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

The Partial Hydrogenation of Difurfuralacetone and Related Compounds

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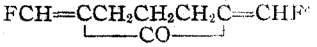
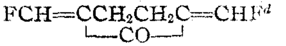
Selective hydrogenation studies, previously applied to furfuralacetofuran,[2] have been extended to a series of furfural- and difurfural-ketone and aldehyde condensation products. Total reduction of such products to tetrahydrofuryl-substituted alcohols has been reported.[3,4] but the furyl alcohols have not been described.

The condensation products (Table I) of furfural with acetone (I and II), methyl ethyl ketone (III), cyclohexanone (IV) and cyclopentanone (V); furylacrolein with 2-acetylfuran (VI), and acetone (VII); and benzaldehyde with 2-acetylfuran (VIII), were hydrogenated at 100–135° in ethanol solution over a copper chromite ($CuCr_2O_4$) catalyst. The hydrogen absorption in all cases corresponded approximately to that calculated for the reduction of the unsaturated ketone bridge.

TABLE I

CONDENSATION PRODUCTS

Formula, F = α-furyl-	No.	Crystn. solvent	M. p., °C.	Yield, %	Reacn. medium, ml./mole H_2O	Reacn. medium, ml./mole EtOH	Empirical formula	Analyses, % Calcd.	Analyses, % Found
$FCH{=}CHCOCH_3$[a]	I		37–39						
$FCH{=}CHCOCH{=}CHF$	II	*n*-Heptane	59–60	98[b]	2500	...	$C_{13}H_{10}O_3$		
$FCH{=}C(CH_3)COCH{=}CHF$	III	EtOH–H_2O	61–62	56	200	320	$C_{14}H_{12}O_3$	C, 73.64 H, 5.30	C, 74.1 H, 5.17
 $FCH{=}\underbrace{CCH_2CH_2CH_2C}_{CO}{=}CHF$[c]	IV	EtOH	144–145				$C_{16}H_{14}O_3$		
 $FCH{=}\underbrace{CCH_2CH_2C}_{CO}{=}CHF$[d]	V	EtOH	163–164	85[b]	1000	100	$C_{15}H_{12}O_3$		
$F(CH{=}CH)_2COF$	VI	EtOH–H_2O	80–81	90	150	500	$C_{13}H_{10}O_3$	C, 72.85 H, 4.71	C, 72.7 H, 4.72
$F(CH{=}CH)_2CO(CH{=}CH)_2F$[e]	VII	Benzene	128–129[f]				$C_{17}H_{14}O_3$		
$C_6H_5CH{=}CHCOF$	VIII	EtOH–H_2O	89–89.5[g]	87[h]	500	250	$C_{13}H_{10}O_2$		

[a] Prepared by the method of Leuck and Cejka, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 283. [b] Based on dry weight of crude. [c] Prepared by the method of E. Boedtker, *J. Pharm. Chim.*, **6**, 204 (1927); *C. A.*, **22**, 585 (1928). [d] Volander and Hobohm, *Ber.*, **29**, 1839 (1896). [e] Prepared by method of ref. 3, [f] Karrer, Cochand and Neuss, *Helv. Chim. Acta*, **29**, 1836 (1946), report m. p. 130°. [g] Weygand and Strobelt, *Ber.*, **68**, 1839 (1935), report m. p. 87–88°. [h] Plus a small amount of $C_6H_5CH(CH_2COF)_2$ m. p. 103–104°. *Anal.* Calcd. for $C_{19}H_{16}O_4$: C, 74.0; H, 5.23. Found: C, 74.1; H, 5.25. Bis-2,4-DNPH (red form) m. p. 227–229°; (orange form) m. p. 236–238°. *Anal.* Calcd. for $C_{31}H_{24}O_{10}N_8$: C, 55.70; H, 3.62; N, 16.76. Found: C, 55.75; H, 3.63; N, 16.2.

Fractional distillation of the hydrogenation products gave 80–90% yields of oily liquids distilling over narrow boiling ranges. Carbon and hydrogen analyses were in accord with the expected furyl alkanols, but, with the exception of the products from I, VI and VIII, hydroxyl values were much too low. Since refractionation did not effect substantial improvement, the once distilled products were treated with phthalic anhydride in pyridine and the pure alkanols obtained by saponification of the purified hydrogen phthalate esters.

The cause of the low hydroxyl analyses was found to be the presence of hydroxyl-free compounds. Two of these compounds from the hydrogenation products of I and II were isolated and gave analyses in accord with the structures IX[5] and XI (Table II). These products are analogous to the 1,9-dioxa-5-spirononane which Adkins[6] obtained from furylacrolein.

