added in several portions, whereupon a clear solution formed. Stirring was continued for 90 minutes at 5°.

In the meantime 0.5 g. of sodium sulfite was added to a mixture of 2.0 g. of hydrated copper sulfate, 4.0 g. of sodium bromide, and 1.5 ml. of 1 *N* sulfuric acid in 10 ml. of water yielding a precipitate of cuprous bromide which was washed repeatedly with water by decantation in a centrifuge tube. This salt, dissolved in 10 ml. of 48% hydrobromic acid, was added to the diazonium solution. The dark mixture was allowed to stand for four hours while coming to room temperature. It was then refluxed for 15 minutes and poured onto cracked ice giving a white precipitate and a brown gum. The mixture was extracted twice with benzene. The benzene solution was washed with water until the washings were neutral, extracted three times with a total of 50 ml. of 1 *N* potassium hydroxide, and washed again until neutral. Only a small amount of material precipitated upon acidification of the aqueous alkaline solution.

The benzene layer was dried over calcium chloride and percolated through an alumina column (1 cm. diameter, 8 cm. high). The column was washed with 20 ml. of benzene and the combined eluates taken to dryness. Methanol (6 ml.) was added to the residue and the mixture was refluxed for five minutes giving a light yellow solution and a mobile brown gum. The solution was decanted through a filter. Crystallization occurred overnight at −10° to give 140 mg. of a mixture of white crystals, m.p. 100–103°, and a tan gum (re-extraction of the brown gum obtained above produced no further crystalline material). Three successive recrystallizations from 3, 2 and 0.7 ml. of methanol eliminated the gum and yielded 20 mg. of 4-bromofluorene, m.p. 112°.

Anal. Calcd. for $C_{13}H_9Br$: Br, 32.60. Found: Br, 32.80.

BETHESDA 14, MARYLAND

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Polyhydroxyalkanes from Furfural Condensation Products

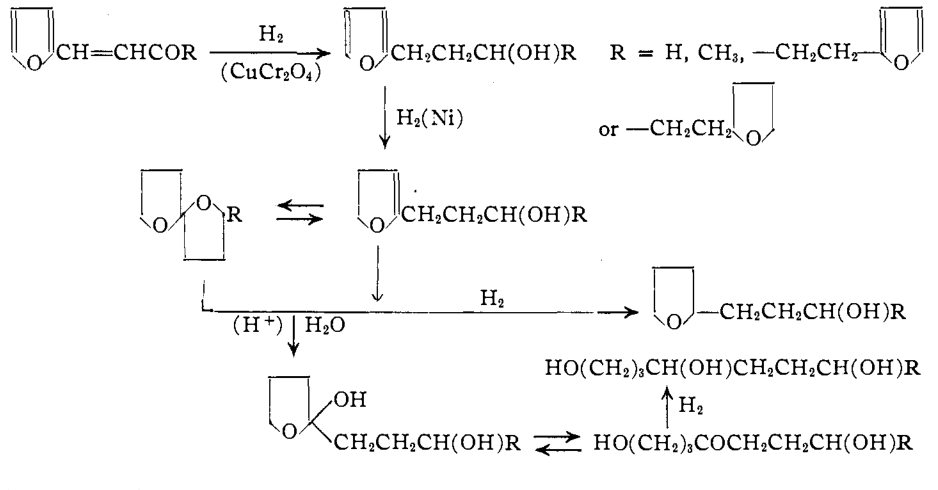
BY CHARLES R. RUSSELL, KLIEM ALEXANDER, W. O. ERICKSON, L. S. HAFNER AND L. E. SCHNIEPP

RECEIVED FEBRUARY 29, 1952

The reaction products from the copper chromite-catalyzed hydrogenation of the condensation products of furfural with acetaldehyde and with acetone are converted to polyols by further hydrogenation in the presence of water and a small amount of formic acid. The preparation of 1,4,7-heptanetriol, 1,4,7-octanetriol, 1-tetrahydrofuryl-3,6,9-nonanetriol and 1,4,7,10,13-tridecanepentaol is described.

