[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF SCHERING CORPORATION]

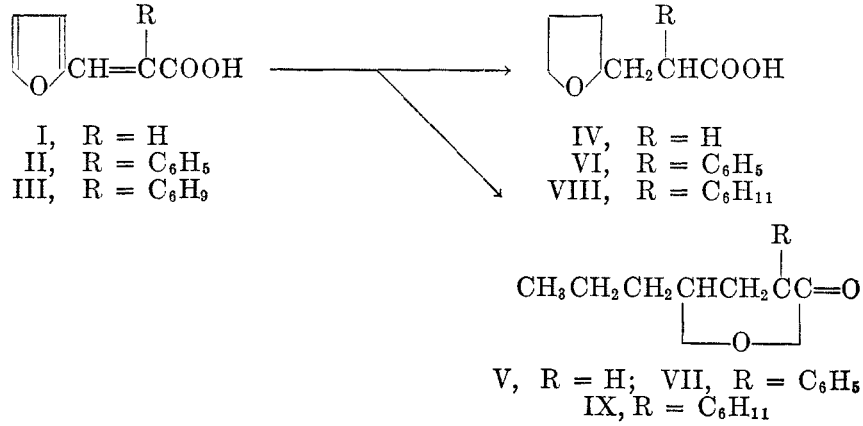
REDUCTIONS WITH NICKEL-ALUMINUM ALLOY AND AQUEOUS ALKALI. PART VIII. HYDROGENOLYSIS OF FURAN DERIVATIVES[1]

DOMENICK PAPA, ERWIN SCHWENK, AND HELEN F. GINSBERG

Received September 18, 1950

In previous publications from this laboratory, the hydrogenolysis of alkoxy groups (1), the methylenedioxy bridge (2), and sulfur compounds (3) by the action of Raney alloy and aqueous alkali have been described. This paper describes the results of further studies on this fission reaction with furan compounds.

The type of hydrogenation and/or cleavage products which are obtained in the hydrogenation of the furan ring are dependent on the nature of the catalyst and reaction conditions. For example, the reductive cleavage of the furan nucleus has been reported to occur over copper chromium oxide catalyst at 175° (4), similar results being obtained with platinum oxide catalyst at room temperature and low pressure (5). More specifically, the reductive cleavage



of furfuryl alcohol has been shown to yield 1,2- and 1,5-pentanediol, further hydrogenation converting both glycols to amyl alcohol. By way of comparison, tetrahydrofurfuryl alcohol is not altered under conditions which readily bring about hydrogenolysis of furfuryl alcohol.

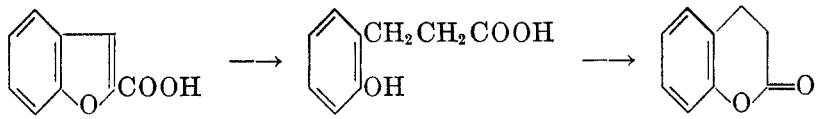
With Raney alloy and aqueous alkali, furan compounds yield approximately equal amounts of two products, one resulting from the hydrogenation of the furan ring, the other a product of the hydrogenolysis of the furan ring. β-(α-Furyl)acrylic acid (I) gives rise to β-tetrahydrofurfurylpropionic acid (IV)

[1] (a) This is part of a paper presented in abstract before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, September, 1944. (b) *Org. Syntheses*, **27**, 68 (1947).

and γ-*n*-propylbutyrolactone[2] (V). *alpha*-Substituted furylacrylic acids, α-phenyl-β-(α-furyl)acrylic acid (II) and α-(Δ^1-cyclohexenyl)-β-(α-furyl) acrylic acid (III) behave in a similar manner, and yield the tetrahydrofuran derivatives (VI and VIII) and the substituted butyrolactones (VII and IX), respectively.

