Bromination of α,β-unsaturated acids of pyridine Preparation of 2-bromoethylenes of the pyridine series

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Received 25 October 1987

Accepted for publication 1 August 1988

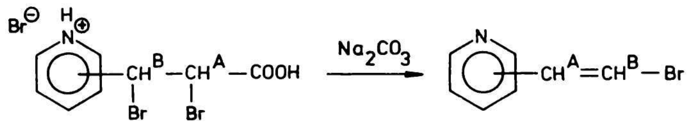
Preparation of bromides of 2,3-dibromo-3-(X-pyridinium)propanoic acids (X = 2, 3, 4) by bromination of the respective (*E*)-3-(X-pyridyl)-2-propenoic acids (X = 2, 3, 4) in chloroform and glacial acetic acid has been described. (*Z*)-X-(2-Bromovinyl)pyridines (X = 2, 3, 4) were prepared by debromination decarboxylation of alkaline 2,3-dibromo-3-(X-pyridyl)propanoates (X = 2, 3, 4) in acetone. The structures of the prepared derivatives were proved by ^{1}H NMR spectra.

Описано получение бромидов 2,3-дибромо-3-(X-пиридиний)пропановых кислот (X = 2, 3, 4) бромированием соответствующих (*E*)-3-(X-пиридил)-2-пропеновых кислот (X = 2, 3, 4) в хлороформе и ледяной уксусной кислоте. Получены (*Z*)-X-(2-бромовинил)пиридины (X = 2, 3, 4) дебромированием и декарбоксилированием щелочных 2,3-дибромо-3-(X-пиридил)пропанатов (X = 2, 3, 4) в ацетоне. Структуры полученных производных были определены ^{1}H ЯМР спектрами.

α,β-Dibromopropanoic acids are interesting from the aspect of their utilization for preparation of vinyl halides [1, 2] that may serve as starting compounds for synthesis of various ethylene and acetylene derivatives [2—5].

It is known from the literature that β-halo acids on heating with weak bases decompose under formation of alkene, carbon dioxide, and halide anion [6]. Debromination decarboxylation, as named by the authors in [7, 8], became a suitable method for preparation of activated vinyl halides of furan [1] and thiophene [2, 9]. Attempts to prepare pyrrole [10] and pyridine [11] derivatives by this method have been unsuccessful thus far.

For preparation of (*Z*)-X-(2-bromovinyl)pyridines (X = 2, 3, 4) *IIIa—IIIc* bromides of 2,3-dibromo-3-(X-pyridinium)propanoic acid (X = 2, 3, 4) *IIa—IIc* were synthesized by addition of bromine to (*E*)-3-(X-pyridyl)-2-propenoic acids (X = 2, 3, 4) *Ia—Ic*. X-(2-Bromovinyl)pyridines (X = 2, 3, 4) *IIIa—IIIc*



IIa–IIc *IIIa–IIIc*

a 2-pyridyl

b 3-pyridyl

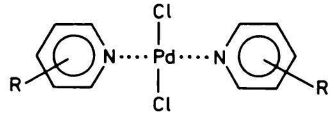
c 4-pyridyl

Scheme 1

(Scheme 1), not described in the literature so far, were obtained by decomposition of *IIa—IIc* with sodium carbonate in acetone.

The conditions for bromination of *Ia—Ic* were optimized. The best yields (above 90 %; Table 1) were achieved by heating of these compounds in chloroform or glacial acetic acid to 80 °C with mole excess of bromine. On heating the reaction components in glacial acetic acid above 100 °C we failed to isolate the appropriate α,β-dibromopropanoic acid *IIa* in the case of 3-(2-pyridyl)-2-propenoic acid *Ia*. However, from the pitchlike mass a negligible amount of a mixture of 2-(2,2-dibromovinyl)pyridine (*V*) and 2-(1,2-dibromovinyl)pyridine (*VI*) in the ratio of 3 : 5 was obtained [12]. These products resulted from successive brominations, dehydrobrominations, and decarboxylation.

