

treated as follows: The addition of bromine to a cold petroleum ether solution gave solid dipentene tetrabromide, m. p. after recrystallization from ethyl acetate 126°, mixed m. p. unchanged. A second portion was treated with maleic anhydride after the method of Birch<sup>15</sup>; the distillate indicated 10%  $\alpha$ -terpinene based on the steam volatile fraction. The maleic anhydride adduct of  $\alpha$ -terpinene was isolated. A third portion was oxidized with cold neutral permanganate to give 17% of the steam volatile product as a saturated oil identified as *p*-cymene by the aroyl benzoic acid, m. p. and mixed m. p. 123.16. Cut no. 4 was not identified. Cut no. 5 gave terpinolene tetrabromide, m. p. and mixed m. p. 116–117°,<sup>17</sup> in 63%

(15) Birch, *Proc. Roy. Soc. N. S. Wales*, **71**, 54–59 (1937); *C. A.* **31**, 8109 (1937).

(16) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, 1935, pp. 76–77.

(17) Wallach, *Ann.*, **227**, 283 (1884).

yield based on the cut 5 indicating a high proportion of terpinolene. The residue was not investigated.

### Summary

1. The cyclobutane ring in  $\alpha$ -pinene is broken by treatment with 1-chloro-4-naphthalene sulfonic acid in an analogous fashion to 3,4,5,5-tetramethyl-2-hexene.

2. This reaction, and the general acid catalyzed isomerization of  $\alpha$ -pinene, and presumably  $\beta$ -pinene as well, to monocyclic terpenes is discussed from the point of view of the Whitmore mechanism with which it appears to be in complete harmony.

WILMINGTON, DELAWARE

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## Substituted Styrenes. II. The Preparation of *p*-Iodo-, *p*-Nitro- and *p*-Dimethylaminostyrene and $\alpha$ -Vinylthiophene

BY ROGER W. STRASSBURG,<sup>1</sup> R. A. GREGG AND CHEVES WALLING

In connection with copolymerization studies<sup>2</sup> it has been found necessary to synthesize a number of substituted styrenes in this Laboratory.<sup>3</sup> This paper reports the preparation of the hitherto undescribed *p*-iodostyrene and new syntheses of *p*-nitrostyrene and  $\alpha$ -vinylthiophene. New physical constants are also reported for *p*-nitrostyrene and *p*-dimethylaminostyrene.

*p*-Iodostyrene has been prepared in three steps from commercially available *p*-aminoacetophenone by diazotization and conversion to *p*-iodoacetophenone (52% yield), reduction with aluminum isopropylate (92.5%), and dehydration over potassium acid sulfate (60%) in an over-all yield of 29%.

*p*-Nitrostyrene has been prepared by the treatment of  $\beta$ -bromo- $\beta$ -(*p*-nitrophenyl)-propionic acid with sodium carbonate solution.<sup>4</sup> We have followed what appears to be a more practical two-step synthesis from  $\beta$ -phenylethyl bromide by nitration followed by dehydrobromination in aqueous triethanolamine. We have, however, been unable to confirm the melting point previously reported for this styrene.<sup>4</sup>

*p*-Dimethylaminostyrene was prepared from *p*-dimethylaminobenzaldehyde and methylmagnesium bromide by a method similar to that employed by Marvel, Overberger, Allen and Saunders,<sup>5</sup> but in larger quantity. Our physical constants differ somewhat from theirs.

$\alpha$ -Vinylthiophene has been prepared by the de-

hydration of methyl- $\alpha$ -thienylcarbinol.<sup>6,7</sup> We have prepared the material in 28.7% yield by the reaction of  $\alpha$ -thienylmagnesium bromide with vinyl chloride in the presence of cobaltous chloride in a manner analogous to the synthesis of styrene reported by Kharasch and Fuchs.<sup>8</sup> An attempt to prepare *m*-methoxystyrene from *m*-iodoanisole by the same method, however, was unsuccessful.