Compound XI was further hydrogenated over Raney nickel to give XII which was also obtained, along with XIII, by two-stage hydrogenation of II, first over $CuCr_2O_4$ and then over Raney nickel.

The structure and route of formation of these spiro-compounds will be discussed in a later communication.

Experimental.

Condensation Products.—(Table I) Except for compounds V and VIII, the condensation products were prepared by mixing the appropriate aldehyde (furfural, furylacrolein, benzaldehyde) and ketone (acetone, methyl ethyl ketone, cyclohexanone, cyclopentanone, acetylfuran) in molar ratio, cooling to 0–5° and adding, with stirring, 0.45–0.50 mole/mole of sodium hydroxide in water or aqueous alcohol. The temperature was held at 0–5° for

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[2] Alexander and Smith, THIS JOURNAL, **71**, 735 (1949).

[3] Hinz, Meyer and Schücking, *Ber.*, **76B**, 676 (1943).

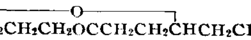
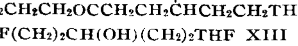
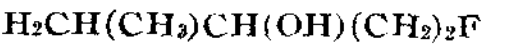
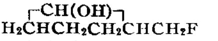
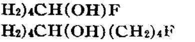
[4] Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wis., 1937.

(5) Hinz (ref. 3) isolated this same compound and provisionally assigned it a methyldioxaoctahydroindene structure in accord with Adkins' proposal (ref. 6a); in view of ref. 6b, IX is more probable.

(6) (a) Burdick and Adkins, THIS JOURNAL, **56**, 438 (1934); (b) Farlow, Burdick and Adkins, *ibid.*, **56**, 2498 (1934).

TABLE II

HYDROGENATION PRODUCTS

Compound: F = α-furyl; THF = α-tetrahydrofuryl	From	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	Yield, %	Empirical formula	Analyses,[a] % Calcd. C	Calcd. H	Calcd. OH	Found C	Found H	Found OH[b]	Hydrogen phthalates Neut. equiv. Calcd.	Neut. equiv. Found	Sapn. equiv. Calcd.	Sapn. equiv. Found
$FCH_2CH_2CH(OH)CH_3$[c]	I	127–128	55	1.4744	1.0192	85	$C_8H_{12}O_2$	68.5	8.63	12.13	68.2	8.6	12.1				
 $\overbrace{CH_2CH_2CH_2OCCH_2CH_2C}^{O}HCH_3$ IX	I	80	46	1.4412	0.9854	10	$C_8H_{14}O_2$	67.6	9.92	0.00	67.5	9.82	0.55				
$F(CH_2)_2CH(OH)(CH_2)_2F$[d] X	II	112–114	0.14	1.5092	1.1006	70	$C_{13}H_{16}O_3$	70.9	7.32	7.72	70.7	7.53	7.6	368[h]	365	184	185
 $\overbrace{CH_2CH_2CH_2OCCH_2CH_2C}^{O}HCH_2CH_2F$ XI	II	84–85	0.08	1.4888	1.087	15–25	$C_{13}H_{18}O_3$	70.2	8.16	0.0	69.7	8.02	0.0				
 $\overbrace{CH_2CH_2CH_2OCCH_2CH_2C}^{O}HCH_2CH_2THF$ XII	II, XI	90–95	0.09	1.4720	1.0403	70[e]	$C_{13}H_{22}O_3$	68.95	9.80	0.0	68.65	9.66	0.0				
$THF(CH_2)_2CH(OH)(CH_2)_2THF$ XIII	II,[f] X	132–134	0.18	1.4793	1.0354	90	$C_{13}H_{24}O_3$	68.4	10.58	7.45	67.8	10.59	7.5				
$FCH_2CH(CH_3)CH(OH)(CH_2)_2F$	III	110–112	0.14	1.5074	1.0833	55	$C_{14}H_{18}O_3$	71.73	7.74	7.26	71.8	8.02	6.9	382[i]	372	191	195
 $FCH_2\overbrace{CHCH_2CH_2CH_2C}^{CH(OH)}HCH_2F$	IV	134–138	0.18	1.5276[g]		55	$C_{16}H_{20}O_3$	73.8	7.74	6.53	74.1	7.85	6.1	408[j]	404	204	200
 $FCH_2\overbrace{CHCH_2CH_2C}^{CH(OH)}HCH_2F$	V	128–132	0.18	1.5228	1.1258	80	$C_{15}H_{18}O_3$	73.1	7.36	6.90	73.2	7.46	6.7	394[k]	390	197	199
$F(CH_2)_4CH(OH)F$	VI	134–140	0.8	1.5088	1.0929	95	$C_{13}H_{16}O_3$	70.9	7.32	7.72	70.8	7.23	7.0				
$F(CH_2)_4CH(OH)(CH_2)_4F$	VII	148–152	0.15	1.5046	1.044	50	$C_{17}H_{24}O_3$	73.9	8.75	6.15	73.75	8.32	6.15	424[l]	421	212	212
$C_6H_5(CH_2)_2CH(OH)F$	VIII	109–111	0.22	1.5441	1.0934	93	$C_{13}H_{14}O_2$	77.18	6.98	8.41	76.8	7.08	8.1				

