The Preparation of 3-Chloro-1-phenyl-2-butene

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(Received December 15, 1966)

It has been demonstrated that diethylaluminum chloride alone or mixed catalysts containing diethylaluminum chloride and nickel or cobalt compounds promoted the reaction of chloroprene with benzene to yield 3-chloro-1-phenyl-2-butene as the main product, while chloroprene is readily polymerized to a solid polymer in the presence of aluminum trichloride or ethylaluminum dichloride.

A four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a dropping funnel was flushed with dry nitrogen and then charged with 150 m*l* of benzene and 0.5 m*l* of pure diethylaluminum chloride. From the dropping funnel, 20 m*l* of chloroprene was added, drop by drop, at 50—60°C. The solution became dark red and then gradually turned to a bluish purple. After one hour, the reaction was stopped by adding methanol. A light yellow liquid was then obtained by distillation under reduced pressure, bp 90—93°C/10 mmHg. The results of elemental analysis were as follows; Found; C, 70.6; H, 6.8%. Calcd for $C_{10}H_{11}Cl$: C, 72.7; H, 6.6%. The gas chromatogram of the distillate showed that it contained three components and that the area ratio was 1.16 : 5.84 : 1. The fractions of the second (p-2) and the third peak (p-3) were each purified by preparative gas chromatography, and the mass spectrum of each fraction was measured in order to determine the molecular weight. Since both fractions indicated the same molecular peak at $m/e=166$ and since their relative intensities at $m/e=166$ and 168 corresponded exactly to the abundance ratio of ^{35}Cl to ^{37}Cl, the products must be $C_{10}H_{11}Cl$. In the infrared spectra of p-2 and p-3, the characteristic adsorption bands (2000—1700 cm^{-1}) of mono-substituted benzene were observed, and the NMR spectrum of the distillate showed the following chemical shifts: 2.9 $\tau(C_6H_5-)$, 4.56 $\tau(-CH=C)$, 6.65 $\tau(-CH_2-)$, and 8.12 $\tau(-CH_3)$. The value of the coupling constants reported by Newman[1] suggested that the product consisted mainly of 3-chloro-1-phenyl-*cis*-2-butene (p-2). A doublet at 8.42 τ indicated the presence of the partial structure, $-C=CH-CH_3$, and showed a formation of a small quantity of 2-chloro-1-phenyl-2-butene (p-3). It is considered that p-1 is probably 3-chloro-1-phenyl-*trans*-2-butene.

An improved result was obtained by using the mixed catalysts. Halides or nitrate of nickel and cobalt were effective as transition metal components, nickel and cobalt compounds coordinated with tertiary phosphines or ditertiary phosphines were the most active (Table 1).

TABLE 1. REACTION OF CHLOROPRENE WITH BENZENE*1

Catalyst*2	Product, g	Residue, g
$(C_2H_5)_2AlCl$	2.1	2.7
$CoCl_2(DPE)_2-(C_2H_5)_2AlCl$	8.8	3.2
$Ni(NO_3)_2(DPE)_2-(C_2H_5)_2AlCl$	6.9	3.0

*1 Benzene 200 m*l*, metal complex 0.1 g, diethylaluminum chloride 0.47 g (0.5 m*l*), and chloroprene 9.6 g (10 m*l*).

*2 DPE = Ethylene bis(diphenylphosphine)

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[1] M. S. Newman, G. Fraenkel and W. N. Watson, *J. Org. Chem.*, **28**, 1851 (1963).