The hydrolytic cleavage of furan rings under hydrogenating conditions has been shown to be a useful way of preparing 1,4-dihydroxy-substituted compounds. Leuck, Pokorny and Peters[2] used the method to prepare di- and trihydroxypentanes from furfural and furfuryl alcohol. Methylfuran has been similarly converted to 1,4-pentanediol.[3] The method is apparently applicable to any furan having an alkyl or hydroxyalkyl substituent in the 2-position. The course of the reaction is most readily explained in terms of the mechanism proposed by Topchiev[4] for the formation of acetopropanol from methylfuran. Confirmatory evidence for this mechanism, which involves the initial formation of a 4,5-dihydrofuran, has been presented by Swadesh, Smith and Dunlop.[5]

Previous work[6] on the hydrogenation of furfural condensation products made available several γ-(2-furyl)-alkanols which should yield 1,4,7-triols under the conditions of the hydrolytic-hydrogenation reaction. Three of these, 1-furylpropanol-3,1-furylbutanol-3 and 1,5-difurylpentanol-3 were selected, on the basis of ready availability of the raw materials for their preparation, for a study of conditions leading to optimum yields of cleavage products.



In addition to the purified furylalkanols, pure spirononanes[7] and the crude reaction mixtures, obtained by copper chromite-catalyzed hydrogenation of furylacrolein and the mono- and difurfuralacetones, were investigated as source materials for the preparation of triols. It was found that the 1,6-dioxaspiro[4.4]nonanes gave higher yields of triols than the corresponding furyl-

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] G. J. Leuck, J. Pokorny and F. N. Peters, Jr., U. S. Patent 2,097,493 (1937).

[3] L. E. Schniepp, H. H. Geller and R. W. Von Korff, THIS JOURNAL, **69**, 672 (1947).

[4] K. S. Topchiev, *Compt. rend. acad. sci.* (*U.R.S.S.*), **19**, 497 (1938) [*C. A.*, **32**, 8411 (1938)].

[5] S. Swadesh, S. Smith and A. P. Dunlop, *J. Org. Chem.*, **16**, 476 (1951).

[6] K. Alexander, G. H. Smith, L. S. Hafner and L. E. Schniepp, THIS JOURNAL, **72**, 5506 (1950).

[7] K. Alexander, L. S. Hafner and L. E. Schniepp, *ibid.*, **73**, 2725 (1951).

TABLE I

EFFECT OF ACID CONCENTRATION, AMOUNT OF CATALYST AND NATURE OF SOLVENT ON THE YIELD OF 1-THF-3,6,9-NONANETRIOL FROM 1,5-DIFURYLPENTANOL-3[a]

Run no.	1,5-Difurylpentanol-3 (A), mole	Catalyst (B), g.	Ratio g. (B)/100 g. (A)	Formic acid (C), ml.	Solvent[b] (D), ml.	Total volume (E), ml.	Ratio ml. (C)/100 ml. (E)	Time, hr.	Yield of triol, %
1	0.75	7.0	4.24	0.6	220	370	0.162	4.5	37.2
2	.75	7.0	4.24	.3	220	370	.081	3.0	38.6
3	.75	7.0	4.24	.0	220	370	...	5.0	19.4[c,d]
4	.75	5.0	3.03	.6	220	370	.162	7.0	35.2
5	.375	7.0	8.5	.3	295	370	.081	2.0	49.8
6	.375	1.8	2.18	.3	295	370	.081	9.5	32.0
7	.75	7.0	4.24	.6	H_2O 143 EtOH 77	370	.162	7.0	36.5
8	.375	7.0	8.5	.3	H_2O 30 EtOH 265	370	.081	2.0	13.0[d]

[a] All runs were conducted at pressures of 170–200 atmospheres. [b] Water, unless otherwise designated. [c] Product contained small amounts of impurities which were difficult to remove. [d] DiTHF pentanol was main product.

alkanols. The crude mixtures of alkanols, spirononanes and intermediate carbonyl compounds from the copper chromite reductions of condensation products[6] gave as good yields as the pure furylalkanols under comparable reaction conditions. For preparative purposes, therefore, the following two-stage operation was adopted.

The furfural condensation product was reduced in alcohol over a copper chromite catalyst to approximately the furylalkanol stage after which the catalyst and alcohol were removed. Water, formic acid and a nickel catalyst were added to the residue and the hydrogenation was continued until absorption ceased. The final reaction mixture which now consisted of water, tetrahydrofuryl alkanol and triol was then separated by fractional distillation. The reaction course may be illustrated as already shown.

