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A Palladium-catalyzed Alkoxycarbonylation of Ethynylmercury Compounds

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Synopsis. Bis(phenylethynyl)mercury reacts with carbon monoxide and alcohol at room temperature in the presence of palladium(II) salt to form dialkyl phenylmaleate, accompanied by small amounts of alkyl phenylpropiolate and dialkyl phenylfumarate. An alkoxycarbonylation at 100 °C afforded a trialkoxycarbonylation product, accompanied by dialkoxycarbonylation products. The alkoxycarbonylation of bis(ethylethynyl)mercury proceeds similarly.

The palladium-promoted alkoxycarbonylation of alkyl,[1] aryl,[2] and vinyl-mercury compouns[3] has been described. Heck[4] has also reported the palladium-catalyzed carbonylation of olefins and acetylenes with methoxycarbonylmercuric chloride. In this paper, we wish to report the palladium-catalyzed alkoxycarbonylation of bis(phenylethynyl)mercury (**1**) and bis(ethylethynyl)mercury (**2**).

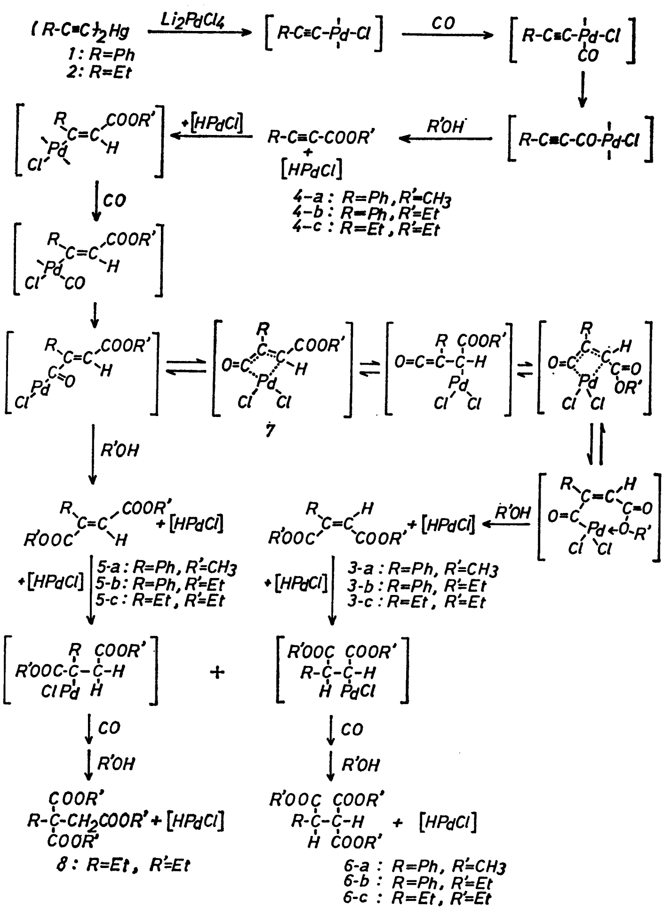
The methoxycarbonylation of **1** was carried out at room temperature under a carbon monoxide pressure of 20 atm in the presence of lithium tetrachloropalladate(II) in methanol to give dimethyl phenylmaleate (**3a**) as the main product. Small amounts of methyl phenylpropiolate (**4a**) and dimethyl phenylfumarate (**5a**) were also produced. The methoxycarbonylation of **1** at 100 °C resulted in the formation of **3a**, **4a**, **5a**, and trimethyl 2-phenyl-1,1,2-ethanetricarboxylate (**6a**). In ethanol, the corresponding ethyl esters were obtained. Similarly, the alkoxycarbonylation of **2** at room temperature afforded dialkoxycarbonylated products, and the reaction at 100 °C led to the formation of trialkoxycarbonylation products. These results are presented in Table 1.

