 28, 94 (1948). ^d Not isolated. ^e Melting point; D. Seyferth, *J. Org. Chem.*, 22, 478 (1957). ^f A. N. Nesmeyanov and E. G. Perevalova, *Izvest. Akad. Nauk, SSSR, Otdel Khim. Nauk*, 1002 (1954); *C. A.*, 49, 6892 (1955). ^g J. C. Sauer and J. D. C. Wilson, *J. Am. Chem. Soc.*, 77, 3793 (1955). ^h M. F. Shostakovskii, A. M. Shur and B. F. Filimonov, *Zhur. Priklad. Khim.*, 30, 816 (1957); *C. A.*, 51, 17757 (1957). ⁱ Melting point; M. Hopff, *Bull. soc. chim. France*, 1283 (1958). ^j Chlorine, %.

Trichloroacetic acid reacts so rapidly that the intermediate vinylmercuric ester could not be detected. However, vinyl trichloroacetate is isolated from the reaction in a 40–50% yield. In addition, vinylmercuric chloride is formed in this reaction. The isolation of this material is not too surprising in view of the secondary product formation usually associated with trichloroacetic acid, but the evolution of ethylene as the only gaseous product is peculiar, for the decomposition of trichloroacetic acid often liberates oxides of carbon.

Vinylmercuric acrylate is obtained from divinylmercury and acrylic acid in heptane. In the absence of a diluent, polymer formation is observed. The vinylmercuric esters of acrylic, benzoic and acetic acids have similar thermal stability as would be expected from comparable dissociation constants. The stability of vinylmercuric esters is also influenced by the solvent as shown in Table II.

TABLE II
DECOMPOSITION OF VINYL MERCURIC ESTERS

$$\text{RCO}_2\text{HgCH}=\text{CH}_2 \xrightarrow{\Delta} \text{RCO}_2\text{CH}=\text{CH}_2 + \text{Hg}$$

| Vinyl mercuric ester, R = | Solvent | Temp., °C. | Time, hr. | % Hg formed |
|---------------------------------|----------------------------------|------------|-----------|-------------|
| CH ₃ - | C ₂ H ₅ OH | 80 | 3 | 48 |
| | None | 100 | 5 | 85 |
| | HOAc | 100 | 1.5 | 90 |
| ClCH ₂ - | None | 25 | 72 | ~100 |
| | None | 100 | 1 | ~100 |
| C ₆ H ₅ - | Heptane | 100 | 12 | 65 |
| | None | 200 | 0.5 | ~100 |

A number of organomercuric acetates were prepared, isolated and purified prior to being heated in acetic acid to demonstrate the effect of unsaturation on the stability of the carbon-mercury bond. These data are summarized in Table III. The stability of phenyl-, cyclopropyl- and methylmercuric acetates indicates participation of the double bond in the decomposition. The effect of a double bond in a position other than adjacent to the mercury atom will be discussed in a future publication.

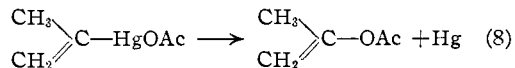
TABLE III
DECOMPOSITION OF MERCURIC ACETATES

$$\text{CH}_3\text{CO}_2\text{HgR} \longrightarrow \text{CH}_3\text{CO}_2\text{R} + \text{Hg}$$

| Mercuric acetate R = | Solvent | Temp., °C. | Time, hr. | % Hg formed ^a |
|---------------------------------|---------|------------|-----------|--------------------------|
| CH ₂ =CH- | HOAc | 100 | 1.5 | 90 |
| Cyclopenten-1-yl | HOAc | 120 | 3 | 61 |
| Cyclohexen-1-yl | HOAc | 120 | 3 | 86 |
| C ₆ H ₅ - | HOAc | 150 | 4 | 0 |
| Cyclopropyl | HOAc | 150 | 4 | 0 |
| CH ₃ - | HOAc | 150 | 4 | 0 |

^a The vinyl and substituted vinyl acetates were either isolated or identified spectroscopically. When mercury was not produced, the starting material was recovered.