The stability of the tetrahydrofuran ring to this reduction procedure strongly suggests that hydrogenation and hydrogenolysis occur as two competitive reactions. In view of the fact that β-(α-tetrahydrofuryl)propionic acid can be quantitatively recovered unchanged notwithstanding prolonged treatment with excessively large amounts of Raney alloy, it is to be concluded that hydrogenolysis of the furan ring must precede hydrogenation in order to yield the lactones V, VII, and IX. It is of interest to note that these three α-substituted furan compounds yielded hydrogenolysis products in which the oxygen atom remained linked to the substituted α-carbon of the furan ring.

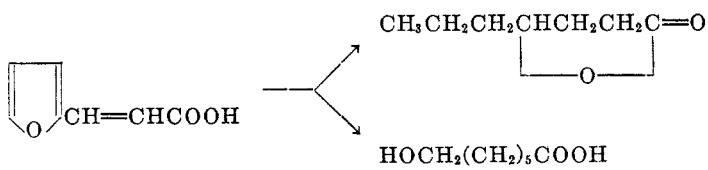
Two aromatic derivatives of furan were studied. Diphenylene oxide (X) yielded a small amount of phenolic material, which coupled deep red with nitrodiazobenzene and which probably is *o*-hydroxydiphenyl (XI). It may be assumed that the very low yield of XI is due to the poor solubility of X in the reaction medium, notwithstanding the use of organic solvents. On the other hand, coumarilic acid (XII) gave good yields of the hydrogenolysis product, β-(*o*-hydroxyphenyl)propionic acid (XIII), isolated in the form of its lactone (XIV). In addition to XIV, a small amount of intractable oil was isolated from the reduction of XII.



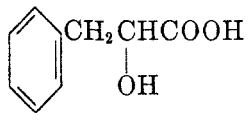
XII XIII XIV

The amount of the latter substance was insufficient to establish its identity and it is probable that this product is either β-phenyl-α-hydroxypropionic acid (XV) or dihydrocoumarilic acid (XVI). The former substance would arise from XII by rupture of the oxygen bond adjacent to the benzene ring, whereas XVI being a hydrogenated furan derivative would be unaltered by the alloy procedure (*cf.* compounds II, VI, VIII). The stability of dihydrocoumarilic acid (XVI) was confirmed by preparing this substance from XII by sodium amalgam reduction and submitting it to the action of Raney alloy. In two reduction experiments a minimum of 92% of recrystallized dihydrocoumarilic acid was recovered.

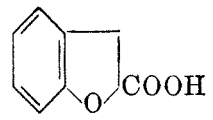
[2] The reductive cleavage of β-(α-furyl)acrylic acid was described[1a] as proceeding in the following manner:



This interpretation of the course of the reaction was based on, as was later established, insufficient analytical data.

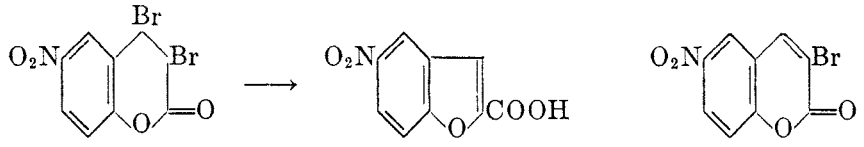


XV



XVI

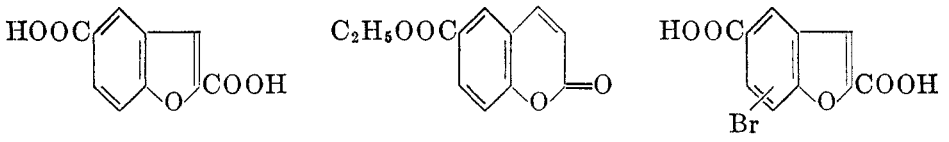
In previous studies on the hydrogenolysis of ethers from the benzene ring (1), it was shown that *meta*-directing groups in either the *o*- or *p*-position to an ether linkage facilitate hydrogenolysis of these groups. It, therefore, was of interest to determine whether a *meta*-orienting group in the *p*-position to the oxygen atom of XII would exert a similar effect.



