3,4-dichloro-5-isopropylphenol. One of the chlorine atoms must have entered the free *o*-position of carvacrol (see Table I for analysis).

5-Chloro-2-methoxyphenol.—Chlorination of guaiacol gave a 68% yield of a mono-chloro derivative, b.p. 225–230°. It gave, by condensation with chloroacetic acid, a product of m.p. 134–135° (see Table I for analysis) and upon methylation 4-chloroveratrole. This was proven by nitration of the latter to the known 5-nitro-4-chloro-1,2-dimethoxybenzene, m.p. 118°.[13]

The chlorination product of guaiacol is 5-chloro-2-methoxyphenol; it was not identical with the other possible derivative **4-chloro-2-methoxyphenol**, which was prepared as follows: (a) *o*-anisidine was converted into *sym*-di-(2-methoxyphenyl)-urea, m.p. 190° (from petroleum ether), by treatment with phosgene in toluene in presence of dimethylaniline.

Anal. Calcd. for $C_{15}H_{16}O_3N_2$: N, 10.3. Found: N, 10.2.

Chlorination with sulfuryl chloride in tetrachloroethane gave *sym*-di-(4-chloro-2-methoxyphenyl)-urea, m.p. 232–234° (from ethanol).

Anal. Calcd. for $C_{15}H_{14}O_3N_2Cl_2$: Cl, 20.8. Found: Cl, 20.8.

The substituted urea was hydrolyzed by means of sodium hydroxide in ethylene glycol to 4-chloro-2-methoxyaniline which was purified by steam distillation and had m.p. 54°.[14]

(b) **4-Chloro-2-methoxyphenol.**—To a solution of 4-chloro-2-methoxyaniline (4 g.) in a mixture of sulfuric acid (4.5 ml.), water (12.5 ml.) and ice (11 g.), a solution of sodium nitrite (2 g.) in water (6 ml.) was added. The resulting diazonium solution was poured into a hot mixture of sulfuric acid (10 ml.) and water (6 ml.) and distilled with steam. 4-Chloro-2-methoxyphenol (1.4 g.) was isolated from the distillate. Its condensation product with chloroacetic acid, (4-chloro-2-methoxy)-phenoxyacetic acid, could not be induced to crystallize; nor did it crystallize when seeded with the chloroacetic acid derivative (m.p. 134–135°) of the monochloroguaiacol, obtained above.

Anal. Calcd. for $C_9H_9O_4Cl$: Cl, 16.4. Found: Cl, 16.2.

Methyl 2-Hydroxy-3,5-dichlorobenzoate.—Chlorination of methyl salicylate with one mole of *t*-butyl hypochlorite gave a 35% yield of the dichloro compound which crystallized from the reaction mixture after removal of the solvents. Distillation of the mother liquor yielded 45% of unreacted methyl salicylate. The dichloro-compound melted at 150°[15] and was hydrolyzed by means of ethanolic potassium hydroxide to 2-hydroxy-3,5-dichlorobenzoic acid, m.p. 216–218°.[16]

Anal. Calcd. for $C_7H_4O_3Cl_2$: Cl, 34.4. Found: Cl, 34.4.

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tetrachloride). However, it is reasonable to assume that concentration has only a minor effect in the infrared absorption of chelate compounds. It is worthy of note that the infrared absorption at 3520 cm.$^{-1}$ (2.84μ) is the fundamental band corresponding to the overtone at 7050 cm.$^{-1}$ as found by Wulf and Liddell for *o*-chlorophenol (THIS JOURNAL, **57**, 1464 (1935); see also L. Pauling, *ibid.*, **58**, 94 (1936)).

[13] C. A. Fetscher and M. T. Bogert, *J. Org. Chem.*, **4**, 77 (1939).

[14] W. Fitzky, U. S. Patent 1,792,156 (*C. A.*, **25**, 1844 (1931)).

[15] Lassar-Cohn and F. Schultze, *Ber.*, **38**, 3301 (1905), report m.p. 150°.

[16] R. Anschütz and H. Mehring, *Ann.*, **346**, 300 (1906), report m.p. 219°.