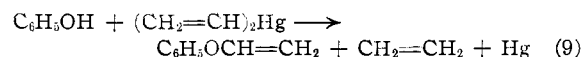
Isopropenylmercuric acetate was prepared, isolated and subsequently decomposed to demonstrate which carbon atom was involved in the formation of the new carbon-oxygen bond. The product isolated was isopropenyl acetate in a purity of greater than 94% as determined by vapor phase chromatography. The carbon-oxygen bond is formed at the carbon atom that originally held the mercury atom.



The vinyl esters of thiolacetic and *p*-toluenesulfonic acid were prepared by this general method. Selected dicarboxylic acids also react with two equivalents of divinylmercury to form the corresponding divinyl esters. Thus, divinyl adipate and divinyl isophthalate have been successfully prepared by this method.

Although alkylmercuric esters are largely covalent¹⁸ the infrared absorption spectrum of vinylmercuric esters indicates an ionized carboxyl group. The characteristic ester carbonyl band is replaced by bands at 6.22–6.45 μ and 7.14–7.70 μ which correspond to the anti-symmetrical and symmetrical vibrations of the COO⁻ structure.¹⁹ The >CH_2 wag which in divinylmercury²⁰ occurs at 9.92 μ , is shifted to 10.10–10.18 μ in vinylmercuric esters and to 10.55–10.68 μ in vinyl esters. The =CH₂ wag occurs at 10.67 μ in divinylmercury,²⁰ 10.60–10.70 μ in vinylmercuric esters but at 11.28–11.67 μ in vinyl esters. The variation in the infrared spectra of the three compounds allows the products to be distinguished in the reaction mixture.

Phenols.—Perhaps an even more pronounced effect of the unsaturation in vinyl and substituted vinyl mercury compounds is observed when these reagents are treated with phenols. Instead of nuclear mercuration of the aromatic ring that is normally observed with saturated aliphatic or aromatic mercury compounds, phenols react with divinylmercury to form aryl vinyl ethers, ethylene and metallic mercury. Aryl vinyl ethers derived



from phenol, *p*-cresol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol and 2,4-dinitrophenol have been prepared by this method in yields ranging from 80–100% (see Table IV). The highly hindered 2,6-di-*t*-butylphenol failed to react with divinylmercury even under more vigorous conditions and could be recovered unchanged. Under the conditions of the reaction, the vinylmercuric aryl ethers were too unstable to isolate except in the case of pentachlorophenol. Vinylmercuric pentachlorophenolate was also prepared by the reaction of vinylmercuric acetate with pentachlorophenol in methanol. The vinylmercuric ether was

(18) E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 118.

(19) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edition, Methuen, London, 1956, p. 174.

(20) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, 360 (1959).

TABLE IV
 DIVINYLMERCURY AND PHENOLS

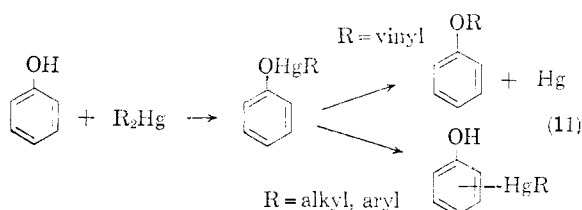
| Phenol | Dissoch. const. (25°) | Reacn. time (at 100°) hr. | B.p., °C. (mm.) | | Vinyl aryl ether Yield, % | Carbon, % | | Hydrogen, % | |
|--------------------------|-----------------------|---------------------------|-----------------|-------------------------|---------------------------|-----------|--------------------|-------------------|-------------------|
| | | | Obsd. | Lit. | | Calcd. | Found | Calcd. | Found |
| Phenol | 1.3×10^{-10} | 3 | 57-59(19) | 155-157 ^a | 96 | 79.97 | 80.13 | 6.71 | 6.48 |
| <i>p</i> -Cresol | 6.7×10^{-9} | 3 | 58-60(5) | 174 ^a | 94 | 80.56 | 80.20 | 7.51 | 7.28 |
| 2,4-Dichloro- | 3.1×10^{-8} | 3 | 86-88(5) | 105(15) ^{a,b} | 85 | 50.83 | 50.67 | 3.20 | 3.33 |
| 2,4,6-Trichloro- | 3.9×10^{-7} | 3 | 75-77(1) | 118(14) ^{a,b} | 80 | 42.99 | 43.17 | 2.26 | 2.12 |
| Pentachloro- | 5.5×10^{-6} | 1 | M.p. 89-90 | M.p. 84-85 ^b | ° | 32.86 | 32.82 ^e | 1.03 ^e | 1.25 |
| 2,4-Dinitro- | 1.0×10^{-4} | 1 | M.p. 51-52 | | 88 | 45.74 | 45.84 ^f | 2.86 | 3.04 ^f |
| 2,6-Di- <i>t</i> -butyl- | | 3 | | | 0 ^d | | | | |

