## RESEARCH ON VINYL ETHERS OF THE FURAN SERIES

## VIII. VINYL ETHERS OF 2- $(\alpha$ -FURYL)ETHANOLS

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Vinyl ethers of  $\beta$ -furyl-,  $\beta$ -(5-methylfuryl)-,  $\beta$ -furfuryloxy-, and  $\beta$ -tetrahydrofurfuryloxyethanols were synthesized.

We have previously shown [1, 2] that 5-bromo-, 5-iodo-, 5-methyl-, and N-disubstituted aminomethylfurfuryl alcohols readily react with acetylene at 135°C in the presence of potassium hydroxide. In order to further ascertain the nature of the effect of a furan ring on the vinylation of an OH group, in this paper we have investigated the reaction of acetylene with heterocyclic alcohols in which the OH group is removed from the furan ring by more than one methylene link. To obtain the starting  $\beta$ -furyl- (I) and  $\beta$ -(5-methylfuryl)ethanols (II), we have for the first time proposed a method for their synthesis through the methyl derivatives of furan and ethylene oxide (alcohol II was unknown up to now):

$$R \xrightarrow{BuLi} R \xrightarrow{CH_2 - CH_2} R \xrightarrow{CH_2 - CH_2} R \xrightarrow{CH_2 - CH_2} CH_2 CH_2 OH$$
  
I R=H; II R=CH<sub>3</sub> I,II

Another route [4] was used to obtain  $\beta$ -furfuryloxy- (III) and  $\beta$ -tetrahydrofurfuryloxyethanols (IV).

The reaction with acetylene was carried out under pressure (15-16 atm) in dioxane in the presence of KOH. The characteristics of the new synthesized compounds (V-VIII) are given in Table 1. They are colorless liquids that are readily polymerized under the influence of ionic catalysts. The structures of the vinyl ethers we re confirmed by the results of hydrogenation and by the IR spectra. The bands at 1620-1640 and 3120 cm<sup>-1</sup> are evidence for the presence of a terminal vinyl group.

The vinylation of the alcohols was studied in comparison with furfuryl (XI), tetrahydrofurfuryl (XII), and 5-methylfurfuryl (XIII) alcohols. We have previously obtained the latter via the Cannizzaro reaction in only low yields (~ 42%). In this paper, we propose a different route for its synthesis through the condensation of 2-lithio-5-methylfuran with formaldehyde. This reaction gave XIII in yields up to 60%. The vinylation conditions and the yields are presented in Table 2, from which it is seen that the further the furan ring is away from the alcohol group, the less actively the compound reacts with acetylene. Alcohol XIII undergoes vinylation to a lesser extent than XI. It is interesting that tetrahydrofuran alcohols require severer conditions than furan alcohols for the addition of acetylene. Thus the vinylation of XI proceeds to give up to 65% of the ether at  $135^\circ$ , while XII forms only traces of the ether under these conditions. Thus the above information indicates that the more donor character the substituent attached to the alcohol group has, the greater the difficulty in vinylating the given compound. Taking into account an anionic (a) or mo-

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Com- pound	Structural formula	bp, °C (mm)	$d_4^{20}$	n <sub>D</sub> <sup>20</sup>
V	(CH <sub>2</sub> ) <sub>2</sub> OCH=CH <sub>2</sub>	56 (13)	0,9997	1,4705
VI	$H_3C - (CH_2)_2OCH = CH_2$	62 (5)	0,9790	1,4720
VII*	CH20(CH2)20CH=CH2	87 (5)	1,0559	1,4760
VIII	СH <sub>2</sub> O(СH <sub>2</sub> ) <sub>2</sub> OCH=CH <sub>2</sub>	83 (3)	1,0134	1,4565
IX	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	65 (6)	0,9475	1,4523
x	CH <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	82 (5)	0,9815	1,4368

TABLE 1. Vinyl and Ethyl Ethers of Furan Alcohols

TABLE 1 (continued)

Com- pound	MR <sub>D</sub>		Francisianal	Found, %		Calc., %	
	found	calc.	formula	с	н	С	н
V VI VII VIII IX X	38,54 43,38 44,89 46,17 43,88 45,36	38,83 43,45 45,09 46,04 43,91 45,75	$\begin{array}{c} C_8 H_{10} O_2 \\ C_9 H_{12} O_2 \\ C_9 H_{12} O_3 \\ C_9 H_{16} O_3 \\ C_9 H_{16} O_3 \\ C_9 H_{14} O_2 \\ C_9 H_{14} O_3 \end{array}$	69,00 71,00 64,64 62,84 69,74 63,03	7,04 7,97 7,20 9,28 9,18 9,69	69,59 71,06 64,30 62,77 70,10 63,52	7,25 7,95 7,20 9,37 9,10 9,47

\*According to the data in [3], this compound has bp 76-77°C (1.5 mm),  $n_D^{25}$  1.4739, and  $d_4^{20}$  1.0569.

