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Preparation of Vinylphenols by Catalytic Cracking of Certain Dioxyarylalkanes

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In connection with the development of the chemistry of high-molecular compounds, investigations in the field of the synthesis of new monomers possessing high reactivity are becoming of great importance. One such group of monomers is the vinylphenols, the synthesis of many of which up to the present time has either not been accomplished or has been studied only very slightly. In the scientific literature there are highly contradictory data concerning the possibility and effectiveness of the synthesis of these compounds. Thus, in 1955 Bader ([1]), having investigated previously proposed methods for preparing *o*-vinylphenol by condensation of phenol with ethylene oxide or with ethylene chlorohydrin ([2]), reported that it is impossible to obtain *o*-vinylphenol by these methods. Bader' s conclusions were later confirmed ([3]). Another isomer of vinylphenol, *p*-vinylphenol, was isolated from natural substances and first characterized in work ([5]); however, attempts to synthesize this compound until recently had been unsuccessful. Only in 1958 was *p*-vinylphenol obtained synthetically from phenol via *p*-acetoxyacetophenone ([5]), but the synthesis is very complicated, consists of 5 stages, and has purely preparative significance. The synthesis of other vinylphenols has been studied to an even lesser extent.

In the present work we propose a new method for preparing vinylphenols, consisting in the catalytic cracking of dioxyarylalkanes in the presence of an aluminosilicate catalyst. The work investigated the catalytic cracking of 1,1-(4′,4″-dioxy)-diphenylethane, 1,1-(4′,4″-dioxy-5′,5″-dimethyl)-diphenylethane, and 2,2-(4′,4″-dioxy)-diphenylpropane.

Cracking was carried out in a flow apparatus (Fig. 1). A solution of the dioxy-diphenylalkane in a suitable solvent was fed from graduated cylinder 4, under piston pressure and at a constant rate, into a tee, where it was mixed with water vapors coming from steam superheater 3. The resulting mixture entered reactor 2—a quartz tube filled with quartz packing and catalyst. The temperature inside the catalyst bed was measured with a chromel-alumel thermocouple and a millivoltmeter and was maintained with an accuracy of $\pm 5°$. The cracking products were collected in a receiver cooled by a stream of water. The solution of the cracking prod
were used.

Fig. 1. Cracking apparatus for unsymmetrical diarylethanes. 1 —tube furnace; 2 —quartz reactor; 3 —steam superheater; 4 —feed of raw material; 5 —water feed; 6 —pump; 7 —laboratory autotransformers

Figure 1: Fig. 1. Cracking apparatus for unsymmetrical diarylethanes. 1 —tube furnace; 2 —quartz reactor; 3 —steam superheater; 4 —feed of raw material; 5 —water feed; 6 —pump; 7 —laboratory autotransformers

Cracking of 1,1-(4′,4″-dioxy)-diphenylethane.

$$HO{-}\langle C_6H_4\rangle{-}CH(CH_3){-}\langle C_6H_4\rangle{-}OH \rightarrow \langle C_6H_5\rangle{-}OH + HO{-}\langle C_6H_4\rangle{-}CH{=}CH_2 \quad (1)$$

1,1-(4′,4″-dioxy)-diphenylethane, obtained by alkylation of phenol with acetylene according to the method described by us ([6]), after recrystallization from ben-

the resin was a white powder with m.p. 122.5°, readily soluble in alcohol, ether, acetone, and acetic acid, and poorly soluble in hydrocarbons.

Cracking was carried out using, as solvents for dioxy-diphenylethane, acetone, ethyl ether, phenol, and acetic acid mixed with benzene, over various aluminosilicate catalysts at different space velocities for feeding the dioxy-diphenylethane solutions. The best results were achieved when cracking in the presence of an aluminosilicate catalyst containing 50% Al_2O_3 and using ether or acetic acid mixed with benzene as solvents for dioxy-diphenylethane.

