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The Regioselective Addition of Alcohols to Isoprene with Rhodium Trichloride Hydrates

Hiroshi Kawazura,* Toshihisa Takagaki, and Yoshio Ishii

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

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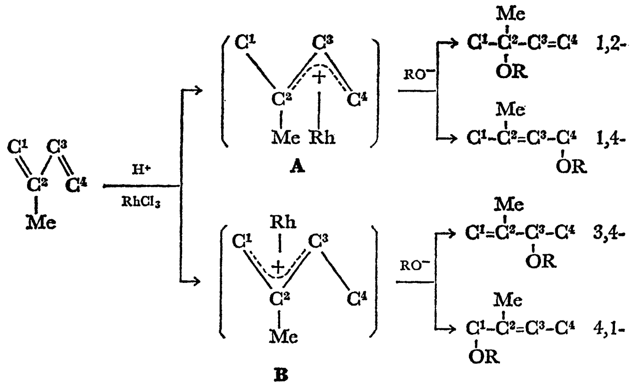
Synopsis. Rhodium trichloride hydrates gave predominantly the 1,2-addition product, 2-alkoxy-2-methylbut-3-ene, in the addition reaction of alcohols to isoprene. The regioselective path was established by assuming the formation of the π-(2-methylbut-3-en-2-yl)rhodium complex.

The almost exclusive formation of 2-alkoxybut-3-ene in the addition reaction of alcohols to 1,3-butadiene with rhodium trichloride hydrates[1)] prompted us to examine the same reaction with isoprene, with special attention, paid to its regioselectivity, which was not noticed in the pioneering work.[2)]

Table 1 summarizes the results of the addition reactions of various alcohols to isoprene carried out at 50 °C for 96 hr under nitrogen in the presence of a catalytic amount of $RhCl_3 \cdot 3H_2O$. The addition products were fractionated by preparative glc, and all the structures, as described in the table, were unambiguously determined by IR and PMR. The predominant formation of 2-alkoxy-2-methylbut-3-ene, a 1,2-addition product, accounting for more than 70% of the total products, proved the regioselectivity of the reaction.

The ionic nature of the reaction is evident, since the total yields of the addition products hold a parallel correlation with the intensities of the OH stretching vibrations of the alcohols, as in the case of butadiene.[1)]

The regioselective path of the reaction may be understood if one assumes the formation of π-allylic rhodium complexes originating from an alcoholic proton attack on isoprene, as is delineated in the following scheme. The overwhelming formation of the **A** complex can be understood in view of the higher electron density of the C^1 carbon in comparison with the C^4 carbon in isoprene. Consequently, the predominant formation of the 1,2-addition product may be well explained as an attack of alkoxy nucleophile on the electron-deficiently stabilized C^2 tertiary carbon in the **A** complex. The nil to minor formations of 3-alkoxy-2-methylbut-1-ene, the 3,4-addition product and the total absences of 1-alkoxy-2-methylbut-2-ene, the 4,1-addition product may be reflections of the electronically unfavored formation of the **B** complex.



Eventually the regioselectivity to the 1,2-addition may be ascribed to the predominant formation of the π-(2-methylbut-3-en-2-yl)rhodium complex, to whose tertiary carbenium carbon occurs the highly directive addition of the alkoxy nucleophile.

Experimental

Reaction of n*-BuOH to Isoprene.* A mixture of n-BuOH (25.0 ml) containing $RhCl_3 \cdot 3H_2O$ (62.0 mg, 0.24 mmol) and isoprene (15.0 ml, 150 mmol) was heated at 50 °C for 96 hr with stirring under nitrogen. The reaction mixture was then filtered, and the filtrate was subjected to preparative glpc (PEG 6000, 3 m, 60 °C, H_2 50 ml/min) to give three