By debromination decarboxylation of the respective α,β-dibromopropanoic acids *IIa—IIc* the desired X-(2-bromovinyl)pyridines (X = 2, 3, 4) *IIIa—IIIc* were obtained. Of these, only the 3-substituted derivative of pyridine *IIIb* was a stable compound. We failed to isolate 4-(2-bromovinyl)pyridine (*IIIc*) in a pure state. Therefore, the products *IIIa—IIIc* were stabilized by converting to palladium(II) complexes *IVa—IVc* with aqueous solution of palladium(II) chloride [13].



IVa–IVc

a R = 2-(2-Bromovinyl)

b R = 3-(2-Bromovinyl)

c R = 4-(2-Bromovinyl)

Table 1

Physical constants of the compounds *II*—*IV*

Compound	Formula M_r	w_i(calc.)/% w_i(found)/% C	H	N	Br	Yield/%	M.p./°C
IIa	$C_8H_7Br_2NO_2 \cdot HBr$	24.64	1.81	3.59	61.48	93[a], 84[b]	127—129
	389.9	24.53	1.78	3.45	62.30		
IIb	$C_8H_7Br_2NO_2 \cdot HBr$	24.64	1.81	3.59	61.48	97[a], 93[b]	154—156
	389.9	24.68	1.88	3.45	61.22		
IIc	$C_8H_7Br_2NO_2 \cdot HBr$	24.64	1.81	3.59	61.48	91[a], 83[b]	147 (decomp.)
	389.9	24.58	1.85	3.44	61.92		
IIIa	C_7H_6BrN	45.69	3.28	7.61	43.42	78	Oil
	184.0	45.55	3.12	7.45	43.78		
IIIb	C_7H_6BrN	45.69	3.28	7.61	43.42	75	Oil
	184.0	45.57	3.43	7.52	43.28		
IVa	$C_{14}H_{12}Br_2N_2 \cdot PdCl_2$	30.83	2.22	5.14	—		212 (decomp.)
	545.4	30.66	2.36	5.31	—		
IVb	$C_{14}H_{12}Br_2N_2 \cdot PdCl_2$	30.83	2.22	5.14	—		205—208
	545.4	30.89	2.21	5.10	—		
IVc	$C_{14}H_{12}Br_2N_2 \cdot PdCl_2$	30.83	2.22	5.14	—		225 (decomp.)
	545.4	30.96	2.42	5.37	—		

a) Prepared by the method *A*; *b*) prepared by the method *B*.

Table 2

^1H NMR spectral data of the compounds *I*, *II* in hexadeuterodimethyl sulfoxide

Compound	δ/ppm							Coupling constants
	H-2	H-3	H-5	H-4	H-6	H^A	H^B	
Ia	—		7.25—8.00 (m)		8.66 (d)	6.84 (d)	7.63 (d)	$J_{5,6} = 4.8$ Hz, $J_{A,B} = 16$ Hz
Ib	8.86 (d)	—	7.47 (dd)	8.15 (m)	8.61 (dd)	6.69 (d)	7.67 (d)	$J_{2,4} = 1.7$ Hz, $J_{5,6} = 5$ Hz, $J_{4,5} = 8.1$ Hz, $J_{A,B} = 16$ Hz
Ic	8.66 (d)	7.73 (d)	7.73 (d)	—	8.66 (d)	6.80 (d)	7.60 (d)	$J_{2,3} = J_{5,6} = 6$ Hz, $J_{A,B} = 16$ Hz
IIa	—		7.50—8.38 (m)		8.76 (d)	5.32 (d)	5.74 (d)	$J_{5,6} = 4.8$ Hz, $J_{A,B} = 11.5$ Hz
IIb	9.31 (d)	—	8.15 (dd)	8.75—9.06 (m)		5.75 (d)	5.94 (d)	$J_{2,4} = 2$ Hz, $J_{4,5} = 7.9$ Hz, $J_{A,B} = 11.6$ Hz
IIc	9.07 (d)	8.45 (d)	8.45 (d)	—	9.07 (d)	5.55 (d)	5.92 (d)	$J_{2,3} = J_{5,6} = 6.5$ Hz, $J_{A,B} = 11.6$ Hz

d = doublet; dd = doublet of doublets; m = multiplet.

