

## BRIEF COMMUNICATIONS

## SYNTHESIS OF UNSATURATED ESTERS OF PYRIDINE- AND QUINOLINEDI-CARBOXYLIC ACIDS

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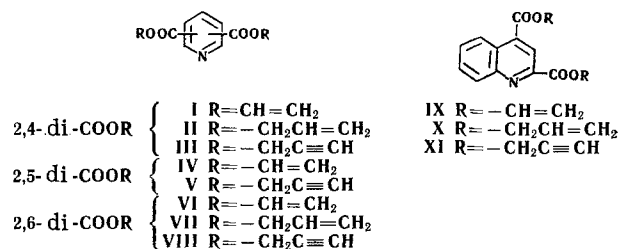
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The divinyl, diallyl, and dipropargyl esters of pyridine-2,4-, pyridine-2,6-, and quinoline-2,4-dicarboxylic acids and the divinyl and dipropargyl esters of pyridine-2,5-dicarboxylic acid have been synthesized.

The divinyl and diallyl esters of dicarboxylic acids are of interest as starting materials for the production of polymers with a cross-linked structure. In recent years, polymers based on the diallyl esters of phthalic acids, which possess a number of valuable properties, have attracted attention. It is also known that the dipropargyl esters of aliphatic and aromatic dicarboxylic acids can be converted by the polydehydrocondensation reaction into polymers with a high thermal stability [1, 2]. Furthermore, the possibility has been shown of polymerizing dipropargyl esters of carbazodicarboxylic acids [3].

In view of this, in the present work we have obtained a series of diallyl, divinyl, and dipropargyl esters of pyridine- and quinolinedicarboxylic acids (I-XI, table) in order subsequently to study the possibility of their polymerization.

Only the diallyl ester of pyridine-2,5-dicarboxylic acid, obtained by direct esterification [4], was known previously.



We obtained the diallyl and dipropargyl esters from the chlorides of the corresponding acids and allyl and propargyl alcohols. The divinyl esters were obtained by the reaction of mercurybisacetaldehyde [5] with the dichlorides of the appropriate acids at room temperature in dichloroethane solution in the presence of pyridine. These divinyl esters consist of colored solid substances, except for compound I which is a high-boiling liquid.

Propargyl esters are colored solid substances. Diallyl quinoline-2,4-dicarboxylate is a colorless solid. The diallyl esters of pyridine-2,4- and -2,6-dicarboxylic acids are high-boiling yellow liquids.

## EXPERIMENTAL

Divinyl pyridine-2,5-dicarboxylate (IV). The dichloride of pyridine-2,5-dicarboxylic acid obtained from 10 g (0.06 mole) of the diacid was added at 20-25° C with stirring to a suspension of 51.3 g (0.18 mole) of mercurybisacetaldehyde in 200 ml of dry dichloroethane and 9.46 g (0.12 mole) of dry pyridine, and the mixture was stirred for 1 hr and filtered. The filtrate was washed 2-3 times with saturated sodium carbonate solution and then with water to neutrality. The dichloroethane was distilled off, the residue was extracted with hot petroleum ether (bp 40-60° C), the petroleum ether was evaporated off, and the substance was recrystallized. Compounds VI and IX were obtained similarly. After the dichloroethane had been distilled off, the residue was extracted with ether. In the synthesis of compound I, after the dichloroethane had been driven off the substance was distilled in vacuum.

Diallyl pyridine-2,4-dicarboxylate (II). In drops, with stirring, 40 ml of allyl alcohol was added to the chloride of pyridine-2,4-dicarboxylic acid obtained from 10 g (0.06 mole) of the diacid. The mixture was boiled in the water bath for 4-5 hr, poured into

