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Vinylphenol Derivatives

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2,5-Dimethoxystyrene, 2-acetoxy-5-methoxystyrene, 2-acetoxystyrene, and 6-methoxy-2-vinylnaphthalene have been prepared by the pyrolysis of α-(2,5-dimethoxyphenyl)ethyl acetate, α-(2-acetoxy-5-methoxyphenyl)ethyl acetate, α-(2-acetoxyphenyl)ethyl acetate, and α-(2-naphthyl)ethyl acetate at 500°. The foregoing styrenes are all readily polymerized by peroxide catalysts. Deacetylation of 2-acetoxy-5-methoxystyrene, using trimethylbenzylammonium hydroxide, gave 2-hydroxy-5-methoxystyrene, which did not polymerize by peroxide catalysis. It was not identical with a monomethyl derivative that appeared as a by-product in the preparation of 2,5-dimethoxystyrene. Acecyclone reacted readily with all the substituted styrenes, except the 2-hydroxy-5-methoxy derivative, to give substituted dihydrofluoranthenes.

A previous publication[1] reported work dealing with the hydrogenation of aromatic ketones and provided a series of carbinols and their corresponding acetates which are readily converted into substituted styrenes by pyrolysis. 2,5-Dimethoxystyrene, 2-acetoxy-5-methoxystyrene, 2-acetoxystyrene, and 6-methoxy-2-vinylnaphthalene have been prepared by pyrolysis at 500° of the acetates: α-(2,5-dimethoxyphenyl)ethyl acetate, α-(2-acetoxy-5-methoxyphenyl)ethyl acetate, α-(2-acetoxyphenyl)ethyl acetate, and α-(2-naphthyl)ethyl acetate.

Updegraff and Cassidy[2] found that low-molecular-weight materials were obtained when vinylhydroquinone was polymerized using free radical-type catalysts. The retarding effect was due to self-termination by the monomer, since the hydroquinone nucleus acted as a polymerization shortstop. Vinylhydroquinone diacetate[3] provided a polymerizable monomer, since the termination effect of hydroquinone was not present when the hydroxyl groups were covered by non-labile residues. For the same purpose, 2,5-dimethoxystyrene, 2-acetoxy-5-methoxystyrene, 2-acetoxystyrene, and 6-methoxy-2-vinylnaphthalene have been synthesized from the acetates by vapor-phase pyrolysis.

Vapor-phase pyrolysis of α-(2,5-dimethoxyphenyl)ethyl acetate led to demethylation as well as elimination of acetic acid. By alkaline extraction of the products, there was obtained a portion of material having elemental analyses corresponding to a vinylhydroquinone monomethyl ether or mixtures of isomers. The pyrolysis product failed to polymerize prior to the alkaline extraction step, while, after extraction, polymerization was easily carried out with benzoyl peroxide as the catalyst. Pyrolysis of α-(2-acetoxy-5-methoxyphenyl)ethyl acetate proceeded smoothly to give 2-acetoxy-5-methoxystyrene, which was deacetylated to give 2-hydroxy-5-methoxystyrene. Deacetylation was carried out using trimethylbenzylammonium hydroxide since neither sodium methoxide nor methanol saturated with hydrogen chloride gave the desired product. Infrared comparison of 2-hydroxy-5-methoxystyrene with the alkali-soluble by-product from the preparation of 2,5-dimethoxystyrene indicated that the materials were similar but not identical, and that the by-product was probably a mixture of isomers rather than a pure compound.

Both 2,5-dimethoxystyrene and 2-acetoxystyrene were readily converted to polymers by using benzoyl peroxide, while, as expected, 2-hydroxy-5-methoxystyrene failed to polymerize.

