cooled and kept at 5° for 12 hr. The liquid was separated by filtration, and the unchanged crystalline potassium hydrogen D-glucarate was suspended in water (300 ml.) and treated as before. The crystals from the second treatment were recovered and again treated with water (300 ml.) as above. The crystalline potassium hydrogen D-glucarate (18.0 g.) which separated after this third heating and cooling was not treated further.

The yellow solutions from the above three heat treatments of the potassium hydrogen salt were combined and deionized by passing through a column of Amberlite IR-120[13] cation exchange resin (H form). The acidic effluent from the cation exchange column was concentrated under reduced pressure (bath temp. 30–35°). The resulting thick, yellow sirup was stirred with a 1:1 mixture of water and acetone (50 ml.) and concentrated in an air stream. Crystallization commenced shortly after the heavy, viscous sirup was seeded with a mixture of D-glucaro-1,4- and 6,3-lactones. The crystallization was continued for 4 days under the air stream. The crystalline matrix was triturated with acetone (100 ml.) and the crystalline 6,3-lactone separated by filtration and washed with acetone (300 ml.). The yield of D-glucaro-6,3-lactone was 15.2 g. (17.6% of the potassium salt converted); m.p. 138–142°, $[\alpha]_D^{23}$ +58.5° (*c* 1.3, water) changing to $[\alpha]_D^{27}$ +23.7° (87 days).

The combined yellow acetone filtrate and washings were concentrated in an air stream and seeded with the 1,4-lactone. Crystallization was allowed to proceed to completion. After about 4 weeks the crystalline mass was triturated with ethyl acetate (125 ml.) and washed by decantation first with ethyl acetate and then with diethyl ether. The yield of D-glucaro-1,4-lactone was 56.0 g. (64% of the potassium salt converted); m.p. 90–100°, $[\alpha]_D^{27}$ +43.6° (*c* 1.2, water) changing to +27° in 8 days.

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(13) A product of the Rohm and Haas Co., Philadelphia, Pa.

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# *p*-Vinylbenzoic Acid

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Several preparations of *p*-vinylbenzoic acid have been reported.[1–4] All are four- to six-step syntheses of low over-all yields (10–20%). A recently published[4] synthesis from ethylbenzene gave a yield of 24% of material of doubtful purity.

The preparation of *p*-vinylbenzoic acid reported here is a three-step synthesis from an ordinary molding-grade polystyrene. The yield, 18%, is only average compared to that of the other methods, but the simplicity of the procedure moderates this objection considerably. Polyvinylacetophenone was prepared by Friedel-Crafts acetylation of polystyrene. Thermal depolymerization yielded *p*-vinylacetophenone, and hypochlorite oxidation of the ketone gave *p*-vinylbenzoic acid.

The low-yield step in the various published syntheses of *p*-vinylbenzoic acid has been the formation of the vinylic double bond. The necessary high temperature or prolonged reaction time causes polymerization of the product. The negative group, carboxy, alkoxycarbonyl, or cyano, on the ring of the styrene molecule renders it more sensitive to polymerization. Previously this low-yield step has been the fourth or fifth reaction in the sequence, which makes it particularly objectionable. The double-bond formation in the present synthesis does not afford a better yield, but it occurs in the second step. Furthermore, the first step, acetylation of polystyrene, can be conducted on a large scale with little additional effort.

The preparation of polyvinylacetophenone and its depolymerization have been described,[5] but the yield reported for the pyrolysis could not be repeated. Heat transfer to the partially pyrolyzed polymer in the spherical flask was poor. A special pyrolysis tube overcame this problem somewhat. This apparatus probably could be used to advantage in many pyrolysis reactions which leave a nonvolatile residue. Redistillation of the pyrolysis product gave *p*-vinylacetophenone contaminated with *p*-methylacetophenone which boils a few degrees lower. Recrystallization from *n*-heptane constituted the best purification.

