A Novel Synthesis of Glycol Mono-ester from an Olefin

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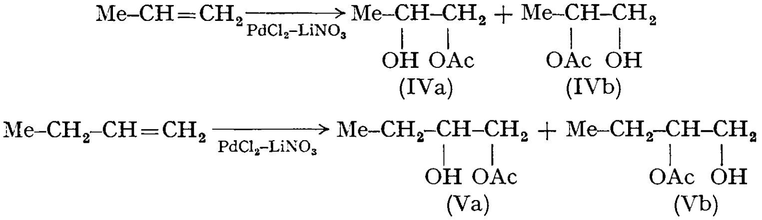
THE reactions of olefins with palladous salt in acetic acid has been reported.[1] Glycol mono-esters have previously been prepared from glycols or alkene oxides, but a recent patent suggests that ethylene reacts with $PdCl_2$–$CuCl_2$ catalyst in acetic acid to give ethylene glycol monoacetate (I). We report a new method of obtaining glycol mono-esters from olefin and organic acid. Use of the binary catalyst system palladium(II) salt–metallic nitrate gave a high conversion of ethylene into (I) under mild conditions with formation of small amounts of acetaldehyde (II) and ethylene glycol diacetate (III), *e.g.* $PdCl_2$ (1·0 mmole) and lithium nitrate (50 mmole) in acetic acid (100 ml.) were stirred at 50° and ethylene was led into the solution at the rate of 5 l./hr.; after 2 hr., the reaction mixture was analysed by g.l.c. The products were (I) (72·1 mmole), (III) (4·8 mmole), and (II) (2·3 mmole). Nitric oxide and a trace of nitrous oxide were also formed during the reaction.

Use of a mixture of ethylene and oxygen gave a larger amount of (I) and no nitric oxide. The yield of (II) was dependent on the concentrations of water and lithium nitrate, and on the reaction temperature. The diacetate (III) was believed to be formed by esterification of (I) during the reaction.

In the absence of oxygen, the rate of formation of (I) was shown by a following equation;

$$r = kP_{C_2H_4}[PdXn]$$

where k = rate constant, $P_{C_2H_4}$ = partial pressure of ethylene, and $[PdXn]$ = concentration of palladium(II) salt. When the molar ratio, $LiNO_3 : PdXn$, was above 10, r was independent of the concentration of lithium nitrate. The activation energy of this reaction was estimated as 11·8 kcal./mole. All palladium(II) salts examined and metallic palladium showed catalytic activity but mercury(II) and thallium(III) salts were inactive. Copper(II) and iron(III) nitrates were also effective, but barium and potassium nitrates were ineffective because of their poor solubility in acetic acid. Lithium nitrate was the most active. Lithium and sodium nitrites were also active, even in the absence of oxygen, whilst nitric oxide was inactive in itself, but became active in the presence of oxygen. In propionic and n-butyric acid, with the same catalyst system, the monopropionate and mono-n-butyrate of ethylene glycol were formed from ethylene at about the same rate as in acetic acid. Similarly, propene and but-1-ene gave mono-acetates of propene glycol and of n-butene glycol. The main products were (IVa) and (Va).



$$Me{-}CH{=}CH_2 \xrightarrow[PdCl_2-LiNO_3]{} \underset{OH\ \ OAc}{Me{-}CH{-}CH_2} + \underset{OAc\ \ OH}{Me{-}CH{-}CH_2}$$

(IVa) (IVb)

$$Me{-}CH_2{-}CH{=}CH_2 \xrightarrow[PdCl_2-LiNO_3]{} \underset{OH\ \ OAc}{Me{-}CH_2{-}CH{-}CH_2} + \underset{OAc\ \ OH}{Me{-}CH_2{-}CH{-}CH_2}$$

(Va) (Vb)

The rate of formation of these glycol mono-esters was in the order, $C_2H_4 > C_3H_6 > 1\text{-}C_4H_8$. In all these reactions, formation of palladium was not observed during mono-ester formation.

It is assumed that the reaction proceeds through π-olefin complex of the palladium(II) salt. The linkage isomerisation of Pd–NO_3 to a Pd–ONO_2 bond is believed to be an important step in the reaction.

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[1] A. Aguilo, "Olefin Oxidation with Palladium Catalyst in Solution" Advances in Organometallic Chemistry, Academic Press, New York, 1967, Vol. 5, p. 321; C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Logos Press, 1967, p. 88.

[2] B.P. 1,058,995/1967.