

PREPARATION AND PROPERTIES

OF

2-VINYLFURAN

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PREPARATION AND PROPERTIES
OF
2-VINYLFURAN

By

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INTRODUCTION

The structural similarity of 2-vinylfuran to styrene, consisting in the attachment of a vinyl group to a cyclic nucleus, suggested an interesting study: whether the reactions applicable to the vinyl group of styrene are possible with 2-vinylfuran. Besides, not very many compounds of 2-vinylfuran have been prepared and studied. It was the original purpose of this work to attempt such a study; however, 2-vinylfuran had to be first prepared and since the results were inconsistent with those in the literature, the problem naturally turned toward this preparation.

The work on the preparation and reactivity of this compound has just barely been touched. The substance is interesting not only as a source of new compounds for the enrichment of the literature of organic chemistry, but for its commercial possibilities as a source of plastic.

HISTORICAL

Marckwald (1) first prepared 2-vinylfuran (also called 2-furyl-ethylene) by the slow distillation of β -2-furylacrylic acid, which decomposes near its sublimation point yielding 2-vinylfuran and carbon dioxide. Liebermann (2) confirmed the decarboxylation reaction but noted that a slightly higher temperature was required than that reported by Marckwald. Liebermann obtained yields of 40% of the theoretical in his work. Moureu, Dufraisse and Johnson (3) also obtained 40% yields of 2-vinylfuran following the procedure of Marckwald. Koton, Votnova and Florinskii (4) reported yields of 42% and observed that the resin-like residue in the reaction vessel had one characteristic of a compound, i.e., a melting point. This olefin has also been prepared by the dehydration of 1-(2-furyl)-1-ethanol by Paul (5). The alcohol was passed over alumina in a nitrogen atmosphere at temperature of 390° to 400°C. Side reactions involving the formation of 2-ethylfuran occurred, lowering the yields. None of the decarboxylations previously mentioned for the preparation of 2-vinylfuran employed a solvent or a catalyst; reaction was carried out by merely heating the dry acid above its melting point. Galimberti (6), however, employed a solvent (quinoline) and a "catalyst" (anhydrous copper sulphate). The yields reported were much higher than previous authors mentioned obtained, with Galimberti getting as high as 80% of the theoretical.

The literature contains a few references involving the preparation of derivatives of 2-vinylfuran from the parent compound. Moureu, Dufraisse, and Johnson (3) made the dibromo derivative by the addition of bromine across the double bond in the vinyl side chain. However,

the compound was not purified because of its extreme instability. The monobromo derivative was made directly from the dibromo compound by the removal of one mole of hydrogen bromide. The position of the remaining bromine atom was in doubt. Further removal of hydrogen bromide formed furylacetylene (3). Several substituted derivatives of 2-vinylfuran have been made; indeed, β -nitro- α -(α -furyl) ethylene (7) was known before the parent compound was prepared. Kasiwagi (8) obtained this and other substituted compounds by a condensation of some nitro-paraffins or polynitrotoluenes with furfural. Several other compounds that might be considered derivatives of 2-vinylfuran should be mentioned here. Schaarschmidt, Georgeacopol and Herzenberg (9) obtained β -isopropyl- α -(α -furyl) ethylene by decarboxylation of the acid prepared by a Perkin synthesis involving the reactants furfural, isovaleric anhydride and sodium isovalerate. Toennies and Staub (10) similarly used isobutyric anhydride and potassium isobutyrate and obtained the olefin β, β -dimethyl- α -(α -furyl) ethylene from the subsequent decarboxylation of the acid. Hale, McNally and Pater (11) reported the preparation of α, α -diethyl- β -(α -furyl)- β -methylethylene.

Since the vinyl side chain in the styrene molecule is attacked by oxidizing agents, one would expect an analogous reaction to occur with 2-vinylfuran. Mild oxidation of 2-vinylfuran with potassium ferricyanide thus gave traces of furoic acid (12).

Paul (13) has reported the 1,4-addition of maleic anhydride to 2-vinylfuran in 80% yields. This ease of the Diels-Alder reaction, not exhibited by the analog styrene, indicates conjugation of the side-chain double bond with one of those in the ring.