Excess hypochlorite causes increased polymer formation in the oxidation reaction. Consequently, the potassium hypochlorite was standardized by titration with thiosulfate in a conventional iodometry procedure, and only the calculated amount was used. The conventional recrystallization of *p*-vinylbenzoic acid from aqueous alcohol does not remove the contaminating polymeric acid. The monomer is highly soluble in ethyl ether; the polymer is quite insoluble in ether. Filtration affords the separation, and the low temperature of this process prevents further polymerization. Titration of the double bond of *p*-vinylbenzoic acid with bromine was found to be a better measure of purity than melting point.

## EXPERIMENTAL

*Polyvinylacetophenone.* This polymer was prepared in 91% yield by a modification[6] of the published[5] procedure with carbon tetrachloride as solvent. An equivalent of aluminum chloride and a 10% excess of acetyl chloride were used. The dried polymer–aluminum chloride complex was decomposed in dilute hydrochloric acid and ice. The polymer was washed thoroughly with water but not reprecipitated.

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(1) C. G. Overberger and R. E. Allen, *J. Am. Chem. Soc.*, **68**, 722 (1946); C. S. Marvel and C. G. Overberger, *J. Am. Chem. Soc.*, **67**, 2250 (1945).

(2) W. S. Emerson, J. W. Heyd, V. E. Lucas, E. C. Chapin, G. R. Owens, and R. W. Shortridge, *J. Am. Chem. Soc.*, **68**, 674 (1946).

(3) E. D. Bergmann and J. Blum, *J. Org. Chem.*, **24**, 549 (1959).

(4) E. R. Bissell and R. E. Spenger, *J. Org. Chem.*, **24**, 1146 (1959).

(5) W. O. Kenyon and G. P. Waugh, *J. Polymer Sci.*, **32**, 83 (1958).

(6) C. C. Unruh, *J. Appl. Polymer Sci.*, **2**, 358 (1959).

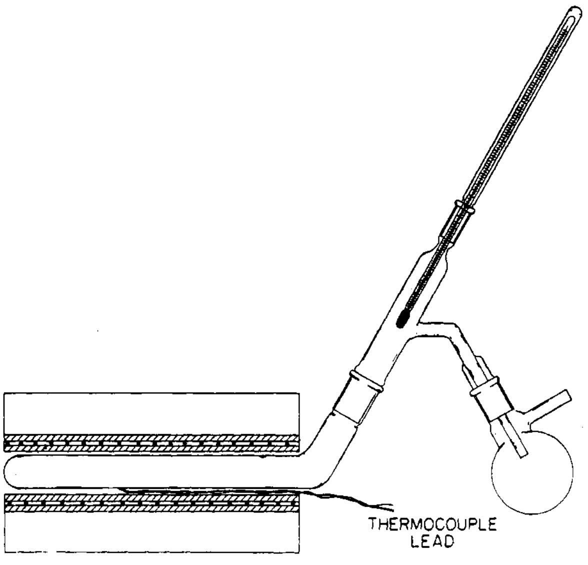

Fig. 1. Pyrolysis apparatus

*p-Vinylacetophenone.* Into the pyrolysis tube illustrated in Fig. 1 was charged 35 g. of polyvinylacetophenone. The tube, with a thermocouple attached, was placed in a stationary combustion furnace inclined about 30° upward toward the opening. The heating zone of the furnace was 12 in. long and extended an inch beyond the polymer charge at the outlet end of the tube. The thermocouple output activated a regulator which registered and controlled the furnace temperature. The furnace was heated to 200° to soften the polymer, vacuum was applied, and the temperature was raised to 400° for depolymerization. The temperature of the distilling product was in the vicinity of 100° at 1–2 mm. The receiver was cooled in ice. When the pyrolysis was completed (60–90 min.), the tube was removed from the furnace, cooled, and recharged. This process was repeated several times before the accumulation of nonvolatile pyrolysis products had to be removed. A total of 110 g. of polymer was pyrolyzed to give 70 g. of crude distillate. The oil was redistilled, in the presence of a small amount of hydroquinone, at 75–80° (0.3 mm.). The 48 g. of crystalline distillate was recrystallized from 40 ml. of *n*-heptane at 0°. The yield was 33 g. (30%); m.p. 34–35°.

