Organomercury Chemistry

Some Novel Reactions of Divinylmercury

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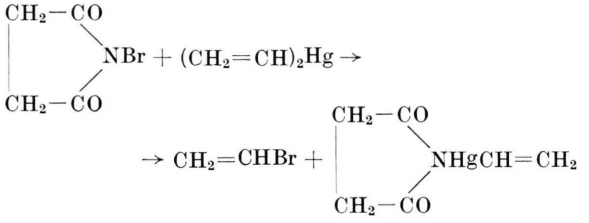
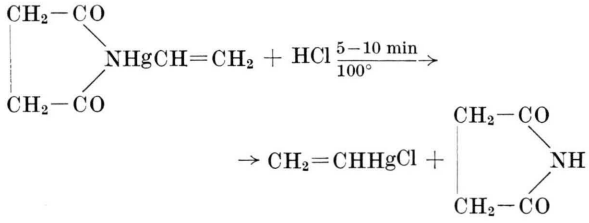
Divinylquecksilber reagiert mit *N*-Bromimiden unter Abspaltung von Vinylbromid und Bildung von *N*-Vinylquecksilberimiden. Dicyclopropylquecksilber wurde durch „Carben-Addition" an die beiden Doppelbindungen von Divinylquecksilber dargestellt. Durch Umsetzung von Divinylquecksilber mit *p*-Toluolsulfinsäure erhält man in guter Ausbeute das Vinyl-*p*-tolyl-sulfon.

The sensitivity of the carbon-mercury bond to cleavage [1] limits the reactions that can be carried out at the point of unsaturation of divinylmercury [2]. Repeated attempts to add halogens to the double bonds of divinylmercury resulted in cleavage of the starting material to a vinylhalide and mercuric halide. Similarly, bromotrichloromethane did not add to the unsaturation of divinylmercury but resulted in C-Hg bond cleavage.

N-Bromoimides react with divinylmercury to form vinylbromide and the corresponding *N*-vinylmercuric imide. Thus, an equimolar mixture of divinylmercury and *N*-bromosuccinimide refluxed in CCl_4 for two hours



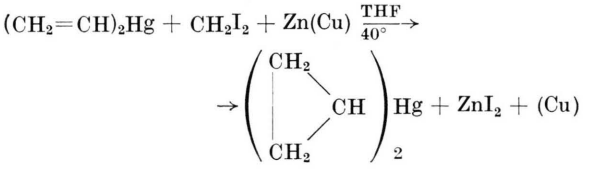
afforded a 95 per cent yield of *N*-vinylmercuric succinimide, m. p. 113 – 114°. (Found: C, 22.13; H, 2.21; N, 4.25. $C_6H_7HgNO_2$ requires C, 22.12; H, 2.17; N, 4.30.) The infrared spectrum shows strong absorption bands at 6.01, 7.38, 7.73 and 8.11 μ. The gaseous product from this reaction was analyzed by mass spectrometry and found to be vinylbromide of 96.4 per cent purity. *N*-vinylmercuric succinimide is easily cleaved by hydrochloric acid to vinylmercuric chloride and succinimide.



Similarly divinylmercury and *N*-bromophthalimide [3] yielded *N*-vinylmercuric phthalimide, m. p. 133 – 135°, (85 per cent yield). (Found: C, 32.39; H, 2.12; N, 3.88. $C_{10}H_7HgNO_2$ requires C, 32.13; H, 1.89; N, 3.75.) In the infrared, strong absorption bands are observed at 5.90, 7.43, 7.66, 8.01, 8.93 and 13.93 μ.

Unlike most vinylmercuric compounds [1], the vinylmercuric imides possess a considerable thermal stability.

The reaction of methylene iodide and zinc with olefins to form cyclopropyl derivatives [4], was successfully applied to divinylmercury. While no reaction was observed in ethyl ether, it did proceed readily in tetrahydrofuran. The dicyclopropylmercury obtained had



b. p. 92 – 95° at 3 mm., and n_D^{20} 1.5937. The infrared spectrum was identical with the one obtained from an authentic sample (b. p. 98 – 99° at 3.7 mm., n_D^{20} 1.5901), prepared from cyclopropyllithium and mercuric chloride. (lit. [2b] b. p. 110 – 112° at 18 mm.). Bubbling dry HCl gas through a benzene solution of dicyclopropylmercury at 75 – 78° for ten minutes gave excellent yields of cyclopropylmercuric chloride, m. p. 186 to 187°. (Found: C, 12.71; H, 1.76; Cl, 12.58. C_3H_5HgCl requires C, 12.99; H, 1.80; Cl, 12.82.) With acetic acid, cyclopropylmercuric acetate, m. p. 80 – 81°, was readily formed [1].

It has been demonstrated that the reaction of sulfinic acid salts with alkyl halides leads to the formation of sulfones [5], whereas alkylchlorocarbonates and sulfinic acid salts result in sulfinate ester formation [6]. Since divinylmercury reacts with a variety of organic acids to form the corresponding vinylesters [1], the reaction with sulfinic acids could result in the formation of vinyl sulfone and/or a vinylsulfinate. Dropwise addition of an ethanolic solution of divinylmercury to freshly prepared *p*-toluenesulfinic acid [7] in ethanol and subsequent heating on the steam bath gave ethylene, mercury metal (89 per cent) and a white solid. Fractional crystallization of the solid from ethanol gave vinyl *p*-tolyl sulfone, m. p. 65 – 66° (lit. [8], m. p. 67°), in a 75 per cent yield. (Found: C, 59.43; H, 5.35; S, 17.21.

