

The bearing of these results upon the mechanism of certain Grignard reactions and the use of bifunctional reactants is discussed.

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## Orientation in the Furan Nucleus. VI. $\beta$ -Substituted Furans

BY HENRY GILMAN AND ROBERT R. BURTNER

### Introduction

The only established case of the directing influence of a mono- $\beta$ -substituted furan is the aldehyde reaction effected by Reichstein and co-workers<sup>1</sup> on 3-methylfuran. They showed that the aldehydic group, introduced by hydrogen cyanide and hydrogen chloride, entered the 2-position to give 3-methyl-2-furfural. Oxidation of this compound gave the known 3-methyl-2-furoic acid.

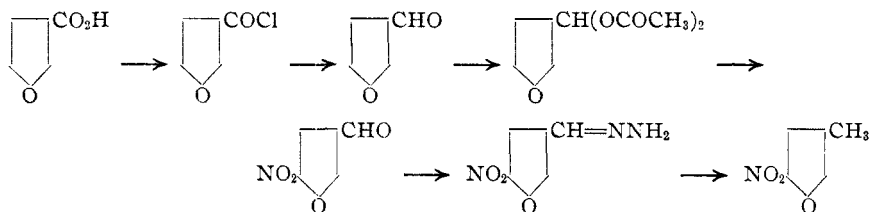
The results now reported on the nitration and halogenation of  $\beta$ -mono-substituted furans make it possible to formulate with some confidence generalizations on the directing influence of such substituents. These may be stated as follows. (1) The entering group goes largely, if not exclusively, to one of the  $\alpha$ -positions. (2) The particular  $\alpha$ -position assumed by the substituent is determined largely by the nature of the group already in the  $\beta$ -position. If the group in the  $\beta$ -position is one which in benzene is largely *o,p*-directing, then the substituent assumes that  $\alpha$ -position contiguous to the  $\beta$ -group; and if the group in the  $\beta$ -position is one which in benzene is largely *m*-directing, then the substituent assumes the more distant or opposite  $\alpha$ -position.<sup>2</sup> With additional studies involving nuclear substitution under varied conditions, it would not be surprising to find some cases where the substituent goes to each  $\alpha$ -position. Furthermore, in view of some anomalous substitution reactions with diphenylene oxide, there is the possibility that a sulfonic acid group, for example, might not assume the same position as a nitro group or a halogen. However, the rules as stated for  $\beta$ -substituted furans are sufficiently well established to warrant the prediction that mono-substitution of a compound like 4-methyl-3-furoic acid will involve the replacement of hydrogen on the 5-

(1) Reichstein, Zschokke and Goerg, *Helv. Chim. Acta*, **14**, 1277 (1931).

(2) It is significant that the rules for orientation of  $\beta$ -substituted furans may apply generally to di- $\alpha$ -substituted furans having unlike groups. For example, the sulfonation of 5-chloro-2-furoic acid gives 5-chloro-4(?) -sulfo-2-furoic acid and this compound with phosphorus pentachloride gives a dichlorofuroic acid identical with the compound previously described as 3,5-dichloro-2-furoic acid. The explanation (Ref. 3) involving 1,4-elimination of halogen hydride to account for the formation of 4,5-dihalogen-2-furoic acids rather than 3,5-dihalogen-2-furoic acids can be supplemented by two 1,2-eliminations, the second of which occurs subsequent to rearrangement of the  $\alpha$ -hydrogen to the 3-position.

position. Other rules on orientation of furan compounds have recently been formulated.<sup>3</sup>

