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HYDRODIMERIZATION OF ACRYLIC ESTERS BY HALOGENOTRIS(TRIPHENYLPHOSPHINE)COBALT COMPLEXES

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Acrylic esters were selectively hydrodimerized to adipic esters by halogenotris(triphenylphosphine)cobalt complexes in alcohol. The yield of a hydrodimer based on cobalt exceeded 100% in the presence of zinc. The addition of halides of alkali metals increased the yield.

Hydrodimerization of vinyl monomers was catalyzed with iron pentacarbonyl in the presence of sodium hydroxide1) or phenol under the irradiation.2) Acrylonitrile was hydrodimerized to adiponitrile by the use of cobalt chloride, powdered manganase, and water in dimethylformamide.3) This catalytic system for acrylic esters, however, resulted in the formation of propionic esters, not of adipic esters, in which metals were deposited contrary to the case of acrylonitrile.

We found a catalytic procedure for hydrodimerizing acrylic esters to adipic esters by halogenotris(triphenylphosphine)cobalt in alcohol and tetrahydrofuran at room temperature. During the reaction the color of the mixture changed yellowish-green to red-brown and finnaly to blue. The yields of a hydrodimer from methyl acrylate were 15, 18, and 30% based on cobalt for chloro-, bromo-, and iodo-complexes, respectively. Hydrogenation of acrylic esters and addition of alcohol to acrylic esters4) were not observed until the solution became blue. After the decomposition of the catalytic species, addition of alcohol to acrylic esters began to occur. Halogenotris(triphenylphosphine)cobalt complexes were prepared from cobalt halides, triphenylphosphine, and zinc in alcohol.5) The mixtures were used as catalysts for the hydrodimerization of acrylic esters. As shown in Table, the yield exceeded 100% based on cobalt in the presence of zinc. The catalytic activity increased in the order Cl < Br < I. The addition of halides of alkali metals, notably potassium iodide, increased the yield.

When CH_3OD and methyl acrylate were used, the hydrogen distribution in dimethyl adipate was $(CH_{2.02}CH_{1.19}D_{0.81}CO_2CH_{3.00})_2$ from its pmr spectrum. The source of the hydrogen added is mainly hydroxyl group of alcohol. Transesterification took place at the same time. There was no formation of α-methyleneglutarate and dihydromuconate which are the main products catalyzed by tertiary phosphines or other transition metal complexes.6)

Acrylonitrile and methyl methacrylate were not hydrodimerized by cobalt(I) complexes. When methyl vinyl ketone was reacted with cobalt(I) complexes at room temperature, a red-brown solution was instantly obtained, but complexes were decomposed after a few minutes. Below 0°C methyl vinyl ketone was hydrodimerized to 2,7-octanedione by cobalt(I) complexes in a low yield.

Table Hydrodimerization of Acrylic Esters by Cobalt(I)-triphenylphosphine Complexes a)

R in $CH_2=CHCO_2R$	X in CoX_2	mmol	PPh_3 mmol	Additive	mmol	Yield of adipic ester mmol
CH_3	Cl	1.0	3.0			1.84
CH_3	Cl	1.0	6.1			2.78
CH_3	Cl	1.1	3.0	MeOH b)		2.23 c)
CH_3	Cl	1.0	3.0	KCl	10.8	2.14
C_2H_5 d)	Cl	1.0	3.0			1.86
CH_3	Br e)	1.0	3.0			2.25
CH_3	I	1.0	3.0			3.52
CH_3	I	1.0	3.0	KI	5.1	6.07

a) A reaction mixture of CoX_2, PPh_3, 8 mmol of Zn powder, 16.6 mmol of alkyl acrylate in 2 ml of methanol and 8 ml of THF was stirred at room temperature for 1-5 days. b) Methanol was used as a solvent. c) A small amount of methyl α-methyleneglutarate and a considerable amount of methyl β-methoxypropionate were formed. d) Two ml of ethanol and 8 ml of THF were used. e) Cobalt bromide hexahydrate was used.

Isomerization of olefins was catalyzed by halogenotris(triphenylphosphine)nickel complexes,7) which did not hydrodimerize acrylic esters even in protic solvents. However, hydrodimerization of acrylic esters was catalyzed by halogenotris(triphenylphosphine)cobalt complexes, which showed no catalytic activity for isomerization of olefins. Both complexes are monovalent and tetrahedral, but they differ from one another in the electronic configuration, which reflects the reaction selectivity.

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