^a C. E. Schildknecht; see ref. 25, p. 623. ^b A. V. Kalabina, A. Kh. Filippova, E. S. Domnina, T. I. Ermolova, M. L. Navtanovich and G. V. Dmitrieva, *Izvest. Sibir. Otdel. Akad. Nauk. S.S.S.R.*, 9 (1958); *C. A.*, 53, 17033 (1959). ^c This reaction yielded the pentachlorophenyl vinylmercuric ether, m. 160-161.3° in 82% yield. The same product was obtained from the reaction of an equimolar mixture of vinylmercuric acetate and pentachlorophenol in methanol. Sublimation of this intermediate at 110-120° at 20 mm. afforded the pentachlorophenyl vinyl ether in 87% yield. ^d The starting phenol was recovered unchanged. ^e Calcd.: Cl, 60.65. Found: Cl, 60.18. ^f Calcd.: N, 13.33. Found: N, 13.31.

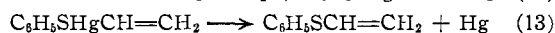
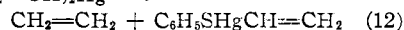
converted into pentachlorophenyl vinyl ether and $\text{CH}_2=\text{CHHgOAc} + \text{C}_6\text{Cl}_5\text{OH} \longrightarrow \text{C}_6\text{Cl}_5\text{OHgCH}=\text{CH}_2 + \text{HOAc}$ (10)

mercury by heating under reduced pressure.

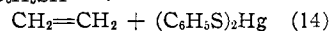
These data suggest that phenols react with organomercury compounds to form the organomercuric phenolate intermediate which can then decompose to give the corresponding aryl ether when R is unsaturated, such as vinyl, or the organomercury moiety can rearrange into the ring¹⁰⁻¹⁴ when R is aliphatic or aromatic. The stability of the intermediate organomercuric aryl ether apparently determines the course of the reaction.



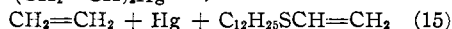
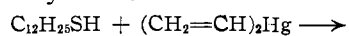
Thiophenol and Alkyl Thiols.—Thiophenol reacts with divinylmercury even at room temperature to give ethylene, mercury and a mixture of vinylmercuric thiophenolate and vinyl phenyl thioether. Similar to the vinylmercuric esters, vinylmercuric thiophenolate releases mercury on $\text{C}_6\text{H}_5\text{SH} + (\text{CH}_2=\text{CH})_2\text{Hg} \longrightarrow$



heating and forms vinyl phenyl thioether. Mercuri-bis-thiophenolate was formed as a secondary product in this reaction. It apparently resulted from the reaction of a second molecule of thiophenol. Even alkylthiols react with divinylmercury to form the corresponding alkyl vinyl thio- $\text{C}_6\text{H}_5\text{SHgCH}=\text{CH}_2 + \text{C}_6\text{H}_5\text{SH} \longrightarrow$



ether although at a much slower rate than thiophenol. Lauryl vinyl thioether was prepared by the reaction of lauryl mercaptan and divinylmercury at 115°.