Until quite recently,  $\beta$ -monosubstituted furans were exceedingly rare. One of the oldest compounds of this type is 3-furoic acid, isolated by Rogerson<sup>4</sup> from *Euonymus atropurpureus*. Confirmation of the structure assigned to this acid was obtained by Reichstein and Zschokke<sup>5</sup> and the authors.<sup>6</sup> We are grateful to Dr. T. A. Henry of The Wellcome Chemical Research Laboratories in London for a mixed melting point determination of our acid with a sample of the original acid isolated by Rogerson. We have generally prepared 3-furoic acid by the following sequence of reactions: malic acid  $\rightarrow$  coumalic acid  $\rightarrow$  methyl coumalate  $\rightarrow$  methyl bromocoumalate  $\rightarrow$  2,4-furandicarboxylic acid  $\rightarrow$  3-furoic acid. It can also be prepared by decarboxylation<sup>7</sup> of furan-tetracarboxylic acid, the furan tricarboxylic acids,<sup>7a</sup> 3,4-furandicarboxylic acid (in good yields), 2,3-furandicarboxylic acid,<sup>5</sup> and in very small yields from the carbonation of 3-furylsodium. The position of the nitro group in the nitroaldehyde prepared from the corresponding 3-furaldehyde was established by the following sequence of reactions



The 2-nitro-4-methylfuran obtained in these reactions had the same melting point as an authentic specimen.<sup>8</sup>

Direct nitration of 3-methylfuran gave the isomeric 2-nitro-3-methylfuran.<sup>9</sup> The identity of this compound was also established by comparison with an authentic specimen kindly provided by Dr. I. J. Rinkes. The 3-methylfuran was synthesized by the following sequence of reactions: 3-furaldehyde  $\rightarrow$  3-furaldehydehydrazone  $\rightarrow$  3-methylfuran. An excellent derivative for 3-methylfuran is the mercurial (3-methyl-2-

(3) Gilman and Wright, "Nuclear Substitution and Orientation of Furan Types," *Chem. Rev.*, **11**, 323 (1932).

(4) Rogerson, *J. Chem. Soc.*, **101**, 1044 (1912). See, also, Salway and Powers, *Pharm. J.*, [4] **36**, 550 (1913).

(5) Reichstein and Zschokke, *Helv. Chim. Acta*, **15**, 268 (1932).

(6) Gilman, Burtner and Wright, *THIS JOURNAL*, **54**, 1696 (1932).

(7) These decarboxylations can be effected in several ways such as by pyrolysis, by catalysis using mercuric salts, and by first replacing an  $\alpha$ -carboxyl group by a mercuri group and then hydrolyzing by acids.

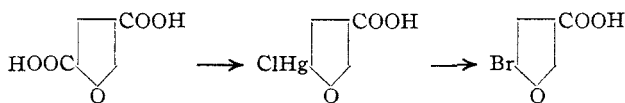
(7a) Reichstein and co-workers [*Helv. Chim. Acta*, **16**, 276 (1933)] have just reported the formation of 3-furoic acid from a furan tricarboxylic acid and from 3,4-furandicarboxylic acid.

(8) Rinkes, *Rec. trav. chim.*, **49**, 1125 (1930). The authors are grateful to Dr. I. J. Rinkes for a specimen of this compound.

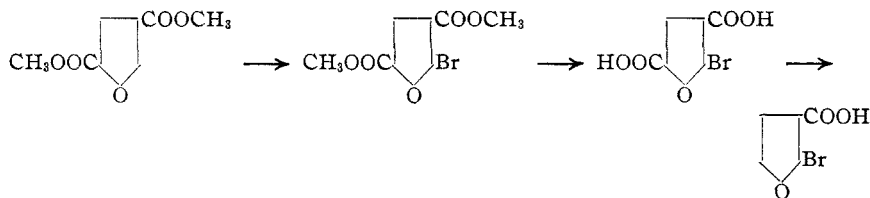
(9) Rinkes, *ibid.*, **49**, 1118 (1930).

furylmercuric chloride), and such mercurials are recommended for the characterization of a wide variety of furans.<sup>10</sup>

The position assumed by the bromine in bromination of 3-furoic acid was established by showing the product to be identical with 2-bromo-4-furoic acid synthesized in the following manner



