to give β-2-fluorenoyl-α-methylacrylic acid as yellowish crystals, m.p. 181–182°, identical to an authentic sample.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.69; H, 5.03. Found: C, 77.25; H, 4.91.

The mother liquor was evaporated and the residue crystallized from light petroleum (b.p. 80–100°) to give β-2-fluorenoylcrotonic acid (1 g.), m.p. 139–141° (m.p. and mixed m.p.). Found: C, 77.32; H, 4.95. When this reaction was repeated using *s*-tetrachloroethane as solvent, the mixture of isomeric acids was obtained in higher yield. However, the two acids were difficult to separate. Authentic samples of both keto-acids were prepared from the corresponding α- and β-methylpropionic acids as previously stated (cf. ref. 4).

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Preparation and Polymerization of *p*-Vinylphenol

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Received February 10, 1959

Recently, syntheses of *p*-vinylphenol have been reported[1,2] by the decarboxylation of *p*-benzoxycinnamic acid followed by hydrolysis of the resulting ester, and by hydrogenation of *p*-acetoxyacetophenone followed by dehydration-hydrolysis. In view of this, it is of interest to describe the successful direct synthesis of *p*-vinylphenol by the decarboxylation of *p*-hydroxycinnamic acid. Although this route to the monomer has been reported to yield only traces of the desired product[3,4] in contrast to the smooth conversion of *o*-coumaric acid to the *o*-vinylphenol,[5] it was found that by use of the decarboxylation procedure of Wiley and Hobson,[6] wherein the cinnamic acid in quinoline is added dropwise to an evacuated, heated vessel containing catalyst and the product immediately distilled out, yields as high as 40% were obtained. The usual decarboxylation procedures even when carried out *in vacuo* gave resinous products.[7–9]

The separation of the monomer from the distillate and its purification are extremely difficult because of the ease with which it polymerizes, especially in the presence of acidic reagents. Best yields were obtained when the distillate was carefully acidified in the cold in the presence of extractant to remove monomer immediately. Extraction with aqueous caustic followed by neutralization with acid or carbon dioxide gave lower yields. The physical properties and color tests of the monomer agreed with those described.[3] Analysis of the monomer with standard bromine–carbon tetrachloride or bromate-bromide solutions indicated that four atoms of bromine were added per mole of monomer.

Attempts to prepare vinylphenols by the reaction of vinyl chloride with phenol in the presence of aluminum chloride as described by Seymour were unsuccessful.[10]

p-Vinylphenol readily polymerizes on standing, even at 0°, or in the presence of free-radical or cationic initiators. The latter may be predicted on the basis of the presence of the electron-releasing phenolic group. Benzene solution viscosities indicated low molecular weight. Addition of the monomer to a mixture of sulfuric and acetic acids gave a swellable but insoluble cross-linked polymer, possibly from alkylation reactions.

Since phenols are generally inhibitors for the radical addition polymerization of vinyl monomers, consideration was given to other modes of polymerization, such as the addition of the double bond of one molecule of vinylphenol to the benzene ring of another molecule. However, the infrared spectra of the polymer obtained with catalytic amounts of either azobisisobutyronitrile or sulfuric acid were essentially identical and indicated vinyl-type addition polymerization.[11] The monomer and polymer spectra are shown in Figs. 1 and 2 for comparison.

Radical initiated polymeric *p*-vinylphenol which sintered at 207–215° and melted at 229° was obtained as a white powder on purification by reprecipitation. Ionic initiation generally gave lower melting polymers in the 175–220° range. A copolymer of styrene and *p*-vinylphenol was prepared from a mixture containing 10 mole % vinylphenol, and resulted in a polymer containing approximately 19 mole % vinylphenol as deduced from absorption spectra and carbon-hydrogen analysis. Its softening range was 164–198°.

EXPERIMENTAL

p-Hydroxycinnamic acid. The method of Vorsatz[12] was used except that aniline was used as the catalyst as sug-

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[10] G. W. Seymour, U.S. Patent **2,006,517**, July 2, 1935.

[11] I am indebted to R. A. Nyquist of the Dow Spectroscopy Laboratory for the infrared spectra and their interpretation.