Characteristics of the Compounds Synthesized

Compound	Mp, °C	Bp, °C (mm)	n <sub>D</sub> <sup>20</sup>	Empirical formula	Found, %		Calculated, %		Yield, %
					C	N	C	N	
I	—	133—134 (3)	1.5450	C <sub>11</sub> H <sub>9</sub> NO <sub>4</sub>	60.21	6.23	60.26	6.51	75
II	—	171—173 (4.5)	1.5220	C <sub>13</sub> H <sub>13</sub> NO <sub>4</sub>	62.93	5.72	63.16	5.66	75
III	78.5—79.5 (from ethanol)	—	—	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	64.57	5.72	64.24	5.76	81
IV	68—69 (from petroleum ether)	—	—	C <sub>11</sub> H <sub>9</sub> NO <sub>4</sub>	59.97	6.73	60.26	6.51	77
V	92—93 (from ethanol)	—	—	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	64.43	5.83	64.24	5.76	87
VI	68—69 (from ether)	—	—	C <sub>11</sub> H <sub>9</sub> NO <sub>4</sub>	60.21	6.77	60.26	6.51	80
VII	—	154—156 (3)	1.5175	C <sub>13</sub> H <sub>13</sub> NO <sub>4</sub>	63.33	5.98	63.16	5.66	84
VIII	124—125 (from ethanol)	—	—	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	64.41	5.94	64.24	5.76	87
IX	124—125 (from ethanol)	—	—	C <sub>15</sub> H <sub>11</sub> NO <sub>4</sub>	66.50	5.80	66.75	5.67	62
X	56.5—57 (from ethanol)	—	—	C <sub>17</sub> H <sub>15</sub> NO <sub>4</sub>	68.83	4.53	68.68	4.72	72
XI	98.5—99.5 (from ethanol)	—	—	C <sub>17</sub> H <sub>11</sub> NO <sub>4</sub>	69.40	4.86	69.62	4.78	89

water, and extracted with dichloroethane and the extracts were dried with anhydrous sodium sulfate. After the elimination of the solvent, the residue was distilled in vacuum. Compounds VII and X were obtained similarly. Diallyl pyridine-2,5-dicarboxylate was obtained by the same method, mp 54° C (from ethanol); according to the literature [4], mp 53° C.

Dipropargyl pyridine-2,4-dicarboxylate (III). In drops, 25 ml of propargyl alcohol was added to the chloride of pyridine-2,4-dicarboxylic acid obtained from 10 g (0.06 mole) of the diacid. The reaction mixture was boiled in the water bath for 4–5 hr, and then the excess of propargyl alcohol was distilled off in vacuum. The residual oil was triturated with ether and recrystallized. Compounds V and X were obtained similarly. In the synthesis of VIII, after being boiled the reaction mixture was treated with saturated sodium carbonate solution and the precipitate was filtered off and recrystallized.

Attempts to obtain the divinyl, diallyl, and dipropargyl esters of pyridine-2,3-dicarboxylic acid were unsuccessful.

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## N-SUBSTITUTED 2,5-DIMETHYL-4-ETHYNYL(VINYL)PIPERID-4-OLS

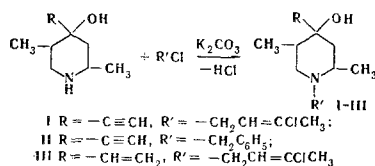
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The  $\gamma$ -isomers of 1-(3-chlorobuten-2-yl)- and 1-benzyl-2,5-dimethyl-4-ethynylpiperid-4-ols (I, II) and of 1-(3-chlorobuten-2-yl)-2,5-dimethyl-4-vinylpiperid-4-ol (III) and the quaternary salts of compounds I–III and of the  $\beta$ -isomers of the 1,2,5-trimethyl-4-ethynyl-(vinyl)piperid-4-ols [1] have been synthesized.

1-Alkenyl-4-ethynyl(vinyl)-2,5-dimethylpiperid-4-ols have been synthesized previously [2–4] and have been used to obtain various esters. Continuing systematic investigations on the synthesis of new physiologically active compounds from 2,5-dimethylpiperid-4-one [5] we have synthesized the  $\gamma$ -isomers of 1-(3-chlorobuten-2-yl)- and 1-benzyl-4a-ethynyl-2e,5e-dimethylpiperid-4e-ols (I, II) and of 1-(3-chlorobuten-2-yl)-2e,5e-dimethyl-4a-vinylpiperid-4e-ol (III) by the reaction of the individual  $\gamma$ -isomers of 4-ethynyl(vinyl)-2,5-dimethylpiperid-4-ols with the corresponding halogen derivatives in absolute butanol in the presence of anhydrous potassium carbonate [8].



