SYNTHESIS OF UNSATURATED ESTERS OF PYRIDINE- AND QUINOLINECARBOXYLIC ACIDS

V. E. Blokhin, Z. Yu. Kokoshko, L. V. Kireeva, and Z. V. Pushkareva

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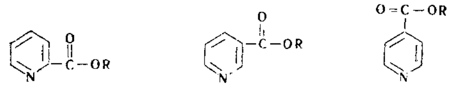
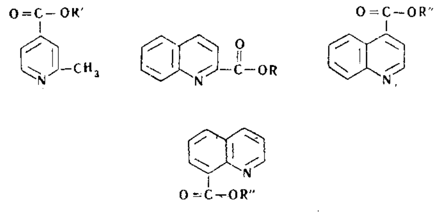
The vinyl esters of pyridine-2- and -4-carboxylic acids, the propargyl esters of pyridine-2-, -3-, and -4-carboxylic acids, the vinyl, allyl, and propargyl esters of quinoline-2-, -4-, and -8-carboxylic acids, and the allyl ester of 2-methylisonicotinic acid have been synthesized.

Interest in unsaturated esters of pyridine- and quinolinecarboxylic acids is due to the possibility of using them in copolymerization reactions. It is also desirable to investigate their biological activity, since poly(vinyl nicotinate) [1, 2] is a long-acting and stable vitamin. At present, the literature contains reports of the synthesis of allyl esters of pyridinecarboxylic acids [3–5] and of the vinyl ester of nicotinic acid [2, 6–9]; however, the difficulty of obtaining vinyl esters from the acids in view of their low solubility and the negative influence of the heteroatom on the course of catalysis is mentioned. Thus, vinyl nicotinate is obtained by direct vinylation with acetylene at high pressure and high temperatures [6, 7, 9] or by the reaction of nicotinic acid with divinylmercury [2].

We have synthesized a number of isomeric unsaturated esters of pyridine- and quinolinecarboxylic acids of the general formulas:





R = $CH_2{=}CH$, $CH{\equiv}C{-}CH_2$; R' = $CH_2{=}CH{-}CH_2$;

R'' = $CH_2{=}CH$, $CH_2{=}CH{-}CH_2$, $CH{\equiv}C{-}CH_2$

The vinyl esters were obtained by the reaction of hydrochlorides of the corresponding acid chlorides with mercurybisacetaldehyde [10, 11]. The reaction takes place readily at room temperature with yields of 35–60%. The vinyl pyridinecarboxylates obtained are colorless liquids which distil in vacuum, readily form hydrochlorides, and crystallize from ethanol or acetone (**I**, **IV** in the table). The vinyl quinolinecarboxylates are low-melting crystalline substances (**VII**, **X**, and **XIII** in the table).

The allyl and propargyl esters were obtained from the hydrochlorides of the corresponding acid chlorides and allyl or propargyl alcohol. The allyl esters are liquids that can be distilled in vacuum (**VI**, **VIII**, **XI**, and **XIV** in the table). The propargyl esters of the

Characteristics of the Substances Synthesized

№ пп.	Compound	Bp, °C (pressure mm)	n_D^{20}	Mp*, °C	Empirical formula	Found, %			Calculated, %			Yield, %	Mp* of the hydrochloride °C
						C	N	Cl	C	N	Cl		
I	Vinyl picolinate**	98—100 (4)	1.5413	—	$C_8H_7NO_2 \cdot HCl$	51.90	7.55	18.87	51.75	7.55	19.13	50—56	102—103 (ac.)
II	Propargyl picolinate**	116—118 (3)	1.5360	—	$C_9H_7NO_2 \cdot HCl$	54.83	7.06	18.25	54.73	7.09	17.97	76	128—129 (ac.)
III	Propargyl nicotinate**	110—112 (4)	1.5328	—	$C_9H_7NO_2 \cdot HCl$	54.87	7.06	17.96	54.73	7.09	17.97	83	150—151 (al.)
IV	Vinyl isonicotinate**	75—77 (4)	1.5260	—	$C_8H_7NO_2 \cdot HCl$	51.83	7.62	19.50	51.75	7.55	19.13	38	171—172 (ac.)
V	Propargyl isonicotinate**	110—111 (5)	—	54.5—55 (ac.)	$C_9H_7NO_2 \cdot HCl$	54.63	6.83	18.10	54.73	7.09	17.97	68	164.5—165 (al.)
VI	Allyl 2-methylisonicotinate**	102—103 (4)	1.5085	—	$C_{10}H_{11}NO_2 \cdot HCl$	56.13	6.73	16.74	56.21	6.56	16.62	81	125—126 (al.)
VII	Vinyl quinaldinate	150—152 (3)	—	70—71 (et.)	$C_{12}H_9NO_2$	72.35	7.26	—	72.25	7.03	—	48	111—111,5 (ac.)
VIII	Allyl quinaldinate	160—161 (4)	1.6030	—	$C_{13}H_{11}NO_2$	73.20	6.73	—	73.29	6.60	—	79	72—73 (ac.)
IX	Propargyl quinaldinate	—	—	110—111 (ac.)	$C_{13}H_9NO_2$	73.86	6.84	—	73.94	6.63	—	73	—
X	Vinyl quinoline-4-carboxylate	134—136 (3)	—	43—44	$C_{12}H_9NO_2$	72.00	7.39	—	72.25	7.03	—	44	—
XI	Allyl quinoline-4-carboxylate	149—151 (4)	1.5936	—	$C_{13}H_{11}NO_2$	73.15	6.69	—	73.29	6.60	—	76	—
XII	Propargyl quinoline-4-carboxylate	—	—	103—104 (ac.)	$C_{13}H_9NO_2$	73.72	7.00	—	73.94	6.63	—	89	—
XIII	Vinyl quinoline-8-carboxylate	—	—	63—64 (pet. et.)	$C_{12}H_9NO_2$	71.98	7.28	—	72.25	7.03	—	27	—
XIV	Allyl quinoline-8-carboxylate	155—156 (5)	1.6005	—	$C_{13}H_{11}NO_2$	73.36	6.59	—	73.29	6.60	—	73	—
XV	Propargyl quinoline-8-carboxylate	—	—	111—112 (al.)	$C_{13}H_9NO_2$	73.93	6.82	—	73.94	6.63	—	81	—

