

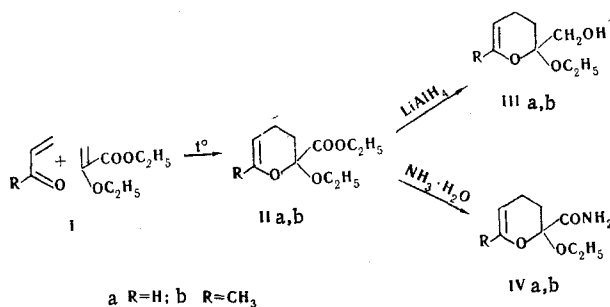
SYNTHESIS OF 2-ETHOXY-2-CARBETHOXY- Δ^5 -
DIHYDROPYRANS AND THEIR DERIVATIVES

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Acrolein and methyl vinyl ketone undergo diene condensation with ethyl α -ethoxyacrylate to give the corresponding 2-ethoxy-2-carbethoxy- Δ^5 -dihydropyrans in 50-60% yields. The reduction of the latter with lithium aluminum hydride gave the hydroxymethyl derivatives of dihydropyrans, while ammonolysis gave amides of 2-ethoxy- Δ^5 -dihydropyran-2-carboxylic acids.

2-Alkoxy- Δ^5 -dihydropyrans can be used as starting materials for the synthesis of amino deoxy sugars and diamino deoxy sugars [1-3]. In this connection, it seemed of interest to ascertain the possibility of the synthesis of Δ^5 -dihydropyrans, which can serve as starting compounds for the synthesis of ketohexoses. For this, we studied the diene condensation of α, β -unsaturated carbonyl compounds with ethyl α -ethoxyacrylate (I) [4].



We found that acrolein and methyl vinyl ketone undergo this reaction at 180°C to give 2-ethoxy-2-carbethoxy- Δ^5 -dihydropyran (IIa) and its 6-methyl derivative (IIb) in 50-60% yields. The IR spectra of IIa,b have absorption bands at 1655-1690 and 1750 cm^{-1} , which are ascribed to the stretching vibrations of the C=C bond and the carbonyl group in the esters, respectively.

Since IIa,b are of interest as starting materials for the synthesis of ketohexoses, some of their transformations were studied: hydroxymethyl derivatives IIIa,b were obtained by reduction with lithium aluminum hydride, while the corresponding amides (IVa,b) were obtained by reaction with 25% ammonium hydroxide.

EXPERIMENTAL

2-Ethoxy-2-carbethoxy- Δ^5 -dihydropyran (IIa). A mixture of 16.8 g (0.117 mole) of ethyl α -ethoxyacrylate (I), 6.55 g (0.117 mole) of acrolein, and 0.1 g of hydroquinone was heated in a glass ampule at 180° for 6 h to give 11.5 g (49%) of dihydropyran IIa with bp 107-108° (14 mm) and n_D^{23} 1.4468. Found: C 60.0, 60.1; H 8.1, 8.1%. $\text{C}_{10}\text{H}_{16}\text{O}_4$. Calculated: C 60.0; H 8.1%.

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2-Ethoxy-2-carbethoxy-6-methyl- Δ^5 -dihydropyran (IIb). This compound was obtained in 65% yield from ester I and methyl vinyl ketone by a similar method and had bp 125-126° (30 mm) and n_D^{24} 1.4480. Found: C 61.7, 61.5; H 8.5, 8.4%. $C_{11}H_{18}O_4$. Calculated: C 61.6; H 8.5%.

2-Ethoxy-2-hydroxymethyl- Δ^5 -dihydropyran (IIIa). A 5-g (0.025 mole) sample of 2-carbethoxydihydropyran IIa was added with stirring and cooling to a suspension of 1.42 g (0.0375 mole) of lithium aluminum hydride in 150 ml of absolute ether. The reaction mass was refluxed for 4 h, cooled, and decomposed with 5 ml of water. The precipitate was removed by filtration and washed with ether. The ether layer was dried with magnesium sulfate, the ether was removed by distillation, and the residue was vacuum distilled to give 3.5 g (89%) of IIIa with bp 101-102° (15 mm) and n_D^{21} 1.4645. Found: C 60.4, 60.7; H 8.7, 8.9%. $C_{11}H_{14}O_3$. Calculated: C 60.7; H 8.9%.

2-Ethoxy-2-hydroxymethyl-6-methyl- Δ^5 -dihydropyran (IIIb). This compound was similarly obtained in 85% yield from 2-carbethoxydihydropyran IIb and had bp 98-100° (10 mm) and n_D^{16} 1.4655. Found: C 63.0, 63.0; H 9.4, 9.4%. $C_9H_{16}O_3$. Calculated: C 62.7; H 9.4%.

2-Ethoxy- Δ^5 -dihydropyran-2-carboxamide (IVa). A total of 25 ml of 25% ammonium hydroxide was added with vigorous stirring to 2.5 g (0.0125 mole) of dihydropyran IIa. After 3 days, colorless, acicular crystals precipitated and were removed by filtration and recrystallized from hexane to give 1.7 g (80%) of amide IVa with mp 110-112°. Found: C 56.1, 56.3; H 7.6, 7.9; N 7.9, 8.0%. $C_8H_{13}NO_3$. Calculated: C 56.0; H 7.7; N 8.2%.

2-Ethoxy-6-methyl- Δ^5 -dihydropyran-2-carboxamide (IVb). This compound was similarly obtained in 73% yield from carbethoxydihydropyran IIb and 25% ammonium hydroxide and had mp 114-115° (from ether). Found: C 58.5, 58.7; H 8.3, 8.0; N 7.5%. $C_9H_{15}NO_3$. Calculated: C 58.3; H 8.2; N 7.5%.

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