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Abstract

Full Text

CHEMISTRY

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FLUORINE-CONTAINING DIVINYLBENZENES

The ability of divinylbenzene to undergo polymerization or copolymerization reactions with styrene, and the preparation on this basis of polymers with varying heat resistance, hardness, and swelling in organic solvents, creates prospects for their use in technology. Recently divinylbenzene has been widely used for the production of ion-exchange resins and for other purposes ([1]). However, before our first brief publication ([2]) and the present work, fluorine-containing divinylbenzenes had not been described, and their polymers, consequently, could not have been characterized.

Of the possible combinations of groups synthesized by us: $-\mathrm{CH}=\mathrm{CH}_2$, $-\mathrm{CF}=\mathrm{CFCl}$, $-\mathrm{C(CF_3)}=\mathrm{CH}_2$, etc., we give several examples. For the synthesis of n-α,β-difluoro-β-chlorovinylstyrene we used n-lithio-α,β-difluoro-β-chlorostyrene, obtained by us ([2]) according to the scheme

$$\mathrm{Br{-}C_6H_4{-}CF{=}CFCl} \xrightarrow{\mathrm{C_4H_9Li}} \mathrm{Li{-}C_6H_4{-}CF{=}CFCl} \qquad (1)$$

It is important to carry out the exchange reaction at a temperature of about -70° and to complete it within 20-30 min. Under these conditions the yield of the organolithium compound is rather high. However, if the reaction mixture is left at -70° for several hours or the temperature is raised, the Gilman test becomes negative. Evidently, under these conditions the aryllithium and butyllithium formed, which have not entered into the exchange reaction, have time to react completely with the fluorine-containing vinyl group (cf. ([3])).

The organolithium fluorinated styrenes obtained by us exhibit all the variety of reactions that have been described for ordinary aromatic organolithium compounds, provided that they can likewise be carried out at low temperature (-70°).

In the present work it is shown that an organolithium compound of the new type enters, for example, into reaction with acetaldehyde. n-α,β-Difluoro-β-chlorovinylphenylmethylcarbinol is formed in 42% yield; dehydration of the latter gives n-α,β-difluoro-β-chlorovinylstyrene

Fig. 1

Figure 1: Fig. 1

$$\mathrm{Li{-}C_6H_4{-}CF{=}CFCl} \xrightarrow{\mathrm{CH_3CHO}} \mathrm{CH(OH)CH_3{-}C_6H_4{-}CF{=}CFCl} \xrightarrow{-\mathrm{H_2O}} \mathrm{CH{=}CH_2{-}C_6H_4{-}CF{=}CFCl} \tag{2}$$

Another type of fluorinated divinylbenzene was synthesized according to the scheme

$$\mathrm{Li{-}C_6H_4{-}CF{=}CFCl} \xrightarrow{\mathrm{CF_2{=}CFCl}} \mathrm{CF{=}CFCl{-}C_6H_4{-}CF{=}CFCl} \tag{3}$$

We carried out a preliminary polymerization of $CH_2 = CHC_6H_4CF = CFCl$. In the presence of benzoyl peroxide the substance polyme-

polymerized at 100° at approximately the same rate as ordinary styrene, with formation of a solid transparent polymer. However, unlike polystyrene, it is insoluble on heating in aromatic hydrocarbons and only slowly swells in them. The polymer is stable at temperatures of about 210°, as is evident from Fig. 1, showing the thermal degradation of the polymer.

The determination of thermal stability was carried out by heating the polymer in air in a platinum crucible, with photographic recording of the weight loss on BP-NV-20 thermogravimetric balances of continuous weighing. The temperature was raised over 3 hr to 400°.

