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HYDROALUMINATION OF ALKENES WITH ALKYLALUMINIUM HALIDES

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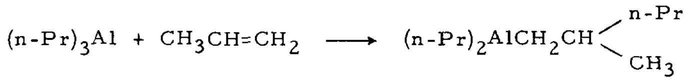
Although the reactions of olefins with aluminium-alkyls (Eq. 1) and alkylaluminium hydrides (Eq. 2) are well-known reactions (1), no references have been found concerning hydroalumination of ethylenic bonds with aluminium organic compounds which do not have hydrogen atoms bonded directly with the metal.



$$(n\text{-}Pr)_3Al + CH_3CH{=}CH_2 \longrightarrow (n\text{-}Pr)_2AlCH_2CH\begin{matrix} n\text{-}Pr \\ CH_3 \end{matrix} \qquad \ldots (1)$$

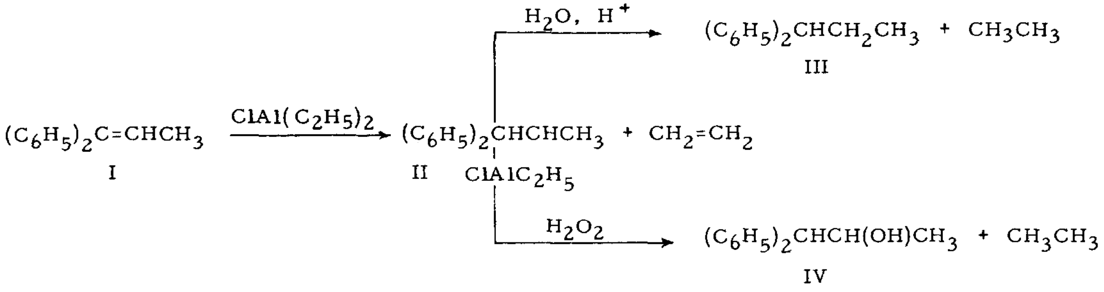
$$R_2AlH + CH_3CH{=}CH_2 \longrightarrow R_2AlCH_2CH_2CH_3 \qquad \ldots (2)$$

Since the alkylaluminiums can act as donors of hydride ions from their alkyl group (2), the possibilities of diethylaluminium chloride, ethylaluminium dichloride and triethylaluminium as hydroaluminating agents of alkenes have been studied.

Being one of the most typical examples of this new kind of reaction 1,1-diphenylpropene (I) adds diethylaluminium chloride in benzene solution at 80°C to form an intermediate (II) which is transformed by hydrolysis into 1,1-diphenylpropane (III) and produces 1,1-diphenylpropan-2-ol (IV, 90 per cent) by oxidation with alkaline hydrogen peroxide.

The formation of ethylene in the hydroalumination process has been confirmed by its IR spectrum and by gas-chromatography. The physical constants of III, b.p. 153°C/20 mm; and

IV, m.p. 62°C (from pentane; acetate, m.p. 77°C, from methanol) coincide with those described (3); the IR and NMR spectra confirm their identity as well.



$$(C_6H_5)_2C{=}CHCH_3 \xrightarrow{ClAl(C_2H_5)_2} (C_6H_5)_2\underset{\displaystyle ClAlC_2H_5}{C}HCHCH_3 + CH_2{=}CH_2$$

I II

$$\xrightarrow{H_2O,\ H^+} (C_6H_5)_2CHCH_2CH_3 + CH_3CH_3$$

III

$$\xrightarrow{H_2O_2} (C_6H_5)_2CHCH(OH)CH_3 + CH_3CH_3$$

IV

Some other examples of this reaction are given in Table I.

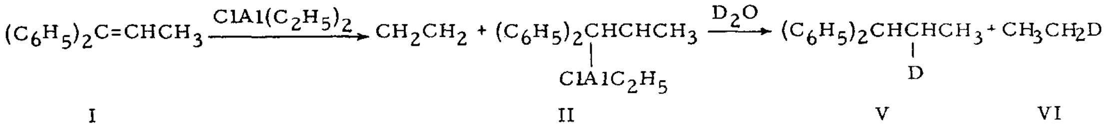
Table I

Conversion of alkenes into alcohols

Olefin	Alcohol	Temp. (°C)	Time (h)	Yield (%)
Styrene	2-Phenylethanol	80	5	70
Propenylbenzene	1-Phenylpropan-2-ol	80	6	75
α-Methylstyrene	2-Phenylpropan-1-ol	80	5	85
1,1-Diphenylethylene	2,2-Diphenylethanol	80	4	90

The reaction of I with ethylaluminium dichloride takes place in a similar fashion; however, triethylaluminium adds very slowly (after 30 hours at 80°C the conversion is only 3 or 4 per cent).

In order to establish the direction of the addition reaction and its mechanism, the hydrolysis of the organometallic intermediate with heavy water has also been studied.

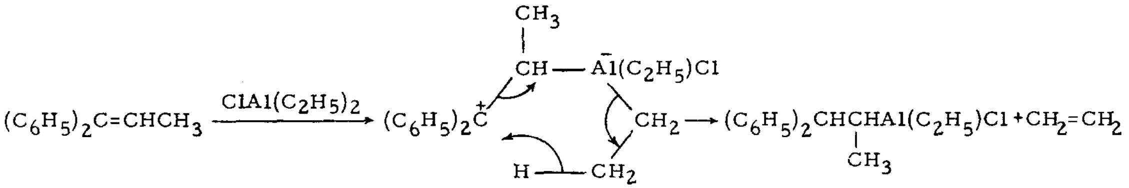


$$(C_6H_5)_2C{=}CHCH_3 \xrightarrow{ClAl(C_2H_5)_2} CH_2CH_2 + (C_6H_5)_2\underset{\displaystyle ClAlC_2H_5}{C}HCHCH_3 \xrightarrow{D_2O} (C_6H_5)_2CH\underset{\displaystyle D}{C}HCH_3 + CH_3CH_2D$$

I II V VI

The position of the deuterium atom on molecule V —which is the same as the position of the hydroxyl group in IV— has been determined by analysis of its NMR spectrum which presents a doublet at $\tau = 9,12$ ppm (CH_3), a quintuplet centered at $\tau = 8.00$ ppm (the gem-proton of the deuterium atom), a doublet at $\tau = 6.29$ ppm (CH) and a signal at $\tau = 2.87$ ppm (aromatic protons). The identification of VI has been carried out by means of its IR spectrum.

The reaction of I with the organometallic compounds can be interpreted as an electrophilic attack of the alkylaluminium at the double bond, with the formation of the more stable of the two possible carbonium ions, followed by the transference of a hydride ion from the carbon atom in position ß with respect to the metallic atom which is now a negative ion.



I

II

Hydroalumination processes of this kind —in which the presence of hydrogen atoms bonded directly with the aluminium is not necessary— have been observed in numerous reactions of halogenated olefins with trialkylaluminium— arene systems (4). These observations will be published shortly.

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