Addition of α-Olefins to Diolefins with Ziegler-type Catalysts

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RHODIUM CHLORIDE can catalyze the addition of ethylene and propene to such diolefins as butadiene, isoprene, and penta-1,3-diene, forming 1,4-diolefins;[1] the synthesis of 1,4-dienes by the reaction of 1,3-dienes with ethylene, in the presence of a catalyst consisting of iron compounds and organo aluminium compounds, has been reported by Hata[2]. It has been also found[3] that cobalt compounds combined with metal alkyls can catalyze the addition of butadiene to olefins such as $\mathrm{R^1CH = CHR^2}$ (where $\mathrm{R^1}$, $\mathrm{R^2}$ is H,$\mathrm{-CH{=}DCH_2}$, or $\mathrm{—COR^3}$) forming 1,3-diolefins $\mathrm{CH_2{=}CH{\cdot}CH{=}CH{\cdot}CHR{\cdot}CH_2R^2}$.

We report the addition of the α-olefins ethylene and propene to diolefins, such as isoprene, penta-1,3-diene, methyl penta-1,3-diene and hexa-1,4-diene, with a three-component catalyst consisting of cobaltous chloride, phosphorous trichloride, and triethylaluminium.

For example, 20·4 g. (0·3 mole) of isoprene, 0·5 mmole of $\mathrm{CoCl_2}$, 1 mmole of $\mathrm{PCl_3}$, 3 mmole of $\mathrm{AlEt_3}$ and 50 ml. of toluene were placed in an autoclave (100 ml.) under an inert atmosphere. Then, ethylene was introduced up to 40 kg./cm.^{2}. After 2 hr. at 40°, the products were isolated and were analysed by gas chromatography. 16·2 g. (0·17 mole) of 4-methylhexa-1,4-diene and 5·4 g. (0·056 mole) of 5-methylhexa-1,4-diene were obtained.

The reaction of 0·3 mole of isoprene with ethylene at 40° for 2 hr. afforded 0·7 mole of 4-methyl-hexa-1,4-diene and 0·056 mole of 5-methylhexa-1,4-diene, and the reaction of 0·3 mole of penta-1,3-diene with ethylene at 40° for 1 hr. gave 0·085 mole of 3-methyl hexa-1,*cis*-4-diene and 0·0095 mole of hepta-1, *cis*-4-diene. The reaction of 0·3 mole of 2-methylpenta-1,3-diene with ethylene at 30° for 2 hr. afforded 0·153 mole of 3,5-dimethylhexa-1,4-diene and 0·040 mole of 4-methylhepta-1,4-diene, and the reaction of 0·3 mole of hexa-1,4-diene with ethylene at 70° for 2 hr. gave 0·045 mole of 3-ethylhexa-1,4-diene and 0·039 mole of 3-methylhepta-1,4-diene. The addition of 0·5 mole of propene to 0·3 mole of buta-1,3-diene at 90° for 1 hr. gave 0·12 mole of 2-methylhexa-1, *trans*-4-diene and 0·008 mole of 2-methylhexa-1, *trans*-3-diene, and the addition of 0·5 mole of propene to 0·3 mole of isoprene at 70° for 1 hr. gave 0·18 mole of 2,4-dimethylhexa-1,4-diene and 0·036 mole of 2,5-dimethylhexa-1,4-diene.

The products (hexadienes) of the last reaction, were analysed and determined by gas chromatography i.r. and n.m.r. spectra. The i.r. spectra showed that one of the double bonds is in a terminal methylene group and the other is $\mathrm{-CR{=}CH-}$. The carbon skeletons were determined by hydrogenation to the alkanes (2,4-dimethylhexane and 2,5-dimethylhexane). In the addition of ethylene to hexa-1,4-diene, isomerisation to the conjugated hexa-1,3- and 2,4-dienes, was presumably followed by reaction of these with ethylene, to give two isomeric nonconjugated dienes, 3-ethylhexa-1,4-diene and 3-methylhepta-1,4-diene.

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