Investigations to find conditions which would give high yields of ring cleavage products involved determinations of the effects of varying the amount of acid, the amount of catalyst, the composition and volume of the reaction medium, and the interdependence of these factors on each other and on the amount of reactant. Such data, relating to the preparation of 1-tetrahydrofuryl-3,6,9-nonanetriol from 1,5-difurylpentanol-3, are given in Table I.

The presence of acid had been indicated to be necessary to promote or catalyze the desired reaction[3,5]; but because of the interdependence of factors in this type of reaction, an absolute optimum concentration of acid in the reaction mixture was not established. Previous work[3] had shown that best results were obtained from methylfuran by using 0.01 to 0.10% formic acid by weight of the reaction mixture Data on runs 1 and 2 show that the change from 0.16 to 0.08 ml. of acid/100 ml. of reaction mixture made no significant difference in yield when other variables were kept constant. When no formic acid was added, the ring cleavage reaction still occurred but to a lesser extent (run 3). It is probable that under the reaction conditions used, water itself is sufficiently acidic to catalyze its addition to the double bond of the dihydrofuran. It has also been observed[6] that dioxaspirononanes are formed from furylalkanols without the addition of acid to the reaction mixture. This indicates that such alcoholic hydroxyl groups are also acidic enough, at elevated temperatures, to catalyze their addition to the double bond of dihydrofurans. However, the data in reference 7 and in Table I show that substantial improvements in the yield of the desired products are obtained by the addition of small amounts of formic acid.

The ratio of catalyst to reactant appears to be of much greater importance. A comparison of the results of runs 1, 2, 4, 5 and 6 in Table I indicates that variations in the ratios of catalyst to acid, acid to water, and of acid to total volume are not of great consequence, whereas variations in the amount of catalyst affected both yield and reaction rate. Although no attempt was made to evaluate time as a reaction variable, all runs being continued until hydrogen absorption ceased, it was observed that the increased reaction rates at high catalyst ratios gave increased yields of triol. This was only true, however, if other conditions favored this course of the reaction. Investigations of the use of alcohol, to determine the effect of homogeneous *vs.* heterogeneous reaction mixtures, showed that a change of solvent alters the course of the reaction. A comparison of runs 1 and 7 indicates that up to 40% alcohol can be tolerated without greatly changing the yield of triol. However, the use of 90% alcohol (run 8) resulted in a high yield of ditetrahydrofurylpentanol. With reactants having appreciable water-solubility, such as furylpropanol and furylbutanol, the ratio of starting material to water can be increased considerably over those shown in Table I (see Experimental part).

The results of an investigation to determine the relative merits of a one- *vs.* a two-step conversion of furfuralacetone to 1,4,7-octanetriol are shown in Table II. Treatment of 1-furylbutanol and of 2-methyl-1,6-dioxaspiro[4.4]nonane, the products of copper chromite catalyzed hydrogenation of furfuralacetone,[6] with hydrogen and water, in the presence of a catalyst and acid, gave better yields of triol than could be obtained by a one-step conversion of furfuralacetone. The use of a large amount of copper chromite catalyst and a low acid concentration gave a reasonably good yield of triol directly from furfural–acetone (run 13) but the product was yellow and difficult to purify.

Of the two types of catalyst investigated, nickel-

TABLE II

EFFECT OF TYPE OF CATALYST AND NATURE OF STARTING MATERIAL ON YIELD OF 1,4,7-OCTANETRIOL[a]

Run No.	Starting material	Mole	Type of catalyst Ni(C), g.	CuCr$_2$O$_4$, g.	Formic acid, ml.	Solvent,[b] ml.	Time, hr.	Max. temp., °C.	Triol yield, %	THF butanol, %
9	1-Furylbutanol-3	0.5	7	..	0.6	301	3.5	198	42	27
10	1-Furylbutanol-3	.5	..	5.5	.6	301	10	230	36	9
11	Furfuralacetone	.5	6	..	.6	301	10.5	217	22.6	41
12	Furfuralacetone	.5	..	5.5	.6	H$_2$O 214 EtOH 87	12	238	25.8	11.8[c]
13	Furfuralacetone	.5	..	14	.3	301	9	234	35.7	18.8[c]
14	2-Methyl-1,6-dioxaspiro[4.4]nonane	.5	4	..	.6	301	7	218	47.8	18.2[d]
15	2-Methyl-1,6-dioxaspiro[4.4]nonane	.5	..	5.5	.6	301	5	234	56.2	16.2[d]

[a] Initial hydrogen pressures for all runs were 170–200 atmospheres. [b] Water, unless otherwise noted. [c] Some furylbutanol and methyl–dioxaspirononane also obtained. [d] Some starting material recovered.

