## AMMONIUM SALTS IN ALKYLATION REACTIONS. 34.\* SYNTHESIS AND INTRAMOLECULAR CYCLIZATION OF UNSATURATED

ESTERS WITH A FURFURYL GROUP

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Unsaturated esters of furfuryl alcohol were synthesized by interphase catalysis. The intramolecular thermal cyclization of the synthesized compound was studied.

Continuing our research on intramolecular thermal cyclization reactions [2] we studied the behavior of unsaturated esters of furfuryl alcohol in this reaction.

Furfuryl acrylate was obtained in 85% yield by the reaction of methyl acrylate with furfuryl alcohol at 160°C in the presence of aluminum ethoxide (8%) and diphenylamine for 5-7 h [3]. In addition to the high reaction temperature, the chief drawback of the method is the need to use a large amount of furfuryl alcohol (a threefold molar excess). We carried out the synthesis of furfuryl acrylate (III) by alkylation of sodium acrylate (I) with furfuryl chloride (II) under interphase-catalysis (IPC) conditions with triethylbenzylammonium chloride (TEBA) as the catalyst at 25-30°C.

$$CH_2 = CHC \stackrel{0}{\underset{ONa}{\leftarrow}} + \underbrace{CH_2 = CHC \stackrel{0}{\underset{OCH_2}{\leftarrow}} + NaCl}_{III}$$

In a repetition of the known method [3] we also isolated a substance, the elementary composition of which corresponds to III, whereas the IR spectrum does not contain the characteristic absorption bands of a terminal vinyl group and a furfuryl group.

We assumed that intramolecular thermal cyclization occurred. In fact, we found that prolonged heating (100 h, 90-92°C) in the presence of Neozone D leads to a cyclization product in 10% yield. Unchanged ester III is recovered. A polymer with  $[\eta] = 0.049$  (in chloroform, at 20°C) is formed in the presence of AlCl<sub>3</sub>. The cyclization was studied on diatomaceous earth; 3a,6-epoxy-3a,6,7,7a-tetrahydro-3H-benzo[c]furan-1-one (IV) was obtained in 50% yield.



The synthesis and cyclization of allyl and propargyl furfuryl ethers (VIIa, b) are known. The reaction of furfuryl alcohol (VI) with the corresponding alkyl halide Va,b under IPC conditions [with a mixture of dimethylbenzylalkyl( $C_{10}H_{21}-C_{18}H_{37}$ ) ammonium chlorides (Catamine AB) as the catalyst] leads to the formation of ethers VIIa, b in high yields (80-90%).



V, VII a  $R = CH_2 = CHCH_2$ ; b  $R = CH = CCH_2$ 

\*See[1] for Communication 33.

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 457-495, April, 1990. Original article submitted July 27, 1989. Ethers VIIa, b do not undergo cyclization on heating on a boiling-water bath either in the presence of diatomaceous earth or when it is absent.

The behavior of VIIa at 170°C in an argon atmosphere was studied. It was found that in 18 h ether VIIa undergoes cyclization (with spontaneous warming up to 200°C) to 3a,6epoxy-1,6,7,7a,tetrahydro-H-benzo[c]furan (VIII).



It is known that intramolecular cyclization proceeds slowly in quaternary ammonium salts that contain a propargyl group in addition to a furfuryl group as compared with the allyl analogs. This is explained by the repulsive interaction of the bonds of the propargyl group with the p electrons of the oxygen atom in the furfuryl fragment [4]. In all like-lihood, this interaction also becomes a hindrance in the cyclization of VIIb, which leads to partial resinification of the latter at 175-185°C in argon. The yield of the cyclization product - 3a, 6-epoxy-1,3-dihydro-6H-benzo[c]furan (IX) - is low.



## EXPERIMENTAL

The IR spectra of suspension of the compounds in the mineral oil were recorded with a UR-20 spectrometer. The PMR spectra of solutions in  $CDCl_3$  were obtained with a Perkin-Elmer R-12B spectrometer (60 MHz) with tetramethylsilane (TMS) as the internal standard.

Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates in a chloro-form-hexane system (1:1) with development with iodine vapors.

The results of elementary analysis of III, IV, VIIa, b, XIII, and IX for C and H were in agreement with the calculated values.

<u>Furfuryl Acrylate (III,  $C_8H_8O_3$ )</u>. A solution of 0.12 ml (100 mmole) of furfuryl chloride in 60 ml of ether was added dropwise with stirring in the course of 30 min at 25-30°C to a mixture of 9.4 g (0.1 mole) of I, 2.28 g (10 mmole) of TEBAC, and 50 ml of ethyl ether, after which the mixture was stirred for 10 h. It was then washed with ether (two 25 ml portions), and fractional distillation gave 10.64 g (70%) of III with bp 95-104°C (18 mm),  $n_D^{20}$  1.4819,  $d_4^{20}$  1.1125, and  $R_f$  0.82. IR spectrum: 920, 1640 (CH=CH); 1510, 1580, 1610, 3140, 3180 (furan ring); 1730 cm<sup>-1</sup> (C=O). PMR spectrum: 5.07 (2H, s, CH<sub>20</sub>), 5.6-5.9 (3H, m, CH<sub>2</sub>=CH), 6.01 (2H, m, 3-H, 4H), 7.27 ppm (1H, m, 5-H).

