monochloride vapor to synthesize diiodotyrosine in 38.5% yield. The following method gives 80 to 85% of a product that can more easily be rendered absolutely white than diiodotyrosine iodinated by the method of Oswald.

Five grams of tyrosine was suspended in 20 cc. of acetic acid, and 10 g. of iodine monochloride in 20 cc. of acetic acid added. The tyrosine immediately went into solution. The reaction mixture was warmed to 60° and 80 cc. of water added in three portions, warming the solution to 60° after each addition. The total time of heating was thirty minutes. Sodium bisulfite was added to destroy the excess iodine monochloride, and ammonia to precipitate the diiodotyrosine. One reprecipitation from dilute hydrochloric acid gave an entirely colorless product, decomposing with evolution of iodine at 201° (cor.), heated at 10° per minute.

DEPARTMENT OF CHEMISTRY
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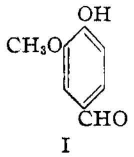
Some Derivatives of Creosol

BY JOHN H. FLETCHER AND D. S. TARBELL

It was recently necessary to prepare 3,4-dimethoxy-5-propenyltoluene (VI) in connection with some other work. It seems worth while to report the observations and new compounds which resulted from the synthetic work.

The starting material was vanillin (I) from which creosol (II) was prepared by a Clemmensen reduction. This reaction has been reported by Kawai and Sugiyama,[1] but neither yields nor experimental details were given. These workers also carried out the synthesis of the allyl ether of creosol (III) and its subsequent rearrangement to 6-allylcreosol (IV); our work checks theirs. Methylation of IV followed by alkali-induced isomerization of the allyl side-chain in diethylene glycol solution produced 3,4-dimethoxy-5-propenyltoluene (VI). If IV was first isomerized and then methylated, VI was obtained but in poorer yield than by the former method. Compound VII, 6-propenylcreosol, is a solid, m. p. 61–62°; all the other derivatives described above are high-boiling liquids.

Two solid derivatives were prepared and analyzed as checks. Oxidation of III gave 2-methoxy-4-methylphenoxyacetic acid (VIII); both V and VI gave 2,3-dimethoxy-5-methylbenzoic acid (IX) when treated with aqueous permanganate.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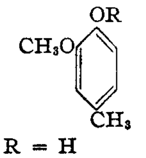
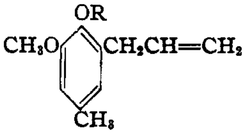
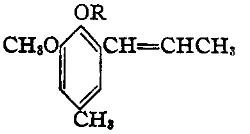
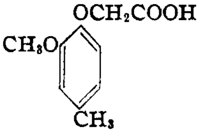
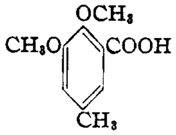

II, R = H
III, R = $CH_2CH=CH_2$


IV, R = H
V, R = CH_3


VI, R = CH_3
VII, R = H


VIII


IX

Experimental[2]

Creosol (II).—The modified procedure of Martin[3] was used with the following amounts: 200 g. of mossy zinc, 150 cc. of water, 350 cc. of concentrated hydrochloric acid, 200 cc. of toluene, and 90 g. of vanillin (Eastman Kodak Company). This mixture was refluxed for twenty-four hours. The yield of creosol was 51.7 g. (63%), b. p. 105–106° (15 mm.), n^{23}_D 1.5355.[4]

Creosol Allyl Ether (III).—To a solution of 50 g. (0.36 mole) of creosol in 180 cc. of acetone was added 90 cc. of water containing 18 g. (0.45 mole) of sodium hydroxide; after mixing well, 54.5 g. (0.45 mole) of allyl bromide was added and the mixture refluxed for one hour. Dilution was made with 500 cc. of water and the solution was extracted with three 90-cc. portions of petroleum ether (b. p. 60–70°). The ether extract was washed twice with 5% alkali, twice with water, and was dried over calcium chloride. The solvent was distilled and the residual oil subjected to vacuum distillation; yield, 55.4 g. (86%), b. p. 128–130° (15 mm.), n^{24}_D 1.5270.

2-Methoxy-4-methylphenoxyacetic Acid (VIII).—A solution of 4.7 g. (0.03 mole) of potassium permanganate in 200 cc. of water was prepared. To this were added 1.3 g. (0.01 mole) of sodium carbonate monohydrate and 1.8 g. (0.01 mole) of creosol allyl ether (III). The mixture was shaken at intervals for fifteen minutes; heat was evolved and a brown solid separated. After standing overnight the mixture was filtered; the filtrate was acidified with hydrochloric acid and evaporated to 50 cc. On cooling, white crystals were obtained; yield, 0.6 g. (31%), m. p. 111–113°. The product was recrystallized from water; m. p. 115–116°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 61.3; H, 6.0.

6-Allylcreosol (IV).—Fifty-five grams of creosol allyl ether (III) was heated in an oil-bath to 210° whereupon gentle boiling set in and the liquid darkened. After five minutes the material was allowed to cool. It was distilled

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[1] Kawai and Sugiyama, *Ber.*, **72B**, 367 (1939).

[2] Analyses by Mr. Robert W. King.

[3] Martin, THIS JOURNAL, **58**, 1438 (1936).

