methylfuran in 20 g. of acetic anhydride was added dropwise with stirring at −12° 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° 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° and identified as 2-nitro-3-methylfuran by a mixed melting point determination.[9]

Summary

A study of nuclear substitution reactions of some new β-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 α-position; (2) if the β-group is an *o,p*-director in the benzene series, the entering group goes to the contiguous α-carbon atom, and if the β-group is a *m*-director in the benzene series the entering group goes to the more remote or opposite α-carbon atom.

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The Decomposition of Certain Iodophenols

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Phenol when treated with excess alkali and iodine has long[1] been known to produce a deep red substance which is often but incorrectly called tetraiododiphenoquinone.[2] It has more recently[3] 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

$$C_6H_5OH + 4NaOH + 3I_2 \longrightarrow C_6H_2I_3ONa + 3NaI + 4H_2O \qquad (I)$$

$$xC_6H_2I_3ONa + I_2 \longrightarrow (C_6H_2I_2O)x + xNaI + I_2 \qquad (II)$$

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

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(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).

The behavior of the six methyl and methoxyl phenols is recorded here.

Five of the six phenols were first completely iodinated and the pure iodo products treated with dilute sodium hydroxide or concentrated sodium carbonate solution. If decomposition did not take place spontaneously a small amount of a dilute standard iodine–potassium iodide solution was added. The amounts of chromo-resinoid formed, iodine split out and iodine remaining in the resinoid were determined.

Complete data on decomposition of salts calculated on the basis of the free phenols are given in Table I.

TABLE I

1	Phenol	Triiodo[5] resorcinol monomethyl ether	Triiodo-*m*-cresol	Diiodo-guaiacol	Diiodo-*o*-cresol	Diiodo-*p*-cresol
2	Number of detns. avgd.	3	8	5	19	7
3	Sample weight, g.	0.4151	0.250	0.250	0.250	0.250
4	Elementary I_2 added (g.) High	None	None	.0250	.0387	.437
	Low	None	None	.0125	.0077	.126
5	Total I added (g.) = I_2 + KI	None	None	.0478	.0503	.463
6	Iodine recovered (g.)	0.1057	0.0635	.1313	.1315	.509
7	Iodine split out (g.) = 6 − 5	.1057	.0635	.0835	.0812	.046
8	% I split out	25.47	25.40	33.40	32.48	18.4
9	Calcd. % I split out for loss of one I atom	25.29	26.12	33.77	35.36	35.36
10	Resinoid found (g.)	0.3053	0.1835	0.1620	0.1674	0.225
11	% resinoid formed	73.06	73.40	64.80	66.96	90.0
12	Calcd. % resinoid for loss of one I atom	74.51	73.66	65.97	64.35	64.35
13	Sum of resinoid % and split I % (8 + 11)	98.53	98.80	98.20	99.44	108.4
14	Calcd. sum of resinoid and split 1 (9 + 12)	99.80	99.78	99.74	99.71	99.71
15	% of one atom of I lost	100.7	97.7	98.9	92.0	51.0
16	% I calcd. for	$(C_7H_4I_2O_2)_x$ 67.88	$(C_7H_4I_2O)_x$ 70.94	$(C_7H_5IO_2)_x$ 51.18	$(C_7H_5IO)_x$ 54.72	$(C_7H_5IO)_x$ 54.72
17	% I found in resinoid (Carius analysis)	67.64	70.48	50.68	54.67	58.49
18	Color of resinoid	Red	Blue green	Red	Brown	Faint yellow

Hydroquinone monomethyl ether (the sixth phenol) under conditions which should produce a chromo-resinoid produced instead black substances varying in iodine content from 1.4 to 13.2% and having little resemblance to the other products.

Preparations

Diiodoguaiacol.—Iodine–potassium iodide solution containing 6.6 g. of free iodine was quickly added to 1.5 g. of guaiacol dissolved in 800 cc. of concentrated ammonium hydroxide. After one and one-half minutes a small amount of sodium sulfite was added. Excess ammonia was blown out and finally boiled out, the cooled residue acidified and extracted with ether. The residue from ether was taken up in heptane and

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(5) The positions of the iodine atoms in the two new phenols and in the well-known iodo cresols have never been determined. There can be little doubt, however, that they occupy positions ortho and para to the hydroxyl groups.

decolorized with norit. The residue from evaporation of heptane was steam distilled and the part not passing with steam was, after extraction with ether, crystallized from alcohol to the constant melting point of 92.4°.

Anal. (Carius). Calcd. for $C_7H_6I_2O$: I, 67.53. Found: I, 67.30.

Triiodoresorcinol Monomethyl Ether.—A solution containing 24.8 g. (0.2 mole) of resorcinol monomethyl ether in 250 cc. of ammonium hydroxide and a solution containing 153 g. (0.6 + mole) of iodine and 155 g. of potassium iodide in 250 cc. of water were run at approximately equal rates during about one-half hour into 1200 cc. of concentrated ammonium hydroxide which was mechanically stirred. Stirring was continued for about two hours, after which excess iodine was removed with sulfite.

The precipitate of ammonium salt was filtered off, the cake suspended in water, acidified and refiltered. Suspension in water and filtration were repeated; yield of crude, 80 g., 80%.

Purification was accomplished by solution in alcohol, decolorization with norit and final crystallization from hot glacial acetic acid to constant melting point 123°.

Anal. (Carius). Calcd. for $C_7H_5I_3O_2$: I, 75.88. Found: I, 75.72.

Summary

Diiodoguaiacol and triiodoresorcinol monomethyl ether have been prepared.

The sodium salts of these and also of diiodo-*o*-cresol and triiodo-*m*-cresol have been shown to lose sodium iodide, leaving highly colored amorphous residues of definite composition, the second and fourth spontaneously, and the first and third in the presence of small quantities of iodine.

The sodium salt of diiodo-*p*-cresol has been shown to lose only a part of its sodium iodide under similar conditions.

Hydroquinone monomethyl ether does not iodinate under conditions which introduce iodine into the above phenols but decomposes in a different manner.

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