<u>3a,6-Epoxy-3a,6,7,7a-tetrahydro-3H-benzo[c]furan-1-one (IV,  $C_8H_2O_3$ )</u>. A 1-g (6.6 mmole) sample of ester III precipitated on 5 g of diatomaceous earth was placed in a round-bottomed flask equipped with a refluxer, and the flask was heated at 80°C for 60 h. The contents were then extracted in a Soxhlet extractor with 200 ml of chloroform for 6 h. An oily viscous mass was obtained from the extract after removal of the chloroform with a rotary evaporator. Slow (dropwise) precipitation of this mass in 150 ml of absolute ether gave light-yellow crystals with mp 119-121°C and R<sub>f</sub> 0.69. IR spectrum: 1740 (C=O) 1630 cm<sup>-1</sup> (CH=CH). PMR spectrum: 1.10-1.45 (3H, m, CH=CH<sub>2</sub>), 3.82 (2H, m, CH<sub>2</sub>O), 5.12 (1H, m, OCH), 6.50 ppm (2H, m, CH=CH).

<u>Allyl Furfuryl Ether (VIIa,  $C_8H_{10}O_2$ .</u> A 10.2-ml (60 mmole) sample of Va was added dropwise in the course of 20 min at 55-60°C to a mixture of 5.54 ml (50 mmole) of alcohol VI, 3.15 g (5 mmole) of Catamine AB, and 10 ml of 10 N KOH solution, after which the reaction mixture was maintained at the indicated temperature for 1 h. It was then cooled to 20°C to 20°C and extracted with ether (three 50-ml portions), and the extract was dried with magnesium sulfate. Fractional distillation gave 6.21 g (90%) of ether VIIa with bp 173.5-174°C,  $nD^{20}$  1.4716, and  $d_4^{20}$  1.0025. IR spectrum: 920, 1640, 3080 (CH<sub>2</sub>=CH); 1500, 1550, 1600, 3130, 3170 (furan ring); 1070-1100 cm<sup>-1</sup> (COC). PMR spectrum: 3.85 (2H, d, OCH<sub>2</sub>CH=), 4.08 (2H, s, CH<sub>2</sub>O), 4.92-5.15 (2H, m, CH<sub>2</sub>=CH), 5.22-5.92 (1H, m, CH=CH<sub>2</sub>), 6.03 (2H, m, 3-H, 4-H), 7.08 ppm (1H, m, 5-H). <u>3a,6-Epoxy-1,6,7,7a-tetrahydro-3H-benzo[c]furan (VIII,  $C_8H_{10}O_2$ )</u>. A 1.6-g (11.6 mmole) sample of ether VIIa and 0.1 g of hydroquinone were placed in a three-necked flask equipped with a reflux condenser, a tube for admission of argon, and a thermometer, and the mixture was maintained at 170°C on an oil bath equipped with a thermoregulator. In the course of 6 h the temperature of the mixture rose spontaneously to 200°C. After 18 h from the start of the reaction, the reaction mixture was cooled and washed with absolute ether. The precipitate was dissolved in 15 ml of absolute alcohol and precipitated in 150 ml of absolute ether to give VIII in the form of light-yellow crystals (35% yield) with mp 149-150°C and Rf 0.63. IR spectrum: 1630 cm<sup>-1</sup> (C=O) PMR spectrum: 1.20-1.65 (3H, m, CH=CH<sub>2</sub>), 3.80-4.35 (5H, m, 2CH<sub>2</sub>O, OCH), 5.35-6.00 (m, 2H, CH=CH).

<u>Propargyl Furfuryl Ether (VIIb,  $C_{\rm a}H_{\rm a}O_{\rm 2}$ )</u>. A 7.1-ml (60 mmole) sample of halide Vb was added dropwise in the course of 20 min at 55-60°C to a mixture of 5.54 ml (50 mmole) of VI, 3.51 g (5 mmole) of Catamine AB, and 10 ml of 10 N aqueous KOH solution, and the mixture was maintained at the indicated temperature for 1 h. It was then cooled to 20°C and extracted with ether (three 50-ml portions), and the extact was dried with magnesium sulfate. Fractional distillation gave 5.44 g (80%) of ether VIIb with bp 110-114°C and  $n_D^{20}$  1.4821. IR spectrum: 2130 (C=CH); 1500, 1570, 1600, 3130, 3136 cm<sup>-1</sup> (furan ring). PMR spectrum: 2.15 (1H, m, HC=C), 3.85 (2H, d, OCH<sub>2</sub>), 4.15 (2H, m, CH<sub>2</sub>O), 6.04 (2H, m, 3-H, 4-H), 7.05 ppm (1H, m, 5-H).

<u>3a,6-Epoxy-1,3-dihydro-6H-benzo[c]furan (IX,  $C_{g}H_{g}O_{2}$ ). A 3-g (22 mmole) sample of ether</u> VIIb and 0.1 g of hydroquinone were placed in a three-necked flask equipped with a reflux condenser, a tube for the admission of argon, and a thermometer, and the mixture was maintained at 178° on an oil bath equipped with a thermoregulator. In the course of 4 h the temperature of the mixture rose spontaneously to 185°C. The mixture was cooled and washed with absolute ether, and the precipitate was dissolved in 15 ml of absolute alcohol and precipitated in 150 ml of absolute ether to give IX in the form of a light-yellow crystalline substance (15% yield) with mp 180-183°C and R<sub>f</sub> 0.61. IR spectrum: 1630 cm<sup>-1</sup> (CH=CH). PMR spectrum: 3.8-04.5 (5H, m, 2CH<sub>2</sub>O, OCH), 5.7-6.8 ppm (3H, m, CH=CH and CH=).

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