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

The Preparation and Properties of 1-Vinylpyrene

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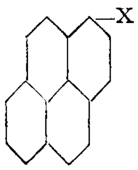
The synthesis and investigation of the properties of 1-vinylpyrene (I) was undertaken as part of a program in which various polymerizable aromatic compounds were being studied. Interest in the physical and particularly the electrical properties of polymers having large aromatic nuclei stimulated the present work on the vinylpyrene.

Two different methods for the preparation of I were successfully carried out. In the first method, 1-acetylpyrene (II) was hydrogenated to the 1-(α-hydroxyethyl)-pyrene (III) with subsequent dehydration to I.



I X = —CH=CH$_2$
II X = —COCH$_3$
III X = —CHOHCH$_3$
IV X = —CHO
V X = —CH=CHCOOH

Bachmann and Carmack[1] prepared II as yellow crystals, m. p. 80–90°, and III as pale yellow crystals, m. p. 112–112.5°, from the hydrogenation of II with aluminum isopropoxide. The method used in the present work was to hydrogenate II in the presence of a copper–chromium oxide catalyst.[2] Some ethylpyrene is formed, even under the mildest conditions, when II is treated with more than equimolecular amounts of hydrogen. An excellent yield of 1-ethylpyrene was prepared by using a large amount of hydrogen. This is in agreement with results reported by Homer Adkins for aryl- and poly-aryl carbinols bearing an aryl group in the 2 position with respect to the hydroxy group.[3]

The second procedure for the preparation of I involved the treatment of 1-pyrenylaldehyde (IV) with malonic acid to give the 1-pyrenylacrylic acid (V) which was decarboxylated to I.

IV was prepared from phosphorus oxychloride, formylmethylaniline and pyrene as described by Vollman, *et al.*[4] Bergmann and Bograchov[4] prepared V from IV using piperidine as the condensation catalyst. The decarboxylation of V to I was attempted by the method of Walling and Wolfstirn[5] by which they decarboxylated cinnamic acids. The method, however, was not satisfactory in this case as the product obtained was almost entirely polymerized. A vapor phase modification of this method gave good results and has the added advantage that continuous rather than batch reactions may be carried out.

Experimental

1-(α-Hydroxyethyl)-pyrene (III).—Twenty-four grams of II, 0.119 mole, dissolved in 120 cc. of absolute methyl alcohol was agitated with 1.4 g. of copper–chromium oxide catalyst[2] and 0.12 mole of hydrogen for seven hours at 80° in a 270-cc. bomb. The initial pressure of 260 pounds per square inch fell to zero during this time; 17 g., 70% yield, of III, m. p. 113°, was obtained on recrystallization from benzene.

1-Ethylpyrene.—Twelve grams of II, 0.059 mole, dissolved in 120 cc. of absolute methyl alcohol was placed in a 270-cc. bomb with 0.7 g. of copper–chromium oxide catalyst. 0.55 mole of hydrogen was introduced into the bomb which was then agitated for one-half hour at 83–88°; 10 g., 83% yield, of the ethyl compound was obtained which had a melting point of 95° as previously reported.[6]

1-Vinylpyrene (I) from III.—Sixty-two grams of III dissolved in 200 cc. of dioxane was added dropwise into the top of a vertical stainless steel column $^1/_2$ in. in diameter and 18 in. long. The column was packed with alumina pellets[7] and was maintained at a temperature of 340–360° and a pressure of 6 mm. during the reaction. Much charring of the product was observed under these conditions; 10 g., 18% yield, of light yellow 1-vinylpyrene, m. p. 87–89°, along with a considerable quantity of polymer was obtained.

Anal.[8] Calcd. for $C_{18}H_{12}$: C, 94.69; H, 5.30. Found: C, 94.35; H, 5.69.

1-Vinylpyrene (I) from V.—Nine grams of V in 150 cc. of benzene and 25 cc. of quinoline were allowed to pass down through a stainless steel column packed with copper borate-alumina pellets.[5] The temperature of the tube was kept at 520–580° and a pressure of 10–20 mm. was maintained on the system during the reaction. The product was washed with cold 2.4 *N* hydrochloric acid and then several times with water. The benzene was removed and the residue taken up with alcohol. This alcohol solution was boiled with activated charcoal and filtered; 5 g., 66% yield, of I, m. p. 87–89°, crystallized out of the light yellow solution.

Polymers of 1-Vinylpyrene.—Six grams of I dissolved in benzene was treated with boron trifluoride etherate to give a quantitative yield of a white powder, softening point about 220°, when precipitated out with methyl alcohol. This powder was molded into a disk at 160° using 40,000 p. s. i. pressure. This polymer had a dielectric constant of 3.2 and a power factor of 0.07% at one megacycle.

Polyvinylpyrene was also prepared by heat alone and with catalysts such as benzoyl peroxide and *t*-butyl perbenzoate.

Copolymers of 1-Vinylpyrene.—Copolymers have been obtained by polymerizing one part of I with one part of each of the following monomers: vinyl acetate, styrene, acenaphthylene, N-vinylphthalimide, N-vinylcarbazole, acrylonitrile and maleic anhydride. The softening points of these copolymers ranged from 155° for styrene and 180° for vinyl acetate to above 220° for the acenaphthylene and maleic anhydride products.

Summary

The properties of 1-vinylpyrene and its preparation by two methods have been described. Polymers and copolymers of 1-vinylpyrene have been made.

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[1] Bachmann and Carmack, THIS JOURNAL, 63, 2494 (1941).

[2] Adkins, "Reactions of Hydrogen." Wisconsin Press, 1937, p. 12.

[3] Adkins, *ibid.*, p. 69.

[4] Bergmann and Bograchov, THIS JOURNAL, 62, 3016 (1940).

[5] Walling and Wolfstirn, *ibid.*, 69, 852 (1947).

[6] Vollmann, Becker, Corell, Streeck and Langbein, *Ann.*, 531 1–159 (1937); *C. A.*, 32, 1492 (1938).

[7] Harshaw Chemical Company, Cleveland, Ohio.

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