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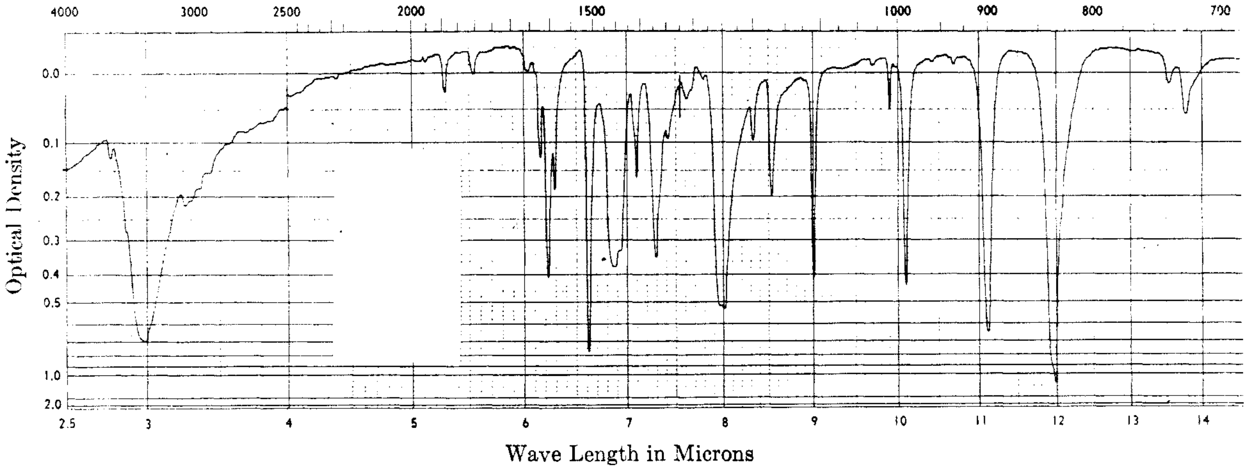

Fig. 1. Infrared spectra of *p*-vinylphenol monomer

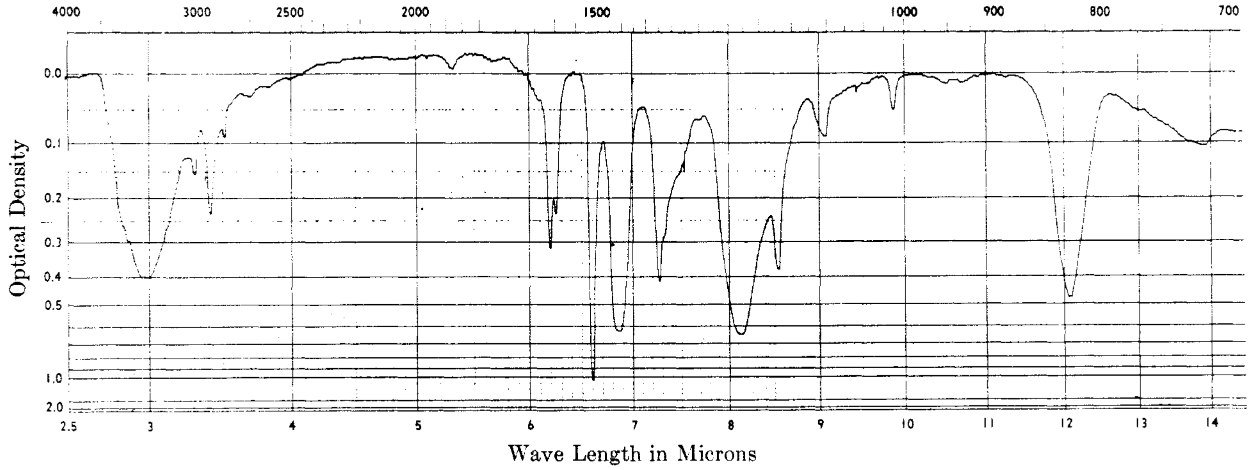

Fig. 2. Infrared spectrum of *p*-vinylphenol polymer

gested by Overberger.[9] From 104 g. (1.0 mole) malonic acid, 122 g. (1.0 mole) *p*-hydroxybenzaldehyde, and 5 ml. aniline in 150 ml. distilled pyridine, 146 g. (89%) of *p*-hydroxycinnamic acid was obtained, m.p. 206–208°. Three crystallizations from a 1:3 mixture of methanol and water gave a crystalline product in 41% yield, m.p. 213.0–214.5° (lit.[9] m.p. 210.5–211°). Attempts to speed the reaction by heating gave lower yields and lower melting product.