The literature contains a few references to patents covering the polymerization of 2-vinylfuran (14, 15, 16, 17, 18, 19). A plastic

is obtained whose formation is accelerated by oxygen-bearing catalysts. Studies by Moureu, Dufraisse, and Johnson (20) have shown that atmospheric oxygen is also an accelerator in this reaction. The thermosetting nature of this plastic contrasts sharply with the thermoplastic behavior of polystyrene.

Various physical aspects of 2-vinylfuran such as its thermochemistry (21), its Raman spectrum (22), and other physical constants (23) have been studied.

Experimental

Preparation of 2-vinylfuran

A. Decarboxylation of 2-vinylfuran with variation of catalyst.

The method for preparing 2-vinylfuran proposed by Galimberti (6), i.e., the decarboxylation of furylacrylic acid using coal tar bases as solvents and a catalyst such as anhydrous copper sulfate, was selected. This decision was based on two factors: the relatively high yields claimed by Galimberti and the general agreement in recent literature that decarboxylations proceed more smoothly in quinoline.

Principal Reagents and Equipment. The furylacrylic acid, m.p. 138-139°, was prepared according to the directions given by Johnson (24). No attempt was made to obtain an absolutely pure sample; the melting point was the only criterion of purity. The quinoline used as a solvent was an Eastman Kodak product. It was purified after each decarboxylation by distillation unless otherwise stated. All the decarboxylations were carried out in a 500 ml. distilling flask, heated with an open flame unless otherwise stated. The product was collected in an ice-cooled test tube which served as condenser and receiver.

Procedure. Fifteen grams of furylacrylic acid in 45-50 ml. of quinoline was decarboxylated in the presence of various catalysts, the quantities of which ranged from one-hundredth mole to one mole per mole of the acid. The reaction mixture was slowly heated to the boiling point of the quinoline and a fraction was collected within this range. The quinoline was then distilled over and ready for the next decarboxylation. The fraction containing the 2-vinylfuran was washed with water, dried over anhydrous calcium chloride

and then redistilled through a 3-ball Snyder column; the product which boiled from about 95 to 105° C. was collected. Hydroquinone was used in all the purified 2-vinylfuran to inhibit oxidation and polymerization (20). This procedure was used throughout the following experiments excepting for such deviation as can be noted on the data sheet (Table I).

Observation. Throughout the experiments in which the variation of catalyst was studied a metallic deposit was noted in the reaction vessel after the run was completed. The deposition of the metal always preceded the evolution of 2-vinylfuran, as evidenced by the change in color, e.g., of the green of copper salts to the reddish brown of copper.

The residue of one of the runs was extracted with 5% aqueous potassium hydroxide. The alkaline extract acidified with hydrochloric acid gave no precipitate such as would be noted if any free furylacrylic acid were present. The thick gummy material remaining in the distillation flask was slightly soluble in warm benzene or acetone.

B. Decarboxylation of 2-vinylfuran with variation of solvent.

Other methods of decarboxylation, such as the use of steam in preparing benzene from sodium benzoate (25), of primary amines in the decarboxylation of phenylglyoxylic acid and benzoic acid (26), and of soda lime in the preparation of benzene from phthalic acid (27), suggested the experiments tabulated in Table II.

Since no decarboxylation of an isolated salt of furylacrylic acid had been tried, silver furylacrylate was made and tested, the silver being chosen because of the smooth performance of silver carbonate as a catalyst.

TABLE I

Run No.	Wt. of furyl-acrylic acid, g.	Kind of catalyst	Wt. of catalyst, g.	Vol. of quinoline, ml.	Technique of run	B.p. of product, °C.	Yield, % theo.
1	15	CuSO ₄ (anhyd.)	1.6	50	Distillation (a)	95-99°	19
2	10	CuSO ₄	1	50	Flushing (b)	---	33
3	15	CuCl ₂	1.3	50	Distillation	98-108°	24
4	15	CuO	0.4	50	Fractionation (c)	99-108°	15
5	36	CuCO ₃	?	146	Distillation	99-108°	21
6	25	CuCO ₃	2	210	Fractionation	99-109°	47
7	50	CuCO ₃	2	250	Distillation	95-105°	38
8	50	CuCO ₃	2	250	Distillation	95-105°	27
9	10	CuCO ₃	1	50	Distillation	95-105°	24
10	20	CuCO ₃	1.7	50	Flushing (c)	95-105°	26.5
11	19	CuCO ₃	1	50	Distillation	95-100°	17
12	15	CuCO ₃ ZnCO ₃	1	50	Distillation	95-105°	40
13	30	CuCO ₃ ZnCO ₃	1	Moistened	Distillation	85-150°	15
14	45	ZnCO ₃	45.5	100	Distillation	---	Traces
15	50	ZnCO ₃	5	100	Distillation	---	Traces
16	7.5	CoCO ₃	--	50	Distillation	---	30
17	15	Raney Ni	0.01	25	Distillation	---	Traces