### Experimental

***p*-Iodoacetophenone.**—Diazotization of 270 g. (2 moles) of *p*-aminoacetophenone with sulfuric acid and sodium nitrite, treatment of the diazo compound with excess potassium iodide solution, and vacuum distillation of the resulting oil gave 245 g. (52%) of light yellow *p*-iodoacetophenone, b. p. 137–140° (9 mm.), m. p. 83–84° (lit. 85°).

***p*-Iodophenylmethylcarbinol.**—In a 5-liter round bottom flask equipped with a 1 meter helices-packed fractionating column was placed 235 g. (0.96 mole) of *p*-iodoacetophenone and 2900 cc. of dry isopropyl alcohol in which 40 g. (1.48 moles) of aluminum had been dissolved, and the mixture slowly distilled. After several hours, when the distillate no longer gave a test for acetone with 2,4-dinitrophenylhydrazine, the excess alcohol was distilled off and, after cooling, the residue decomposed with 350 cc. of concentrated hydrochloric acid and 1000 g. of ice. After standing overnight the mixture was extracted with benzene, the benzene dried by azeotropic distillation, and then distilled off. The residue was vacuum-distilled at 2 mm. through a 6-in. Vigreux column until the forerun had been removed, and then without a column. There was obtained 211 g. (92.5%) carbinol, b. p. 99–120° (2–5 mm.), m. p. 40–42°. Inadvertently all of the carbinol was used before a sample was set aside for analysis. However, its method of preparation and subsequent reaction leaves little doubt as to its identity.

***p*-Iodostyrene** was prepared by dehydrating the carbinol over potassium acid sulfate essentially as described by Brooks<sup>9</sup> for similar compounds. Employing 211 g.

(1) Present address, University of Minnesota, Minneapolis, Minn.

(2) Walling, Briggs, Wolfstirn and Mayo, unpublished work.

(3) For the first paper in this series, see Walling and Wolfstirn, *THIS JOURNAL*, **69**, 852 (1947).

(4) Basler, *Ber.*, **16**, 3003 (1883).

(5) Marvel, Overberger, Allen and Saunders, *THIS JOURNAL*, **68**, 736 (1946).

(6) Mowry, Renoll and Huber, *ibid.*, **68**, 1105 (1946).

(7) Kuhn and Dann, *Ann.*, **547**, 293 (1941).

(8) Kharasch and Fuchs, *THIS JOURNAL*, **65**, 504 (1943).

(9) Brooks, *ibid.*, **66**, 1295 (1944).

(0.84 mole) of carbinol and 2 g. of potassium acid sulfate, 161 g. of crude styrene was obtained. Recrystallization from 275 cc. of 95% ethanol gave 118 g. (60%) of pure product as white plates with a licorice-like odor, m. p. 44–44.5°, sparingly soluble in cold methanol and ethanol, soluble in cold acetone, dioxane and petroleum ether. Although stable for months in the ice box in the solid state, a portion heated overnight at 60° with a trace of benzoyl peroxide was completely converted to the glassy light yellow polymer.

*Anal.* (on polymer) Calcd. for  $(C_8H_7I)_n$ : I, 55.1. Found: I, 54.88, 54.59.

**$\beta$ -(*p*-Nitrophenyl)-ethyl bromide** was prepared by the nitration of 1000 g. of Eastman Kodak Co.,  $\beta$ -phenylethyl bromide with fuming nitric acid in an acetic acid-acetic anhydride mixture at –5 to 0° essentially as described by Foreman and McElvain.<sup>10</sup> The procedure was simplified somewhat and a more rapid addition of nitric acid effected by cooling the reaction mixture by the direct addition of solid carbon dioxide. A partial separation of product was accomplished by filtration of the reaction mixture on a sintered glass filter at 0°. The precipitate, on washing with water and recrystallizing from petroleum ether containing 10–20% benzene, gave 300 g. of  $\beta$ -(*p*-nitrophenyl)-ethyl bromide, m. p. 69–70.5° (lit. 69–70°<sup>10</sup>). On pouring the mother liquors from the reaction mixture on ice, taking up in benzene, washing, drying and removing solvent, 907 g. of oils was obtained which, when fractionated on a short path still at 0.03 mm., yielded an additional 260 g. of product plus lower-boiling oils consisting chiefly of the *o*-isomer. The total yield thus amounted to 45%.  $\beta$ -(*p*-Nitrophenyl)-ethyl bromide was also prepared in 38.5% yield by nitrating 1000 g. of  $\beta$ -phenylethyl bromide in fuming nitric acid alone at –20 to –30° as described by Sobotka,<sup>11</sup> but this appeared a less attractive method.