The palladium-catalyzed alkoxycarbonylation of **1** and **2** undoubtedly proceeds by means of an initial mercury-palladium exchange reaction, carbon monoxide insertion into the resultant ethynyl palladium compounds, and subsequent alcoholysis to give **4** and [HPdCl]. The formation of **3** and **5** could be explained by considering the re-addition of [HPdCl] to **4**. A proposed reaction mechanism is shown in Scheme 1. That the elimination and addition of [HPdCl] on unsaturated carbon-carbon bond proceed *via* a *cis* stereochemistry is well-known.[5] Consequently, the

TABLE 1. ALKOXYCARBONYLATION OF BIS(PHENYLETHYNYL)-MERCURY (**1**) AND BIS(ETHYLETHYNYL)MERCURY (**2**)

Mercurial	ROH	Temp °C	Product	Yield %[a]
1	CH_3OH	25	Methyl phenylpropiolate (**4a**)	4
			Dimethyl phenylmaleate (**3a**)	58
			Dimethyl phenylfumarate (**5a**)	4
1	CH_3OH	100	**4a**	3
			3a	43
			5a	10
			Trimethyl 2-phenyl-1,1,2-ethanetricarboxylate (**6a**)	12
1	C_2H_5OH	25	Ethyl phenylpropiolate (**4b**)	5
			Diethyl phenylmaleate (**3b**)	62
			Diethyl phenylfumarate (**5b**)	6
1	C_2H_5OH	100	**4b**	2
			3b	48
			5b	11
			Triethyl 2-phenyl-1,1,2-ethanetricarboxylate (**6b**)	8
2	C_2H_5OH	25	Ethyl 2-pentynoate (**4c**)	6
			Diethyl ethylmaleate (**3c**)	40
			Diethyl ethylfumarate (**5c**)	10
2	C_2H_5OH	100	**4c**	1
			3c	46
			5c	4
			Triethyl 1,1,2-butanetricarboxylate (**6c**)	6
			Triethyl 1,2,2-butanetricarboxylate (**8**)	2

a) Yields are based on the mercurial used.



Scheme 1.

reaction pathway of the formation of **5** may very probably include a *cis* addition of [HPdCl] to **4**, but the *cis-trans* isomerization (**5**→**3**) can not be explained only in terms of a palladium-hydride addition-elimination mechanism in the present case. Furthermore, the product, **5**, did not isomerize to **3** under the present reaction conditions.

Schoenberg *et al.*[6] reported that the palladium-catalyzed butoxycarbonylation of (*Z*)-*β*-bromostyrene gave a mixture of (*E*)- and (*Z*)-butyl cinnamate, and, with reference to the formation of the (*E*)-isomer, they suggested that the *cis-trans* isomerization proceeds probably *via* a ionic carbene-type intermediate or a *π*-acryloylpalladium-type intermediate. As they have pointed out, the mechanism of the formation of **3** probably involves a *π*-acryloylpalladium-type intermediate (**7**), and the overwhelming formation of **3** compared with **5** is consistent with this process, because a coordination of the palladium atom to the alkoxycarbonyl group occurs. In the alkoxycarbonylation of **1** and **2** at 100 °C, the formation of **6** and/or **8** proceeds *via* a re-addition of [HPdCl] to **3** and/or **5**. **8a** and **8b** could not be detected because of their poor yields.

Experimental

Materials. The bis(phenylethynyl)mercury (**1**) and bis(ethylethynyl)mercury (**2**) were prepared according to the method described by Johnson and McEwen.[7]

General Procedure for the Alkoxycarbonylation of 1 and 2. A lithium tetrachloropalladate(II) solution was prepared by stirring 0.82 g (20 mmol) of lithium chloride with 1.77 g (10 mmol) of palladium(II) chloride overnight at room temperature in 80 ml of methanol or ethanol. In this solution, 5 mmol of mercurial (**1** or **2**) was then carbonylated under a carbon monoxide pressure of 20 atm for 6 h with shaking. The reaction mixture was then filtered to remove a precipitated palladium and distilled under reduced pressure to remove the solvent. The products were isolated by preparative gas chromatography or column chromatography (Al_2O_3–hexane), analysed by gas chromatography on 1-m SE 30 (5% on celite) column with a Hitachi K-53 gas-chromatograph, and identified by comparing their retention time and IR and NMR spectra with those of an authentic sample. The reactions carried out are listed in Table 1.

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