2-Vinylphenol has been known since 1908, but no improvement in its synthesis has been achieved since that time. Fries and Fickewirth,[4] who first synthesized 2-vinylphenol by pyrolytic distillation of *o*-coumaric acid, reported that its polymer was produced as a by-product of the pyrolysis. The same synthesis was used by Marvel and Rao,[5] who then acetylated the 2-vinylphenol to prepare 2-acetoxystyrene, which could be readily polymerized. 2-Vinylphenol apparently acts as a polymerization selfinhibitor similar to vinylhydroquinone. Smith and Niederl[6] prepared 2-vinylphenol by the action of ethylene oxide on phenol, but the experimental details regarding their process were meager and the present authors were unable to duplicate that method. A recent survey summarized a number of methods for the preparation of 2-vinylphenol.[7]

4-Acetoxystyrene was prepared by Alderman and Hanford[8] by hydrogenation of 4-hydroxyacetophenone to α-(4-hydroxyphenyl)ethanol and pyrolysis of the corresponding acetate. Synthesis of 2-acetoxystyrene was not indicated by Alderman and Hanford. The critical step undoubtedly was the hydrogenation of 2-hydroxyacetophenone to α-(2-hydroxyphenyl)ethanol, since Nightingale and

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[1] Williams, *J. Org. Chem.*, **19**, 1205 (1954).

[2] Updegraff and Cassidy, *J. Am. Chem. Soc.*, **71**, 407 (1949).

[3] Reynolds, Cathcart, and Williams, *J. Org. Chem.*, **18**, 1709 (1953).

[4] Fries and Fickewirth, *Ber.*, **41**, 367 (1908).

[5] Marvel and Rao, *J. Polymer Sci.*, **4**, 703 (1949).

[6] Smith and Niederl, *J. Am. Chem. Soc.*, **53**, 807 (1931).

[7] Bader, *J. Am. Chem. Soc.*, **77**, 4155 (1955).

[8] Alderman and Hanford, U. S. Patent 2,276,138 (1942).

TABLE I

REACTION PRODUCTS OF STYRENES WITH ACECYCLONE

Styrene R—CH═CH₂	R in Adduct 9,10-Diphenyl-8-(R) 7,8-dihydro-fluoranthene	M.P. °C.	Formula	Analysis Calc'd C	H	Found C	H
2-Acetoxy-5-methoxy-	2-Acetoxy-5-methoxyphenyl	170–171	$C_{38}H_{28}O_4$	85.4	5.4	85.5	5.1
2-Hydroxy-5-methoxy-	2-Hydroxy-5-methoxyphenyl	109–110	$C_{38}H_{28}O_4$	83.2	5.3	83.3	5.8
2,5-Dimethoxy-	2,5-Dimethoxyphenyl	171–171.5	$C_{39}H_{30}O_4$	87.5	5.9	87.8	5.6
2-Acetoxy-	2-Acetoxyphenyl	162–163	$C_{36}H_{26}O_2$	88.2	5.3	87.9	5.0
6-Methoxy-2-vinyl-naphthalene	6-Methoxy-2-naphthyl	169–170	$C_{40}H_{28}O_2$	91.4	5.5	91.2	5.7

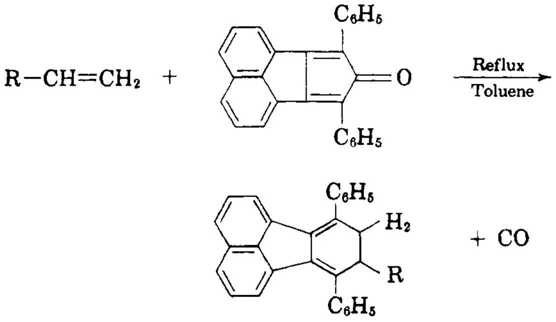
Radford[9] demonstrated that 2- and 4-hydroxyl-substituted acetophenones yield not the desired carbinols but the corresponding alkyl derivatives when copper chromite was used as the catalyst during hydrogenation at 115–130° and 250 atm. Recently, it has been found that 2- and 4-hydroxyacetophenones can be hydrogenated to the corresponding carbinols, under carefully controlled conditions of catalyst, temperature, and pressure.[1] Thus, 2-hydroxyacetophenone has been transformed into α-(2-acetoxyphenyl)ethyl acetate which, in turn, was pyrolyzed to give 2-acetoxysytrene in over-all yield of 64.8%.