XVII XVIII XIX

For this study, the readily accessible 3,4-dibromo-6-nitrocoumarin (XVII) was selected, since treatment with alcoholic alkali should yield 5-nitrocoumarilic acid (XVIII). However, from the reaction of XVII and alcoholic alkali, none of the expected 5-nitrocoumarilic acid was obtained. Attempts to remove two molecules of hydrogen bromide by refluxing the dibromonitrocoumarin with pyridine were also unsuccessful, the reaction yielding a monobrominated 6-nitrocoumarin of probable formula XIX. This finding is in agreement with previously reported dehydrohalogenations of compounds of this type with pyridine (6). Further attempts to convert XVII to XVIII were abandoned in view of the apparent difficulties of such a transformation and the probable conversion of XVIII to the corresponding amino compound by Raney alloy prior to hydrogenolysis of the furan ring.[3]

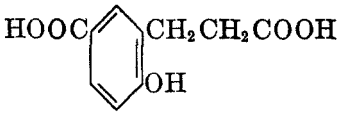
The high yields of hydrogenolyzed products obtained in the case of *ortho*- and *para*-carboxyaryl alkyl ethers (1) suggested the preparation of 5-carboxycoumarilic acid (XX). Since the literature preparation (7) of XX is unsatisfactory, from the standpoint of yield and number of steps and intermediates, a procedure based on the Pechmann synthesis of coumarins (8) was used for securing this compound. This synthesis is based on the condensation of a substituted phenol, in this case ethyl *p*-hydroxybenzoate, with malic acid in the presence of sulfuric acid to give the 6-carbethoxycoumarin (XXI).



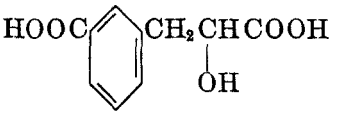
XX XXI XXII

[3] In the case of *p*-nitroanisole only 20% of the hydrogenolysis and reduction product, aniline, was obtained (1).

Although this reaction gave poor yields, the accessibility of starting materials and ease of manipulation afforded sufficient material for investigation. Following the general procedure for the synthesis of coumarilic acids, the 6-carbethoxycoumarin was brominated and dehydrohalogenated. The product isolated from these reactions analyzed for a bromocarboxycoumarilic acid (XXII); the latter being further identified by the preparation and analysis of the diester. The position of the bromine atom in XXII was not determined. From XXII, on treatment with Raney alloy, there was obtained in 60% yield a carboxylic acid which coupled deep red with nitrodiazobenzene. On the basis of its analysis, neutral equivalent, and coupling reaction, this acid is very likely β-(2-hydroxy-5-carboxyphenyl)propionic acid. None of the alternate hydrogenolysis product, β-(3-carboxyphenyl)-α-hydroxypropionic acid (XXIV) was obtained.

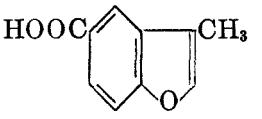


XXIII

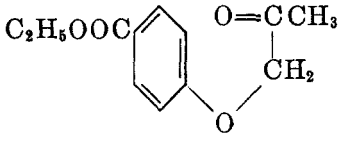


XXIV

Simultaneously with our studies on the synthesis of XX, we investigated the preparation of 3-methyl-5-carboxybenzofuran (XXV). The requisite intermediate for XXV, *p*-carbethoxyphenoxyacetone (XXVI) was obtained readily



XXV



XXVI

by the reaction of chloroacetone and ethyl *p*-hydroxybenzoate (9a). However attempts to effect ring closure of XXVI resulted either in recovery of the compound or resinification. Stoermer reported a similar result with *p*-nitrophenoxyacetone, although the corresponding *p*-methyl compound gave good yields of the cyclized product, 3,5-dimethylbenzofuran (9b).

The labilizing effect of a *para*-substituted carboxyl group on the hydrogenolysis of ether groups by the Raney alloy procedure was also observed in the case of *p*-carboxyphenoxyacetic acid. Whereas approximately 70% of the phenoxyacetic acid was recovered unchanged, the *p*-carboxy compound was quantitatively hydrogenolyzed to benzoic acid. It is to be noted, however, that phenoxyacetic acid yielded about 30% of the hydrogenolysis product, benzene, a result not observed with the previously studied alkoxy ethers (1). This apparent exception is very likely due to the solubility of the phenoxyacetic acid in the reaction medium in contrast to the insolubility of the aralkyl ethers.

