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**Studies on 4-Pyrones and 4-Pyridones. II.\***  
**The Preparation and Rearrangement of 3-Allyloxy-4-pyrone\*\***

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Preparation of 3-allyloxy-4-pyrone (II), the Claisen rearrangement of II to 3-hydroxy-2-allyl-4-pyrone (IV) and synthesis of a number of related compounds are described.

In recent years several papers describing examples of Claisen rearrangement in the 4-pyrone series (allyl kojate<sup>1,2</sup>,  $\alpha$ -deoxykojyl allyl ether<sup>3</sup>) have been published. As part of our studies on 4-pyrones the rearrangement of 3-allyloxy-4-pyrone (allyl ether of pyromeconic acid) has been investigated. In the present communication the preparation and properties of the hitherto undescribed 3-allyloxy-4-pyrone (II) and of several related compounds (IV—IX) is reported.

Pyromeconic acid (3-hydroxy-4-pyrone, I), needed as starting material, could be readily prepared by complete decarboxylation of meconic acid (3-hydroxy-4-pyrone-2,6-dicarboxylic acid), under reduced pressure. Although yields of I obtained in this reaction by different authors<sup>4-13</sup> are rather low, we were able to obtain an average yield of 65%.

3-Allyloxy-4-pyrone (II) was prepared by refluxing a mixture of the sodium salt of I with an equivalent amount of allyl bromide in methanol. It could be isolated as a colourless oil having b. p. 107—110° at 2.5—3 mm. For identification purposes 3-methoxy-4-pyrone (III) was also prepared<sup>11</sup>. In ultraviolet analysis the spectra of II and III showed to be very similar.

It was observed that during distillation of II at higher temperatures and pressures rearrangement takes place and crystalline 3-hydroxy-2-allyl-4-pyrone (IV) is obtained in good yield. Compound IV could be distilled at 135—140°/16 mm. and crystallized from water, having m. p. 88—89°. Evidence for the free hydroxyl group of IV is given by the positive colour test with ferric chloride (violet colour) and by reaction with diazomethane affording 3-methoxy-2-allyl-4-pyrone (VIII). The colour test of VIII with ferric chloride was negative.

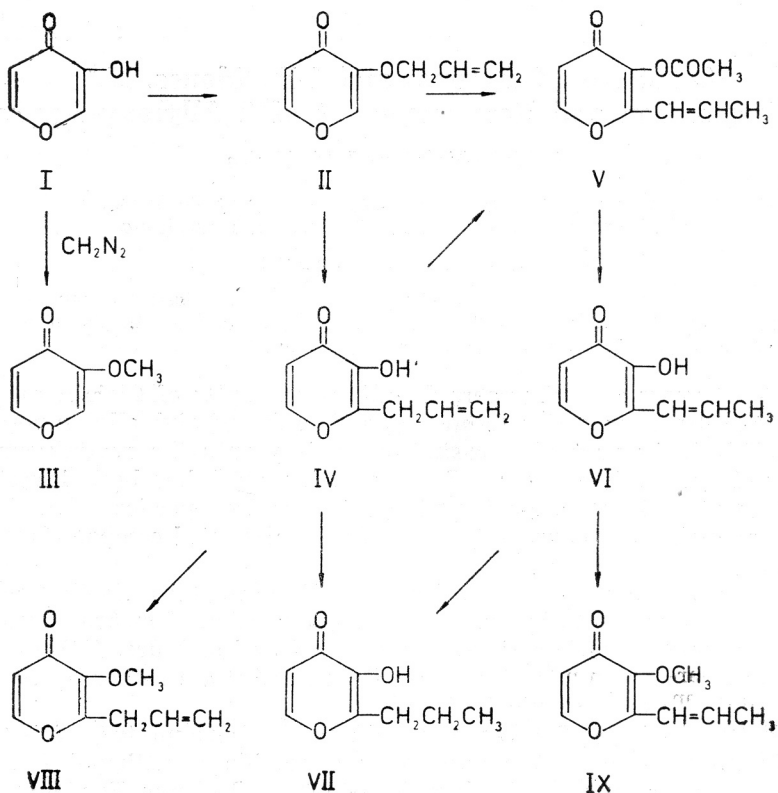
Heating of either II or IV with acetic anhydride yielded 3-acetoxy-2-propenyl-4-pyrone (V). Deacetylation of V with hydroxylamine according to Beélik and Purves<sup>14</sup> gave 3-hydroxy-2-propenyl-4-pyrone (VI). The structure of VI is supported by the positive ferric chloride test, the ultraviolet spectrum and

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by hydrogenation. Compound VI shows an expressive bathochromic shift (350 Å) with respect to IV. Catalytic hydrogenation of both VI and IV led to 3-hydroxy-2-propyl-4-pyrone (VII).