The product was sufficiently pure that homopolymerizations and copolymerizations of 2-acetoxystyrene were possible, using either benzoyl peroxide or ultraviolet radiation.

6-Methoxy-2-vinylnaphthalene was formed without any evidence of concurrent demethylation during pyrolysis of the corresponding acetate. When 6-methoxy-2-vinylnaphthalene was treated with maleic anhydride in refluxing dioxane, a copolymer was obtained. The polymerization was more efficient when benzoyl peroxide was present. However, when the components were heated in the absence of peroxide in toluene, the diene adduct, 7-methoxy-2,3,4-trihydrophenanthrene-3,4-decarboxylic anhydride, was obtained.

Treatment of the styrenes with acecyclone, according to the method described previously by Allen and Van Allan,[10] provided an excellent means of forming derivatives for characterization in nearly quantitative yields. The carbonyl bridged compound formed initially is decarbonylated during the period of heating.

In the case of 2-hydroxy-5-methoxystyrene, it was found impossible to form the acecyclone adduct directly, owing to side reactions which occurred at the elevated temperature of reaction. The side reactions may have involved polymerization and/or oxidation of the monomeric material, since 2-hydroxy-5-methoxystyrene is the vinyl-substituted analog of the phenol, 4-methoxyphenol, an antioxidant. The desired adduct was prepared by deacetylation of the adduct of 2-acetoxy-5-methoxystyrene. The physical constants for the acecyclone-styrene adducts are listed in Table I.



Acecyclone

where R can be:
2,5-dimethoxyphenyl
2-acetoxy-5-methoxyphenyl
2-acetoxyphenyl
6-methoxy-2-naphthyl.

EXPERIMENTAL

2,5-Dimethoxystyrene. A mixture of 65 g. (0.29 mole) of α-(2,5-dimethoxyphenyl)ethyl acetate[1] and 60 g. of thiophene-free benzene was passed dropwise during 2 hours through a 25-mm. O. D. Pyrex tube packed for 30 inches with glass beads and maintained at 500–510° by means of an electrically controlled furnace. The pyrolyzate was swept through the tube by a slow stream (1.0 l./hour) of dry nitrogen and collected in a Dry Ice-carbon tetrachloride-chloroform-cooled trap. The pyrolyzate was washed twice with water, dried over magnesium sulfate, and distilled through a 12-inch Vigreux-type column, giving the following fractions: (1) b.p. 54.5–65.5° (0.35 mm.), 1.5 g., n_D^{25} 1.5400; (2) b.p. 65.6–69° (0.3 mm.), 3.2 g., n_D^{25} 1.5525; (3) b.p. 69–75° (0.3 mm.), 7.2 g., n_D^{25} 1.5602; (4) b.p. 75–85° (0.3 mm.), 10.0 g., n_D^{25} 1.5625; (5) b.p. 88–103° (0.3 mm.), 9.0 g., n_D^{25} 1.5665. None of these fractions polymerized when heated at 70° with benzoyl peroxide. The fractions were combined, and, after the addition of 50 ml. of benzene, were washed with three 25-ml. portions of 10% aqueous sodium hydroxide, followed by two 25-ml. portions of saturated aqueous sodium chloride. The organic material was dried over magnesium sulfate and distilled through a 12-inch Vigreux-type column to give the following fractions: (6) 50–51° (0.3 mm.), 0.85 g., n_D^{25} 1.5472; (7) 55–56° (0.3 mm.), 1.0 g., n_D^{25} 1.5510; (8) 59–61° (0.3 mm.), 1.2 g., n_D^{25} 1.5570; (9) 62–65° (0.33 mm.), 2.25 g., n_D^{25} 1.5590; (10) 65–69° (0.3 mm.), 3.05 g., n_D^{25} 1.5589; (11) 69–73° (0.3 mm.), 4.5 g., n_D^{25} 1.5575; (12) 75–76° (0.3 mm.), 2.0 g., n_D^{25} 1.5550. One-tenth-gram samples of fractions 6 to 12 were heated for 72 hours with 0.1 g. of dioxane and 0.001 g. of benzoyl peroxide

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(9) Nightingale and Radford, *J. Org. Chem.*, **14**, 1092 (1948).