The isomeric 2-bromo-3-furoic acid was prepared as follows, and shown to be unlike the bromo acid prepared by bromination of 3-furoic acid



$\beta$ -Substituted furans are now more available as a consequence of the diazotization of  $\beta$ -aminofurans. For example, George F. Wright has shown that ethyl 4-amino-5-acetamino-2-furoate is readily diazotized to give a diazonium compound which lends itself to replacement and coupling reactions.  $\alpha$ -Aminofurans are diazotized with considerable difficulty as is the case in the thiophene series,<sup>3</sup> but fortunately it is possible to introduce a wide variety of substituents into the  $\alpha$ -positions without recourse to the diazonium compounds. Other diazo compounds, however, are readily prepared from  $\alpha$ -substituted furans. For example, furyl-diazomethane can be prepared by the oxidation of furfuralhydrazone, and with benzoyl chloride gives furyl benzoate. These aliphatic diazo compounds present an avenue of approach to furfuryl compounds which should be of value in elucidating the mechanism of rearrangement of such compounds first noted by Johnson and by Reichstein.

### Experimental Part

**2,4-Furandicarboxylic Acid, 2,4-C<sub>4</sub>H<sub>2</sub>O(COOH)<sub>2</sub>.**—The preparation of coumalic acid was in accordance with the directions of Pechmann.<sup>11</sup> Inasmuch as the directions for the subsequent transformations appear to be inadequate, a few working details will be given. These are based on numerous experiments.

Methyl coumalate<sup>11</sup> was prepared by adding 547 g. (5.5 moles) of concd. sulfuric acid to 280 g. (2 moles) of coumalic acid contained in a 3-necked flask provided with a stirrer. Considerable heat is evolved. Methyl alcohol (280 g. or 8.75 moles) is added rapidly to the stirred mixture, no attempt being made to control the temperature. After heating the mixture on a boiling water-bath for one hour, it is cooled, poured into an equal volume of ice water, filtered, and the filtrate extracted twelve times with a total

(10) Gilman and Vanderwal, *Rec. trav. chim.*, **52**, 267 (1933).

(11) Pechmann, *Ann.*, **264**, 261 (1891).

of about two liters of ether. The extract is dried over sodium sulfate and after removal of the solvent the air-dried ester is secured in a 55% yield. A small but significant quantity of the ester may be recovered on long standing from the aqueous layer of the original extraction.

Methyl bromocoumalate<sup>12</sup> was prepared by the addition at room temperature over a one-hour period of 250 g. (1.55 moles) of bromine to a stirred solution of 152 g. (1 mole) of the crude ester in 500 cc. of chloroform. Stirring is continued for three hours and then the excess bromine is removed by evaporation under reduced pressure, after which 200 cc. of ether is added and about 500 cc. of the mixed solvent removed by distillation. The residual material is chilled, the solid ester filtered and washed with ether, then shaken in a flask with about 150 cc. of ether, after which it is filtered and washed as before. The concentration process is repeated on the combined filtrates until no ester separates on chilling. The yield is 65%. Excessive concentration of the mother liquors is to be avoided, otherwise apparently intractable, viscous oils result.

2,4-Furandicarboxylic acid<sup>12</sup> was prepared by dissolving, with shaking, 200 g. (0.86 mole) of the bromo ester in a solution of 400 g. of potassium hydroxide in 800 cc. of water. The solution is then refluxed for one-half hour, chilled and carefully acidified by adding 310 g. of concd. sulfuric acid in 290 cc. of water at such a rate that the temperature of the mixture does not rise above 10°. The solid is filtered, washed with water to remove sulfuric acid, dried in the air and extracted with acetone in a Soxhlet extractor. The solid obtained after distilling off the acetone is washed with petroleum ether and crystallized from a minimum of hot water. A small additional quantity of acid can be had from the original filtrate by evaporation to dryness and then extracting with acetone. Although the yield averages only 50%, the time required is reduced.