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

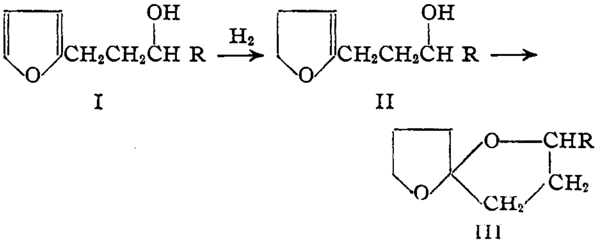
1,6-Dioxaspiro[4.4]nonanes from γ-(2-Furyl)-alkanols

BY KLIEM ALEXANDER, L. S. HAFNER AND L. E. SCHNIEPP

1,6-Dioxaspiro[4.4]nonane and 2-methyl-1,6-dioxaspiro[4.4]nonane were prepared in significant yield from 1-(2-furyl)-propanol-3 and 1-(2-furyl)-butanol-3, respectively. A mechanism for the formation of 1,6-dioxaspiro[4.4]nonanes from γ-(2-furyl)-alkanols is proposed.

The formation of 1,6-dioxaspiro[4.4]nonane[2] (III, R = H) on hydrogenation of β-(2-furyl)-acrolein was observed by Adkins and co-workers.[3,4] Furfuralacetone[5,6] and difurfuralacetone[6] were found to yield the same type of products.

The route of formation of these spiranes has not been adequately explained. Burdick and Adkins[3] concluded that β-(2-furyl)-propionaldehyde was an intermediate in the conversion of furylacrolein to 1,6-dioxaspiro[4.4]nonane and that 1-(2-furyl)-propanol-3 was not. Their tabulated experimental data show, however, that the furylpropanol was hydrogenated over Raney nickel whereas the best yields of spirane had been obtained with nickel-on-kieselguhr catalysts. Recent investigations with furfuralacetone and its hydrogenation products showed that Raney nickel promoted rapid and complete reductions to 1-tetrahydrofurylbutanol-3 and that copper chromite and nickel-on-kieselguhr always gave appreciable amounts of 2-methyl-1,6-dioxaspiro[4.4]nonane (III, R = CH_3). The observation that 1-furylbutanol-3 gave higher yields of the spirane than did 1-furylbutanone-3 prompted a reinvestigation of furylpropanol. It was found that reduction of furylpropanol over a nickel-on-kieselguhr catalyst gave a 38% yield of 1,6-dioxaspiro[4.4]nonane. It is, therefore, concluded that the γ-(2-furyl)-alkanol (I) structure is an intermediate in the formation of these spiranes. A mechanism for the ring closure, involving the intramolecular addition of the hydroxyl group into the double bond of a 4,5-dihydrofuryl intermediate (II), is proposed:



I

II

III

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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] A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940, p. 109; previously named 1,9-dioxa-5-spirononane, ref. 4.

[3] H. E. Burdick and H. Adkins, THIS JOURNAL, **56**, 438 (1934).

[4] M. Farlow, H. E. Burdick and H. Adkins, *ibid.*, **56**, 2498 (1934).

[5] A. Heinz, G. Meyer and G. Schucking, *Ber.*, **76B**, 676 (1943).

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

This mechanism is analogous to those previously proposed by Topchiev[7] and others[8] for the formation of acetopropanol from 2-methylfuran and by Swadesh and Dunlop[9] for the conversion of furfuryl alcohol to 2,5-bis-(trimethyleneoxy)-*p*-dioxane.

Since the structure of the hydroxyl-free product from furfuralacetone hydrogenation had not been satisfactorily established,[5,6] this material was treated with hydriodic acid and the resulting diiodoketone reduced to yield octanone-4. By analogy to the structure proof for 1,6-dioxaspiro[4.4]nonane[4] this evidence shows that the product in question is 2-methyl-1,6-dioxaspiro[4.4]nonane (III, R = CH_3).

Analytical data and physical properties of the hydroxyl-free compound obtained in admixture with 1,5-ditetrahydrofurylpentanol-3, from the hydrogenation of difurfuralacetone,[6] indicate that this product is 2-(β-2-tetrahydrofurylethyl)-1,6-dioxaspiro[4.4]nonane (III, R = $CH_2CH_2\underbrace{CHCH_2CH_2CH_2}_{O}$)

$CH_2CH_2\underbrace{CHCH_2CH_2CH_2}_{O}$

Evidence of analogous products in the hydrogenation mixtures from other furfural–ketone condensation products[6] indicates that spirane formation is a general reaction of γ-(2-furyl)-alkanols on hydrogenation over copper chromite or nickel-on-kieselguhr catalysts.

Experimental

Catalysts and Apparatus.—The nickel-on-kieselguhr catalyst was prepared according to the procedure of Adkins.[10] All hydrogenations were conducted in a rocker-type, high-pressure hydrogenation bomb assembly.

