[CONTRIBUTION FROM THE PITTSFIELD LABORATORY, APPARATUS DEPARTMENT, GENERAL ELECTRIC COMPANY]

The Preparation and Properties of 2-Vinylbenzofuran

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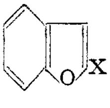
The synthesis and investigation of the properties of 2-vinylbenzofuran was undertaken as part of a program in which various polymerizable aromatic compounds were being studied. The favorable electrical properties possessed by non-polar vinyl aromatic polymers stimulated the present work. The 2-vinylbenzofuran was synthesized by the hydrogenation of the ketone to the carbinol and subsequent dehydration to the vinyl compound.



I $X = —COCH_3$
II $X = —CHOHCH_3$
III $X = —CH = CH_2$

Since the 2-position on the benzofuran nucleus does not acetylate by a Friedel–Crafts reaction, I was prepared by a condensation reaction between salicylaldehyde and chloroacetone in the presence of alcoholic potassium hydroxide using a modification of the method reported by Stormer.[1] Shriner and Anderson[2] prepared II by the hydrogenation of I with platinum oxide. The method used in this work was to hydrogenate I in the presence of a copper–chromium oxide catalyst.[3]

Polymers of III are thermoplastic and for this reason it is believed that the furan double bond does not enter into the polymerization. Otherwise a thermosetting polymer would result due to crosslinking. It is unlikely that a linear butadiene type polymerization occurs because of the nonlinear relationship due to the angle between the vinyl group and the benzofuran nucleus. Rapid polymerization of III occurs at elevated temperatures. At room temperature and exposed to the atmosphere a hard, glass-like polymer is formed after 2 days. Emulsion polymerization techniques are successfully applied resulting in quantitative polymer yields.

Experimental

2-Acetylbenzofuran (I).—One-hundred grams of salicylaldehyde[4] dissolved in 400 ml. of ethyl alcohol was heated with 50 g. of alcoholic KOH until solution of the salt was achieved. The calculated amount of chloroacetone[4] (75.8 g.) was slowly added from a dropping funnel while stirring contents with a mechanical stirrer in a one-liter flask. After the vigorous reaction subsided, about 15 minutes, the mixture was diluted with an equal amount of water and the excess alcohol distilled off. The partly oily, partly crystalline, precipitated acetylbenzofuran was shaken in ether, dried over anhydrous Na_2SO_4 and the ether solution distilled. At 11 mm. and 136° the solidified product distilled over. A yield of 87 g., 67% of I, m.p. 76°, was obtained on recrystallization from ethyl alcohol.

(2) (**α-Hydroxyethyl)-benzofuran** (II).—Eighty-two and one-half grams of I dissolved in 1500 ml. of methanol was agitated in the presence of 2 g. of copper–chromium oxide catalyst[3] for 6 hours at 150° under a pressure of 1800 p.s.i. of molecular hydrogen using a 3-liter capacity hydrogenation bomb. A yield of 68 g., 81% of II, m.p. 41° was obtained on recrystallization from ligroin.

2-Vinylbenzofuran (III).—Sixty-eight and one-half grams of (II) dissolved in 500 ml. of benzene was passed through a vertical stainless steel column one inch in diameter and eighteen inches long. The reaction column was packed with alumina pellets[5] and maintained at a temperature of 520 ± 10°. A pressure of 10–20 mm. was maintained on the system during the reaction. After evaporating the benzene, the product was distilled on a steam-bath and the oily residue redissolved in ether and dried over anhydrous Na_2SO_4. The product was distilled at a pressure of 1–2 mm. obtaining 35 g., 58% yield of a colorless liquid (III) possessing a characteristic sweet odor, b.p. 74° (1.8 mm.), $n^{25.5}_D$ 1.6125, D^{25}_4 1.0598.

Anal.[6] Calcd. for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.18; H, 5.59.

Polymers of III.—(a) Ten grams of III dissolved in benzene was treated with 1 ml. of boron trifluoride etherate[4] obtaining a quantitative yield of polymer when precipitated from the benzene solution with methanol. The softening point range was 285–290°.

Anal. Polymer (III).[6] Calcd. for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 82.79; H, 5.95.

(b) Ten grams of III was added to a rubber gasketed glass pressure bottle. To this 100 ml. of an emulsion solution consisting of 600 g. of water, 14 g. of stearic acid and 6 g. of KOH were added. After adding 0.1 g. of $K_2S_2O_8$ catalyst, the pressure bottle was capped, immersed in an oil-bath kept at 45° and mechanically agitated back and forth in a horizontal plane for fifteen hours. The white polymer was coagulated by pouring into 500 ml. of dilute HCl. After dissolving the coagulated polymer in benzene it was purified by precipitating it in methanol.

Polymers of III were also prepared by heat alone and with the following catalysts: benzoyl peroxide, tertiary butylperbenzoate and 1-hydroxycyclohexylhydroperoxide.

Copolymers of III.—Using emulsion polymerization techniques, copolymers of III with the following monomers have been prepared: isoprene, butadiene, styrene, vinyldibenzofuran and N-vinylcarbazole.

Summary

The synthesis and properties are given for 2-vinylbenzofuran. Polymers and copolymers of the monomer have been prepared.

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[1] Stormer, *Ber.*, **57**, 75 (1924).

[2] Shriner and Anderson, THIS JOURNAL, **61**, 2705 (1939).

[3] Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 12.

[4] Eastman Kodak Company, Rochester, N. Y.

[5] Harshaw Chemical Company, Cleveland, Ohio.

[6] Analyses were made by Dr. Carl Tiedcke.