New Catalysts for Olefin–Formaldehyde Concentrations: Palladium Compounds

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IN the Prins reaction, *i.e.*, acid-catalyzed condensation of olefins with formaldehyde to give 1,3-dioxans, glycols, *etc.*, selectivity and the yield of 1,3-dioxan are generally low.[1-3] We report high catalytic activity and high selectivity in 1,3-dioxan formation when palladium compounds, *e.g.*, a catalyst system consisting of palladium chloride and cupric chloride, are used as catalyst.

A benzene solution of 3-methylbut-1-ene, commercial (37% aq.) formaldehyde (2 moles), and 0·01 mole of catalyst were shaken in a sealed tube at 50° for 18 hr. (heterogeneous reaction). A small amount of metallic palladium separated in the latter stage of the reaction. The combined yield of 4,4,5-trimethyl-1,3-dioxan (I), b.p. 64°/30 mm. Hg and 4-isopropyl-1,3-dioxan (II), b.p. 50°/20 mm. Hg, and the isomer ratio (II)/[(I) + (II)] were measured by gas chromatography and are shown in the Table. With acid catalysis, (I) and (II) were obtained in low yield, along with considerable amounts of glycols and other high-boiling products. Palladium chloride, especially in the presence of cupric chloride, exhibited much higher catalytic activity, and gave predominantly the product (I), which would be produced after isomerization. Glycol and other by-products were scarcely detected in the reaction mixture.

An oxygen atmosphere was not essential to 1,3-dioxan formation (compare runs 6 and 7), suggesting a different function for the palladium

TABLE. *Condensation of 3-methylbut-1-ene with formaldehyde*

Run	Catalyst	Yield (I)+(II) %	Isomer Ratio (I)/[(I)+(II)]
1	H_2SO_4	3	77
2.	HCl	3	—
3.	$PdCl_2$	6	47
4.	HCl + $CuCl_2$[a]	3	90
5.	$PdCl_2$ + HCl[b]	8	55
6.	$PdCl_2$ + $CuCl_2$[a]	61, 58[d]	14, 16[d]
7.	$PdCl_2$ + $CuCl_2$[a,c]	54	14
8.	$PdCl_2$ + $FeCl_3$[a]	29	10
9.	$PdCl_2$ + $NiCl_2$[a]	14	29
10.	$PdCl_2$ + $HgCl_2$[a]	8	—
11.	$PdCl_2$ + $SnCl_2$[a]	7	—
12.	$PdCl_2$ + $CuCl_2$[a,e]	70	14

[a] Catalyst : cocatalyst = 1 : 3, except run 11, 1 : 1.

[b] pH in aqueous layer was controlled to 2·0 by addition of HCl.

[c] Reaction in nitrogen atmosphere. Other reactions were carried out in air.

[d] Reaction without solvent.

[e] pH in aqueous layer was controlled to 6·0 by $Na_2B_4O_7,10H_2O$.

catalyst in the Hoechst–Wacker process,[4] although the reaction of the isolated 3-methylbut-1-ene–palladium chloride complex with formaldehyde gave (I) in 21% yield.

Palladium nitrate and acetate were also catalytically active, but the palladium complexes of triphenylphosphine, pyridine, dimethylglyoxime acetylacetone, and diethyl sulphide were inactive. Paraformaldehyde could be used instead of formalin. The reaction was not affected by the addition of hydrocarbon or chlorinated hydrocarbon solvent, but basic solvents such as tetrahydrofuran or dimethylformamide decreased the yield of products.

Although normal olefins such as but-1-ene (2%), *cis*-but-2-ene (2%), *trans*-but-2-ene (2%), and styrene (4%) gave low yields of 1,3-dioxans, branched olefins as isobutene (67%) and 2-methylpen-1-ene (41%) gave good yields.

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