***p*-Nitrostyrene.**—Fifty grams (0.217 mole) of the nitrophenylethyl bromide, 300 cc. of triethanolamine and 150 cc. of water were refluxed in a 1 liter round-bottom flask equipped with Stark and Dean trap and reflux condenser. The styrene soon began to separate in the trap as a heavy yellow liquid and the rate of reflux was maintained at the capacity of the condenser in order to remove the styrene from the reaction zone as quickly as possible. In approximately ninety minutes, when separation of the styrene had almost ceased, an additional 50 g. of bromide was added, and the procedure repeated until 200 g. in all had been decomposed. The crude yield in several experiments varied between 110 and 118 g. (85–91%), m. p. 18–19°. The product could be purified by fractional freezing, molecular distillation, or recrystallization at 0° from petroleum ether. The highest recovery, however, was obtained by two recrystallizations from methanol at about –40° followed by drying *in vacuo* at 0°. Under these conditions 100 g. of crude product gave approximately 80 g. of pure *p*-nitrostyrene, m. p. above 21°, usually 21.4°. Exhaustive purification by all the methods listed above of several samples of *p*-nitrostyrene prepared, in turn, from different lots of the bromide invariably led to material m. p. 21.4°, at variance with the m. p. of 28° reported by Basler in 1883.<sup>4</sup> *p*-Nitrostyrene is a yellow liquid, crystallizing in thick needles from petroleum ether and having a pleasant, but persistent, aromatic odor.

*Anal.* (on polymer) Calcd. for  $(C_8H_7O_2N)_n$ : C, 64.42; H, 4.74; N, 9.40. Found: C, 64.65, 65.07; H, 4.99, 5.18; N, 9.07, 9.03.

***p*-Dimethylaminostyrene.**—To the Grignard reagent prepared from 50 g. (2.08 moles) of magnesium and 160 g. (1.68 moles) of methyl bromide in 1500 cc. of ether in a 12-liter flask equipped with dropping funnel, stirrer and reflux condenser, 200 g. (1.34 moles) of Eastman *p*-dimethylaminobenzaldehyde in 3500 cc. of ether were added over ninety minutes and stirring continued for an

additional hour. The reaction mixture was then decomposed by the cautious addition of 120 cc. of saturated ammonium chloride solution containing 1% concentrated hydrochloric acid. After standing overnight, the ether was decanted and the granular precipitate containing magnesium and ammonium salts washed with two small portions of ether. The ether solutions were combined and the ether distilled. The residue (180 g.) was divided into two portions and the dehydration completed by distilling as rapidly as possible from a Claisen flask at 1 mm. until the temperature of the vapors reached 140°. The combined distillates (67 g.) were then fractionated in a molecular still at approximately 1 micron. The results indicate the distillate to be homogeneous except for a

Fraction	Wt., g.	$n_D^{20}$	M. p., °C.
I	2.0	....	..
II	18.0	1.6118	16.7
III	20.5	1.6123	16.8
IV	16.5	1.6118	16.4
V	5.0	1.6124	16.0

small forerun. Fractions II–V combined amount to 60 g. or 30.4%. Another preparation, starting with 100 g. of *p*-dimethylaminobenzaldehyde and carried out in the same manner except that the final distillation was performed at 0.5 mm. through a short column, gave 24.0 g. of product (24%),  $n_D^{20}$  1.6110. Marvel, *et al.*,<sup>5</sup> for a single smaller preparation of *p*-dimethylaminostyrene have reported an index of refraction  $n_D^{20}$  1.6010 but no melting point. *p*-Dimethylaminostyrene prepared as described above was obtained as a water-white liquid turning faintly yellow on standing. It possesses a faint, flowery odor quite unlike dimethylaniline and in the solid condition in the ice-box appears stable for months.