**3-Furoic Acid, 3-C<sub>4</sub>H<sub>3</sub>OCOOH.**—Decarboxylation of the dibasic acid (in 2-g. to 40-g. lots) by a modification of Johnson's method gives 75–80% of 3-furoic acid. The dibasic acid (20 g.) is thoroughly mixed with 2 g. of copper bronze and together with 25 g. of crude base<sup>13</sup> is placed in a 125-cc. distilling flask provided with a right-angled side-arm 18 mm. in diameter and 30 cm. in length. The end of this tube extends below the surface of 10% sodium hydroxide contained in a 200-cc. wide-mouthed bottle connected in series with a similar wash bottle with alkali. The reaction mixture is heated in a metal bath, while a vigorous stream of nitrogen is passed through to sweep the acid, as fast as it forms, into the alkaline solution. Decarboxylation starts at 270° and reaches a maximum rate at 285°, at which point the temperature is held for one hour or the completion of reaction. The combined alkaline solutions are washed with ether to remove the crude base carried over, chilled, acidified with dilute hydrochloric acid and the 3-furoic acid filtered and air-dried. Additional acid can be recovered by thoroughly extracting the filtrate with ether.

**3-Furoyl Chloride, 3-C<sub>4</sub>H<sub>3</sub>OCOC1.**—The acid chloride was prepared by refluxing 13 g. (0.11 mole) of 3-furoic acid with 25.2 g. (0.2 mole) of thionyl chloride and 120 cc. of benzene for nine hours. The benzene and excess thionyl chloride are removed by distillation through a fractionating column to reduce loss of 3-furoyl chloride, and the residue distilled under reduced pressure to give a 77% yield of acid chloride distilling at 65° (47 mm.) and melting at 29°. The amide melts at 169°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>Cl: Cl, 27.19. Found: Cl, 27.10.

**Ethyl 3-Furoate, C<sub>4</sub>H<sub>3</sub>OCOC<sub>2</sub>H<sub>5</sub>.**—The ester was prepared from 3-furoyl chloride and absolute ethanol; b. p. 65–67° (14 mm.); *n*<sub>D</sub><sup>20</sup> 1.4592; sp. g.<sub>20</sub><sup>20</sup> 1.038.

*Anal.* Calcd. for C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>: C, 60.0; H, 5.76. Found: C, 59.56; H, 6.01.

(12) Feist, *Ber.*, **34**, 1993 (1901).

(13) The fraction distilling at 160–220° (15 mm.) was used. The authors are grateful to Mr. W. R. Gerges of the Barrett Co., Philadelphia, for a liberal supply of the crude pyridine oil.

**Ethyl 2-Nitro-4-furoate**,  $\text{NO}_2\text{C}_4\text{H}_3\text{OCOOC}_2\text{H}_5$ .—A solution of 1.4 g. (0.01 mole) of ethyl 3-furoate in 2.1 g. of acetic anhydride was added dropwise with stirring, at  $-15^\circ$ , to a mixture of 3.5 g. of fuming nitric acid and 5.6 g. of acetic anhydride. After stirring for one-half hour, the mixture was poured upon 30 g. of cracked ice, then brought almost to neutrality with 50% potassium hydroxide and extracted with ether. The mixture after adding 8 cc. of pyridine was allowed to stand overnight at room temperature, the solvent removed by distillation, and the residue carefully acidified with 10% hydrochloric acid to give 0.9 g. or 50% of the nitro ester which after crystallization from ethyl alcohol melted at  $56^\circ$ .

*Anal.* Calcd. for  $\text{C}_7\text{H}_7\text{O}_5\text{N}$ : C, 45.40; H, 3.78. Found: C, 45.58; H, 3.72.

**2-Nitro-4-furoic Acid**,  $\text{NO}_2\text{C}_4\text{H}_2\text{OCOOH}$ .—The nitro ester was hydrolyzed by refluxing with a 1:1 mixture of concd. sulfuric acid and water to give the nitro acid, which when crystallized from hot water melted at  $138^\circ$ . The same acid was obtained by the direct nitration of 3-furoic acid.

