the monooxygen activation as a model of cytochrome P-450.

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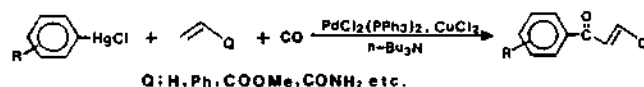# Palladium-Catalyzed Carbonylative Vinylation of Arylmercuric Chlorides with Carbon Monoxide and Olefins

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Department of Industrial Chemistry, Hanyang University, Haengdang-Dong 17, Seoul, 133-791 Korea
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The palladium-catalyzed vinylation of vinyl halides with olefins provides a convenient method for the preparation of the corresponding conjugated dienes.[1] We reported methods for the palladium-catalyzed vinylation of vinylmercuric chlorides with olefins under mild conditions, which afforded the conjugated dienes in good yields,[2] and for the palladium-catalyzed cabonylative vinylation of aryl halides with olefins in the presence of carbon monoxide, which resulted in the formation of aryl vinyl ketones or aryl vinyl-α-diketones.[3]

We have now found that arylmercuric chlorides react under mild conditions with carbon monoxide and olefins in the presence of a palladium catalyst, a base, and CuCl₂ to afford the corresponding aryl vinyl ketones in moderate to good yields.

The results obtained are summarized in the Table 1. In a typical procedure (entry 1) a mixture of phenylmercuric chloride (1.57 g, 5 mmol), styrene (0.69 m*l*, 6 mmol), tri-*n*-

Table 1. Palladium-Catalyzed Carbonylative Vinylation of Arylmercuric Chlorides with Carbon Monoxide and Olefins[a]

Entry	Arylmercuric chloride	Olefin	Product (% Yield[b])
1			(71)
2[c]			(30)
3[d]			(35)
4			(70)
5			(81)
6			(68)

[a] All reactions were carried out for 12 hours in the same manner as described in the text, unless otherwise noted. Disappearance of the starting material was monitored by TLC. [b] Yiels of isolated products. [c] PdCl₂(CH₃CN)₂ was used as a catalyst. [d] Reacted under atmospheric pressure of CO.

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butylamine (3.57 ml, 15 mmol), dichlorobis (triphenylphosphine) palladium(II) (0.035 g, 0.05 mmol), and cupric chloride (1.34 g, 10 mmol) in acetonitrile (5 ml) was stirred under 10 atm of CO at 80°C for 12 hours. The reaction mixture was then diluted with aq. ammonium chloride, extracted with ether, washed several times with distilled water, dried over $MgSO_4$, and evaporated. Chromatography of the residue (0.94 g) on silica gel using hexane/ethyl acetate=3/1 as eluent gave 0.74 g (71%) of (E)-1,3-diphenyl-1-oxo-2-propene: IR (KBr) 1670 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ7.31-7.82 (m, 10H), 7.92-8.18(m, 2H); mp. 59°C; m/e(M$^+$) calcd for $C_{15}H_{12}O$ 208.2592, found 208.2590.

Satisfactory results were obtained by using PdCl$_2$(PPh$_3$)$_2$ as a catalyst. Triphenylphosphine was found to be a better ligand than others[4] regarding the yields of aryl vinyl ketones (entries 1 and 2). And also, the increase of CO pressure enhanced the yields of the desired aryl vinyl ketones (entries 1 and 3).

The mechanism of the present carbonylative vinylation of arylmercuric chlorides with CO and olefins involves (a) transmetallation of the palladium(II) catalyst with the mercurial moiety to give arylpalladium(II) complex,[5] (b) CO insertion to give the aroylpalladium(II) complex, (c) reaction with olefins according to the Heck's vinylation mechanism to afford aryl vinyl ketones and Pd(O)[1c], and (e) reoxidation of Pd(O) to Pd(II) with CaCl$_2$.

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Carrier-Mediated Transport of Some Transition Metal Cations Through Bulk Liquid Membrane Containing Azacrown Ether

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Studies were reported of the variation of cation transport rate through a bulk chloroform membrane containing a neutral macrocyclic carrier with cation (substrate) concentration in the source phase[1,2]. The transport rates (j_c) for potassium salts (KCl, KI, KSCN and KNO$_3$) were found to vary as the square of the cation activity in region of $1 \times 10^{-2} \sim 1$ M using dibenzo-18-crown-6(DBC) as membrane carrier. An associative mechanism, carrier-mediated transport of complexed ion-pair was applied to explain the results[3,4].

To better understand the relationship between carrier properties and transport rates in connection with the above results, extensive numerical simulations were proposed to describe simply and quantitatively various transport mechanisms[3,5]. They are approaches with adaptation and extension of earlier developed kinetic treatments[6,8]. The first model was to depict the carrier-mediated transport of a single substrate species such as aminoacids through the liquid membrane. Depending on the substrate concentration (C_a) and extraction coefficient (k), two kinds of regimes may be observed: at $kC_a \ll 1$, the transport rate is very low and first order with respect to the substrate concentration. At $kC_a \gg 1$, the rate increases up to its maximum and becomes independent of C_a and k. The second model was to describe substrate competition. Although the goal of the most transport experiments through liquid membrane is to achieve the selective removal of a given substrate, experimental results revealed that the selectivity for two substrates is not directly related to the relative transport rates of the two substrates measured in separate experiments[5]. The third one was to describe the facilitated transport of complexed ion-pair. This is the system most widely studied especially in relation to the transport of cation together with anions by neutral ligands like crown ethers and cryptands[1,2,4,9,10]. Due to simultaneous extraction and transport of two species, concentration appears at the second power in the transport rate equation. It is the case described in the opening of this paper.

The principal aim of this paper is to report unusual carrier-mediated transport phenomena of some transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, all chlorides) through bulk chloroform membrane containing azacrown ether. One of the azacrowns was 1,12,15-triaza-3,4 : 9,10-dibenzo-5,8-dioxocycloheptadecane (N$_3$O$_2$). The other was 6,9,12-triazabicyclo[15,3,1]-heneicosa-1(21), 17,18-triene-2,6-dione(PAC). The synthetic methods of the carriers and experimental procedures to obtain transport rates were just the same as described elsewhere[1,4,9,11].

N$_3$O$_2$ PAC
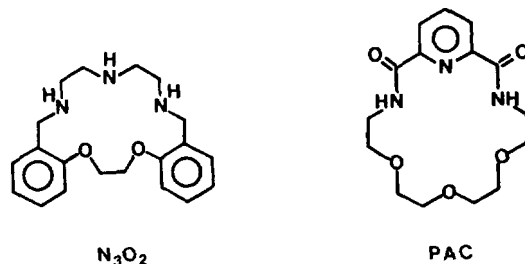
Since the membrane phase was stirred during the experiments, the rate was diffusion-limited and diffusion of the complexes through the membrane phase can not be rate-determining. The k values determined by extraction method[12] were larger than 1×10^2 for all the investigated systems and the first model could be excluded in the discussion. There-