Table 1. Addition reaction of alcohols to isoprene

Alcohol (25 ml)	$RhCl_3 \cdot 3H_2O$ mmol	Addition products 1,2- 2-Alkoxy-2-methyl-but-3-ene mmol	%[a)]	1,4- 4-Alkoxy-2-methyl-but-2-ene mmol	%[a)]	3,4- 3-Alkoxy-2-methyl-but-1-ene mmol	%[a)]	Total mmol	%[a)]	Intensity of ν_{OH}[b)] (l mol^{-1} cm^{-1}) 10^4
Me-	0.22	22.6	15.1	4.6	3.1	0	0	27.2	18.1	0.53
Et-	0.20	24.9	16.6	7.7	5.1	trace	—	32.6	21.7	0.62
Pr^n-	0.32	23.0	15.3	2.1	1.4	4.5	3.0	29.6	19.7	—
Bu^n-	0.24	33.0	22.0	5.7	3.8	8.1	5.4	46.8	31.2	0.72
Bu^i-	0.21	11.4	7.6	0.9	0.6	2.0	1.3	14.3	9.5	—
Bu^s-	0.21	2.3	1.5	0.9	0.6	0	0	3.2	2.1	0.58
Bu^t-	0.22	0		0		0		0		0.42

a) On the basis of fed isoprene 150 mmol. b) Cited from Ref. 3.

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* Present address: Faculty of Pharmaceutical Sciences, Josai University, Keyaki-dai, Sakado, Saitama 350-02.

addition products. Isolated were 2-*n*-butoxy-2-methylbut-3-ene (1,2-addition product) (4.77 g (33.0 mmol); bp 12—13 °C/2 mmHg; IR (liquid, cm^{-1}) 1650 ($\nu_{C=C}$), 1093 (ν_{C-O}), 1000 and 920 (δ_{CH} in $-CH=CH_2$); PMR (CCl_4 with TMS, τ) 4.21 (1H, dd, $J=18$ and $J=10$ Hz, proton at C^3), 5.01 (1H, dd, $J=18$ and $J=2$ Hz, *trans* proton at C^4), 5.04 (1H, dd, $J=10$ and $J=2$ Hz, *cis* proton at C^4), 6.75 (2H, t, $J=6.0$ Hz, $-CH_2O-$), 8.58 (4H, m, $-(CH_2)_2-$), 8.75 (6H, s, protons of two methyls at C^2), and 9.08 (3H, t, $J=6.2$ Hz, methyl protons in butoxy)), 3-*n*-butoxy-2-methylbut-1-ene (3,4-addition product) (1.07 g (8.1 mmol); bp 12—13 °C/2 mmHg; IR (liquid, cm^{-1}) 1650 ($\nu_{C=C}$), 1090 ($\nu_{C=C}$), and 920 (δ_{CH} in $>C=CH_2$); PMR (CCl_4 with TMS, τ) 5.16 (2H, m, protons at C^1), 6.21 (1H, q, $J=6.0$ Hz, proton at C^3), 6.75 (2H, t, $J=6.0$ Hz, $-CH_2O-$), 8.35 (3H, s, methyl protons at C^2), 8.58 (4H, m, $-(CH_2)_2-$), 8.77 (3H, d, $J=6.0$ Hz, protons at C^4-methyl), and 9.08 (3H, t, $J=6.2$ Hz, methyl protons in butoxy)), and 4-*n*-butoxy-2-methylbut-2-ene (1,4-addition product) (0.81 g (5.7 mmol); bp 23—25°C/2 mmHg; IR (liquid, cm^{-1}) 1650 ($\nu_{C=C}$), 1095 (ν_{C-O}), and 1000 (δ_{CH} in $>C=CH-$); PMR (CCl_4 with TMS, τ) 4.78 (1H, t, $J=6.0$ Hz, proton at C^3), 6.21 (2H, d, $J=6.2$ Hz, protons at C^4), 6.73 (2H, t, $J=6.0$ Hz, $-CH_2O-$), 8.30 (3H, s, C^1-methyl protons), 8.38 (3H, s, methyl protons at C^2), 8.56 (4H, m, $-(CH_2)_2-$), and 9.10 (3H, t, $J=6.3$ Hz, methyl protons in butoxy).

Reaction of the Other Alcohols to Isoprene. According to the procedure described above, the addition reaction and the products analysis were carried out for the other alcohols to give the glpc fractions, which were determined, as is shown in the table, by their IR and PMR, in which were found a characteristic pattern attributable to the 1,2-, 3,4-, or 1,4-addition product.

References

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