*Anal.* Calcd. for  $\text{C}_6\text{H}_5\text{O}_5\text{N}$ : C, 38.21; H, 1.91. Found: C, 38.63; H, 1.69.

**2-Bromo-4-furoic Acid**,  $\text{BrC}_4\text{H}_2\text{OCOOH}$ .—3-Furoic acid in chloroform was brominated at  $5^\circ$  to give a 32.4% yield of the bromo acid which melted at  $130^\circ$  after crystallization from hot water. Neutralization equivalent: calcd., 191; found, 190.

*Anal.* Calcd. for  $\text{C}_5\text{H}_3\text{O}_3\text{Br}$ : Br, 41.88. Found: Br, 41.67, 41.75.

The same bromo acid was obtained by adding 20 g. (0.1 mole) of the di-sodium salt of 2,4-furandicarboxylic acid in 200 cc. of water to a solution of 27.1 g. (0.1 mole) of mercuric chloride in 500 cc. of water. After standing for one hour at room temperature, the mixture was filtered and the filtrate heated to boiling. Carbon dioxide was evolved promptly, accompanied by the formation of a cream colored precipitate. Gas evolution was complete at the end of three hours, when the mixture was chilled and filtered to give 8 g. of solid. A part (3.47 g.) of this mercurial was suspended in 15 cc. of glacial acetic acid and treated with 2.4 g. (0.015 mole) of bromine at  $17^\circ$ ; the mixture was then stirred for one hour at room temperature, the excess bromine removed under reduced pressure, and the mixture poured into 25 cc. of ice water. The filtered solution, after heating to boiling, was again chilled and saturated with hydrogen sulfide to remove mercury, and after removal of the solvent a small quantity of the 2-bromo-4-furoic acid was obtained.

**5-Bromo-2,4-furandicarboxylic Acid**,  $\text{BrC}_4\text{HO}(\text{COOH})_2$ .—This experiment was carried out by E. W. Smith. Four grams (0.022 mole) of dimethyl 2,4-furandicarboxylate and 8 g. (0.05 mole) of bromine were heated in a sealed tube at  $160^\circ$  for eight hours. Hydrolysis was effected by alcoholic potash to give 3.7 g. of the bromo dibasic acid which when crystallized from hot water melted at  $250^\circ$ . Neutralization equivalent: calcd., 235; found, 235.4.

*Anal.* Calcd. for  $\text{C}_6\text{H}_3\text{O}_5\text{Br}$ : Br, 34.04. Found: Br, 33.6.

The  $\alpha$ -bromine was removed by heating an ammoniacal solution for fifteen minutes with zinc dust to give 2,4-furandicarboxylic acid.

**2-Bromo-3-furoic Acid**,  $\text{BrC}_4\text{H}_2\text{OCOOH}$ .—One and four-tenths g. (0.006 mole) of 5-bromo-2,4-furandicarboxylic acid and 1.62 g. of mercuric chloride was refluxed with 25 cc. of water, and when no carbon dioxide was evolved after fifteen minutes, 2.4 cc. of 10% sodium hydroxide was added and the solution refluxed to cause the immediate evolution of carbon dioxide. In working up in a customary manner, using hydrogen sulfide to precipitate the mercury not removed by a prior treatment with sodium hydroxide, 0.3 g. of the bromo acid was obtained. This melted at  $158^\circ$  on crystallization from hot water. Neutralization equivalent: calcd., 191; found, 191.9.

*Anal.* Calcd. for  $\text{C}_5\text{H}_3\text{O}_3\text{Br}$ : Br, 41.88. Found: Br, 41.71.