The stability of vinylmercuric aryl thioethers as compared to vinylmercuric aryl ethers is undoubt-

edly due to the greater affinity of mercury for sulfur than for oxygen. While the thio-alcohols react with divinylmercury under moderate conditions, 2-ethylhexanol failed to react with divinylmercury under more vigorous conditions.

Experimental

Divinylmercury and Acids.—As a general rule, equimolar amounts of the acid and divinylmercury were combined in the absence of a solvent when the vinyl esters were desired. The weaker acids, such as acetic and benzoic acid, were heated together with divinylmercury on the steam-bath. An inert solvent was required to prevent polymer formation in the reaction of acrylic acid with divinylmercury. Stronger acids such as *p*-toluenesulfonic and the chloroacetic acids were added dropwise to the divinylmercury at room temperature. After the initial reaction subsided, the mixture was heated on the steam-bath to complete the reaction. When the vinylmercuric esters were desired, the reaction was carried out in a suitable diluent such as benzene or hexane. The infrared spectra of the esters produced in the reactions were compared with those of authentic samples. In all cases, ethylene (determined with a mass spectrometer) was the only gaseous product produced in these reactions.

The following examples are typical of the reactions carried out with divinylmercury and acids investigated.

Divinylmercury and Acetic Acid.—A mixture containing 25.5 g. (0.1 mole) of divinylmercury and 13.2 g. (0.22 mole) of acetic acid was heated on a steam-bath for 30 min. The reaction mixture was taken up in 100 ml. of ethyl ether and washed with 5% sodium bicarbonate and water. The organic layer was dried over anhydrous sodium sulfate and distilled at atmospheric pressure. A product boiling at 71-73° was shown to be identical to an authentic sample of vinyl acetate. The product yield was 74% of the theoretical. The mercury was recovered as the free metal.

To 25.5 g. (0.1 mole) of divinylmercury was added 6.0 g. (0.1 mole) of acetic acid at room temperature. At 40° an exothermic reaction commenced which raised the reaction temperature to 90°. The product gas was collected, then analyzed in a mass spectrometer and found to be ethylene of 98.7 mole per cent. purity. The reaction mixture precipitated white crystals on cooling to room temperature. The white solid was filtered off and recrystallized from petroleum ether. The crystalline solid melting at 92-93°, 40% yield, was identified by chemical and physical properties to be vinylmercuric acetate. In addition to vinylmercuric acetate, vinylacetate and metallic mercury in a yield of 58% were also found in this reaction. The yield of vinylmercuric ester in this reaction could be increased to over 80% by carrying out the reaction in a solvent and keeping the temperature below 50°.

A 5.7-g. (0.02 mole) sample of vinylmercuric acetate was placed in a distilling flask and heated at atmospheric pressure. As the temperature was increased above 70°, vinyl acetate distilled out of the reaction vessel and metallic mercury was deposited. The recovery of mercury was quantitative and the vinyl acetate that distilled out proved to be spectroscopically identical to an authentic sample.

Divinylmercury and Adipic Acid.—A mixture containing 12.7 g. (0.05 mole) of divinylmercury, 3.7 g. (0.025 mole) of adipic acid and 25 ml. of xylene was heated to reflux for 1 hour and the hot solution was decanted from the free mercury; 4.7 g. Upon cooling, a white crystalline solid, subsequently identified as divinylmercuric adipate, melted at 138–139.5° after recrystallization from benzene. Distillation of the mother liquor gave 1.9 g. (38%) of divinyl adipate, b.p. 76–78° (0.5 mm.), n_D^{20} 1.4549.

A 1.7-g. sample of divinylmercuric adipate was heated in the absence of a solvent for 3 hours at 130°. The resulting liquid was separated from the mercury, and distilled at reduced pressure to yield 73% of divinyl adipate, b.p. 70–72° (0.3 mm.), n_D^{20} 1.4545.

