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The Carbonylation of Furan and Thiophene Mercuric Compounds with Palladium Salt

Taeko IZUMI, Toshio IINO, and Akira KASAHARA

Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992

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Heck¹⁾ has reported that diarylketones were formed in moderate yields from arylmercuric salts and carbon monoxide with a transition-metal-salt catalyst. Furthermore, we have ourselves described the carbonylation of 1,1'-bis(chloromercuri)-ferrocene in the presence of a palladium salt.²⁾ In this report, we wish to report on the carbonylation reactions of chloromercuri-derivatives of furan and thiophene in methanol with a palladium salt.

The carbonylation of 2-chloromercurifuran (I-1) was carried out at 100 °C under a carbon monoxide pressure of 50 atm in the presence of lithium chloropalladite in methanol; the main products were 2,2'-difurylketone (II-1) and methyl furoate (III-1), plus a small amount of 2,2'-bifuryl (IV-1). The carbonylations of 5-methoxycarbonyl-2-chloromercurifuran (I-2) and 2-chloromercurithiophene (I-3) were performed under the same conditions. The mechanism of the formation of II-1 from I-1, as has been pointed out by Heck,¹⁾ probably involves the reaction of an acylpalladium

compound with a furylpalladium compound or I-1. III-1 and IV-1 are probably formed by side reactions.

On the other hand, the carbonylation of 2,5-dichloromercurifuran (V-1) under the same conditions gave a mixture of 5,5'-dimethoxycarbonyl-2,2'-difurylketone (II-2), 2,5-dimethoxycarbonylfuran (III-2), and the keto-ester polymer (VIII). The structure of VIII was identified by means of the measurement of the molecular weight and by means of the spectral data. In the IR spectrum, very intensive absorption bands at 1735 cm⁻¹ due to ester stretching, at 1630 cm⁻¹ due to carbonyl stretching, and at 880 cm⁻¹ due to the furan ring were observed. However, the carbonylation of 2,5-dichloromercurithiophene (V-2) yielded a mixture of 5,5'-dimethoxycarbonyl-2,2'-dithienylketone (VI) and 2,5-dimethoxycarbonylthiophene (VII).

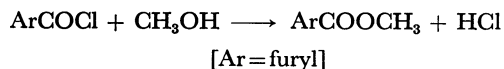
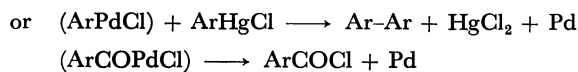
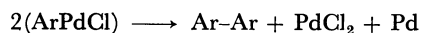
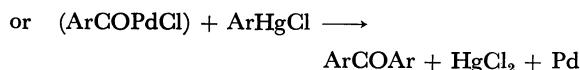
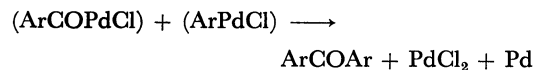
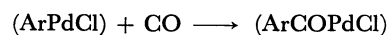
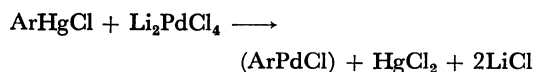
Experimental

All the melting and boiling points are uncorrected. The IR spectra were recorded on a Hitachi 215 spectrometer, while the NMR spectra were obtained in CDCl₃ at 90 MHz with a Hitachi R-22 NMR spectrometer, using TMS as the internal standard.

Materials. The 2-chloromercurifuran (I-1) and 2,5-dichloromercurifuran (V-1) were synthesized by the method of Gilman *et al.*³⁾ The 2-chloromercurithiophene (I-3) and 2,5-dichloromercurithiophene (V-2) were prepared by the method of Cherbuliez and Giggey.⁴⁾

The 5-methoxycarbonyl-2-chloromercurifuran (I-2) was synthesized from methyl furoate, mercuric chloride, and sodium acetate by a modification of the method of Gilman and Wright³⁾ Mp 243—245 °C. Yield, 60%. Found: C, 19.69; H, 1.15%. Calcd for C₈H₅O₃HgCl: C, 19.95; H, 1.36%.

General Procedure for The Carbonylation of Chloromercuric Compounds. A lithium chloropalladite solution was prepared by stirring 0.84 g (20 mmol) of lithium chloride with 1.77g

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