TABLE III

YIELD OF POLYOLS FROM DIFFERENT STARTING MATERIALS

Run no.	Starting material	Mole	Ni(C) catalyst, g.	Formic acid, ml.	Solvent,[a] ml.	Yield triol, %	Yield THF alkanol	Yield pentaol, %	Time, hr.	Max. temp., °C.
16	1,5-Difurylpentanone-3	0.375	7.0	0.3	295	46.5	31.6	15.1	4.5	200
17	1,5-Difurylpentanol-3	.375	7.0	.3	295	49.8	31.4	15.6	2.0	200
18	2-(β-2-Furylethyl)-1,6-dioxaspiro[4.4]-nonane	.375	7.0	.3	295	55.4	26.5	14.8	3.0	208
19	2-(β-2 THF ethyl)-1,6-dioxaspiro[4.4]-nonane	.375	7.0	.3	295	51.0	37.9	0	2.7	207
20	Difurfuralacetone	.375	7.0	.3	H$_2$O 208 EtOH 87	37.1	36.0	15.7[b]	4.0	202
21	1,5-Difurylpentanol-3 (crude)	.375	7.0	.3	295	38.6	36.5	19.4[b]	3.0	200
22	1-Furylbutanol-3	.50	6.0	.6	300	42.0	27.0	..	3.5	198
23	Furfuralacetone	.50	6.0	.6	300	22.6	41.0	..	10.5	217
24	2-Methyl-1,6-dioxaspiro[4.4]nonane	.50	4.0	.6	300	47.8	18.2	..	7.0	218
25	Furylacrolein	.50	6.0	.6	304	41.0	38.4	..	4.0	200
26	1-Furylpropanol-3 (crude)	.50	6.0	.5	304	35.0	32.5	..	1.5	203

[a] Water, unless otherwise noted. [b] Dark-colored, contained some resins.

TABLE IV

PHYSICAL PROPERTIES OF ALKANETRIOLS AND THEIR AQUEOUS SOLUTIONS[a]

Compound	B.p., °C.	Mm.	d^{20}_4	n^{25}_D	M^{20}_D Calcd.	Obsd.	Viscosity centistokes (C.S.) 100°F.	210°F.	F.p.,[b] °F.	Aqueous solutions Viscosity at 100°F. C.S. 75%[c]	50%	25%	Pour point[d] 75%, °F.
1,4,7-Heptanetriol	146	0.1	1.084	1.4773	39.10	38.67	1200.4	36.72	−35	45.07	6.64	1.81	−65
1,4,7-Octanetriol	148	0.16	1.051	1.4748	43.72	43.40	2659.6	48.17	+ 5	58.81	7.96	2.00	−30
1-Tetrahydrofuryl-3,6,9-nonanetriol	189	0.03	1.081	1.4908	66.30	66.08	2705.7	61.85	+ 3	77.80	9.43	2.10	−35

[a] Determinations by Herbert E. Smith of this Laboratory. [b] Solidification to a clear glass. [c] Per cent. triol by weight. [d] Pour point determination by ASTM procedure D97-47, Part 5, 736 (1949).

on-Celite gave definitely better results on the conversion of furylbutanol whereas copper chromite showed an advantage with the dioxaspirononane. In the one-step operations, copper chromite was superior because it did not promote such rapid saturation of the furan ring. This property probably accounts for the higher yield of triol from spirononane with copper chromite, since in this case further hydrogenation of the ring is undesirable.

A comparison of the yields of triols and their coproducts from the hydrolytic hydrogenation of different starting materials under generally comparable conditions is given in Table III. The pentaol listed as a product from difurfural–acetone and its partial hydrogenation products is believed to be 1,4,7,10,13-tridecane pentaol which would be obtained by cleavage of both furan rings. The yield of this product from crude starting materials could not be accurately determined because of contamination with resinous materials from which it was not easily separated. As would be expected, on the basis of the proposed reaction mechanism, none of this pentaol was obtained from 2-(tetrahydrofurylethyl)-1,6-dioxaspiro[4.4]nonane, whereas some was obtained in all cases where both furyl rings were available for reaction.