1,6-Dioxaspiro[4.4]nonane.—1-Furylpropanol-3,[3] 126 g. (1.0 mole), dissolved in sufficient absolute alcohol to make a total volume of 370 ml., was hydrogenated over 6 g. of freshly reduced nickel-on-kieselguhr catalyst. The initial pressure was 2300 p.s.i. and 1.6 moles of hydrogen was absorbed in 90 minutes over a temperature range of 70–125°. Fractional distillation of the product yielded 48.6 g. (38%) of 1,6-dioxaspiro[4.4]nonane: b.p. 81–82° (60 mm.), $n^{25}D$ 1.4465, and 74 g. (57%) of 1-tetrahydrofuryl-propanol-3: b.p. 144° (60 mm.), $n^{25}D$ 1.4563.

2-Methyl-1,6-dioxaspiro[4.4]nonane.—One mole (140 g.) of 1-furylbutanol-3 was hydrogenated in dry cyclohexane (total volume 370 ml.) in the presence of 0.3 ml. of 90% formic acid over 6 g. of nickel-on-kieselguhr catalyst. The initial pressure was 2300 p.s.i. and 1.4 moles of hydrogen was absorbed in 90 minutes over the temperature range of 90–120°. Fractional distillation of the products gave 77 g. (54%) of a colorless liquid (A) having a terpene-like odor and b.p. 80° (46 mm.), $n^{25}D$ 1.4412, $d^{25}{}_4$ 0.985.

Anal.[11] Calcd. for $C_8H_{14}O_2$: C, 67.60; H, 9.92; OH, 0.00. Found: C, 67.5; H, 9.82; OH, 0.55.

The higher boiling product, 58 g. (40%), b.p. 145° (58 mm.), $n^{25}D$ 1.4541, was 1-tetrahydrofurylbutanol-3.

Hydrogenation in absolute alcohol gave 40–50% yields of the spirane with corresponding increases in tetrahydrofurylbutanol formation. Elimination of the formic acid reduced the yield only slightly (to 51%). Addition of sodium methoxide apparently stopped spirane formation entirely.

Diiodoöctanone.—A mixture of 14.2 g. of the liquid (A), b.p. 80° (46 mm.), and 66 ml. of hydriodic acid, sp. gr. 1.7, was heated to boiling. The heavy oil which formed was separated, washed, taken up in ether, washed to neutrality, and the ether solution dried over magnesium sulfate. Removal of the ether left 34.9 g. of a dark oil which gave a positive test for carbonyl.

Anal. Calcd. for $C_8H_{14}OI_2$: C, 25.3; H, 3.71; I, 66.7. Found: C, 26.1; H, 3.84; I, 65.8.

Attempted distillation caused decomposition with evolution of hydrogen iodide.

Octanone-4.—Reduction of the above diiodo ketone with a zinc–copper couple in absolute alcohol yielded octanone-4; hydantoin, m.p. 173–174°.[12] A mixed melting point of this derivative with the hydantoin from an authentic sample of octanone-4 showed no depression.

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

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

[9] S. Swadesh and A. P. Dunlop, *J. Org. Chem.*, **14**, 692 (1949).

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

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

[12] H. R. Henze and R. J. Speer, THIS JOURNAL, **64**, 522 (1942).

[CONTRIBUTION FROM THE GEORGE M. MOFFETT RESEARCH LABORATORIES, CORN PRODUCTS REFINING COMPANY]

Uronoside Formation Catalyzed by Cation Active Resin[1]

BY ELIZABETH M. OSMAN, KENNETH C. HOBBS AND WAYNE E. WALSTON

The reaction between methanol and glucuronolactone is catalyzed by cation exchange resin as well as by mineral acids. In addition to the γ-lactone of methyl β-glucofururonoside, a known product of the acid-catalyzed reaction, a second compound was isolated from the resin-catalyzed reaction; this was identified as the γ-lactone of methyl α-glucofuruonoside. Rotation data indicate that the latter compound undergoes mutarotation to the β-isomer as the reaction is prolonged.

Owen, Peat and Jones[2] have reported the preparation of the γ-lactone of methyl β-glucofururonoside by allowing methanol and glucuronolactone to react for several days at room temperature in the presence of hydrogen chloride. When the reaction product was boiled with methanolic hydrogen chloride, the lactone ring opened to yield an ester which was identified as the methyl ester of methyl glucopyruronoside, a shift of the acetal ring apparently having occurred during the course of the reaction.

Cation exchange resins have found increasing use as substitutes for mineral acid catalysts and offer the advantage that they can be removed by merely filtering the reaction mixture. In order to determine whether uronoside formation could be promoted by this type of catalyst, a methanolic solution of glucuronolactone was refluxed in the

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[2] L. N. Owen, S. Peat and W. J. G. Jones, *J. Chem. Soc.*, 339 (1941).