EXPERIMENTAL

All melting points have been corrected. The procedure for carrying out the reductions was similar to that previously described (10) except where noted.

1. *Reduction of β-(α-furyl)acrylic acid.* Twenty grams of this acid was treated with 50 g. of nickel-aluminum alloy in 1 liter of 10% sodium hydroxide. After acidification, the reaction mixture was extracted three times with ether; the ether extracts were combined and extracted with 5% sodium carbonate. The ether solution was dried, evaporated, and the residue distilled to give 7.2 g. of γ-(*n*-propyl)butyrolactone, b.p. 103°/10 mm.

Anal. Calc'd for $C_7H_{12}O_2$: C, 65.57; H, 9.45.
Found: C, 65.47; H, 9.45.

The *hydrazide* prepared in the usual manner melted at 88°; literature m.p. 89° (11).

The sodium carbonate extracts after acidification were extracted with ether, and the ether extracts were dried and evaporated. The residue on distillation gave 6.6 g. of β-(tetrahydrofuryl)propionic acid, b.p. 113–114°/1 mm.; n_D^{20} 1.4592; literature b.p. 135–137°/4 mm., n_D^{19} 1.4562 (12).

Anal. Calc'd for $C_7H_{14}O_3$: C, 58.29; H, 8.39.
Found: C, 58.38; H, 8.67.

The *ethyl ester* prepared in the usual manner boiled at 84–88°/2 mm., n_D^{25} 1.4382; previously reported b.p. 115–116°/18 mm. (13).

Anal. Calc'd for $C_9H_{16}O_3$: C, 62.74; H, 9.37.
Found: C, 63.09; H, 9.62.

The *p-phenylphenacyl ester* (14) melted at 110.5–111.5° after recrystallization from methyl alcohol.

Anal. Calc'd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.56.
Found: C, 74.72; H, 6.48.

The *p-bromphenacyl ester* (14) melted at 73.5–74.5° on recrystallization from dilute methyl alcohol.

Anal. Calc'd for $C_{15}H_{17}BrO_4$: C, 52.76; H, 5.03.
Found: C, 52.80; H, 5.34.

Separation of the lactone and β-(tetrahydrofuryl)propionic acid can be effected by fractional distillation. The γ-(*n*-propyl)butyrolactone boils at 80–82°/3 mm., and the β-(tetrahydrofuryl)propionic acid at 123–125°/3 mm.

2. *Preparation and reduction of β-(tetrahydrofuryl)propionic acid.* Ethyl β-(α-furyl)acrylate was prepared in the usual manner; b.p. 92–94°/4 mm., n_D^{20} 1.4588 (13). The ethyl ester was hydrogenated with Raney nickel catalyst in alcohol at 1300 p.s.i. at room temperature, the calculated amount of hydrogen being absorbed in 11 hours. After filtration of the catalyst and evaporation of the alcohol, the ethyl β-(tetrahydrofuryl)propionate distilled at 74–76°/4 mm., n_D^{25} 1.4388. Redistilled for analysis, b.p. 73°/2 mm.

Anal. Calc'd for $C_9H_{16}O_3$: C, 62.74; H, 9.37.
Found: C, 62.62; H, 9.48.

β-(Tetrahydrofuryl)propionic acid (25 g.), obtained by saponification of the ester, in 1000 cc. of 10% sodium hydroxide was treated with 100 g. of Raney alloy. The reduction was worked up in the usual manner and the residue distilled, b.p. 82–84°/3 mm., n_D^{25} 1.4382. The *p*-phenylphenacyl ester melted at 110–111°; mixture m.p. with the *p*-phenylphenacyl ester prepared under #1 showed no depression. The *p*-bromophenacyl ester was also prepared and melted at 73–74°; mixture m.p. 73.5–74.5°.