Experimental Part

Preparation of *n*-α,β-difluoro-β-chlorovinylphenylmethylcarbinol. To a solution of 3.84 g (0.04 mole) of butyllithium in 40 ml of anhydrous ether, cooled with liquid nitrogen to −80°, with vigorous stirring, over 5 min there is added a solution of 15.2 g (0.06 mole) of *n*-bromo-α,β-difluoro-β-chlorostyrene in 20 ml of anhydrous ether. The reaction mixture is stirred at −70° for half an hour, cooled to −90°, and a twofold excess of acetaldehyde is added so that the temperature of the mixture does not exceed −70-80°. Stirring is continued for another 30 min, the mixture is allowed to warm to zero, and it is poured into ice water; the ether layer is separated, the aqueous layer is extracted with ether (400 ml), the extracts are dried with sodium sulfate, the ether is distilled off on a water bath, and the thick oily residue is distilled in vacuum. The distillate is fractionated. *n*-α,β-Difluoro-β-chlorovinylphenylmethylcarbinol is obtained in 42% yield, b.p. 107-116° (4 mm), n_D^{20} 1.5455, d_4^{20} 1.2800.

Fig. 1

Found %: C 55.06, 55.02; H 4.22, 4.23; Cl 16.17, 16.59; F 17.03
$C_{10}H_9OF_2Cl$. Calculated %: C 54.94; H 4.15; Cl 16.24; F 17.38

Molecular weight: found 217, calculated 218.67.

Preparation of *n*-α,β-difluoro-β-chlorovinylstyrene. Into a Claisen flask, under nitrogen, are placed 11 g (0.05 mole) of *n*-α,β-difluoro-β-chlorovinylphenylmethylcarbinol, 0.15 g (0.001 mole) of freshly fused acid potassium sulfate, and, as inhibitor, a small crystal of picric acid. A vacuum of 75 mm is created. The reaction mixture is heated on a metal bath at 140°, gradually raising the temperature to 200°. The pressure is slowly lowered to 7 mm. At the end, the starting carbinol distills over. The distillate is dissolved in ether, dried with sodium sulfate, and fractionated. The substance is obtained in up to 50% yield (of theoretical), b.p. 66–69° (2 mm), n_D^{20} 1.5650, d_4^{20} 1.2563.

Found %: C 59.98, 59.99; H 4.09, 4.02; F 18.18, 18.27; Cl 17.52, 17.43
$C_{10}H_7F_2Cl$. Calculated %: C 59.88; H 3.49; F 18.96; Cl 17.68

Molecular weight: found 198, calculated 200.5.

Polymerization. *n*-α,β-Difluoro-β-chlorovinylstyrene is sealed in an ampoule with benzoyl peroxide (0.004 mole per 1 mole of monomer) and heated on a water bath. After 2.5 hr a solid, transparent product is formed, insoluble in organic solvents and slightly swelling in benzene and xylene.

Preparation of bis-α,β-difluoro-β-chlorovinylbenzene. To a solution of 10.9 g (0.17 mole) of butyllithium in 140 ml of ether at −75° (cool—

···cooled with liquid nitrogen) over the course of ten minutes, 43 g (0.17 mole) of *n*-bromo-α,β-difluoro-β-chlorostyrene in 50 ml of ether is added. The reaction mixture is stirred for another half hour, then cooled to −85° and, over the course of 2 hours, 40 g (0.34 mole) of trifluorochloroethylene is added. Fifteen minutes after introduction of the gas, the reaction is complete (the Gilman test is negative).

The reaction mixture is left until morning; during this time the temperature of the mixture rises to zero. After the usual work-up, the ether is distilled off and the residue is distilled in vacuo. A substance is obtained with b.p. 100–105° (5 mm),

n_D^{20} 1.5430, d_4^{20} 1.4240.

Found, %: C 44.41, 44.30; H 1.57, 1.78; Cl 26.57, 26.45; F 27.47, 28.25
$C_{10}H_4F_4Cl_2$. Calculated, %: C 44.28; H 1.48; Cl 26.20; F 28.04

Mol. wt.: found 260, calculated 271.1.

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Note: Figure translations are in progress. See original paper for figures.