Divinylmercury and Isophthalic Acid.—A mixture of 12.7 g. (0.05 mole) of divinylmercury, 4.2 g. (0.025 mole) of isophthalic acid and 25 ml. of toluene was heated to reflux for two hours. The product was distilled under reduced pressure. The distillate solidified on cooling and after recrystallization from ethanol, 3.5 g. (54%) of divinyl isophthalate m. 60–61° was obtained. The product was identical with an authentic sample of divinyl isophthalate.

Isopropenylmercuric Acetate.—An ethanol solution containing equimolar amounts of mercuric acetate and diisopropenylmercury²¹ was allowed to stand one hour at room temperature before the solvent was removed under vacuum. The residue melted at 102–103° after two recrystallizations from ethanol.

Anal. Calcd. for $C_8H_8HgO_2$: C, 19.97; H, 2.67; Hg, 66.71. Found: C, 20.01; H, 2.6; Hg, 66.7.

Decomposition of Isopropenylmercuric Acetate.—Six grams (0.02 mole) of isopropenylmercuric acetate was decomposed by heating to 125° at atmospheric pressure. The entire distillate, 1.7 g. (85%), boiling at 120–126° was subjected to vapor phase chromatographic analysis and analyzed to be isopropenylacetate of 94.2% purity. An authentic sample of isopropenyl acetate, prepared from ketene and acetone, was used for standardization.

Cyclopropylmercuric Acetate.—Prepared by the reaction of dicyclopropylmercury¹⁸ with acetic acid in petroleum ether, m.p. 81–82°.

Anal. Calcd. for $C_8H_8HgO_2$: C, 20.00; H, 2.67. Found: C, 20.01; H, 2.78.

Di-1-cyclopentenylmercury.—A solution containing 103 g. (1 mole) of freshly distilled 1-chlorocyclopentene²² in 100 ml. of tetrahydrofuran was added dropwise during 75 minutes to 13.9 g. (2 g. atoms) of lithium wire in 500 ml. of tetrahydrofuran maintained at –10°. The unreacted lithium was removed prior to the addition of 68 g. (0.25 mole) of mercuric chloride in 150 ml. of tetrahydrofuran at 0°. The reaction mixture was stirred for 3 hours at room temperature and then hydrolyzed with water at 0°. The aqueous layer was extracted with ethyl ether and the combined organic layers were dried prior to removal of the solvents. The residue was recrystallized from ethanol to yield 71 g. (85%) of di-1-cyclopentenylmercury melting 63.5–64.5°.

Anal. Calcd. for $C_{10}H_{14}Hg$: C, 35.87; H, 4.21; Hg, 60.0. Found: C, 35.37; H, 4.02; Hg, 60.4.

17-Cyclopentenylmercuric acetate was prepared by treating di-1-cyclopentenylmercury with acetic acid in heptane; m.p. 119–120° (from ethanol).

Anal. Calcd. for $C_7H_{10}HgO_2$: C, 25.72; H, 3.06. Found: C, 25.83; H, 3.30.

Di-1-cyclohexenylmercury was prepared from 1-cyclohexenyllithium²³ and mercuric chloride in tetrahydrofuran.

(21) A. N. Nesmeyanov, A. E. Borisov and N. V. Novikova, *Doklady Akad. Nauk, S.S.S.R.*, **96**, 289 (1954); *C. A.*, **49**, 5276.

(22) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

(23) E. A. Braude and J. A. Coles, *ibid.*, 2014 (1959).

The product is a colorless viscous liquid, b.p. 122–125° (0.4 mm.), d_4^{25} 1.832, n_D^{20} 1.5918.

Anal. Calcd. for $C_{12}H_{18}Hg$: C, 39.72; H, 4.99; Hg, 55.3. Found: C, 39.73; H, 4.98; Hg, 55.1.

1-Cyclohexenylmercuric acetate was prepared by treating equimolar amounts of di-1-cyclohexenylmercury and acetic acid; m.p. 119–120° (lit.²⁴ m.p. 116–116.5°).

Anal. Calcd. for $C_8H_{12}HgO_2$: C, 28.18; H, 3.52. Found: C, 27.80; H, 3.64.