*Anal.* Calcd. for  $C_{10}H_{13}N$ : C, 81.59; H, 8.89; N, 9.52. Found: C, 80.90, 81.05; H, 8.86, 9.02; N, 9.39, 9.39.

In the first rapid distillation of the styrene a very viscous residue always resulted. From analysis, it appears to be almost pure polymer of *p*-dimethylaminostyrene (*Anal.*: C, 82.09, 82.18; H, 8.82, 8.90; N, 9.30, 9.33). It seems likely that higher yields could be obtained by either carrying out the preliminary dehydration in smaller quantities or at a lower pressure.

**$\alpha$ -Vinylthiophene.**—In a 2-liter round-bottom flask equipped with stirrer, dropping funnel and condenser cooled to –78° was placed 100 cc. of anhydrous ether, 205 g. (3.3 moles) of vinyl chloride and 0.52 g. (0.004 mole) of anhydrous cobaltous chloride, maintained at –10 to 0° with external cooling. From the dropping funnel the filtered Grignard reagent from 140 g. (0.86 mole) of  $\alpha$ -bromothiophene<sup>12</sup> in 400 cc. of ether was added over approximately two hours, and the whole allowed to warm to room temperature overnight. The reaction mixture was next hydrolyzed with a mixture of ice and acetic acid, the ether layer separated, washed with sodium carbonate solution, and dried over calcium chloride. Removal of the ether and fractionation through a 16-inch Vigreux column gave 26.7 g. (28.7%)  $\alpha$ -vinylthiophene, b. p. 73° (69 mm.),  $n_D^{25}$  1.5697 (lit. b. p. 62–3 (50 mm.),  $n_D^{25}$  1.5698<sup>6</sup>). A sample, oxidized with alkaline permanganate, gave  $\alpha$ -thienylcarboxylic acid, m. p. 125°.<sup>13</sup> A similar experiment using approximately ten times as much cobaltous chloride gave a yield of 26.6%  $\alpha$ -vinylthiophene,  $n_D^{25}$  1.5696.

The successful preparation of  $\alpha$ -vinylthiophene by this method led us to attempt the analogous preparation of *m*-methoxystyrene from *m*-methoxyphenylmagnesium iodide. However, the product obtained was an oil boiling continuously over the range 31–64° (3.5 mm.) which reduced potassium permanganate in acetone, reacted

(10) Foreman and McElvain, *THIS JOURNAL*, **62**, 1435 (1940).

(11) Sobotka, *Ber.*, **62**, 2191 (1929).

(12) The writers are indebted to Mr. C. J. Pennino for the preparation of the  $\alpha$ -bromothiophene.

(13) Voerman, *Rec. trav. chim.*, **26**, 295 (1907).

rapidly with bromine in carbon tetrachloride with the evolution of hydrogen bromide, and polymerized on standing. Although the chemical properties correspond to a methoxystyrene, the boiling range indicates a mixture of products.

### Summary

1. *p*-Iodostyrene has been prepared in a three step synthesis from *p*-aminoacetophenone.
2. A new synthesis for *p*-nitrostyrene from

$\beta$ -phenylethyl bromide has been developed.

3.  $\alpha$ -Vinylthiophene has been prepared by the reaction of  $\alpha$ -thienylmagnesium bromide with vinyl chloride in the presence of cobaltous chloride.