[4] de Vries, *Rec. trav. chim.*, **28**, 283 (1909), gives for creosol n^{25}_D 1.5353.

at diminished pressure giving 46.2 g. (84%) of colorless liquid, b. p. 135–138° (18 mm.), $n^{23}\text{D}$ 1.5344.

An alcoholic solution of the product gave a deep blue-green color with ferric chloride. The **α-naphthylurethan** of 6-allylcreosol was prepared in 70% yield; after one recrystallization from ligroin it melted at 132–132.5°.

Anal. Calcd. for $C_{22}H_{21}O_3N$: C, 76.1; H, 6.1. Found: C, 76.1; H, 6.3.

3,4-Dimethoxy-5-allyltoluene (V).—To 130 cc. of 2 *N* sodium hydroxide solution in a glass-stoppered bottle was added 46.2 g. (0.26 mole) of 6-allylcreosol (IV) and one-third of a portion of 32.8 g. (0.26 mole) of dimethyl sulfate; the mixture was shaken vigorously at intervals for five minutes, after which another third of the dimethyl sulfate was added; the final addition was made after a similar period. An oily layer separated and was extracted with ether. The ether extract was washed twice with water and dried over calcium chloride. After removal of the ether, distillation at diminished pressure gave 43.0 g. (86%) of colorless liquid, b. p. 125–135° (12 mm.), $n^{23}\text{D}$ 1.5240.

2,3-Dimethoxy-5-methylbenzoic Acid (IX).—Two grams of 3,4-dimethoxy-5-allyltoluene was treated with aqueous permanganate as described above in the preparation of 2-methoxy-4-methylphenoxyacetic acid. The product was crystallized from petroleum ether (b. p. 60–70°) containing a little benzene; yield, 0.1 g. of white crystals, m. p. 91.5–92.5°. The product dissolved with effervescence in 5% sodium bicarbonate solution.

This compound was also obtained in 20–30% yield by the oxidation of 3,4-dimethoxy-5-propenyltoluene (VI).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 61.4; H, 6.3.

6-Propenylcreosol (VII).—Ten grams of potassium hydroxide pellets was dissolved in 100 cc. of diethylene glycol by heating to 160° in an oil-bath; to the hot solution was added 17.5 g. (0.1 mole) of 6-allylcreosol (IV). Heating (150–170°) was continued for one hour. When cool, the mixture was poured into 200 cc. of water and acidified with hydrochloric acid. The brown oily layer was extracted with petroleum ether (b. p. 60–70°), the solvent evaporated, and the residue distilled through a Widmer column. The boiling point rose gradually, and no clean-cut fractions appeared; a total of 10.5 g. of liquid, b. p. 86–120° (1 mm.), was collected. The residue from the distillation (3.5 g.) solidified upon cooling, and extraction with petroleum ether gave 1.9 g. of light tan crystals, m. p. 60–62°. The crude material was dissolved in dilute alkali, treated with Norit, and precipitated with dilute hydrochloric acid; the purified product, m. p. 61–62°, was still not white.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.1; H, 8.0.

3,4-Dimethoxy-5-propenyltoluene (VI).—Twenty grams of potassium hydroxide pellets was dissolved in 200 cc. of diethylene glycol by heating and stirring. When the temperature of the solution had reached 165° water began to boil off; after most of this had been removed, 41.0 g. (0.213 mole) of 3,4-dimethoxy-5-allyltoluene (V) was added. For the next twenty minutes the solution was stirred and the temperature maintained at 175–185°. After cooling to 120° the dark red liquid was poured into 400 cc. of cold water, whereupon an oily layer separated. The latter was extracted with petroleum ether (b. p. 60–70°) and the ether solution dried over calcium chloride. After removal of the solvent, distillation at diminished pressure gave 16.1 g. (39%) of colorless liquid, b. p. 109–111° (1 mm.), $n^{24}\text{D}$ 1.5468.

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The Heat of Polymerization of Some Vinyl Compounds

BY G. GOLDFINGER, D. JOSEFOWITZ AND H. MARK

The heat liberated in polymerization reactions is sometimes considerable and may interfere with the easy control of the process. Moreover, knowledge of the magnitude of the heat evolution may also be of use in connection with kinetic and equilibrium considerations. We have, therefore, undertaken the direct measurement of the heat of polymerization of several important substances.

Luschinsky[1] has already determined the heat of polymerization of styrene from measurements of the heats of combustion of the monomer and the polymer. These measurements can indeed be made with great accuracy, but as these heats may well be 100 times larger than the heat of polymerization, the errors in the latter may be magnified 100-fold. We have, therefore, resorted to the methods of adiabatic calorimetry and have utilized for this purpose a 100-cc. cylindrical Dewar flask submerged in a 1-liter oil-bath whose temperature could be raised uniformly by means of an insulated heater and a rapid stirrer. The flask contained 50 cc. of water in which was submerged an hermetically sealed glass tube containing 8 g. of the monomer. The adiabaticity was controlled to within ±0.25° by means of a galvanometer sensitive to 0.05°. The polymerization was initiated by heat. The temperature rise of the liquid in the Dewar flask and hence the heat evolved was measured to 0.25°.

The substances studied were purified by repeated vacuum distillation of commerical materials.

Measurements were made on four or five samples of each substance. The individual molar heats of polymerization (*H*) obtained with styrene were typical and were as follows, expressed in calories

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[1] W. V. Luschinsky, *Z. physik. Chem.*, **A183**, 384 (1938).