TABLE I
(Continued)

Run No.	Wt. of furyl-acrylic acid, g.	Kind of catalyst	Wt. of catalyst, g.	Vol. of quinoline, ml.	Technique of run	B.p. of product, °C.	Yield, % theo.
18	15	Raney Ni	0.5	25	Distillation	---	41
19	15	PbO	2.2	50	Fractionation	98-105°	65
20	15	PbO	2.2	50	Distillation	98-105°	24
21	15	PbO	1.5	50	Distillation	---	32
22	50	PbO	2	5 (moisten)	Distillation	95-99°	28
23	50	PbO	10	275	Distillation	95-110°	28
24	10	Cu (powder)	1	50	Distillation	---	Traces
25	10	Ag ₂ CO ₃	1.9	50	Flushing	95-105°	37
26	10	Ag ₂ CO ₃	2	50	Distillation	97-99°	31

- (a) In these runs the slow heating of the mixture in quinoline was done in a distilling flask, and little refluxing occurred.
- (b) In these runs natural gas was bubbled through the reaction mixture, which was heated on a hot plate. The gas served to flush the 2-vinylfuran out of the reaction mixture.
- (c) In these runs a 3-ball Snyder column was used to return excess quinoline to the reaction vessel. A better crude product was thus obtained.

Principal Reagents, Equipment and Procedure. The equipment and methods employed in the study of various solvents were in general the same as used when the catalyst was studied. Data are in Table II.

Measurement of Carbon Dioxide from the
Decarboxylation of Furylacrylic Acid

Since 2-vinylfuran can easily polymerize under the conditions of the reaction and probably does, an estimate of the extent of decarboxylation can not be arrived at from the yield of this olefin. The measurement of the other product of the decarboxylation, i.e., carbon dioxide, should afford a better means of establishing the extent of the reaction.

Principal Reagents and Equipment.

The original apparatus consisted of the following pieces in the order named:

- a. A tank filled with hydrogen.
- b. A dehydrite-filled absorption tower.
- c. A soda lime-filled absorption tower. (Both of these towers were used to purify the hydrogen gas.)
- d. A trap to catch any backflow from the reaction vessel.
- e. A reaction vessel consisting of a 250 ml. flask connected by means of a 24/40 joint to a short air reflux condenser ending in a side arm leading into an ice-cooled 250 ml. distillation flask as receiver.
- f. A hot plate as heating unit for the reaction flask.
- g. A gas scrubbing tower filled with 50% sulfuric acid.
- h. A U-tube filled with Dehydrite to dry the gases before they are passed into the CO₂ absorption bulb.

TABLE II

Run No.	Wt. of furylacrylic acid, g.	Kind of catalyst	Wt. of catalyst, g.	Kind of Solvent	Vol. of solvent, ml.	Technique of run	B.p. of product, °C.	Yield, % theo.
1	30	CuCO ₃	2	None		Distillation		Traces
2	50	CuCO ₃	50	None		Distillation		None
3	15	CuCO ₃ ZnCO ₃	1	Aniline	50	Distillation		Traces
4	15	CuCO ₃	1	Water	25	Distillation		Traces
5	5	CuCO ₃	2	Ethylene Glycol	100	Distillation		Traces
6	10	CuCO ₃	1	Diethanol-amine	35	Distillation		None
7	10	CuCO ₃	1	Triethanol-amine	30	Distillation		None
8	10	None		Diethanol-amine	50	Fractionation		Traces
9	10	None		Amine	40	Distillation		Traces
10	2	Soda lime	2	None		Distillation		None
11	59 (of silver salt) (b)			Quinoline	50	Distillation	97-105°	26
12	59 (of silver salt) (b)			Water	Moisten	Distillation		None

Remarks: (a) In the experiments where traces of 2-vinylfuran were detected, a metallic deposit was noticed on the walls of the reaction flask, but not to the extent caused by the decarboxylation of silver furylacrylate.