p-Vinylphenol. *p*-Hydroxycinnamic acid, 82 g. (0.5 mole), was dissolved in 300 g. distilled quinoline. This solution was added dropwise to 5 g. copper powder in a 125-ml. Claisen flask heated to about 225° and *in vacuo* at such a rate that very little liquid remained in the flask. A light yellow distillate was obtained at 110–130° (4–8 mm.). Hydroquinone was present in the quinoline solution and in the distillate receiver. The distillate was taken up in 150 ml. peroxide-free ether, mixed with 200 g. crushed ice, and 1200 ml. cold 3*N* sulfuric acid added slowly with stirring. The ether layer was removed, and the aqueous portion extracted with small portions of ether. The combined ether extracts were washed with ice cold water, dried over Drierite, and the ether evaporated *in vacuo*. A light brown solid weighing 44 g. was obtained. This product was recrystallized from 500 ml. petroleum ether (b.p. 60–70°) at −15° giving about 5 g. insoluble polymer, and 25 g. (41%) of white, crystalline plates, m.p. 71–72.5° (lit.[3] m.p. 73.5°). Recrystallization raised the melting point to 72–73.5°. Ferric chloride solution and concentrated hydrochloric acid gave a blue coloration. Titration with standard bromate-bromide[13] or bromine-carbon tetrachloride solutions gave values of 4.09 and 4.07 added bromine atoms per mole monomer, respectively. The monomer is soluble in alcohols, acetone, and dilute sodium hydroxide, and partly soluble in water, benzene, and petroleum ether.

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.53; H, 6.47.

Carrying out the above procedure with the exception that the distillate was first extracted with 10% aqueous caustic and then neutralized with acid or carbon dioxide gas yielded only polymer as a solid or viscous oil from which very little monomer could be extracted with petroleum ether.

Polymerization and copolymerization of p-vinylphenol. *p*-Vinylphenol, 5 g., and 0.005 g. azobisisobutyronitrile was heated for 16 hr. at 60°. An amber, brittle, glassy solid resulted which was dissolved in methyl ethyl ketone and precipitated by pouring into hexane. Reprecipitation yielded 4.9 g. of a white, powdery solid which sintered at 207–215° and melted at 229°.

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C, 77.83; H, 6.94.

To prepare the styrene copolymer, 2.4 g. *p*-vinylphenol and 18.72 g. styrene (0.1 and 0.9 mole fractions, respectively) were mixed with 0.02 g. azobisisobutyronitrile and polymerized for 25 hr. at 60°. The product was dissolved in methyl ethyl ketone and precipitated in hexane twice, yielding a white solid, 4.0 g., melting range 164–198°.

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[13] R. H. Boundy and R. F. Boyer (eds.), *Styrene*, ACS Monograph No. 115, Reinhold Publishing Co., New York, 1952, p. 141.

Anal. Found for copolymer: C, 89.72; H, 7.16. This indicates an approximate composition of 19 mole % vinylphenol, and was confirmed by infrared absorption.

For observing the effects of various catalysts, about 1 g. monomer was dissolved in 10 ml. solvent and placed in a test tube with a trace of initiator. With benzoyl peroxide where no solvent was used, the sample was heated at 60° for 24 hr. With boron trifluoride–etherate and aluminum chloride in hexane and tetrachloroethane, respectively, the polymer precipitated immediately on addition of the initiator, and blue color appeared which darkened on standing. Similarly, polymer was obtained by adding a catalytic amount of sulfuric acid to the monomer in hexane and allowing to stand at room temperature. When the monomer was added to a mixture of sulfuric and glacial acetic acids (1:9 volume ratio), an immediate exothermic reaction occurred. The solution became purple in color, darkened on standing, and increased markedly in viscosity. All of the polymers formed except this one were soluble in ethanol and reprecipitated from water. This polymer was also insoluble in dioxane, acetone, and dimethylformamide, although swellable, and was isolated by pouring the reaction mixture into water.

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The Nitration of Acenaphthene with $UO_2(NO_3)_2{\cdot}H_2O{\cdot}N_2O_4$

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Received February 19, 1959

While investigating the behavior of UO_3 in red fuming nitric acid, the compound $UO_2(NO_3)_2{\cdot}H_2O{\cdot}N_2O_4$ was prepared. This material has been previously made by Gibson and Katz[1] by reaction of liquid N_2O_4 with hydrated uranium trioxide. The compound shows interesting chemical properties. It reacts violently with aniline and similar substances to produce immediate combustion. It dissolves in many common organic solvents being similar in this respect to uranyl nitrate hexahydrate. With ethyl alcohol and ether it dissolves liberating a colorless gas; in glacial acetic acid it dissolved without gas evolution indicating that this would be a good solvent. A glacial acetic acid solution reacted at room temperature with acenaphthene to give the 5-nitro derivative, while an acetic anhydride solution reacted in the cold to give 5,6-dinitroacenaphthene.