4. New physical constants are reported for *p*-nitro- and *p*-dimethylaminostyrene.

PASSAIC, NEW JERSEY

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

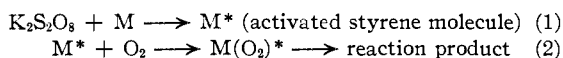
## The Mechanism of Emulsion Polymerizations. III. Oxygen as a Comonomer in the Emulsion Polymerization of Styrene<sup>1</sup>

BY F. A. BOVEY AND I. M. KOLTHOFF

From previous studies,<sup>1a</sup> using the bottle technique, it was found (a) that the induction period caused by oxygen in the emulsion polymerization of styrene is approximately inversely proportional to the concentration of potassium persulfate used as "catalyst," (b) that the induction period is proportional to the amount of oxygen initially present, provided that the initial oxygen pressure is constant, and (c) that the length of the induction period is almost independent of the amount of soap in the charge. From experiments carried out at different initial oxygen pressures, it was further found that for a given amount of oxygen the induction period is somewhat dependent upon the initial oxygen pressure, *i. e.*, that the rate of oxygen disappearance is evidently not quite independent of the oxygen partial pressure in the bottle.

From the fact that the length of the oxygen induction period is nearly independent of the amount of soap in the charge, it was inferred that the main locus of initiation of activated styrene molecules by persulfate is the true water phase and not the soap micelle.

It was postulated that the initiation reaction and the absorption of oxygen were related as shown in (1) and (2)



The first reaction was presumed to be slow, and was regarded as the rate-determining step, whereas the second reaction was presumed to be very rapid. This mechanism requires, however, that the rate of disappearance of oxygen be independent of the oxygen pressure. The apparent failure of the oxygen disappearance to follow exactly a zero order law might be due to the relatively ineffective mixing of the liquid and gas phases under the conditions of these experiments, which

were carried out in 8-oz. bottles rotated end-over-end at about 35 r. p. m. In the previous work the rate of disappearance of oxygen was estimated from the length of the induction period with the assumption that no normal polymerization occurs in the presence of any oxygen in the system. It appeared desirable to make direct measurements of the rate of oxygen disappearance during the induction period in order to establish whether this rate corresponds to a zero order reaction when the system is stirred efficiently. Under the same experimental conditions the relation between the rate of oxygen uptake on the one hand and the concentration of soap and/or persulfate on the other could be determined.

In addition, we have isolated and studied the properties of the reaction product which is formed during the induction period in the presence of oxygen.

### Experimental

#### Materials

**Styrene.**—Dow styrene with a purity of at least 99.5% was used. This material was distilled *in vacuo* just before use, although it may be safely stored for one or two days at 0–10°.

**Water.**—Conductivity water was used throughout.

**Emulsifier.**—Commercial soap (S. F.) flakes supplied by Procter and Gamble were employed. This material is largely composed of the sodium salts of stearic, palmitic and oleic acids, and contains only very small amounts of soaps of polyunsaturated fatty acids. The same lot of this material was used in all this work.

The sodium linoleate employed in Run 1, Fig. 3, was prepared from a sample of linoleic acid supplied by Dr. W. C. Ault of the Eastern Regional Laboratories.

**Potassium Persulfate.**—Merck reagent potassium persulfate, especially purified "for D. D. Van Slyke's Micro-Kjeldahl determination of nitrogen" was found to be satisfactory. It gave the same results as a product twice recrystallized from conductivity water.

**Polymerization Recipe.**—The following recipe, in which the amounts of several of the constituents were varied systematically, was used:

Styrene: 50.0 g. (55.2 ml. at 25°), designated as 100 parts.

Water: 90.0 g., or 180 parts, in separate portions of which the soap and catalyst were dissolved.

Soap: 2.50 g., or 5 parts based on styrene. This quantity of emulsifier will be denoted as "1-X," and other amounts as fractions or multiples thereof.

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government's synthetic rubber program.

(1a) I. M. Kolthoff and W. J. Dale. *THIS JOURNAL*, **69**, 441 (1947).