3. *Reduction of α-phenyl-β-furylacrylic acid.* The acid (15) (25 g.) was dissolved in 750 cc. of 10% sodium hydroxide and 50 g. of Raney alloy was added. The acidified filtrate was then extracted with ether and the combined ether extracts extracted with 5% sodium carbonate. The ether solution was dried and evaporated; the residue on distillation gave 13 g. of α-phenyl-γ-*n*-propylbutyrolactone, b.p. 145–147°/1 mm., n_D^{20} 1.5225.

Anal. Calc'd for $C_{13}H_{16}O_2$: C, 76.42; H, 7.90; Sap. equiv., 204.1.
Found: C, 76.08; H, 8.12; Sap. equiv., 202.8.

The sodium carbonate extracts were combined, acidified, and extracted with ether. The residue, after removal of the ether, was distilled, yield 8 g., b.p. 174–177°/1 mm. This product was very viscous and for convenience in handling was converted to the *ethyl ester*, b.p. 135°/1 mm., n_D^{20} 1.5061.

Anal. Calc'd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12; Sap. equiv., 250.2.
Found: C, 72.66; H, 8.45; Sap. equiv., 252.2.

4. *Reduction of α-(Δ¹-cyclohexenyl)-β-furylacrylic acid.* This acrylic acid (16) (25 g.) was reduced as described for the phenyl derivative. The ether extracts of the acidified solution were dried and after removal of the ether, the residue was fractionated since separation of the neutral and acidic fractions by sodium carbonate was difficult because of the emulsions formed. Fraction I, which was α-cyclohexyl-γ-*n*-propylbutyrolactone, was obtained in a yield of 10 g. and boiled at 130–132°/3 mm., n_D^{25} 1.4795.

Anal. Calc'd for $C_{13}H_{22}O_2$: C, 74.22; H, 10.55; Sap. equiv., 210.2.
Found: C, 74.55; H, 10.62; Sap. equiv., 208.8.

The second fraction, which was identified as α-cyclohexyl-β-tetrahydrofurylpropionic acid, was obtained in a yield of 9 g. and boiled at 174°/2 mm., n_D^{25} 1.4950.

Anal. Calc'd for $C_{13}H_{22}O_3$: C, 68.97; H, 9.80; Neut. equiv., 226.2.
Found: C, 69.50; H, 9.97; Neut. equiv., 226.6.

The substituted propionic acid was esterified in the usual manner and the *ethyl ester* was distilled; b.p. 125°/2 mm., n_D^{20} 1.4792.

Anal. Calc'd for $C_{15}H_{26}O_3$: C, 70.81; H, 10.30; Sap. equiv., 254.2.
Found: C, 71.26; H, 10.30; Sap. equiv., 256.

5. *Reduction of coumarilic acid.* Coumarilic acid was prepared by the hydrolysis of 3,4-dibromocoumarin by alcoholic sodium hydroxide. Bromination of coumarin with chloroform as the solvent did not give satisfactory yields of the desired dibromide (17a). When coumarin was brominated in the vapor phase as described for 6-nitrocoumarin (18), a good yield of the dibromide was obtained. Coumarin (50 g.) was spread on a large watch glass, placed in a desiccator containing 60 g. (15% excess) of bromine, and allowed to stand overnight. The crude dibromide was recrystallized from chloroform and petroleum ether, yield 86 g., m.p. 100–101°. A mixture of 86 g. of 3,4-dibromocoumarin and 500 cc. of 10% alcoholic sodium hydroxide was refluxed for several hours and then 500 cc. of water was added. The alcohol was evaporated *in vacuo* and the aqueous solution on acidification yielded 46 g. of coumarilic acid, m.p. 176–181°. Recrystallized from acetone and water, m.p. 189–190°, literature m.p. 190–191° (17b).

The coumarilic acid (25 g.) was reduced in 1 liter of 10% sodium hydroxide with 60 g. of Raney alloy. The acidified filtrate was exhaustively extracted with ether and on evaporation of the ether, 18 g. of an oily residue was obtained. This product, b.p. 123–125°/2 mm., m.p. 20–22°, was identified as 3,4-dihydrocoumarin (19) which on hydrolysis gave *o*-hydroxhydrocinnamic acid, m.p. 82°; literature m.p. 82° (20).