Fig. 1. Cracking apparatus for unsymmetrical diarylethanes. **1** —tube furnace; **2** —quartz reactor; **3** —steam superheater; **4** —feed of raw material; **5** —water feed; **6** —pump; **7** —laboratory autotransformers.

During distillation of the cracking catalysts, in almost all cases three fractions were obtained: fraction I —phenol; II —phenol mixed with ethylphenol and *p*-vinylphenol; III —*p*-vinylphenol with a small admixture of ethylphenol. If cracking proceeded selectively and the concentration of *p*-vinylphenol in the cracking products was high, then *p*-vinylphenol usually crystallized from fraction III in the form of pale greenish leaflets.

With an increase in the space velocity of feeding the dioxy-diphenylethane solution, the yield of fraction III and the conversion of dioxy-diphenylethane into light products increased. Below is a description of the most effective experiments on the cracking of dioxy-diphenylethane.

A solution of 36 g of dioxy-diphenylethane in 50 ml of ether and 70 ml of benzene, at a rate of 1 ml/min (space velocity 2.4 hr^{-1}), and water at a rate of 4 ml/min were fed into a reactor containing 25 ml of aluminosilicate catalyst (~50% Al_2O_3). The cracking temperature was 550°. The molar dilution of dioxy-diphenylethane by vapors of water and solvents (the ratio of the number of moles

of water and solvents to the number of moles of dioxy-diphenylethane) was ~200. The contact time was 0.03 sec. As a result of vacuum distillation of the cracking products without access of air in a flask with a 30-cm-high dephlegmator, 11 g of fraction 69-74°/3 mm were obtained (n_D^{20} 1.5498; mol. wt. 98; OH 18.4%), 2.5 g of fraction 74-90°/3 mm (n_D^{20} 1.5632; mol. wt. 118; OH 14.2%), and 6.2 g (43.3% of theoretical) of fraction 90-95°/3 mm (n_D^{20} 1.5789). The residue in the flask (9.5 g) was unconverted dioxy-diphenylethane. Fraction 90-95°/3 mm crystallized shortly after distillation. After recrystallization and drying in a vacuum desiccator, the crystals were white, shiny leaflets with m.p. 64-65°. After several recrystallizations from benzene, a constant melting point of 71.5-72° was reached. Literature data for *p*-vinylphenol: m.p. 73.5° ([4]). Crude crystals of *p*-vinylphenol readily dis-

dissolved in benzene, alcohol, and ether; in water—poorly; however, upon brief standing in a vacuum desiccator the solubility decreased owing to polymerization. Crystals of *p*-vinylphenol dissolved in alkali, the solution turning brown; upon addition of *p*-vinylphenol to concentrated sulfuric acid, a bright red coloration was observed. An aqueous solution of *p*-vinylphenol, upon addition of a ferric chloride solution, became blue-green in color.

On standing in air, *p*-vinylphenol rapidly polymerizes in the dark to an insoluble white resin. However, in an atmosphere of inert gas it can be preserved for 50 hours or more. For identification of *p*-vinylphenol its allyl ether was obtained by the method of (5). Constants of the allyl ether of *p*-vinylphenol obtained: b.p. 81°/4 mm; n_D^{20} 1.5562. (Literature data (5): b.p. 82–83°/4 mm; n_D^{20} 1.5578.) From the cracking products, in addition to *p*-vinylphenol, we isolated and identified phenol and ethylphenol in the fractions 69–74°/3 mm and 74–90°/3 mm, and phenetole in small quantity in the fraction 69–74°/3 mm. The formation of phenetole indicates that during the cracking process part of the diethyl ether reacts with phenol. When cracking dioxy-diphenylethane in a solution of acetic acid and benzene, no ether compounds were found among the cracking products. The cracking was carried out under conditions approximately analogous to those used for cracking in the benzene–ether solvent.

