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The Carbonylation of Furan and Thiophene Mercuric Compounds with Palladium Salt

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Heck[1] 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.

$$
\begin{aligned}
&\mathrm{ArHgCl} + \mathrm{Li_2PdCl_4} \longrightarrow \\
&\qquad\qquad (\mathrm{ArPdCl}) + \mathrm{HgCl_2} + 2\mathrm{LiCl} \\
&(\mathrm{ArPdCl}) + \mathrm{CO} \longrightarrow (\mathrm{ArCOPdCl}) \\
&(\mathrm{ArCOPdCl}) + (\mathrm{ArPdCl}) \longrightarrow \\
&\qquad\qquad \mathrm{ArCOAr} + \mathrm{PdCl_2} + \mathrm{Pd} \\
\text{or}\quad &(\mathrm{ArCOPdCl}) + \mathrm{ArHgCl} \longrightarrow \\
&\qquad\qquad \mathrm{ArCOAr} + \mathrm{HgCl_2} + \mathrm{Pd} \\
&2(\mathrm{ArPdCl}) \longrightarrow \mathrm{Ar\text{-}Ar} + \mathrm{PdCl_2} + \mathrm{Pd} \\
\text{or}\quad &(\mathrm{ArPdCl}) + \mathrm{ArHgCl} \longrightarrow \mathrm{Ar\text{-}Ar} + \mathrm{HgCl_2} + \mathrm{Pd} \\
&(\mathrm{ArCOPdCl}) \longrightarrow \mathrm{ArCOCl} + \mathrm{Pd} \\
&\mathrm{ArCOCl} + \mathrm{CH_3OH} \longrightarrow \mathrm{ArCOOCH_3} + \mathrm{HCl} \\
&\qquad\qquad [\mathrm{Ar} = \text{furyl}]
\end{aligned}
$$

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 streching, at 1630 cm^{-1} due to carbonyl streching, 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 $CDCl_3$ 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 Wright[3] Mp 243—245 °C. Yield, 60%. Found: C, 19.69; H, 1.15%. Calcd for $C_6H_5O_3HgCl$: 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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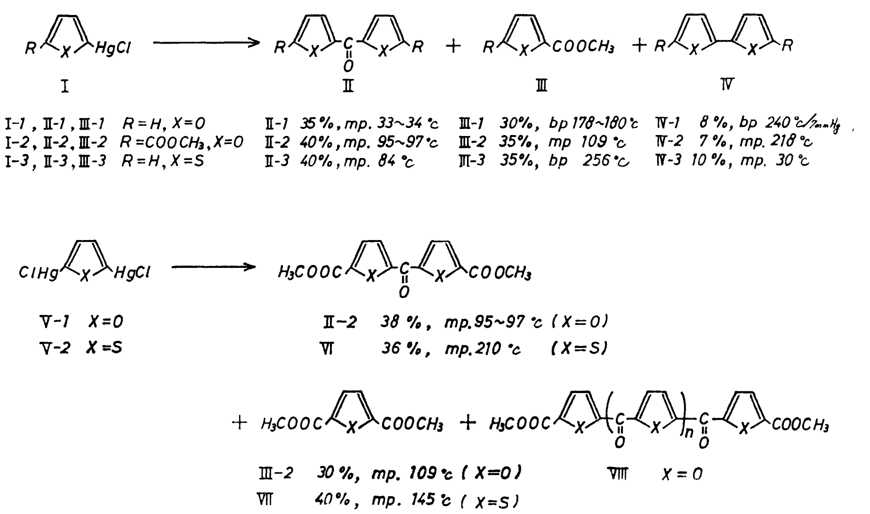

Fig. 1.

(10 mmol) of anhydrous palladium chloride overnight at room temperature in 100 ml of methanol. Into this solution, chloromercuric compound in an equivalent amount was then carbonylated at 100 °C under a carbon monoxide pressure (50 atm) for 6 hr with shaking. The reaction mixture was filtered to remove precipitated palladium, and the solvent was distilled under reduced pressure. The residue was dissolved in benzene and then purified by column chromatography on neutral alumina, or separated by preparative gas chromatography (Hitachi K-53 gas chromatograph, SE-30 column). The structures of the products were confirmed by an observation of the IR and NMR spectra and by comparing the retention time with those of authentic samples. The following results were obtained.

a) The carbonylation of I-1 afforded 2,2′-difurylketone (II-1) (35%, mp 33—34 °C (lit,[5] 33—34 °C)), methyl furoate (III-1) (30%, bp 178—180 °C (lit,[6] 181 °C)), and 2,2′-bifuryl (IV-1) (8%, bp 240 °C/7 mmHg (lit,[7] 240—245 °C/7 mmHg)).

b) The carbonylation of I-2 afforded 5,5′-dimethoxycarbonyl-2,2′-difurylketone (II-2) (40%, mp 95—97 °C, IR 1735, 1640, 880 cm^{-1}, NMR δ 3.88 (s, 6, -COOCH$_3$), 7.15 (d, 2, H on C$_3$ and C$_{3'}$), 7.34 (d, 2, H on C$_4$ and C$_{4'}$). Found: C, 56.05; H, 3.53%. Calcd for $C_{13}H_{10}O_7$: C, 56.12; H, 3.62%). 2,5-Dimethoxycarbonylfuran (III-2) (35%, mp 109 °C (lit,[8] 111—112 °C)), and 5,5′-dimethoxycarbonyl-2,2′-bifuryl (IV-2) (7%, mp 218 °C, IR 1728, 878 cm^{-1}, NMR δ 3.89 (s, 6, -COOCH$_3$), 6.87 (d, 2, H on C$_3$ and C$_{3'}$), 7.22 (d, 2, H on C$_4$ and C$_{4'}$). Found: C, 57.51; H, 3.96%. Calcd for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03%).

c) The carbonylation of I-3 afforded 2,2′-dithienylketone (II-3) (40%, mp 84 °C (lit,[9] 87—88 °C)), 2-methoxycarbonylthiophene (III-3) (35%, bp 256 °C (lit,[10] 117 °C/30 mmHg)), and 2,2′-bithienyl (IV-3) (10%, mp 30 °C(lit,[11] 33 °C)).

d) The carbonylation of V-1 afforded II-2 (38%), III-2 (30%), and the ketoester polymer (VIII) 7%, IR 1735 (C=O, ester), 1630 (C=O, ketone), 880 (furan ring), mol wt 1212 (in benzene)).

e) The carbonylation of V-2 afforded 5,5′-dimethoxycarbonyl-2,2′-dithienylketone (VI) (36%, mp 210 °C, IR 1710, 1610, 700 cm^{-1}, NMR δ 3.91 (s, 6, -COOCH$_3$), 7.23 (d, 2, H on C$_3$ and C$_{3'}$), 7.44 (d, 2, H on C$_4$ and C$_{4'}$), Found: C, 50.25; H, 3.07%; Calcd for $C_{13}H_{10}O_5S_2$: C, 50.33; H, 3.25%), and 2,5-dimethoxycarbonylthiophene (VII), (40%, mp 145 °C (lit,[12] 148—149 °C)).

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