6. *Reduction of phenoxyacetic acid.* Phenoxyacetic acid (25 g.) was dissolved in 750 cc. of 10% sodium hydroxide. This solution was then placed in a 2-liter flask equipped with a condenser and adaptor for the addition of the alloy. The alloy was added slowly to the above mixture at 25° and then the reaction mixture was heated for several hours on the steam-bath and steam-distilled. The steam-distillate, which amounted to approximately 100 cc., was saturated with potassium carbonate and the benzene which separated amounted to 4.6 g. The steam-distillation residue was filtered from the nickel, acidified, and thoroughly cooled. On extraction with ether and evaporation, 16.5 g. of phenoxyacetic acid was obtained which melted at 96–98°. Mixture melting point with an authentic sample showed no depression.

7. *Reduction of p-carboxyphenoxyacetic acid.* *p*-Carboxyphenoxyacetic acid (20 g.) was reduced in the usual manner with 1000 cc. of 10% sodium hydroxide and 70 g. of Raney alloy. After acidification, the solution was thoroughly cooled and the precipitate filtered; yield, 12.8 g., m.p. 112–116°. Recrystallized from water, it had m.p. 122–123°. Mixture m.p. with benzoic acid, 122–123°; Neut. equiv., 122; Found: 122.

8. *Reduction of dihydrocoumarilic acid.* Dihydrocoumarilic acid, m.p. 116–117° was obtained by the sodium amalgam reduction of coumarilic acid (21). The dihydrocoumarilic

acid (25 g.) was reduced in a liter of 10% sodium hydroxide with 60 g. of Raney alloy. The reaction mixture was worked up as described for coumarilic acid. After recrystallization of the reduction product from a mixture of benzene and petroleum ether, there was obtained 23 g. of dihydrocoumarilic acid, m.p. and mixture m.p. 116–117°. A very small amount of oil remained after evaporation of the benzene.

9. *Attempted preparation of 5-nitrocoumarilic acid.* 6-Nitrocoumarin (22) (50 g.) was brominated as described for coumarin. The crude 3,4-dibromo-6-nitrocoumarin on recrystallization from chloroform and petroleum ether was obtained in a yield of 75%; m.p. 155–156°; literature m.p. 151° (18).

The 3,4-dibromo-6-nitrocoumarin (27 g.) was refluxed for four hours with 200 cc. of ethyl alcohol containing 50 cc. of 50% sodium hydroxide. The reaction mixture, after pouring into water, was extracted with ether and after evaporation of the ether a black, semi-solid residue was obtained from which no crystalline material could be isolated.

The dibromonitrocoumarin (20 g.) was refluxed for three hours with 100 cc. of pyridine. The reaction mixture was then poured into 20% sulfuric acid and the solid material filtered; yield, 12 g., m.p. 248–252°. The substance is very likely 3-bromo-6-nitrocoumarin (6).

Anal. Calc'd for $C_9H_4BrNO_4$: C, 40.00; H, 1.48; N, 5.19.

Found: C, 40.28; H, 1.50; N, 5.41.

10. *Preparation and reduction of 6-carboxybromocoumarilic acid.* A mixture of 41.4 g. (0.3 mole) of *p*-hydroxybenzoic acid, 40.2 g. (0.3 mole) of malic acid, and 500 cc. of concentrated sulfuric acid was heated at 75–85° until the evolution of gas bubbles had almost ceased (8). The mixture was allowed to cool, then poured into ice-water and filtered. The precipitate was dissolved in sodium bicarbonate, treated with Norit, filtered, and acidified. The 6-carboxycoumarin was obtained as a fine, white precipitate; yield, 6 g., m.p. 270–271°; literature m.p. 267–268° (8). The methyl ester was prepared in the usual manner from methyl alcohol and sulfuric acid. After removal of most of the methyl alcohol, water was added and the ester extracted with chloroform. The chloroform extract was freed from unreacted acid by washing with sodium bicarbonate solution, dried, and evaporated to a small volume. On addition of petroleum ether the 6-carbomethoxycoumarin was obtained, m.p. 173–174.5°; literature m.p. 174° (8).

