

[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 (CuCr₂O₄) catalyst. The hydrogen absorption in all cases corresponded approximately to that calculated for the reduction of the unsaturated ketone bridge.

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 IX⁵ and XI (Table II). These products are analogous to the 1,9-dioxa-5-spiroonane which Adkins⁶ 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 CuCr₂O₄ and then over Raney nickel.

The structure and route of formation of these

TABLE I
CONDENSATION PRODUCTS

Formula, F = α-furyl-	No.	Crystn. solvent	M. p., °C.	Yield, %	Reacn. medium, ml./mole		Empirical formula	Analyses, %	
					H ₂ O	EtOH		Calcd.	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 ₂ O	61–62	56	200	320	C ₁₄ H ₁₂ O ₃	C, 73.64 H, 5.30	C, 74.1 H, 5.17
FCH=CCH ₂ CH ₂ CH ₂ C=CHF ^c	IV	EtOH	144–145				C ₁₆ H ₁₄ O ₃		
FCH=CCH ₂ CH ₂ C=CHF ^d	V	EtOH	163–164	85 ^b	1000	100	C ₁₅ H ₁₂ O ₃		
F(CH=CH) ₂ COF	VI	EtOH-H ₂ O	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) ₂ CO(CH=CH) ₂ F ^e	VII	Benzene	128–129 ^f				C ₁₇ H ₁₄ O ₃		
C ₆ H ₅ CH=CHCOF	VIII	EtOH-H ₂ O	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 C₆H₅CH(CH₂COF)₂ m. p. 103–104°. *Anal.* Calcd. for C₁₉H₁₆O₄: 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 C₃₁H₂₄O₁₀N₈: 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

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) Parlow, Burdick and Adkins, *ibid.*, **56**, 2498 (1934).