This method of decarboxylation involves  $\alpha$ -carboxylic groups.<sup>10</sup>

**3-Furaldehyde**,  $C_4H_3OCHO$ .—The catalytic reduction of 3-furoyl chloride by the method of Rosenmund<sup>14a</sup> was that used for other furaldehydes.<sup>14b</sup> The average yield of numerous reductions is 55%, and from our present experience it appears desirable to effect reduction in 5-g. lots. The compound responds to the usual aldehydic tests, but unlike 2-furfural it gives no aniline acetate color test. It is relatively stable in the cold and in the absence of direct light, but like 2-furaldehyde appears to polymerize in direct sunlight. An extensive study by N. O. Calloway on the stability of furan compounds shows that many furan compounds hitherto considered unstable are relatively stable when oxygen is excluded; b. p. 70–72° (43 mm.), 144° (732 mm.);  $n_D^{20}$  1.4945; sp. g.<sub>20</sub><sup>20</sup> 1.111.

*Anal.* Calcd. for  $C_4H_3O_2$ : C, 62.50; H, 4.17. Found: C, 63.01; H, 4.44.

The phenylhydrazone melts at 149.5°.

**3-Furaldehyde Diacetate**,  $C_4H_3OCH(OCOCH_3)_2$ .—The diacetate was obtained by refluxing 0.18 mole of the aldehyde with 0.31 mole of acetic anhydride and 0.12 mole of glacial acetic acid for four hours at a bath temperature of 160–170°. The foreruns of the distillation under reduced pressure were re-worked with acetic anhydride and acetic acid. The yield of diacetate distilling at 130° (15 mm.) and melting at 50° on crystallization from petroleum ether was 66%.

*Anal.* Calcd. for  $C_8H_{10}O_6$ : C, 54.54; H, 5.05. Found: C, 54.48; H, 4.90.

**2-Nitro-4-furfural**,  $NO_2C_4H_3OCHO$ .—The diacetate was nitrated in the customary manner for most furan compounds using fuming nitric acid in acetic anhydride, then making neutral to methyl orange with sodium hydroxide and finally treating with pyridine. The viscous brown oil was refluxed with a 1:2 mixture of concd. sulfuric acid and water to give a 22% yield of the nitroaldehyde which when crystallized from petroleum ether melted at 76°.

*Anal.* Calcd. for  $C_5H_3O_4N$ : N, 9.92. Found: N, 9.94.

The authors are grateful to B. L. Woolley for this micro Dumas analysis. Direct nitration of 3-furfural in acetic anhydride gave 2-nitro-4-furfural diacetate which melted at 87° when crystallized from petroleum ether.

**2-Nitro-4-methylfuran**,  $NO_2C_4H_2OCH_3$ .—The hydrazone was obtained in the usual manner by treating 3.2 g. (0.022 mole) of the nitroaldehyde in 45 cc. of methyl alcohol with 2.2 g. of hydrazine hydrate at 0°, and melted with decomposition at 122°. It was reduced by the quinoline-copper bronze procedure<sup>15</sup> by heating with 30 cc. of quinoline and 2 g. of copper bronze for five hours at 90–95°, at the end of which time the evolution of nitrogen was practically complete. The compound was identified as 2-nitro-4-methylfuran.<sup>8</sup>

**3-Methylfuran**,  $C_4H_3OCH_3$ .—The Wolff-Kischner reduction of 3-furfural hydrazone from 16.9 g. of 3-furfural gave a 72% yield of 3-methylfuran.<sup>16</sup> The mercurial was prepared in the usual manner by shaking 0.41 g. (0.005 mole) of 3-methylfuran in 4 cc. of ethanol with a solution of 1.35 g. of mercuric chloride and 0.82 g. of sodium acetate in 25 cc. of water. The 3-methyl-2-furylmercuric chloride so obtained melted at 142° after crystallization from alcohol.

*Anal.* Calcd. for  $C_5H_6OClHg$ : Hg, 63.28. Found: Hg, 63.57 and 63.75.