If desired, the pyrolysis can be conducted in a flask immersed in a molten metal or salt bath at 400° with a somewhat reduced yield.

*p-Vinylbenzoic Acid.*[7] To 31 g. (0.21 mole) of *p*-vinylacetophenone in 150 ml. of dioxane was added dropwise, with stirring, 530 ml. (0.63 mole) of a 1.19*M* solution of potassium hypochlorite[8] over a 45-min. period. The temperature was maintained at 35° with slight cooling. The mixture was stirred an additional 30 min. at 35°. The small amount of excess hypochlorite was discharged by the addition of 1 ml. of acetone as indicated by acidic iodide solution. The mixture was cooled, extracted with one portion of ether, and the aqueous phase was added to 75 ml. of concentrated hydrochloric acid mixed with ice. The product was recovered by filtration and washed with cold water. The damp cake was dissolved in 150 ml. of warm ethanol containing a little hydroquinone, and hot water was added to incipient crystallization. Crystallization was completed at 5°. The acid was dried *in vacuo* at room temperature; yield, 27 g.

This acid was warmed in 150 ml. of ethyl ether to dissolve the monomeric acid. Filtration through Perlite removed the polymeric material, and 600 ml. of petroleum ether was added to the filtrate. Crystallization was completed at 5°. The product was collected and washed with the same mixed solvent. Bromine titration of the double bond[9] indicated 100.0% vinylbenzoic acid. The melting point was 138–141°; yield, 21 g. (67%).

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[7] The hypochlorite oxidation of *p*-vinylacetophenone was mentioned by W. J. Dale and B. D. Vineyard before the Division of Organic Chemistry at the 137th Meeting, ACS, Cleveland, Ohio, April 1960.

[8] M. S. Newman and H. L. Holmes, *Org. Syntheses*, Coll. Vol. II, 428 (1943).

(9) This analysis was a "dead-stop" end-point titration with pyridinium bromide perbromide as titrant and mercuric acetate as catalyst, developed and performed by E. P. Przybylowicz and A. D. Baitsholts, of these Laboratories.

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# The Reaction of 9,10-Dihydro-9,10-ethano-9-anthranol and 2,6-Di-*t*-butylphenol with Lithium Aluminum Hydride

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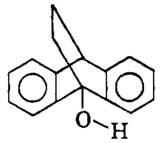
Lithium aluminum hydride when treated with excess methyl, ethyl or isopropyl alcohol liberates four equivalents of hydrogen while *t*-butyl and *t*-amyl alcohols liberate but three equivalents.[1] Two compounds which might liberate only two equivalents of hydrogen are the bridgehead alcohol (I) prepared in these laboratories and 2,6-di-*t*-butylphenol.[2] These compounds were tested and it was found that compound I was comparable with *t*-butyl alcohol and liberated three equivalents of hydrogen. However, 2,6-di-*t*-butylphenol was found to be of the next order of hindrance and it liberated only two equivalents of hydrogen.



As no precipitate was formed, it is likely that the evolution of only two equivalents of hydrogen is due to the inability of three 2,6-di-*t*-butylphenoxide groups to fit around an aluminum atom rather than to insolubility of the complex causing precipitation before a third equivalent of the phenol could react.

Aqueous sodium hydroxide solutions do not dissolve 2,6-di-*t*-butylphenol, but it seems doubtful that the lowered acidity of this hindered phenol would cause it to be unreactive with the bis-2,6-

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[1] H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, 80, 5372 (1958).

[2] During the course of a visit at Colorado, Professor H. C. Brown suggested that compound I would be considerably more hindered than *t*-butyl alcohol in its reaction with lithium aluminum hydride.