(b) Silver salt of furylacrylic acid. Furylacrylic acid was dissolved in dilute ammonium hydroxide and the excess ammonia boiled off, so that the solution was neutral to litmus. Silver nitrate solution was added until a slight excess produced no more precipitation. The salt was filtered off, washed three times with cold water and then allowed to dry in the dark.

- i. This absorption bulb filled with alternate layers of Dehydrite and Ascarite.

The apparatus as described proved satisfactory for blank runs involving the flushing of hydrogen gas through the train. However, a blank run using quinoline under the condition of the decarboxylation, i.e., heated, was complicated by a frothing in the H_2SO_4 scrubbing tower. Another H_2SO_4 scrubbing tower inserted in series in the line gave no better results. As soon as H_2SO_4 was depleted in the first tower, presumably by reaction with quinoline, the second tower commenced to froth. Layers of capryl alcohol placed in the H_2SO_4 towers cut the frothing appreciably but vapors of the alcohol were carried into the drying U-tube and CO_2 absorption bulb.

Several additional modifications were then made in the scrubbing system to remedy the frothing and the carry-over of capryl alcohol. The pieces described below were substituted in the train:

- (e) To retain quinoline better, the side arm leading from the air condenser was fitted with a water jacket, and the vertical exit tube from the receiver was similarly jacketed.
- (g) A scrubbing tower containing 20% H_2SO_4 covered with a layer of mineral oil as a defrothing agent.
- (g₁) A scrubbing tower containing 50% H_2SO_4 covered with a layer of mineral oil as a defrothing agent.
- (g₂) A scrubbing tower containing mineral oil only.

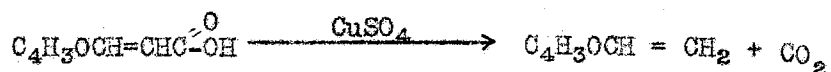
Procedure.

To test the hydrogen purification train, hydrogen gas was flushed through the whole assembly for one-half hour. This also displaced air from the absorption bulb prior to weighing. A one-hour and two-hour flushing of hydrogen through the apparatus gave a negligible

weight increase in the carbon dioxide absorption bulb. This showed that the hydrogen was fairly pure.

A one-hour flushing under the conditions of the reaction, i.e., through the hot solvent quinoline containing no furylacrylic acid or metal catalyst, constituted a blank determination of the apparatus and solvent. For an actual run, approximately 0.01 mole of acid and .001 mole of catalyst (anhydrous copper sulfate) were weighed out and put in the reaction flask with about 25 ml. of quinoline. The reaction was timed from this moment. Hydrogen gas was flushed through the reaction mixture which was heated by the hot plate. At the end of one hour, the carbon dioxide absorption bulb was removed from the train, allowed to come to room temperature in the balance case (about one-half hour), and then weighed.

The method of calculation employed to determine the per cent decarboxylation is described best by an example:



M. W.	138.12		94.11	44.01
G.	1.5692	0.1596		0.5
Moles	0.011	0.0011		0.011

Calculation for sample No. 4 (see attached data sheet):

Wt. sample	=	1.5632 g.
Wt. catalyst	=	0.1555 g.
Wt. CO ₂ obs.	=	0.4279 g.

TABLE III

Run No.	Sample Wt., g.	Length of run, hours	Catalyst wt., g.	Blank runs, wt. gain, g.	Wt. CO ₂ obs., g. (uncorr.)	Wt. acid- S CO ₂ wt.	% Decarboxy- lation
1	1.7715	1	0.3034	0.00239 0.00239	0.4203	1.3344	75
2	1.5773	2	0.2535	0.0020 0.0026	0.4935	1.5681	99
3	1.5585	0.75	0.3017	0.0039	0.2105	0.6956	42
4	1.5632	1	0.1555	0.0353 0.0425	0.4279	1.2418	79
5	1.8163		0.1885		0.0806		
6	1.5100	1	0.6159	0.0015	0.4825	1.5355	102
7	1.5379	1	0.1754	0.0001 0.0002	0.2277	0.7266	47
8	1.4924	1	0.1682	0.0002	0.3087	0.9849	66

Remarks:

- (a) Runs No. 1 and No. 2 employed capryl alcohol as the defrothing agent.
- (b) Run No. 3 was stopped short because of excessive frothing.
- (c) Run No. 5 was stopped because apparatus became plugged up.