## EXPERIMENTAL

1-(3-Chlorobuten-2-yl)-4-ethynyl-2,5-dimethylpiperid-4-ol (I). With vigorous stirring, a solution of 9 g (0.072 mole) of 1,3-dichlorobuten-2-ene in 20 ml of absolute butanol was added dropwise to a mixture of 10 g (0.065 mole) of the  $\gamma$ -isomer of 4-ethynyl-2,5-di-

methylpiperid-4-ol (IV) and 18 g of powdered anhydrous potassium carbonate in 50 ml of absolute butanol, and the mixture was heated at 80–85° C for 7 hr. On the following day, the precipitate of salts was filtered off and washed, the butanol was distilled off in vacuum, and the residue was crystallized from absolute benzene, giving 10.8 g (68%) of I, mp 98–99° C. Found, %: N 5.77, 5.89. Calculated for  $\text{C}_{13}\text{H}_{20}\text{ClNO}$ , %: N 5.79. The hydrochloride of the piperidol I was obtained by the addition of an ethereal solution of dry hydrogen chloride to an ethereal solution of I. Yield 77%, mp 214–215° C (from ethanol with the addition of acetone). Found, %: Cl 12.76, 12.39; N 5.04, 4.93. Calculated for  $\text{C}_{13}\text{H}_{20}\text{ClNO} \cdot \text{HCl}$ , %: Cl 12.76; N 5.04.

The methiodide of the piperidol I was obtained by heating a mixture of 1.5 g (0.006 mole) of the piperidol and 0.96 g (0.006 mole) of methyl iodide in 20 ml of absolute benzene at 75–80° C for 2 hr. Yield 0.47 g (20%), mp 158–160° C (from acetone). Found, %: N 3.53, 3.55. Calculated for  $\text{C}_{14}\text{H}_{23}\text{ClINO}$ , %: N 3.65. The methiodides of II and III were obtained similarly.

1-Benzyl-4-ethynyl-2,5-dimethylpiperid-4-ol (II) was obtained in a similar manner to I from IV and benzyl chloride. Yield of II 74%, mp 60–61° C (from gasoline). Found, %: C 78.79; H 8.90, 8.81; N 6.08, 6.11. Calculated for  $\text{C}_{16}\text{H}_{21}\text{NO}$ , %: C 79.01; H 8.64; N 5.76%. Hydrochloride of the piperidol II, mp 238–239° C (from ethanol). Found, %: Cl 12.70, 12.77; N 5.27, 5.29. Calculated for  $\text{C}_{16}\text{H}_{21}\text{NO} \cdot \text{HCl}$ , %: Cl 12.70; N 5.01.

The methiodide of the piperidol II, yield 56%, mp 116–117° C (from acetone). Found, %: N 3.71, 3.83. Calculated for  $\text{C}_{17}\text{H}_{24}\text{INO}$ , %: N 3.64.

1-(3-Chlorobuten-2-yl)-2,5-dimethyl-4-vinylpiperid-4-ol (III) was obtained from the  $\gamma$ -isomer of 2,5-dimethyl-4-vinylpiperid-4-ol in a similar manner to I. Yield 71%, mp 82–83° C (from gasoline). Found, %: N 5.60, 5.45. Calculated for  $\text{C}_{13}\text{H}_{22}\text{ClNO}$ , %: N 5.75. Hydrochloride of III, mp 215–216° C. Found, %: Cl 12.41, 12.30; N 5.27, 5.18. Calculated for  $\text{C}_{13}\text{H}_{22}\text{ClNO} \cdot \text{HCl}$ , %: Cl 12.64; N 5.00. The methiodide of the piperidol III, yield 37%, mp 161–