(10) Allen and Van Allan, *J. Org. Chem.*, **17**, 845 (1952).

at 90°. Fractions 6 to 12 were submitted for elemental analysis; the results of the carbon-hydrogen analyses are as follows: (6) C, 77.0; H, 7.3; (7) C, 74.5; H, 8.8; (8) C, 74.1; H, 7.0; (9) C, 73.6; H, 7.1; (10) C, 73.6; H, 7.3; (11) C, 73.3; H, 7.5; (12) C, 73.1; H, 7.5.

The calculated analysis for 2,5-dimethoxystyrene, $C_{10}H_{12}O_2$, is: C, 73.2; H, 7.4. Fractions 9 to 12 are, thus, essentially pure 2,5-dimethoxystyrene. Fractions 6 to 12 were submitted for infrared analysis which confirmed the observation that all fractions except No. 1 contained substantial amounts of 2,5-dimethoxystyrene.

The combined alkaline extracts were acidified with dilute hydrochloric acid and were extracted with two 25-ml. portions of benzene. The combined extract was dried over magnesium sulfate and distilled using a small Claisen-type flask to yield 1.0 g. of material, b.p. 84–94° (0.3 mm.). Under the assumption that the material was a vinylhydroquinone monomethyl ether, the following analysis was obtained:

Anal. Calc'd for $C_9H_{10}O_2$: C, 72.0; H, 6.7. Found: C, 71.7; H, 6.3.

The infrared curve of the alkaline-extracted material further confirmed the product as a vinylhydroquinone monomethyl ether or a mixture of its isomers.

2-Acetoxy-5-methoxystyrene. α-(2-Acetoxy-5-methoxyphenyl)ethyl acetate was synthesized as previously reported.[1] A mixture of 274 g. (1.18 moles) of α-(2-acetoxy-5-methoxyphenyl)ethyl acetate and 274 ml. of thiophene-free benzene was passed dropwise at 500° at the rate of 70 ml. per hour through the pyrolysis system. The pyrolyzate was washed with water, saturated sodium bicarbonate, and finally with water. After drying over magnesium sulfate, distillation from a modified Claisen flask gave material boiling at 90–102° (0.3–0.7 mm.). Redistillation through an 8-inch Vigreux-type column gave 200 g. of 2-acetoxy-5-methoxystyrene, b.p. 85–92° (0.25 mm.), n_D^{25} 1.5394–1.5432 (91% of theory). A fraction distilling at 88–92° was submitted for analysis.

Anal. Calc'd for $C_{11}H_{12}O_3$: C, 68.8; H, 6.3. Found: C, 68.9; H, 6.9.

2-Hydroxy-5-methoxystyrene. A mixture of 19.2 g. (0.1 mole) of 2-acetoxy-5-methoxystyrene (n_D^{25} 1.5374), 120 ml. of absolute ethanol, and 12 ml. of Triton-B (40% aqueous trimethylbenzylammonium hydroxide) was refluxed for 2 hours. The reaction mixture was diluted with water to a volume of 500 ml. and extracted with 500 ml. of ether. The extract was shaken with cold, dilute sulfuric acid, water, dilute sodium carbonate, water, and dried over Drierite. Distillation gave 10 g. (66% of theory) of 2-hydroxy-5-methoxystyrene, b.p. 78–79° (0.65 mm.), n_D^{25} 1.5782.

Anal. Calc'd for $C_9H_{10}O_2$: C, 72.0; H, 6.7. Found: C, 72.4; H, 7.3.

o-Acetoxystyrene. A solution of 45 g. (0.2 mole) of α-(*o*-acetoxyphenyl)ethyl acetate[1] in 45 ml. of thiophene-free benzene was passed dropwise during 1.1 hours through the pyrolysis tube at 500°. The pyrolyzate was washed with two 200-ml. portions of water, and the organic material was dried over magnesium sulfate. Distillation through a 12-inch Vigreux-type column gave 23.5 g. (72% of theory) of *o*-acetoxystyrene, b.p. 57.5° (0.4 mm.), n_D^{25} 1.5358. Marvel and Rao[2] reported the following constants: b.p. 97–98° (7 mm.), n_D^{25} 1.5324.