Av. wt. blank = 0.0389 g.

Corr wt. CO₂ = 0.3890 g.

Wt. acid \rightleftharpoons CO₂ obs. = 1.5692/0.5 x 0.389 = 1.228 g.

% decarboxylation = 1.228/1.56 x 100 = 78.3

All pertinent data for each run are recorded on the data sheet (Table III).

Properties of 2-Vinylfuran

A. Physical Properties

Density:

A small weighing bottle having a ground glass stopper was constructed and then calibrated. The weight of the distilled water contained at 25° C. was 2.5814 g. This corrected to vacuo, by means of the following relationship,

$$M = M_{\text{obs}} + M_{\text{obs}} \left(\frac{d_{\text{air}}}{d_{\text{water}}} - \frac{d_{\text{air}}}{d_{\text{wts.}}} \right)$$

gave 2.5841 g. The volume of the small bottle at 25° C. was thence 2.5841/0.99707 = 2.591 ml. A change in temperature within the limits of the determination had no effect on the calculated volume.

The density of freshly distilled 2-vinylfuran, b.p. 97-99° C., was determined at 15°, 20°, 25°, and 30° C. The precision of reading the meniscus of the 2-vinylfuran sample was at the most \pm 0.002 g.

All pertinent data are assembled in the following table:

Table IV

Temp., °C.	Wt. of 2-vinylfuran, g.	Av. wt. and precision, g.	Density, calc., g/ml.	Density (vacuo), g/ml.
	2.4638			
15	2.4625	2.4644		
	2.4622	\pm 0.0013	0.9505	0.9515
	2.4651			

Table IV (Continued)

Temp., °C.	Wt. of 2-vinylfuran, g.	Av. wt. and precision, g.	Density, calc., g/ml.	Density (vacuo), g/ml.
20	2.4468	2.4479	0.9440	0.9450
	2.4446			
	2.4492			
	2.4509			
25	2.4403*	2.4354	0.9415	0.9425
	2.4367			
	2.4345			
	2.4350			

*Omit because the deviation from the mean of the others is greater than four times the average deviation.

30	2.4224	2.4267 ±0.0004	0.9365	0.9376
	2.4214			
	2.4265			

The average value for $\Delta d / \Delta t$ is 9×10^{-4} g/ml/°C. The correction of the weights of 2-vinylfuran involved the following mathematics:

Notation

C_w	Correct mass
W	Observed mass
d_d	Density of air taken as 0.0012 g/ml.
d_s	Density of 2-vinylfuran
d_{wt}	Density of the brass weight taken as 8.4 g/ml.
V_c	Volume of weighing bottle (corrected)

Derivation

$$C_w = W \left(1 + \frac{d_a}{d_s} - \frac{d_a}{d_{wt}} \right); \quad C_w = d_s \cdot V_c$$

$$d_s V_c = W \left(1 + \frac{d_a}{d_s} - \frac{d_a}{d_{wt}} \right)$$

$$d_s^2 - \frac{W}{V_c} \left(1 - \frac{d_a}{d_{wt}} \right) d_s - \frac{W}{V_c} d_a = 0$$

$$d_s = \frac{1}{2} \frac{W}{V_c} \left(1 - \frac{d_a}{d_{wt}}\right) + \frac{1}{2} \sqrt{\left[\frac{W}{V_c} \left(1 - \frac{d_a}{d_{wt}}\right)\right]^2 + 4 \frac{W}{V_c} d_a}$$

Surface Tension:

