[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE PREPARATION AND PROPERTIES OF SOME NEW FURAN DERIVATIVES[1]

BY FREDUS N. PETERS, JR., AND RICHARD FISCHER

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Forty-six years ago Pawlinoff and Wagner[2] prepared ethyl furyl carbinol, the first known alkyl furyl carbinol, from furfural and zinc diethyl. In 1901, Grignard[3] obtained iso-amyl furyl carbinol by the use of furfural and iso-amylmagnesium halide. During the same year Hale, McNally and Pater[4] reported negative results in their attempt to obtain phenyl furyl carbinol from the reaction between furfural and phenylmagnesium halide and a similar failure has been reported by Mahood and Jordan.[5] While the manuscript from which this paper is abstracted was being prepared, Pierce and Adams[6] reported the preparation of crude phenyl furyl carbinol and of *n*-butyl furyl carbinol and ethyl furyl carbinol, the latter compound having previously been prepared by Douris.[7] Jolkver[8] and Jaworsky[9] prepared *n*-propyl and allyl furyl carbinol, respectively.

This paper describes the preparation and properties of several heretofore unreported alkyl furyl carbinols, impure phenyl furyl carbinol, several esters of these substances and a few unidentified oxidation and chlorination products.

The organomagnesium furyl complexes obtained in the preparation of these carbinols by the Grignard reaction are pale to orange-yellow in color and, with one exception, insoluble in ether. The exception is the *n*-butyl derivative, which in this respect is similar to titanium *n*-butoxide, which is also an ether-soluble substance, while the lower aliphatic titanium alkoxides are ether insoluble. Isobutylfurylmagnesium bromide was obtained more nearly white than any of the other insoluble magnesium furyl complexes.

All of the carbinols are colorless liquids when pure. They are slightly soluble in water, the solubility and density decreasing with increasing molecular weight. They are all completely miscible with alcohol, nitro-

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[1] This paper is part of a dissertation presented in 1925 by Fredus N. Peters, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Pawlinoff and Wagner, *Ber.*, **17**, 1967 (1884).

[3] Grignard, *Ann. chim. phys.*, [7] **24**, 468 (1901).

[4] Hale, McNally and Pater, *Am. Chem. J.*, **35**, 68 (1901).

[5] Mahood and Jordan, *Science*, **60**, 453 (1924).

[6] Pierce and Adams, THIS JOURNAL, **47**, 1098 (1925).

[7] Douris, *Compt. rend.*, **157**, 722 (1923).

[8] Jolkver, *Rec. trav. chim.*, **28**, 439 (1909).

[9] Jaworsky, *Ber.*, **42**, 435 (1909).

benzene, benzene, chloroform and ether. Phosphorus pentachloride, acetyl chloride, benzoyl chloride and concentrated hydrochloric acid resinify the carbinols, the first two reagents acting with almost explosive violence. Light and air change the carbinols more or less rapidly to reddish brown, viscous liquids which solidify upon standing for some time. Treatment with metallic sodium liberates hydrogen and produces a dark brown mass, soluble in alcohol or ether. The methyl and phenyl furyl carbinols are the most unstable toward acids, whereas the isopropyl furyl carbinol is practically unchanged within two hours by 10% hydrochloric acid and when the pure substance is sealed in a glass tube it remains colorless for several months. Methyl furyl carbinol in a sealed tube in an atmosphere of hydrogen was only slightly colored within one year and after four years it has changed very little more. The other alcohols which were less carefully protected became dark brown liquids in this time. The alkyl furyl carbinols have very little odor and none that can be ascribed as distinctly due to the furan nucleus, the odor being dependent more on the nature of the radical attached to the secondary carbon atom.

The preparation of the esters was not attempted in every case but where tried the only successful method was the treatment of an ethereal solution of the carbinol with acetic anhydride using anhydrous sodium acetate as a catalyst. This method did not give results with the methyl and phenyl derivatives, these being resinified by even small quantities of acetic acid. Treatment of the magnesium complex of furfural and ethyl bromide with acetyl chloride or with benzoyl chloride resulted in resinification of the substance within one hour. The magnesium complex was also treated with ethyl acetate according to the method of Stadnikoff.[10] However, nothing but ethyl acetate and the unchanged carbinol were isolated at the close of the experiment. The use of pyridine according to the method of Einhorn also failed to produce an ester of methyl furyl carbinol. Attempts to prepare an ester of ethyl furyl carbinol by the Schotten–Baumann or Einhorn methods failed. Pawlinoff reported failure in attempts to prepare this ester.

Molecular refractions were calculated using the values for atomic refractions given by Roth and Eisenlohr[11] and in every case checked very well with the values obtained from the Lorentz–Lorenz formula. Molecular weights were determined cryoscopically using benzene as a solvent.

It was impossible to prepare phenyl furyl carbinol in a pure state, the product always being contaminated with diphenyl and some unidentified products. Attempts to oxidize *n*-butyl furyl carbinol with potassium permanganate in acid solution gave a colorless liquid, b. p. 90–95° (3 mm.),

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[10] Stadnikoff, *Ber.*, 57, 1 (1924).

[11] Roth and Eisenlohr, "Refraktometrisches Hilfsbuch," Veit and Co., Leipzig, **1911**, p. 128.

insoluble in 10% hydrochloric acid or sodium hydroxide. This product was slightly acidic and slowly decolorized bromine water; it gave no phenyl hydrazone, semicarbazide or sodium bisulfite addition products. This material resinified to a yellow, viscous gel within one week.

