
PREPARATION AND PROPERTIES OF 2-VINYLFURAN

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2-Vinylfuran has been prepared by the dehydration of 1-(2-furyl) ethanol-1 (Paul 1935) and by the decarboxylation of β-(2-furyl)acrylic acid (Liebermann 1894; Moureu, Dufraisse, and Johnson 1927; Galimberti 1940; Koton, Votinova, and Florinskii 1941; Paul and Tchelitcheff 1947). The latter route has usually been preferred because of the ease of preparing the starting material. Galimberti reported obtaining yields of 80 percent and Paul and Tchelitcheff 71 percent by using quinoline as solvent and cupric sulfate as catalyst in the decarboxylation.

Very few reactions of 2-vinylfuran have been described. Moureu, Dufraisse, and Johnson added bromine to form the exceedingly unstable dibromide, which was used to make the monobromo-olefin and thence 2-ethinylfuran (furylacteylene). Mild oxidation of 2-vinylfuran with potassium ferricyanide gives traces of furoic acid (Brown 1937), and maleic anhydride combines with it in a Diels-Alder reaction (Paul 1939). All other references (Imperial Chemical Industries 1929; Sorenson 1933; I. G. Farbenindustrie 1938a, 1938b, 1939; Mighton 1945, 1946) are to polymerization of 2-vinylfuran for the manufacture of plastic materials, which are thermosetting rather than thermoplastic like the ones made from styrene.

In our hands the quinoline-copper method of preparation did not give yields even approaching that claimed by Galimberti. We have therefore tested some of the variables in the procedure in search of the optimum. The method used was essentially that of Walling and Wolfstirn (1947) for decarboxylations; dry distillation of the acid with soda lime or copper carbonate, or of silver β-(2-furyl)acrylate, gave only traces of 2-vinylfuran.

Variations in size of run and of volume of solvent used were apparently without effect on yield, but the nature of the solvent is important. Only traces of 2-vinylfuran were produced from the acid and copper carbonate catalyst heated in water, ethylene glycol, or aniline; and none at all in diethanolamine and triethanolamine. Quinoline alone gave measurable though small yields.

Quinoline was used in all experiments involving comparisons of catalysts: the crude product, boiling at 95°-105° and stabilized with hydroquinone, was the basis of yield calculation. From ten to fifty grams of acid were decarboxylated at a time. The ratios of catalyst to acid (expressed as percentages), catalysts, and yields of 2-vinylfuran in the several runs are respectively as follows: 10—$CuSO_4$ 19, 33; 9—$CuCl_2$ 24; 3—CuO 15; 4—$CuCO_3$ 17, 27, 38; 8—$CuCO_3$ 21, 27, 47; 10—$CuCO_3$ 24; 10—Cu powder traces; 3—$CuCO_3$ + $ZnCO_3$ 15; 6—$CuCO_3$ + $ZnCO_3$ 40; 10 or 100—$ZnCO_3$ traces; 10—$CoCO_3$ 30; 0.1 Raney Ni traces; 3—Raney Ni 41; 4—PbO 28; 10—PbO 32; 15—PbO 24; 20—PbO 28; 20—Ag_2CO_3 31, 37. It is obvious that any one of the several heavy metals tried is as effective as another.

We observed reduction of silver and copper salts to metal during decarboxylation, but unlike Walling and Wolfstirn we did not find ready-made copper powder effective. The erratic nature of the yields indicates that some factor other than type and amount of catalyst—undoubtedly polymerization—is the limiting factor. Since 2-vinylfuran, unlike styrene, exhibits diene behavior in the Diels-Alder reaction (Paul 1939), it can polymerize in several ways.

Some effort was made to establish extent of the decarboxylation by sweeping out the carbon dioxide by means of hydrogen, scrubbing out quinoline vapors with acid, and absorbing and weighing the carbon dioxide. The apparatus and technique were not fully developed, but successive runs gave the following percentages of the theoretical amount of carbon dioxide: 75, 99, 79, 102, 47, and 56. Evidently the low yields of olefin are due to subsequent reaction, not to failure of formation.

All physical properties of 2-vinylfuran were measured on freshly distilled samples because of the tendency of stored ones to alter by polymerization. The density was found pyknometrically to be 0.950 g/ml at 15°, 0.945 at 20°, 0.941 at 25°, and 0.937 at 30°. Literature values are 0.9445 at 18 (Moureu, Dufraisse, and Johnson 1927; Landrieu, Baylocq, and Johnson 1929), 0.9316 at 25° (Hughes and Johnson 1931), and 0.936 at 13° (Galimberti 1940). Surface tension by means of the Traube stalagmometer proved to be 29.8 dynes/cm at 26°; from this the parachor may be calculated to be 233.6. The value calculated from atomic parachors is appreciably lower—227.6. Refractive index at 26° is 1.4985; whence molar refraction is 29.29—again higher than the one calculated from atomic constants, 27.95. The molar refraction from Paul's (1935) value of 1.4817 at 13°, obtained on material prepared by a different method and considered impure by him, is 28.61; that calculated from the value 1.4981 at 25° by Hughes and Johnson is 29.58. The optical exaltation and the similar deviation from the calculated parachor are not unexpected in a compound with conjugated double bonds. The viscosity measured with an Ostwald pipette calibrated with water was found to be 5.35 millipoises at 26°.

An attempt to produce furoylformic acid by oxidizing 2-vinylfuran with potassium permanganate by the method of Hurd, McNamee, and Green (1939) gave only a trace of furoic acid and none of the desired product. Similarly an experiment designed to produce 2-vinylfuran oxide via oxidation of 2-vinylfuran with monoperphthalic acid (the latter made according to directions of Böhme (1940) and the oxidation done by the procedure of Hibbert and Burt (1928) for styrene) gave no definite product.

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