A solution of 30 g of dioxydiphenylethane in 15 ml of acetic acid and 20 ml of benzene, at a rate of 1 ml/min, and water, at a rate of 10 ml/min, entered a reactor containing 25 ml of aluminosilicate catalyst (50% Al_2O_3). The molar dilution and contact time were the same as in the preceding experiment. Cracking temperature 550°. As a result of distillation of the catalyst, the following were obtained: 3 g of phenol as a fraction 68–74°/4 mm, 1.2 g of intermediate fraction 74–88°/4 mm, and 5.2 g of *p*-vinylphenol as a fraction 88–102°/4 mm (yield 35.4% of theoretical).

Cracking of 1,1-(4′,4″-dioxy-5′,5″-dimethyl)-diphenylethane.

$$\mathrm{HO{-}\underset{CH_3}{C_6H_3}{-}CH(CH_3){-}\underset{CH_3}{C_6H_3}{-}OH \rightarrow \underset{CH_3}{C_6H_4}{-}OH + HO{-}\underset{CH_3}{C_6H_3}{-}CH{=}CH_2} \quad (2)$$

1,1-(4′,4″-dioxy-5,5″-dimethyl)-diphenylethane (ethylidene-di-*o*-cresol) was obtained by us by alkylation of *o*-cresol with acetylene in alcoholic solution (7). It is a white crystalline substance: m.p. 89.5°; b.p. 206–210°/3 mm.

A solution of 30 g of ethylidene-di-*o*-cresol in 20 ml of acetic acid and 90 ml of benzene was passed into a reactor containing 25 ml of aluminosilicate catalyst (~50% Al_2O_3), at a rate of 1 ml/min. Water was fed at a rate of 4 ml/min. Cracking temperature 550°. After distilling off the benzene, the catalyst was distilled under vacuum in a Claisen flask in the presence of hydroquinone. As a result of the distillation, the following fractions were obtained: fraction 78–87°/4 mm, 6.8 g; fraction 87–98°/4 mm, 0.4 g; fraction 98–110°/4 mm, 9.3 g. The residue in the distillation flask (10.4 g) consisted mainly of unchanged ethylidene-di-*o*-cresol. Fraction 78–87°/4 mm—*o*-cresol: molecular weight 110; n_D^{20} 1.5483; OH 14.0% (literature data: n_D^{20} 1.5453; molecular weight 108; OH 15.7%). The intermediate fraction 87–98°/4 mm is apparently a mixture of *o*-cresol, 4-ethyl-*o*-cresol, and 4-vinyl-*o*-cresol: molecular weight 136; n_D^{20} 1.5690; OH 13.8%. Fraction 98–110°/4 mm was 4-vinyl-*o*-cresol, a white crystalline substance with m.p. 73–74°, soluble in common solvents and readily converting on standing in air into a sticky resin, upon treatment of which with benzene a polymer of 4-vinyl-*o*-cresol precipitates as a white insoluble powder.

Cracking of 2,2-(4′,4″-dioxy)-diphenylpropane

$$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH \rightarrow HO{-}C_6H_5 + HO{-}C_6H_4{-}C(CH_3){=}CH_2. \quad (3)$$

For the cracking, 2,2-(4′,4″-dioxy)-diphenylpropane (diphenylolpropane) was taken, purified by distillation and recrystallization of a technical product obtained from the GIPI-4 Institute: b.p. 225–230°/8 mm, m.p. 157–159°.

A solution of 30 g of diphenylolpropane in 15 ml of acetone and 100 ml of benzene was subjected to cracking under conditions analogous to those described above. The catalyzate (25 g) was distilled under vacuum into fractions: fraction 68–80°/4 mm, 4.8 g; fraction 80–98°/4 mm, 6.2 g; and fraction 98–108°/4 mm, 8.1 g. The residue in the flask was 5.3 g. The fraction 98–108°/4 mm crystallized into a yellow-green crystalline mass. After recrystallization, white scaly crystals with m.p. 80.5° were obtained. Literature data for *p*-isopropenylphenol [5]: b.p. 125°/20 mm, m.p. 83–84°. On standing in air, the crystals of *p*-isopropenylphenol rapidly turned into a reddish resin, sparingly soluble in ordinary organic solvents.

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Note: Figure translations are in progress. See original paper for figures.