Treatment of ethyl furyl carbinol with diethyl sulfate and potassium hydroxide gave no appreciable yield of the expected ether. The product obtained by treating ethyl furyl carbinol with metallic sodium was refluxed with ethyl bromide and a small quantity of material of aromatic odor was isolated but the amount was too small for characterization. Dry hydrochloric acid gas diluted with carbon dioxide was passed through an ethereal solution of *n*-butyl furyl carbinol. A liquid, b. p. 90–95° (5 mm.), containing chlorine was isolated. This chloride upon refluxing with sodium ethoxide precipitated sodium chloride and a small quantity of liquid with a pronounced terpene-like odor was obtained.

Experimental

Reagents.—The furfural used in this work was obtained through the courtesy of The Miner Laboratories of Chicago, to whom the authors are deeply grateful. The magnesium employed was in the form of turnings furnished for this purpose. The ether and organic halides were dried and purified by conventional methods.

TABLE I

SECONDARY ALCOHOLS, $C_4H_3OCH(OH)R$

R	Yield, %	Boiling points, °C.	d^{25}_{25}	n^{25}_{25} D	C	F
Methyl	67	76–77 (23 mm.)	1.0771	1.4785	1.4751	1.4874
Ethyl	82	57–8 (6 mm.), 89–90 (23 mm.), 106–107 (55 mm.), 113 (71 mm.), 120 (95 mm.)	1.0474*	1.4759*	1.4724*	1.4877*
n-Propyl	55	76–77 (5 mm.), 84–5 (9 mm.), 91–2 (12 mm.)	1.0179	1.4768	1.4727	1.4862
Isopropyl	75	99–100 (38 mm.)	1.0111	1.4715	1.4680	1.4800
n-Butyl	72	94–6 (2 mm.)	0.9931	1.4710	1.4675	1.4788
Isobutyl	40	102–3 (10 mm.)	0.9904	1.4687	1.4646	1.4762
Phenyl	26	122–5 (2 mm.), 138–42 (10 mm.), 170–180 (39 mm.) decompn.	1.1423	1.5522	....	....

* Temperature, 20°

R	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		R_m Calcd.	R_m Found
Methyl	$C_6H_8O_2$	64.26	64.51	64.55	7.21	7.05	7.01	29.94	29.48
Ethyl	$C_7H_{10}O_2$	66.62	66.36	66.37	7.99	7.71	7.71	34.56	34.00
n-Propyl[a]	$C_8H_{12}O_2$	68.53	68.96	68.64	8.63	8.66		39.18	38.88
Isopropyl	$C_8H_{12}O_2$	68.53	68.63	68.34	8.63	8.50	8.43	39.18	38.77
n-Butyl	$C_9H_{14}O_2$	70.09	70.12		9.15	9.11		43.80	43.37
Isobutyl	$C_9H_{14}O_2$	70.09	70.13		9.15	8.94	8.99	43.80	43.32
Phenyl[b]	$C_{11}H_{10}O_2$	75.83	76.59	76.69	5.79	6.14	6.08	49.43	48.71

[a] Mol. wt., calcd., 140; found, 146. [b] Mol. wt., calcd., 174; found, 191, 189.

TABLE II

ALKYL FURFURYL ACETATES, $C_4H_3OCRH(OOC—CH_3)$

R	Yield, %	Boiling points, °C.	d_{25}^{25}	n_{25}^{25} D	C	F
Ethyl	40	98 (37 mm.), 102–3 (40 mm.)	1.0427[a]	1.4589	1.4552	1.4662
Isopropyl	67	99–100 (35 mm.)	1.0162	1.4641	1.4606	1.4712
Isobutyl	35	119–20 (30 mm.)	1.0004	1.4600	1.4556	1.4664

[a] Temperature, 26°.

R	Formula	Carbon, % Calcd.	Found		Hydrogen, % Calcd.	Found		R_m Calcd.	Found
Ethyl	$C_9H_{12}O_3$	64.24	64.41	64.23	7.20	7.00	6.98	43.81	44.29
Isopropyl	$C_{10}H_{14}O_3$	65.90	65.72	65.86	7.75	8.20	8.02	48.43	49.46
Isobutyl	$C_{11}H_{16}O_3$	67.29	67.44	67.55	8.22	8.08	8.15	53.04	53.70

Procedure.—In the early work a special apparatus was used in which the organomagnesium halide was formed in a dry, carbon dioxide–oxygen-free atmosphere and then was forced through a glass wool filter into the furfural. The majority of experiments, however, were carried out by forming the Grignard reagent in the usual manner and adding the furfural to the cool and well-stirred solution. Approximately one gram mole of the Grignard reagent was used in each run. Hydrolysis was carried out by pouring the mixture over ice and this was followed by steam distillation without the use of ammonium chloride or other reagent generally added to aid hydrolysis. The distillate was treated with solid potassium carbonate and the organic layer was shaken with freshly prepared bisulfite solution to remove any unreacted furfural. This was followed by treatment with sodium carbonate to neutralize any free acid and then by vacuum distillation.

Tables I and II give the compounds isolated and some of their physical constants.

Summary

1. Methyl, ethyl, propyl, isopropyl, butyl, isobutyl and phenyl furyl carbinols have been described and some of their physical and chemical properties reported.
2. The acetic acid esters of ethyl furyl, isopropyl furyl and isobutyl furyl carbinols have been prepared and some of their physical properties determined.
3. A chloride, which is probably α-*n*-butyl furfuryl chloride and two substances which are very likely the ethyl ethers of ethyl and *n*-butyl furyl carbinols, respectively, were isolated.
4. An unidentified product was isolated from the acid permanganate oxidation of *n*-butyl furyl carbinol.

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