Finally, 3-methoxy-2-propenyl-4-pyrone (IX) was prepared by treatment of VI with diazomethane in ethereal solution. From the ultraviolet spectrum of IX it can be concluded that the side chain double bond is in conjugation with the 4-pyrone ring system. The spectrum of the corresponding allyl derivative (VIII) points at an isolated double bond.

The ultraviolet absorption maxima for compounds II—IX are listed in Table I.

TABLE I  
Ultraviolet Absorption Maxima

Compound	$\lambda_{\max}$ , Å	$\log \epsilon$
II	2700	3.95
III	2700	3.93
IV	2800	3.99
V	2800	4.23
VI	3150	4.26
VII	2800	4.07
VIII	2650	4.01
IX	2940	4.17

## EXPERIMENTAL

All melting and boiling points are uncorrected.

*Pyromeconic acid (I)*

In a 500 ml. distilling flask 50 g. of copper turnings was placed and a mixture of 50 g. of copper powder and 50 g. of partially anhydrous meconic acid added. A thermometer was immersed into the mixture and the flask heated by means of an electrical heating mantle under reduced pressure (13–20 mm.). The temperature was raised during one hour to 245° and during the next one to 330°C. The sublimate was dissolved in chloroform, the suspension filtered and the solvent evaporated. Almost colourless pyromeconic acid having m. p. 117–118° was obtained. Average yield 65%.

*3-Allyloxy-4-pyrone (II)*

A solution of sodium methoxide prepared from 4.6 g. (0.2 g. atom) of sodium and 120 ml. of dry methanol was added to a suspension of 22.4 g. (0.2 mole) of pyromeconic acid in 240 ml. of dry methanol. The mixture was refluxed during 10 minutes and 24.2 g. (0.2 mole) of allyl bromide added at once. Refluxing was continued for 4 hours. The solvent was evaporated and the separated sodium bromide removed by suction. The resulting oily product distilled at 107–110°/2.5–3 mm.; yield 24.5 g. (80%). On standing for several days the oil partially crystallized and a small amount of crystals melting at 81–83° could be separated by filtration. After recrystallization from water the crystalline product melted at 88–89° and was identified as IV. The oily ether (II) was purified by distillation at 108–109°/3 mm. to give a colourless oil,  $d_{26}^{26} = 1.2066$ ,  $n_D^{26} = 1.5468$ .

Anal.  $C_8H_8O_3$  (152.14) calc'd.: C 63.15; H 5.30%  
found: C 63.38; H 5.42%

*3-Methoxy-4-pyrone (III)*

It was prepared from pyromeconic acid and diazomethane according to Bickel<sup>11</sup>. For ultraviolet analysis the substance was sublimated at 135°/19 mm. Colourless crystals having m. p. 94.5–95° were obtained.

*3-Hydroxy-2-allyl-4-pyrone (IV)*

3-Allyloxy-4-pyrone (19.3 g., 0.127 mole) was distilled at 137–140°/15 mm. After cooling the oily distillate crystallized in the receiver. Recrystallization from a mixture of ethanol-water (1:5) afforded 10.5 g. of colourless crystals melting at 85–86°. The solvent was evaporated and the residue repeatedly distilled at 135–140°/16 mm. There was obtained 4.0 g. of colourless crystals having m. p. 85–86° and 3.5 g. of a pale yellow oil. The total yield of IV was 14.5 g. After recrystallization from a mixture of ethanol-water (1:5), colourless prisms of pure IV, m. p. 88–89° were obtained. They were soluble in water, ethanol, chloroform, benzene and dioxane. An analytical sample was recrystallized from water, m. p. 88–89°.

Anal.  $C_8H_8O_3$  (152.14) calc'd.: C 63.15; H 5.30%  
found: C 62.99; H 5.24%

*3-Acetoxy-2-propenyl-4-pyrone (V)*

A mixture of 3-hydroxy-2-allyl-4-pyrone (0.76 g., 0.005 mole) and acetic anhydride (5 ml.) was refluxed for 7 hours, the excess of anhydride evaporated *in vacuo* and the residue distilled at 135–145°/0.15 mm. There was obtained 0.7 g. of a viscous yellow oil which crystallized on standing. Recrystallization from ether gave colourless crystals, m. p. 81–82°. The acetate is soluble in water and the common organic solvents, except petroleum ether.