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*The solvent for crystallization is given in brackets: ac.) acetone, al.) ethanol, et.) ether, pet. et.) petroleum ether.

**Analyses given for the hydrochlorides.

pyridinecarboxylic acids are liquids readily setting at room temperature (**II**, **III**, and **V** in the table). The propargyl esters of the quinolinecarboxylic acids are crystalline substances (**IX**, **XII**, and **XV** in the table).

EXPERIMENTAL

Vinyl picolinate. The hydrochloride of picolinoyl chloride obtained from 20 g (0.163 mole) of the acid was added at 20–25° C with stirring to a suspension of 46.7 g (0.163 mole) of mercurybisacetaldehyde [10] in 200 ml of dry dichloroethane and 12.6 ml of dry pyridine. The reaction mixture was stirred for an hour and filtered. The filtrate was washed several times with saturated sodium carbonate solution and then with water to neutrality. The dichloroethane was driven off and the residue was distilled in vacuum.

Compounds **IV**, **VII**, and **X** were obtained similarly from the hydrochlorides of the corresponding acid chlorides. In the case of vinyl quinoline-8-carboxylate (**XIII** in the table), after the dichloroethane had been driven off the residual oil was extracted repeatedly with hot petroleum ether (bp 40–60° C). The precipitate that deposited was filtered off and recrystallized from petroleum ether.

Allyl quinaldinate. In drops, with cooling, 40 ml of allyl alcohol was added to the hydrochloride of the quinaldinoyl chloride obtained from 28 g (0.163 mole) of the acid. The reaction mixture was boiled in the water bath for 3–4 hr and was then cooled, poured onto ice, made alkaline with saturated sodium carbonate solution to pH 8–9, and extracted with dichloroethane. The extract was dried with sodium sulfate and then the solvent was driven off and the residue was distilled in vacuum.

Compounds **XI** and **XIV** were obtained similarly.

Allyl 2-methylisonicotinate. A mixture of 7.5 g (0.054 mole) of 2-methylisonicotinic acid, 10 ml of conc. H_2SO_4, and 20 ml of allyl alcohol was boiled in the water bath for 3 hr and was then cooled, poured onto ice, made strongly alkaline with a saturated solution of sodium carbonate, and extracted with ether. The extract was dried with sodium sulfate, the solvent was driven off, and the residue was distilled in vacuum.

Propargyl picolinate. In drops, with cooling, 25 ml of propargyl alcohol was added to the hydrochloride of the picolinoyl chloride obtained from 20 g (0.163 mole) of the acid. The reaction mixture was boiled in the water bath for 3–4 hr and was then cooled, poured onto ice, made alkaline with a saturated solution of sodium carbonate to pH 8–9, and extracted with dichloroethane. The extract was dried with sodium sulfate, the solvent was driven off, and the residue was distilled in vacuum.

Compounds **III** and **V** were obtained similarly. In the case of compounds **IV**, **XII**, and **XV**, after the reaction mixture had been made alkaline, the precipitate was filtered off and crystallized.

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Kirov Ural Polytechnic Institute, Sverdlovsk