The surface tension of 2-vinylfuran was determined at 26°C. in an air bath by means of a Traube stalagnometer. The instrument was calibrated with distilled water. The average volume delivered between calibration marks for water was 2.53 ml., which was found equivalent to 21.73 drops. An equal volume of 2-vinylfuran gave an average number of 49.66 drops on three trials. The surface tension of water was taken as 72.0 dynes/cm. The following relationship was used in the calculation:

$$\gamma = \frac{\gamma_0 N_0}{d_0} \cdot \frac{d}{N}$$

$$\gamma_0 = 72.0 \text{ dynes/cm.}$$

$$N = 49.66 \text{ drops}$$

$$N_0 = 21.73 \text{ drops}$$

$$d = 0.9425 \text{ g/ml.}$$

$$d_0 = 0.99707 \text{ g/ml.}$$

$$\gamma = 29.78 \text{ dynes/cm.}$$

Parachor:

The parachor was calculated from the data already observed in the previous experiment on surface tension.

$$[P] = \frac{M}{d} \cdot (\gamma)^{1/4}$$

$$\gamma = 29.8 \text{ dynes/cm.}$$

$$M = 94.11$$

$$d = 0.9425 \text{ g/ml.}$$

$$[P] = 233.6$$

The parachor calculated from Mumford and Phillips values for atomic parachors was 227.6.

Refractive Index and Molecular Refraction:

The refractive index, which was determined at 26° C. by use of an Abbe refractometer, was 1.4985. The molecular refraction was calculated from the Lorentz-Lorenz equation.

$$R = \frac{(N^2 - 1) \cdot M}{(N^2 + 2) \cdot d}$$

M = 94.11
 d = 0.9425 g/ml.
 N = 1.4985
 R = 29.29

The molecular refraction calculated from literature values is 27.95.

Viscosity:

The viscosity was determined at 25° C. by use of an Ostwald pipette in a constant-temperature bath. The pipette was calibrated with distilled water, which gave an average flow time between calibration marks of 91.18 seconds. The value of the viscosity taken for water was 8.95 millipoises. An equal volume of 2-vinylfuran gave an average flow time of 57.56 seconds.

The viscosity was calculated from the following relationship:

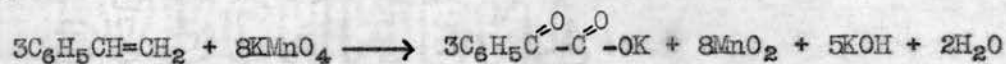
$$N = \frac{d \cdot t}{d_1 \cdot t_1} N_1$$

d = 0.9425 g/ml.
 d₁ = 0.99707 g/ml.
 t = 57.56 seconds
 t₁ = 91.18 seconds
 N₁ = 8.95 millipoises
 N = 5.35 millipoises

B. Chemical Properties

Reaction of 2-Vinylfuran with Potassium Permanganate:

Styrene reacts with potassium permanganate (28) in the following manner,



and since the structure of 2-vinylfuran resembles that of styrene with respect to the vinyl group, it appeared that a similar reaction might take place. The quantities of reactants involving 2-vinylfuran were calculated from a like equation.

Procedure:

Eighty-nine and nine-tenths grams of potassium permanganate was dissolved in 1500 ml. of water and heated to 70° C. Twenty grams of 2-vinylfuran was added to 11 grams of sodium hydroxide in 100 ml. of water. This mixture was placed in a 2-liter round-bottom flask fitted with an air condenser. The potassium permanganate solution was slowly added in six portions with shaking and cooling after each addition. One hundred milliliters of ethyl alcohol were then added to reduce the unreacted permanganate. The manganese dioxide formed during the reaction was filtered off and washed with distilled water. The washings were combined and added to the total volume of the solution, which was then evaporated down to 400 ml. and treated with concentrated hydrochloric acid until neutral to litmus paper. The solution was extracted with 200 ml. of ether. The ether layer was dried over anhydrous calcium chloride and then the ether was distilled off, leaving one-tenth gram of a crude, yellow, crystalline solid. The solid was purified by crystallization from water and then sublimed. The melting point

of the substance was 125-127° C. The melting point of furoic acid is 133° C.

Reaction of 2-vinylfuran with monoperphthalic acid:

The preparation of styrene oxide by the action of perbenzoic acid on styrene is described in detail by Burt and Hibbert (29). The preparation of the oxide of 2-vinylfuran has not been reported in the literature, and since a comparison is being made of the chemistry of styrene and 2-vinylfuran, this reaction was tried.

