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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS

X. CARBONYLATION REACTION OF CYCLOPROPANE CATALYZED BY PALLADIUM CHLORIDE[1]

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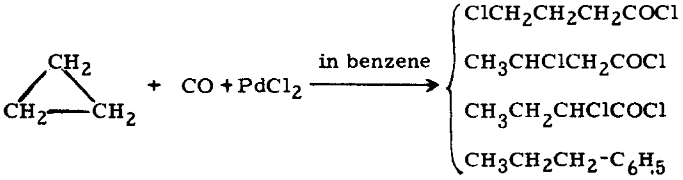
We have reported reactions between olefins, carbon monoxide and palladium chloride to form β-chloroacyl chlorides[2]. It was of considerable interest to study the carbonylation reaction of cyclopropane in view of the fact that olefins and cyclopropane show considerable similarities. We have found that cyclopropane can be carbonylated easily in the presence of palladium chloride in benzene to form α-, β-, and γ-chlorobutyryl chlorides, accompanied with n-propylbenzene. To our knowledge, this work represents the first instance of a carbonylation reaction of cyclopropane catalyzed by a transition metal.



Cyclopropane (5 ml.) in benzene was stirred for several hours in an autoclave with palladium chloride (10 g.) and then carbon monoxide was introduced (100 kg./cm^2.). The mixture was heated for 20 hours at 90°. Formation of the acid chlorides was confirmed by infrared spectra of one of the crude products, and the conversion of the acid chlorides into methyl esters. Isolation of each ester from the distilled mixture (1.6 g.) was done by preparative gas chromatography. These esters were identified as α-, β-, and γ-chlorobutyrates by infrared and n.m.r. spectra and gas chromatography. The ratio of α-, β-, and γ-isomers was about 5 : 1 : 2 in one case and somewhat variable depending on the reaction conditions.

Simple ring opening should give γ-chlorobutyrate and it was rather surprising that the α-isomer was the predominant product. It seems likely that β-chlorobutyrate was formed from propylene formed from cyclopropane. The formation of a small amount of propylene was confirmed by gas chromatography when cyclopropane was reacted with palladium chloride at 50° under nitrogen in the autoclave. Reaction of olefins with palladium chloride to form β-chloroacyl chloride is known.[2] The carbonylation is possible only through complex formation between cyclopropane and palladium chloride, and the structure of the intermediate complex should be clarified before the mechanism of the reaction can be given. No complex formation between cyclopropane and transition metal was reported except for platinum chloride[3]. In this connection, it should be mentioned that Baird and Aboderin observed that deuterium distribution in the 1-, 2-, and 3-positions of 1-propanol, obtained from the solvolysis of cyclopropane in D_2SO_4, was 0.38, 0.17 and 0.46 deuterium atoms respectively[4].

In addition, n-propylbenzene was found in the reaction mixture. Its amount was about three times as much as that of β-chlorobutyrate.

Apparently n-propylbenzene is a product of the Friedel-Crafts reaction of cyclopropane. No report has previously been given that palladium chloride is active for Friedel-Crafts reactions. Interestingly, n-propylbenzene was not formed from benzene and cyclopropane in the presence of palladium chloride in the autoclave under an atmosphere of nitrogen instead of carbon monoxide.

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