**2-Nitro-3-methylfuran**,  $NO_2C_4H_2OCH_3$ .<sup>17</sup>—A solution of 10 g. (0.12 mole) of 3-

(14) (a) Rosenmund and Zetzsche, *Ber.*, **51**, 578 (1918); (b) Gilman, Burtner and Smith, *THIS JOURNAL*, **55**, 403 (1933).

(15) Gilman and Wright, *ibid.*, **54**, 4108 (1932).

(16) Asahina, *J. Pharm. Soc. Japan*, **431**, 1–34 (1918) [*Chem. Abstracts*, **12**, 1047 (1918)]; Rinkes, *Rec. trav. chim.*, **50**, 1127 (1931); Reichstein and Zschokke, *Helv. Chim. Acta*, **14**, 1270 (1931).

(17) Rinkes [*Rec. trav. chim.*, **49**, 1118 (1930)] found that nitration of 3-methylfuran was not a smooth reaction, and no nitromethylfuran was reported. The corresponding 2-nitro-3-methylfuran was, however, prepared by him from the nitration of 3-methyl-2-furoic acid.

methylfuran in 20 g. of acetic anhydride was added dropwise with stirring at  $-12^{\circ}$  to a nitrating mixture of 50 g. of fuming nitric acid and 80 g. of acetic anhydride. A red coloration developed in the addition of the methylfuran, accompanied by a marked temperature rise. Subsequent to addition the mixture was stirred at  $-15^{\circ}$  for fifteen minutes and then poured, with stirring, into 250 g. of cracked ice. The mixture was diluted to 800 cc. with ice water, extracted with ether, the extract washed with a suspension of sodium bicarbonate until free of mineral acid and then twice washed with water. After drying over sodium sulfate, the ether was removed at reduced pressure, the residual oil treated with an equal volume of pyridine with cooling, the mixture allowed to stand at room temperature for one hour and the excess pyridine removed by neutralization with dilute sulfuric acid. The resulting mixture was extracted with ether and the solvent removed as before, leaving a small amount of a dark oil which was then steam distilled. A few drops of oil collected in the distillate, and on cooling they solidified to pale yellow crystals melting at  $35^{\circ}$  and identified as 2-nitro-3-methylfuran by a mixed melting point determination.<sup>9</sup>

### Summary

A study of nuclear substitution reactions of some new  $\beta$ -substituted furans, for which preparative directions are given, makes it possible to formulate definite rules of orientation for such types: (1) the entering group assumes an  $\alpha$ -position; (2) if the  $\beta$ -group is an *o,p*-director in the benzene series, the entering group goes to the contiguous  $\alpha$ -carbon atom, and if the  $\beta$ -group is a *m*-director in the benzene series the entering group goes to the more remote or opposite  $\alpha$ -carbon atom.

AMES, IOWA

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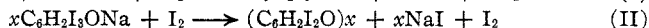
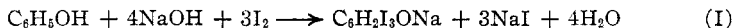
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## The Decomposition of Certain Iodophenols

BY G. H. WOOLLETT, F. W. VAUGHAN, M. L. BURKS AND C. O. HINTON

Phenol when treated with excess alkali and iodine has long<sup>1</sup> been known to produce a deep red substance which is often but incorrectly called tetraiododiphenoquinone.<sup>2</sup> It has more recently<sup>3</sup> been shown to be a highly polymerized non-crystalline product formed by the catalytically induced quantitative loss of alkali iodide from the salt of triiodophenol according to the equations



A similar mechanism has been demonstrated for the action of thymol<sup>4</sup> with alkali and iodine. The chromo-resinoid in this case comes from the decomposition of alkali diiodothymolate without the addition of free iodine.

(1) Lautemann, *Ann.*, **120**, 309 (1861).

(2) Kämmerer and Benzinger, *Ber.*, **11**, 557 (1878).

(3) Hunter and Woollett, *THIS JOURNAL*, **43**, 553 (1921).

(4) Woollett and Everett, *ibid.*, **52**, 4018 (1930).