Physical properties of interest in determining possible utility of the three triols are given in Table IV. The densities were determined in a Fisher–Davidson Gravitometer and the viscosities with Ostwald–Fenske type viscosity pipets. Molecular refractivities were calculated from refractive index values determined at 20° to correspond with the density values. Freezing and pour point values for 50 and 25% triol solutions in water were indefinite because of the separation of ice crystals at temperatures in the range of 15 to 30°F.

Experimental

Catalysts and Apparatus.—The nickel-on-Celite and copper chromite catalyst were prepared according to the procedures of Adkins.[8] All hydrogenations were conducted in a rocker-type, high-pressure hydrogenation bomb assembly.

1,4,7-Heptanetriol.—1-Furylpropanol-3[9] (1009.6 g., 8 moles), 18 g. of freshly reduced nickel-on-Celite catalyst, 1.8 ml. of 90% formic acid and 570 ml. of water were combined in a 3-liter hydrogenation bomb. The initial hydrogen pressure was 200 atmospheres and approximately 16 moles of hydrogen was absorbed over a 6.5-hour period during which the temperature was gradually raised to a maximum of 210°. After removal of the catalyst by filtration and the water by distillation the residue was fractionally distilled. 1-Tetrahydrofurylpropanol-3, 540 g. (51.8%), n^{25}D 1.4557 was collected at 107–109° (14 mm.). The triol fraction boiled over a range of 149–155° (0.1 mm.), n^{25}D 1.4760, yield 461 g. (38.8%).

Redistillation gave an almost quantitative recovery of product b.p. 146° (0.1 mm.), n^{25}D 1.4773.[10]

Anal.[11] Calcd. for $C_7H_{16}O_3$: C, 56.7; H, 10.8; OH, 34.4. Found: C, 56.5; H, 10.8; OH, 34.8.

1,4,7-Octanetriol.—1-Furylbutanol-3, 70 g. (0.5 mole), was mixed with 6 g. of nickel-on-Celite catalyst, 0.6 ml. of 90% formic acid and 300 ml. of water in a 700-ml. hydrogenation bomb. The initial hydrogen pressure was 155 atmospheres and approximately 1.0 mole of hydrogen was absorbed in 3.5 hours during which the temperature had been gradually raised to a maximum of 198°. After removal of the catalyst and water the product mixture was fractionally distilled. The triol fraction was collected at 150–152° (0.17 mm.) and weighed 34.5 g. (42%), n^{25}D 1.4751. The redistilled product boiled at 148° (0.16 mm.), n^{25}D 1.4748.

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.25; H, 11.2; OH, 31.5. Found: C, 59.3; H, 10.8; OH, 31.2.

1-**Tetrahydrofuryl-3**,6,9-**nonanetriol.**—The crude mixture of products obtained from the copper chromite-catalyzed hydrogenation of difurfuralacetone in alcohol was freed of catalyst and alcohol. This material, 440 g. (2.0 moles if assumed to be difurylpentanol) was mixed with 18.7 g. of nickel-on-Celite catalyst, 0.8 ml. of 90% formic acid and 590 ml. of water in a 3-liter hydrogenation bomb. Hydrogen absorption ceased after approximately 3 hours during which the temperature was gradually raised to 200°. Fractionation of the catalyst- and water-free residue gave the following products: (a) 1,5-ditetrahydrofurylpentanol-3, b.p. 144° (0.7 mm.), n^{25}D 1.4793; 167 g. (36.5%).

(b) 1-Tetrahydrofuryl-3,6,9-nonanetriol, b.p. 208–210° (0.12 mm.), n^{25}D 1.4907; 186 g. (38.6%); redistilled b.p. 189° (0.03 mm.), n^{25}D 1.4908.

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 63.4; H, 10.63; OH, 20.7. Found: C, 63.1; H, 10.66; OH, 20.6.

(c) A residue, 102.4 g. (19.4%), containing 1,4,7,10,13-tridecane pentaol.