6-Methoxy-2-vinylnaphthalene. A mixture of 50 g. (0.20 mole) of α-(6-methoxy-1-naphthyl)ethyl acetate[1] and 100 ml. of thiophene-free benzene, preheated to 50°, was passed dropwise at the rate of one drop per second through the pyrolysis tube, which was maintained at 495–505°. The pyrolyzate was washed free from acetic acid with water, dried over magnesium sulfate, and the benzene was distilled. The residue (m.p. 92–93°) was recrystallized from 150 ml. of hexane to give 21 g. (57% of theory) of pure 6-methoxy-2-vinylnaphthalene, m.p. 93–94°. From the hexane mother liquors, there was obtained by evaporation an additional 4 g. of 6-methoxy-2-vinylnaphthalene, m.p. 91–92°.

Anal. Calc'd for $C_{13}H_{12}O$: C, 84.7; H, 6.5. Found: C, 84.2; H, 6.8.

Adduct of 6-methoxy-2-vinylnaphthalene with maleic anhydride. A solution of 1.84 g. (0.1 mole) of 6-methoxy-2-vinylnaphthalene and 0.98 g. (0.1 mole) of maleic anhydride in 50 ml. of toluene was heated under reflux for 24 hours. The reaction mixture was filtered and chilled to give 2.1 g. of 7-methoxy-2,3,4-trihydrophenanthrene-3,4-dicarboxylic acid anhydride, m.p. 246–247°.

Anal. Calc'd for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0. Found: C, 72.6; H, 5.0.

REACTIONS WITH ACECYCLONES

The following procedure illustrates the general technique used to react the various styrenes with acecyclones, as listed in Table I.

9,10-Diphenyl-8-(2-acetoxy-5-methoxyphenyl)-7,8-dihydrofluoranthene. A solution of 1.85 g. (0.0052 mole) of acecyclone and 1.0 g. (0.0052 mole) of 2-acetoxy-5-methoxystyrene in 50 ml. of toluene was refluxed for 24 hours. The reaction mixture was diluted with 500 ml. of dry hexane and heated with Nuchar (C-190). The filtered solution was cooled to −20° to give a near quantitative yield of 9,10-diphenyl-8-(2-acetoxy-5-methoxyphenyl)-7,8-dihydrofluoranthene.

Deacetylation of 9,10-diphenyl-8-(2-acetoxy-5-methoxyphenyl)-7,8-dihydrofluoranthene. To a solution of 0.15 g. (0.0025 mole) of 9,10-diphenyl-8-(2-acetoxy-5-methoxyphenyl)-7,8-dihydrofluoranthene in 15 ml. of absolute ethanol there was added 0.2 ml. (0.005 mole) of Triton-B (40% aqueous trimethylbenzylammonium hydroxide). The mixture was heated on the steam cone until all of the solid had dissolved, after which time the product was precipitated in water. The water slurry was acidified with dilute hydrochloric acid, and the solid was filtered, washed with water, and dried. The yellow-brown solid was recrystallized from hexane to give 9,10-diphenyl-8-(2-hydroxy-5-methoxyphenyl)-7,8-dihydrofluoranthene, m.p. 109–110°.

Anal. Calc'd for $C_{33}H_{28}O_4$: C, 83.2; H, 5.3. Found: C, 83.3; H, 5.8.

Polymerizations. Polymerizations were carried out in order to determine the purity of the monomers, since traces of phenolic by-products would have acted as inhibitors. For this purpose, 1.0-g. samples of the monomers were heated at 90° in 10 ml. of dioxane containing 1% of the monomer weight of benzoyl peroxide. Larger-scale polymerizations and evaluations of the polymers will be reported elsewhere.

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