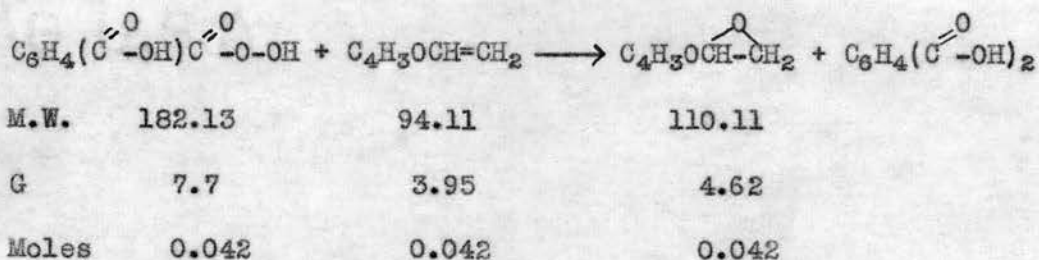
Difficulty was encountered in the preparation of the oxidizing agent, perbenzoic acid. The instability of this reagent and the tediousness of its preparation brought about a literature search for a better oxidizing agent. A more stable and easily prepared one was found in monoperphthalic acid (30, 31). The earlier procedure, described by Bohme (30), involved the less elaborate apparatus and therefore it was selected.

Procedure:

Preparation of monoperphthalic acid. Fifty-five grams of 15% sodium hydroxide and twenty-three grams of 30% hydrogen peroxide were cooled separately in a salt-ice bath and then poured together. To this mixture was added fifteen grams of finely ground and sifted phthalic anhydride with much shaking and in small enough portions that no difficulty would be encountered in the rapid solution of this compound. The alkaline solution was then poured into a 20% sulfuric acid solution, cooled to -10° C. The mixture was filtered through glass wool into a separatory funnel and was successively extracted with one 100 ml. portion and three 50 ml. portions

of ether. The combined ether extracts were washed with three 50 ml. portions of 40% ammonium sulfate solution and then dried 24 hours over freshly heated sodium sulfate. A milliliter of the ethereal solution contained 0.0368 g of monoperphthalic acid. A yield of 7.73 g (42% theoretical) was obtained.

Reaction of 2-vinylfuran and perphthalic acid. The quantity of 2-vinylfuran required to react with the amount of perphthalic acid prepared was calculated from the following equation:



However, a mistake was made in weighing the 2-vinylfuran and a 10% excess was added. Substantially the procedure of Hibbert and Burt (29) was followed. A substance having a boiling point range of 80-100° C. was isolated. After two distillations a product having a boiling point of 100° C. was obtained. The odor of 2-vinylfuran was present and the addition of the unknown to dilute bromine water caused a rapid decolorization. The refractive index of the substance at 22° C. was 1.4730, the refractive index of 2-vinylfuran at 26° C. being 1.4985. The unknown was not characterized beyond this stage because of the difficulty of purification of so small an amount with the available apparatus.

DISCUSSION OF RESULTS

The use of a solvent and a heavy metal carbonate or oxide gives a much smoother reaction than when the decarboxylation is done on the dry acid. The metal carbonate or oxide can not be truly classified as a catalyst because it changes during the reaction. For instance, when silver or copper carbonate was used metallic silver or copper formed a mirror in the reaction vessel. No 2-vinylfuran distilled over until a metallic deposit was formed. The use of copper powder as a catalyst failed completely to give 2-vinylfuran. It would seem from this observation that the metal in an oxidized form is necessary for the decarboxylation.

The metal carbonates giving the best results were those of copper and silver. The one high yield obtained by use of lead oxide could not be duplicated and is now believed erroneous. Although Raney nickel is used primarily as a hydrogenation and dehydrogenation catalyst, it worked fairly well in the decarboxylation. The yields were as good as those in which copper carbonate was used, but no better. The condition of the quinoline, whether distilled or crude, did not seem to affect the reaction, but as Table II has shown, other basic solvents produced only traces of olefin. The yield seemed to increase whenever the 2-vinylfuran was removed by slow distillation or by sweeping it out with natural gas. However a certain amount of olefin was lost in the latter method, because the noncondensed vapors were swept out with the natural gas.