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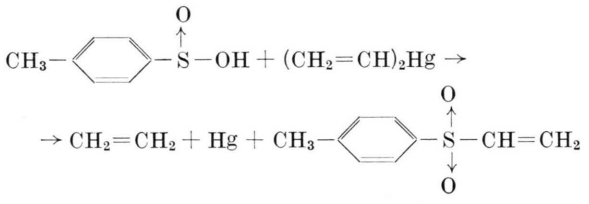

$C_9H_{10}O_2S$ requires C, 59.32; H, 5.53; S, 17.60.) The infrared spectrum showed the characteristic absorptions of a sulfone at 7.52 and 8.69 μ [9].

[9] L. J. BELLAMY, "The Infrared Spectra of Complex Molecules", 2nd. Ed., Methuen, London 1956, p. 360.

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Some Reactions of Vinyl- and Cyclopropylmercury Compounds

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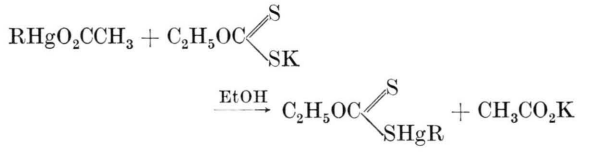
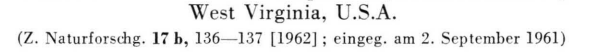
Vinyl- und Cyclopropylquecksilber-ester reagieren mit „Xanthogenaten" unter Bildung der entsprechenden Alkylquecksilber-xanthogenate. Auf ähnliche Weise konnte aus Vinylquecksilber-acetat und Natriumthiocyanat Vinylquecksilber-thiocyanat dargestellt werden. Mit Acetylen setzen sich alkalische Lösungen von organischen Quecksilbersalzen zu Dialkylquecksilberacetylenen um.

SPENGLER and WEBER [1], by treating several mercury addition products with potassium xanthate, obtained organomercury xanthates, which decomposed after a few days accompanied by the deposition of mercury sulfide. Under the same conditions, vinylmercuric and cyclopropylmercuric acetate react with potassium



xanthate in ethanol to give vinylmercuric xanthate (R = CH_2:CH−), green-yellow plates, m. p. 40.5° (Found: C, 17.37; H, 2.37; S, 18.58. $C_5H_8HgOS_2$ requires *C*, 17.21; H, 2.29; S, 18.35) and cyclopropylmercuric xanthate (R = Cyclopropyl), m. p. 87 to 88°, (Found: C, 19.92; H, 2.86; S, 17.41. $C_6H_{10}HgOS_2$ requires C, 19.85; H, 2.78; S, 17.65), respectively. Both compounds show strong infrared absorption bands in the 8.0, 8.2, 9.0 and 9.7 μ region. While cyclopropylmercuric xanthate exhibits considerable stability, vinylmercuric xanthate decomposes after a few days accompanied by the deposition of a grey-black precipitate. Thermal decomposition at 115 to 125 °C under a reduced pressure of 25 mm gave a yellow oil (n_D^{20} 1.5705), which is believed to be vinylxanthate, $C_2H_5OCSSCH=CH_2$. The infrared spectrum of the compound is characterized by two sharp absorption bands at 8.22 μ (C=S) [2, 3] and 9.46 μ (C−O−C) [3].

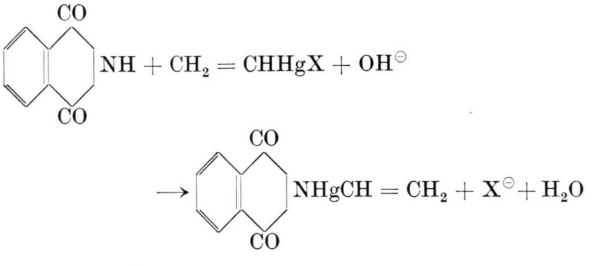
Vinylmercuric acetate also reacts with sodium thiocyanate to yield vinylmercuric thiocyanate, m. p. 138.5 to 139°. The infrared spectrum exhibits a strong



absorption band at 4.83 μ, due to the S−C≡N vibration [4]. (Found: C, 12.39; H, 1.08; N, 5.13; S, 11.38. C_3H_3HgNS requires C, 12.61; H, 1.05; N, 4.90; S, 11.20.)

Thermal decomposition at 100 − 120° under a reduced pressure of 100 mm. gave a colorless liquid of repulsive odor, n_D^{20} 1.5042. The infrared spectrum of this material showed strong absorptions at 4.58 (N=C=S), 4.63 (S−C≡N) and 4.82 μ (N=C=S) [5], indicating the presence of vinylisothiocyanate (lit. [6], b. p. 46° at 100 mm., n_D^{33} 1.505) and vinylthiocyanate (lit. [7], b. p. 54° at 62 mm., n_D^{20} 1.4880). According to a vapor phase chromatographic analysis, the mixture consisted of 30 per cent $CH_2=CHN=C=S$ and 66 per ecnt $CH_2=CHSC\equiv N$.

As already described in the previous communication [8], the reaction of divinylmercury with *N*-bromoimides results in the formation of *N*-vinylmercuric imides. The latter can also be obtained from vinylmercuric salts and imides in the presence of base [9]. Thus, treatment of an alcoholic solution of phthalimide with a solution of vinylmercuric halide in alco-



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