Anal.  $C_{10}H_{10}O_4$  (194.18) calc'd.: C 61.85; H 5.19%  
found: C 62.13; H 5.27%

The same acetate was obtained in a similar way from II, yield 87.5%. Identity of the products obtained from II and IV was established by means of mixed melting point and ultraviolet spectra.

### 3-Hydroxy-2-propenyl-4-pyrone (VI)

To a solution of 0.7 g. (0.01 mole) hydroxylamine hydrochloride in 25 ml. of pyridine 0.97 g. (0.005 mole) of V was added. After keeping the mixture overnight at room temperature 5 ml. of water was added and the solvent evaporated *in vacuo*. Crystallization of the residue from ethanol-water (1:1) afforded 0.38 g. (50%) of almost colourless crystals melting at 118–120°. The compound gave a positive ferric chloride test. After two crystallizations from water-ethanol (1:1) the pure product melted at 122–123°.

*Anal.* C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> (152.14) calc'd: C 63.15; H 5.30%  
found: C 63.24; H 5.39%

### 3-Hydroxy-2-propyl-4-pyrone (VII)

Hydrogenation of 0.76 g. (0.005 mole) of 3-hydroxy-2-propenyl-4-pyrone, melting at 122–123°, in 50 ml. of dry ethanol with 0.25 g. of pre-reduced 10% palladium-on-charcoal catalyst, resulted in the uptake of 105 ml. (0.005 mole) of hydrogen. The catalyst was filtered off, the solvent removed and the residue recrystallized from a mixture of petroleum ether-ethyl acetate (5:1). Colourless leaflets, m. p. 84–85°, giving a positive ferric chloride test were obtained. Compound VII was prepared in a similar way from 3-hydroxy-2-allyl-4-pyrone (IV). The identity was established by means of the mixed melting point and ultraviolet spectra.

*Anal.* C<sub>8</sub>H<sub>10</sub>O<sub>3</sub> (154.16) calc'd: C 62.32; H 6.54%  
found: C 62.56; H 6.94%

### 3-Methoxy-2-allyl-4-pyrone (VIII)

To an ethereal solution of diazomethane (about 1.4 g., 0.033 mole) was added with stirring at 0° an ethereal solution of 3-hydroxy-2-allyl-4-pyrone (1.52 g., 0.01 mole in 200 ml. of ether). After keeping overnight in the refrigerator the solvent was evaporated and the residue distilled at 96–97°/2 mm., yield 0.9 g. (54%) of a pale yellow oil. The analytical sample was obtained by distillation at 112–113°/4 mm.

*Anal.* C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> (166.17) calc'd: C 65.05; H 6.07%  
found: C 64.79; H 6.09%

### 3-Methoxy-2-propenyl-4-pyrone (IX)

To an ethereal solution of diazomethane prepared from about 27.5 g. of nitroso-methylurea was added with stirring at 0° an ethereal solution of 3-hydroxy-2-propenyl-4-pyrone (prepared from 6.1 g., 0.04 mole, and 370 ml. of ether). After keeping overnight in the refrigerator the ether was evaporated and the residue distilled at 119–125°/3.5 mm. Yield 3.0 g. (45%), of a pale yellow oil. The analytical sample was purified by distillation at 126–127°/4.5 mm.

*Anal.* C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> (166.17) calc'd: C 65.05; H 6.07%  
found: C 64.82; H 6.35%

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### IZVOD

#### Studije u redu pirona-(4) i piridona-(4). II. Priprava i premještaj 3-aliloksi-pirona-(4)

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Opisuje se priprava 3-aliloksi-pirona-(4) (II) (aliletera piromekonske kiseline) iz natrijeva piromekonata i alilbromida u metanolu. Opreznom destilacijom kod nižih pritisaka (do 3 mm) dobiva se II, dok kod viših pritisaka (15–20 mm) nastaje, uz Claisenov premještaj, 3-hidroksi-2-alil-piron-(4) (IV).

U radnji su opisani još i ovi spojevi: 3-acetoksi-2-propenil-piron-(4) (V), 3-hidroksi-2-propenil-piron-(4) (VI), 3-hidroksi-2-propil-piron-(4) (VII), 3-metoksi-2-alil-piron-(4) (VIII) i 3-metoksi-2-propenil-piron-(4) (IX).

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