TABLE 2. Vinylation of the Furan Alcohols\*

Starting compound	Expt1. temp.	Exptl. time, h	Yield of vinyl ether, %
I	135 150 170		37 38 56
II	135	1	36
	150	I	65
III	135	0,5	52
	150	0,5	76
IV	190	1	73
XI	135	0,5	65
XII	150	1,5	62
	180	1,5	81
XIII	135	1	32
	150	0,5	34
	170	I	31

\*In all of the experiments, 0.102 mole of the alcohol, 0.018 mole of KOH, and 50 ml of dioxane were used under an acetylene pressure of 15-16 atm.

lecular (b) mechanism [5], it can be assumed that the rate-determining step of the vinylation is dissociation of the alkoxide. Apparently, the greater the electron-donor capacity of the substituent attached to the furan alcohol, the more stable the O-Me bond of the alkoxide.

## EXPERIMENTAL

 $\frac{\beta-\text{Furfuryloxyethanol (III).}}{1.1327, \text{ and } n_D^{20} 1.4839 \ [4]).}$  This compound had bp 108-110° (10 mm) and  $n_D^{20} 1.4845$  (bp 110° (10 mm),  $d_4^{20} 1.4827$ , and  $n_D^{20} 1.4839 \ [4]).$ 

<u> $\beta$ -Tetrahydrofurfuryloxyethanol (IV)</u>. This compound had bp 60-64° (2 mm) and  $n_D^{20}$  1.4605 (bp 113° (7 mm),  $d_4^{20}$  1.0701, and  $n_D^{20}$  1.4565 [4]).

<u> $\beta$ -(5-Methyl-2-furyl)ethanol (II)</u>. Ethylene oxide (20 g) was added with stirring at  $-5^{\circ}$  to a solution of 2-lithio-5-methylfuran prepared from 5 g (0.713 g-atom) of Li, 48.4 g (0.353 mole) of butyl bromide, and 26.4 g (0.321 mole) of  $\alpha$ -methylfuran in 200 ml of absolute ether. The mixture was held at this temperature for ~1 h and diluted with 15% ammonium chloride solution. This mixture was then extracted with ether, and the ether extract was dried over calcined sodium sulfate. The ether was removed, and the reaction products were vacuum-distilled to give 24.4 g (60%) of II with bp 70-71° (3 mm).  $d_4^{20}$  1.0482, and  $n_D^{20}$  1.4810. Found: C 66.27; H 7.99%; MR<sub>D</sub> 34.21.  $C_7H_{10}O_2$ . Calculated C 66.62; H 7.99%; MR<sub>D</sub> 34.56.

Alcohol I with bp 67-68° (6 mm),  $d_4^{20}$  1.0903, and  $n_D^{20}$  1.4820 ( $d_4^{25}$  1.0705 and  $n_D^{25}$  1.4788 [6]) was similarly obtained from  $\alpha$ -lithiofuran.

<u>5</u>-Methylfurfuryl Alcohol (XIII). A stream of formaldehyde, obtained by the decomposition of 20 g of paraformaldehyde, was passed at room temperature into a solution of 2-lithio-5-methylfuran (from 5 g of Li, 48.4 g of  $C_4H_9Br$ , and 26.4 g of  $\alpha$ -methylfuran) in 200 ml of ether. The mixture was stirred for another 0.5 h and worked up as above to give 21 g (60%) of XIII with bp 59-60° (4 mm) and  $n_D^{20}$  1.4812 (bp 70-73° (6 mm),  $d_4^{20}$  1.0769, and  $n_D^{20}$  1.4853 [7]).

<u>Vinyl Ether of  $\beta$ -Furylethanol (V)</u>. The reaction of 11.4 g (0.102 mole) of alcohol I in the presence of 1 g (0.018 mole) of KOH in 50 ml of dioxane in an autoclave under an acetylene pressure of 15-16 atm at 170° gave 6.1 g (56%) of V.

Ethers VI, VII, and VIII were similarly obtained. The vinylation conditions and the yields are presented in Table 2, and the properties of the vinyl ethers are presented in Table 1.

Ethyl Ether of  $\beta$ -(5-Methyl-2-furyl)ethanol (IX). A 3-g sample of II in 50 ml of ethanol was hydrogenated in a long-necked hydrogenation flask over Raney nickel at room temperature until hydrogen absorption ceased, and the mixture was vacuum distilled to give 2.9 g (95%) of IX.

Ether X was similarly obtained in 92% yield. The properties and results of analysis of the corresponding ethyl ethers are presented in Table 1.

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