Divinylmercury and Phenols.—An equimolar mixture of divinylmercury and the appropriate phenol was heated on a steam-bath for 1 to 3 hours. Gas was evolved during this period which was collected, analyzed and found to consist entirely of ethylene. The liquid reaction products were separated from the free mercury and distilled. The yields were 80–96%. The vinyl ethers were compared spectroscopically with authentic samples.

2,4-Dinitrophenyl Vinyl Ether.—2,4-Dinitrophenol (9.2 g., 0.05 mole), and divinylmercury (12.7 g., 0.05 mole) were heated on a steam-bath for 1 hour. Benzene was added to remove the organic material from the free mercury; 9.2 g. (92% recovery). After evaporation of the solvent under reduced pressure, the residue was sublimed at 110° and 0.5 mm. 2,4-Dinitrophenyl vinyl ether was recrystallized from benzene-hexane to deposit yellow needles melting 51–52°.

Divinylmercury and Thiophenol.—To 25.5 g. (0.1 mole) of divinylmercury was added dropwise at room temperature 11.0 g. (0.1 mole) of thiophenol. An exothermic reaction commenced immediately with the accompanying evolution of ethylene and the deposition of metallic mercury. After the initial reaction subsided, the mixture was heated on a steam-bath for 0.5 hour to complete the reaction. The solidified residue was dissolved in hot petroleum ether and decanted from the mercury (6.0 g., 30%). Upon cooling, 17.90 g. of a white solid, m. 61.5–64.5°, separated. Fractional crystallization of the mixture from ethanol gave 13.60 g. of vinylmercuric thiophenolate, m.p. 64–65° (*Anal.* Calcd. for C_8H_8HgS : C, 28.52; H, 2.38; S, 9.52. Found: C, 28.43; H, 2.46; S, 8.94.) and 1.43 g. of mercury-bis-thiophenolate, m.p. 155–156°, lit.¹⁵ m.p. 150–151° (*Anal.* Calcd. for $C_{12}H_{10}HgS_2$: C, 34.40; H, 2.39; S, 15.29. Found: C, 34.21; H, 2.42; S, 14.90). Distillation of the mother liquor yielded 2.75 g. of vinyl phenyl sulfide, b.p. 60–62° (1 mm.), n_D^{20} 1.5873 (lit.²⁵ b.p. 78° (4 mm.), n_D^{20} 1.5883).

A 7.58-g. (0.0225 mole) sample of vinylmercuric thiophenolate was heated to 130° for 3 hours. After cooling, the reaction mixture consisted of mercury metal (4.09 g., 91%), a solid and a liquid. Distillation of the liquid gave 2.32 g. (75.6%) of vinyl phenyl sulfide, n_D^{20} 1.5871. The solid material (0.31 g.) was identical with the mercury-bis-thiophenolate obtained above.

Divinylmercury and Lauryl Mercaptan.—A mixture containing 25.5 g. (0.1 mole) of divinylmercury and 20.3 g. (0.1 mole) of lauryl mercaptan was heated to 115° for 3 hours. The hot reaction mixture was decanted from the deposited mercury (5.7 g., 28.5%). Upon cooling, a waxy solid crystallized, melting 37–53°. Fractional crystallization of the mixture from ethanol-chloroform gave 3.80 g. (16.6%) of vinyl lauryl sulfide, m.p. 50–51°. The sample was dried *in vacuo* (1 mm.) at 40° for 30 hours.

Anal. Calcd. for $C_{14}H_{28}S$: C, 73.62; H, 12.36; S, 14.02. Found: C, 73.86; H, 12.61; S, 13.57.

In addition, 2.1 g. of the mercury salt of lauryl mercaptan, $(C_{12}H_{26}S)_2Hg$, m.p. 79–81°, was obtained.

Anal. Calcd. for $C_{24}H_{50}S_2Hg$: C, 47.80; H, 8.36; S, 10.63. Found: C, 48.07; H, 8.30; S, 10.86.

(24) A. N. Nesmeyanov, *et al.*, *Izvest. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk.*, **50** (1950); *C. A.*, **53**, 6996 (1959).

(25) C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 637.