The nitrating ability of the compound could be explained in the manner proposed for $BF_3{\cdot}N_2O_4$ by Bachman *et al.*[2,3] The uranyl nitrate exhibits electronegative properties similar to those of BF_3 and thus it might have the ability to distort the N_2O_4 in the following manner: $H_2O{\cdot}UO_2(NO_3)_2 + O_2N \vdots \mathit{1}NO_2 = (H_2O{\cdot}UO_2(NO_3)_2 \leftarrow NO_2)^{-}NO_2^{+}$. This distortion produces a nitronium ion which according to present theory is necessary for nitration.

EXPERIMENTAL

The presence of N_2O_4 in the compound was established by treating it with ether and collecting the colorless gas evolved in an inverted test tube filled with ether. The test tube was stoppered and cooled in a dry ice–cellosolve bath and a colorless liquid was obtained. When a small fragment of ice was added to the liquid, a deep blue color was obtained, indicating the presence of N_2O_4 by formation of N_2O_3.[4] The liquid was warmed and the presence of NO_2 determined by odor and color. An analysis of compound gave 56.7% uranium oxide and 10.9% nitrogen (Du Pont Nitrometer). Theoretical for $UO_2(NO_3)_2{\cdot}H_2O{\cdot}N_2O_4$ is 56.7% UO_3 and 11.1% N.

The procedure used in the nitration of acenaphthene was similar to the method employed by Sacks and Mosebach[5] in the preparation of 5 nitroacenaphthene but replacing nitric acid as the nitration agent with $UO_2(NO_3)_2{\cdot}H_2O{\cdot}N_2O_4$. Two g. of acenaphthene were suspended in 16 ml. of glacial acetic acid. A solution containing 7.56 g. of $UO_2(NO_3)_2{\cdot}H_2O.N_2O_4$ dissolved in glacial acetic acid was slowly added to the acenaphthene suspension at room temperature. After most of the nitrating reagent had been added, the material present suddenly dissolved and was immediately followed by the formation of a yellow precipitate. This yellow crystalline product after two recrystallizations with glacial acetic acid gave a melting point of 100–102°. The melting point previously reported for the nitroacenaphthene was 101–102°.

In an attempted preparation of 3-nitroacenaphthene the method of Morgan and Harrison[6] was employed. The reaction was carried out in acetic anhydride below 0°. Again the uranium compound replaced the nitric acid as a nitrating agent. Two g. of acenaphthene were dissolved in 135 ml. of acetic anhydride and cooled to $-5°$; 7.56 g. of $UO_2(NO_3)_2{\cdot}H_2O{\cdot}N_2O_4$ were dissolved in a small amount of acetic anhydride and the resulting solution added slowly to the acenaphthene solution. About 1 hr. was required for the addition of nitrating mixture. The reacting mixture was stirred continuously at a temperature near $-7°$. When only a small amount of the nitrating solution remained to be added, the temperature suddenly rose to 10° and changed from a yellow color to brownish green. The mixture was then cooled again and a yellow-green color was observed. The resulting mixture was added to cold water in order to dissolve the uranyl nitrate and precipitate the nitrated compound. The crude product (1.5 g.) was obtained while the theoretical yield for mononitroacenaphthene is 1.3 g. and 1.6 g. for the dinitroacenaphthene. After recrystallization twice with acetic acid a melting point of 175.5–177° was obtained. After recrystallization a third time followed by drying for 8 hr. under a vacuum, a melting point of 203–205° was observed. This melting point corresponds closely to the 5,6-dinitroacenaphthene whose melting point has been recorded as 210–212.[7] Chemical analysis of the nitro product obtained was as follows: C, 59.39%; H, 3.5%, N, 11.23%; and by difference 0, 25.79%. The theoretical per cents for the dinitroacenaphthene are: C, 59.02%; H, 3.30%; N, 11.47% and 0, 26.20%. The infrared spectra of the compound prepared here were identical to that given by a known sample of 5,6-dinitroacenaphthene. It has been reported[8] that nitrogen

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