The low yields of 2-vinylfuran can be attributed chiefly to its chemical reactivity. It is easily polymerized and the presence of heat helps the reaction. Then, 2-vinylfuran may enter into a Diels-Alder reaction with the solvent, quinoline, thereby reducing the yield. The

procedure developed for the measurement of carbon dioxide gave erratic and thus disappointing results. A more efficient gas scrubbing system and a constant-temperature bath for the reaction flask might have helped tremendously. However, the results do show that the furylacrylic acid is decarboxylated to a far greater extent than the yields of 2-vinylfuran indicate.

The physical properties of 2-vinylfuran, such as the density and refractive index, both of which has been previously reported, were determined, and two new properties, viscosity and surface tension, were studied. The density value 0.9445 (18/4) (3, 21) is the only one of the three literature figures which agrees with the densities herein reported, the others being 0.9316 (25/4) (23) and 0.936 (13/5) (5). These values show no linear relationship, while a $\Delta d/\Delta t$ which has been calculated for densities now determined (Table IV) gives fairly close approximation when used in interpolating densities at various temperatures.

The effect of the several density values in calculation of parachor and particularly molecular refraction can be noticed. Paul's density value 0.936 and refractive index $n_D^{13} = 1.48168$ give a molecular refraction, 28.61, that more closely agrees with the calculated value, 27.95, than the value obtained by Hughes and Johnson (23) from a density value of 0.9316 and refractive index $n_D^{25} = 1.4981$. The refractive index determined in this work gives a molecular refraction of 29.29 which more nearly checks that of Hughes and Johnson. It should be noted that Paul (5) used 2-vinylfuran prepared by dehydrating an alcohol, whereas all other workers have used the product of decarboxylating furylacrylic acid.

The value obtained for the parachor 233.6 is about 3% higher than the calculated parachor, 227.26.

A series of viscosities over a range of temperatures would be of more interest than any single value since the set could be used in the study of the polymerization of 2-vinylfuran. However, this problem was not concerned with this reaction except insofar as it affected the yields of 2-vinylfuran.

The reaction of 2-vinylfuran with potassium permanganate deviated from the expected course leading to the formation of furoylformic acid, and gave furoic acid instead, which was identified by its melting point.

The oxidation of 2-vinylfuran with perphthalic acid was somewhat disappointing since no definite compound could be isolated from the small quantities obtained with the equipment used. The presence of 2-vinylfuran was shown by the decolorization of dilute bromine water but the refractive index gave an indication of other substance or substances present. Although the refractive index of the unknown should have been taken at 26° to permit comparison with the value for 2-vinylfuran, the change in refractive index noted could not have been caused by a 4° temperature change.

The problem of the decarboxylation of furylacrylic acid warrants further investigation by means of different approaches, such as the preparation of homologs of furylacrylic acid and their decarboxylation and the quantitative analysis of the residue for unreacted acid, quantity of catalyst left unchanged, and even possible characterization of the polymers.

The reactions of 2-vinylfuran with reagents that convert styrene into new compounds other than those tried, KMnO_4 or organic peroxides, can form the basis for further extending the chemistry of 2-vinylfuran. Such reactions might well include formation of halohydrins and further application of the Diels-Alder synthesis.

SUMMARY

In the decarboxylation of furylacrylic acid in quinoline, the best yields of 2-vinylfuran, averaging about 30%, were obtained when copper carbonate or silver carbonate in small amount (0.001 mole) was used. The silver salt of furylacrylic acid gave no better results. No other solvent proved to be as good as quinoline. The lowness of yields can be attributed to polymerization of the olefin.

The measurement of carbon dioxide evolved, although erratic, gave a better indication of the extent of the decarboxylation reaction than could be obtained from yields of 2-vinylfuran.

The density, refractive index and surface tension were determined at 25° C and used in the calculation of molecular refraction and parachor. The values thus obtained were slightly higher than either the calculated values or previously determined literature values for molecular refraction and parachor. The viscosity was found at only one temperature, 25° C. The density was also determined at 15, 20 and 30° C. and $\Delta d/\Delta t$ was calculated over this range.

The reaction of 2-vinylfuran with dilute potassium permanganate gave no furoylformic acid but did produce a small yield of furoic acid. The oxidation of 2-vinylfuran with monoperphthalic acid gave indication of having proceeded but no definite compound was isolated from the small quantity of material obtained.

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