Purification of 1,**4**,7,**10**,**13-Tridecanepenta**ol.—A composite sample, 145 g., of residues containing crude pentaol was dissolved in 290 ml. of boiling water, the solution treated with decolorizing carbon and filtered while hot. Removal of the water under reduced pressure left a light-colored residue weighing 141 g. This material was triturated with 200 ml. of boiling acetone, to extract dissolved triol, and left to stand overnight in contact with the acetone. The acetone was removed by decantation and the extraction was repeated with five additional 100-ml. portions of acetone. The residue from this treatment was then dissolved in 5 liters of boiling acetone. After the solution had cooled to room temperature it was placed in a refrigerator for 4 days during which the product slowly separated as a white solid. After removal by filtration and drying to constant weight *in vacuo* over calcium chloride, the white, granular product weighed 84 g. (58% of original crude). This product had no definite melting or freezing point. It liquefied fairly rapidly at 100° and on cooling to room temperature gradually solidified within 2–3 days; n^{60}D 1.4920, n^{25}D of the supercooled liquid, 1.5006.

Anal. Calcd. for $C_{13}H_{28}O_5$: C, 59.1; H, 10.67; OH, 32.2. Found: C, 59.0; H, 10.04; OH, 32.8.

PEORIA 5, ILLINOIS

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[8] H. Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937.

[9] Prepared by $CuCr_2O_4$ catalyzed hydrogenation of furylacrolein in alcohol solution. *Cf.* H. E. Burdick and H. Adkins, THIS JOURNAL, **56**, 438 (1934).

[10] J. Hammonet, *Ann. chim.*, **10**, 5 (1918), reports η^{18}D 1.4738 and η^{18}D 1.447 for the triacetate. H. Hinz, G. Meyer and G. Schücking, *Ber.*, **76**, 676 (1943), report η^{29}D 1.4725 for a triol obtained as a by-product from the hydrogenation of furylacrolein; triacetate η^{23}D 1.4440. 1,4,7-Heptanetriol triacetate prepared from 1-tetrahydrofurylpropanol-3 by treatment with Ac_2O according to procedure of Hinz, *et al.*, PB report 52009, p. 249 (*C. A.*, **41**, 5124 (1947)) and PB report 52020, p. 1050 (*C. A.*, **41**, 6559 (1947)) had b.p. 121° (0.02 mm.), η^{25}D 1.4400, and theoretical saponification equivalent. Methanolysis yielded the triol of η^{25}D 1.4772. The structure of the triol was confirmed by conversion to 1-tetrahydrofurylpropanol-3. This was accomplished by dehydration in toluene with *p*-toluenesulfonic acid as catalyst.

[11] All analyses are micro or semi-micro determinations by C. H. Van Etten and Mary B. Wiele of this Laboratory.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

The Synthesis and Cyclization of Some *o*-Benzylphenones[1,2]

BY FRANK A. VINGIELLO, JAMES G. VAN OOT AND H. HAYDEN HANNABASS

RECEIVED JANUARY 14, 1952

The synthesis of six new *o*-benzylphenones and six new anthracene derivatives has been accomplished. The rates of cyclization of the six new ketones have been measured and the data correlated with an electronic mechanism of aromatic cyclodehydration.

Bradsher and Vingiello[3] have postulated that the cyclization of *o*-benzylphenones proceeds through the following steps: (1) the reversible addition of a proton to the carbonyl oxygen; (2) reaction between the positive central carbon atom and the ortho position of the benzene ring into which cyclization is to occur; (3) elimination of a proton; and finally (4) transannular elimination of water. Vingiello and Van Oot[4] have recently presented data which substantiate Bradsher and Vingiello's conclusion that the rate of cyclization depends, among other things, on the electron density at the ortho position of the benzene ring into which cyclization occurs. We now have additional data to support the statement that a given substituent will change the cyclization rate in a given direction as regards

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[1] Presented before the Division of Organic Chemistry at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952.

[2] This paper has been abstracted from the Doctorate thesis presented by James G. Van Oot to the Virginia Polytechnic Institute in December, 1950.

[3] C. K. Bradsher and F. A. Vingiello, THIS JOURNAL, **71**, 1434 (1949).

[4] F. A. Vingiello and J. G. Van Oot, *ibid.*, **73**, 5070 (1951).