A mixture of 10 g. (0.05 mole) of 6-carbomethoxycoumarin and 8 g. of bromine in 75 cc. of chloroform was exposed to diffuse daylight for 3 days, the color of the solution becoming progressively lighter during this period. Powdered sodium bisulfite was added, the chloroform solution was dried over sodium sulfate and, after filtering off the solids, the solution was evaporated under reduced pressure. The residue was then gradually added to a well-stirred and cooled solution of 25 g. of potassium hydroxide in 60 cc. of absolute alcohol. The mixture was heated slowly to reflux and then refluxed for two hours. Addition of water and acidification yielded 1.2 g. of a white, crystalline product which did not melt at 300° and gave a positive test for bromine. It was purified for analysis by reprecipitaton of the acid from a sodium bicarbonate solution.

Anal. Calc'd for $C_{10}H_5BrO_5$: Neut. equiv., 142.5. Found: Neut. equiv., 142.

The *dimethyl ester* was prepared in the usual manner, m.p. 183–184°.

Anal. Calc'd for $C_{12}H_9BrO_5$: C, 45.90; H, 2.87; Sapon. equiv., 156.5.

Found: C, 45.95; H, 3.04; Sapon equiv., 156.

One gram of the dimethyl ester was dissolved in 25 cc. of 10% sodium hydroxide and 5 g. of Raney alloy was added in the usual manner. After the reaction mixture was worked up, the acidified solution was extracted with ether. The ether extracts yielded 0.6 g. of a white crystalline solid, m.p. 178–178.5°; recrystallized from water, it had m.p. 179.5–180°. The reduction product coupled deep-red with nitrodiazobenzene.

Anal. Calc'd for $C_{10}H_{10}O_5$: C, 57.12; H, 4.79; Neut. equiv., 105.

Found: C, 57.14; H, 5.08; Neut. equiv., 103.9.

11. *Attempted preparation of 3-methyl-5-carboxybenzofuran.* A mixture of 16.6 g. of ethyl *p*-hydroxybenzoate, 12.5 g. of chloroacetone, 45 g. of potassium carbonate, and 225 cc. of

acetone was refluxed for 4 hours. The reaction was then poured into water, acidified, and extracted with ether. The ether extracts were washed with water, dried and, after removal of the ether, the residue was distilled. After a forerun of 6 g., b.p. 70–135°/1 mm., the *p*-carbethoxyphenoxyacetone was obtained as a pale yellow viscous oil; yield, 30 g., b.p. 145–150°/1 mm.; n_D^{25} 1.5326. The analytical sample boiled at 143–145°/1 mm., n_D^{25} 1.5339.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.83; H, 6.35.

Found: C, 64.89; H, 6.69.

The oily ester solidified after standing for several days and on recrystallization from an alcohol-water mixture melted at 54.5–55°.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.83; H, 6.35.

Found: C, 64.54; H, 6.48.

The cyclization experiments were carried out at 0° with concentrated sulfuric acid (4 parts to 1 part of ketone) for 10 minutes, for 30 minutes, and for 2 hours. From each of these runs the starting material was recovered in 96, 78, and 62% yields respectively, m.p. and mixture melting points, 53.5–54°. At 40° for 30 minutes none of the ketone was recovered, the reaction mixture having resinified on distillation.

Acknowledgment. The authors wish to express their appreciation to Mrs. Hilda Breiger and Dr. Peter Hirschler, for their assistance with the experimental work.

SUMMARY

1. Treatment of furylacrylic acid and its α-phenyl and α-(Δ^1-cyclohexenyl) derivatives with Raney alloy and aqueous alkali gives two types of products: (a) the corresponding tetrahydro derivative and (b) the hydrogenolysis product.

2. The tetrahydrofuran nucleus is apparently not altered by this reduction method.

3. Aromatic furan derivatives, such as coumarilic acids, likewise undergo hydrogenolysis of the carbon-oxygen bond.

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