Table 3

^{1}H NMR spectral data of the compounds *III* in deuterochloroform

Compound	δ/ppm							Coupling constants
	H-2	H-3	H-4	H-5	H-6	H^A	H^B	
IIIa	—	8.00 (dd)	7.66 (m)	7.1—7.3 (m)	8.60 (d)	7.25 (d)	6.64 (d)	$J_{5,6} = 4.9$ Hz, $J_{4,6} = 1$ Hz, $J_{3,4} = 7.8$ Hz, $J_{A,B} = 8.5$ Hz
IIIb	8.77 (d)	—	8.10 (m)	7.22 (dd)	8.52 (dd)	7.04 (d)	6.55 (d)	$J_{4,6} = 1.6$ Hz, $J_{5,6} = 4.9$ Hz, $J_{4,5} = 7.8$ Hz, $J_{A,B} = 8.3$ Hz
IIIc	8.59 (d)	7.51 (d)	—	7.51 (d)	8.59 (d)	7.00 (d)	6.63 (d)	$J_{2,3} = J_{5,6} = 6$ Hz, $J_{A,B} = 8.5$ Hz

d = doublet; dd = doublet of doublets; m = multiplet.

X-(2-Bromovinyl)pyridines (X = 2, 3, 4) turn to brown substances insoluble in common organic solvents but very well soluble in methanol and water. So far, this insolubility has been ascribed to a possible polymerization.

It is known from the literature [1, 2] that debromination decarboxylation in acetone always resulted in one isomer (*Z*) of vinyl halide only. In accordance with the theory, only one isomer of *IIIa*—*IIIc* was obtained in all cases. This was ascribed the *Z* configuration on the basis of values of the vicinal coupling constants of the olephinic protons $J_{A,B}$ = 8.3—8.5 Hz.

The structures of all synthesized derivatives were proved by ^{1}H NMR spectra. The values of chemical shifts of protons and coupling constants are presented in Tables 2 and 3.

Experimental

Melting points were determined on a Kofler hot stage. ^{1}H NMR spectra of compounds were measured on a Tesla BS 487 B apparatus at 80 MHz in hexadeuterodimethyl sulfoxide and deuterochloroform, using tetramethylsilane as standard. (*E*)-3-(2-Pyridyl)-2-propenoic acid (*Ia*), m.p. = 202 °C according to [14]; (*E*)-3-(3-pyridyl)-2-propenoic acid (*Ib*), m.p. = 233 °C according to [15]; (*E*)-3-(4-pyridyl)-2-propenoic acid (*Ic*), m.p. = 296 °C according to [16].

Bromides of 2,3-dibromo-3-(X-pyridinium)propanoic acids IIa—IIc

Method A

The mixture of the appropriate acid *Ia*—*Ic* (1.49 g; 0.01 mol) and bromine (3.2 g; 0.02 mol) in chloroform (30 cm^3) was heated for 6 h at boiling point of the solvent. The solvent was distilled off under vacuum and the residue was boiled in acetone. The product was sucked off and crystallized from the mixture of methanol—ether ($\varphi_r = 3:1$).

Method B

The mixture of the appropriate acid *Ia*—*Ic* (1.49 g; 0.01 mol) and bromine (3.2 g; 0.02 mol) in glacial acetic acid (30 cm^3) was heated at 80 °C for 5 h. The solvent was distilled off under vacuum and ether was added to the residue. The precipitate was sucked off and crystallized from the mixture of methanol—ether ($\varphi_r = 3:1$).

(Z)-X-(2-Bromovinyl)pyridines IIIa—IIIc

The mixture of bromide of 2,3-dibromo-3-(X-pyridinium)propanoic acid *IIa*—*IIc* (3.9 g; 0.01 mol) and sodium carbonate (4 g) in acetone (100 cm^3) was heated at the boiling point of the solvent for 6 h. Acetone was distilled off under vacuum and water (40 cm^3) was added to the residue. The product was extracted with chloroform (3 × 20 cm^3), the combined extracts were dried with sodium sulfate. The solvent was distilled off and the residue was analyzed by column chromatography (aluminium oxide, chloroform as the eluent).

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Translated by A. Kardošová