[a] Micro or semimicro determinations by C. H. Van Etten and Mary B. Wiele of this Laboratory. [b] Semimicro method of Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945). [c] 3,5-Dinitrobenzoate, m. p. 63–64°. [d] 3,5-Dinitrobenzoate, m. p. 87–88°. [e] From XI. [f] Raney nickel catalyst. [g] Of supercooled liquid cryst. to solid, m. p. 49–55°. [h] M. p., 93–94°. [i] Sirup. [j] M. p., 95–99°. [k] M. p., 98–101°. [l] M. p., 70–73°.

one hour, then the mixture was allowed to come to room temperature. Stirring was continued until crystallization was complete. Compound V was best prepared by dropwise addition of the ketone to a vigorously stirred mixture of furfural and sodium hydroxide in aqueous alcohol, and for VIII the aldehyde was added gradually to the alkali-ketone mixture.

Hydrogenation Catalysts and Procedure.—The copper chromite and Raney nickel catalysts were prepared according to the procedures of Adkins.[4] The hydrogenations were conducted in a rocker-type, high-pressure hydrogenation bomb assembly.

About 0.3 mole of the compounds to be hydrogenated was dissolved (or suspended) in absolute ethanol, made up to a volume of 370 ml., and hydrogenated over $CuCr_2O_4$ (4–5 g. per 100 g. of compound). The initial hydrogen pressures were 1500–1800 p.s.i. Most of the pressure drop occurred within about twenty minutes at 110–135° and heating was discontinued after an additional ten to twenty minutes. The reaction mixtures were filtered from catalyst, distilled to remove ethanol, and then fractionated at reduced pressure.

Hydrogen Phthalate Esters.—A modification of the procedure of Duveen and Kenyon[7] was used. The main fractions from the distillation of the hydrogenation products were heated with phthalic anhydride in pyridine for one hour on a steam-bath and left to stand overnight. Sodium carbonate solutions of the crude esters were extracted with ether, then acidified. The crude products solidified on long standing and were recrystallized from *n*-heptane or methylcyclohexane.

Furylalkanols.—1-Furylbutanol-3, 1,5-difurylpentanol-1 and 1-furyl-3-phenylpropanol-1 were obtained directly by fractional distillation of the hydrogenation mixtures. All of the others were isolated from the saponification mixtures from their purified hydrogen phthalate esters and purified by distillation under reduced pressure. The properties and analyses of these products and of their hydrogen phthalate esters are given in Table II. Crystalline 3,5-dinitrobenzoates were obtained from 1-furylbutanol-3 and 1,5-difurylpentanol-3. All others were oils.

Hydroxyl-free Compounds.—Compound IX was obtained by refractionation of the low boiling fraction from the hydrogenation of I.

Compound XI was isolated by repeated refractionation of the fore-run from the hydrogenation of II. The sodium carbonate insoluble extract from the hydrogen phthalate of X also yielded compound XI.

Hydrogenation of XI over Raney nickel gave XII in 70% yield. XII was also obtained by fractional distillation of the hydrogenation mixture prepared by reducing II, first over $CuCr_2O_4$ and then over Raney nickel.

Summary

1,5-Difurylpentanol-3 was obtained in approximately 70% yield and 1-furylbutanol-3 in approximately 85% yield by hydrogenating difurfuralacetone and furfuralacetone, respectively, over $CuCr_2O_4$ catalyst. In these two instances side reaction products were isolated, the analytical data of which are consistent with substituted 1,9-dioxa-5-spirononane structures.

Other condensation products were similarly hydrogenated to prepare: 1,5-difuryl-2-methylpentanol-3, 2,6-difurfurylcyclohexanol, 2,5-difurfurylcyclopentanol, 1,5-difurylpentanol-1, 1,9-difurylnonanol-5 and 1-furyl-3-phenylpropanol-1.

Hydrogen phthalate esters of most of these furyl-substituted alcohols were prepared and characterized.

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[7] Duveen and Kenyon, *J Chem. Soc.*, 622 (1936).