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Synthesis of β-Aroylvinyl Derivatives of Triphenylphosphine and Pyridine Based on β-Aroylacrylic Acids

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Abstract—Bromination of β-aroylacrylic acids afforded β-aroyl-α,β-dibromopropionic acids. The latter reacted with pyridine to form 1-(β-aroylvinyl)pyridinium bromides. Reaction of the salts obtained with triphenylphosphine resulted in β-aroylvinyltriphenylphosphonium bromides.

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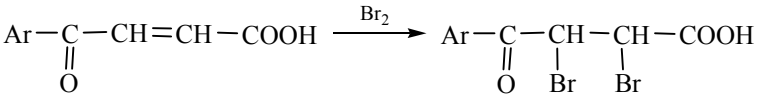
β-Aroylacrylic acids and their derivatives are of interest due their reactivity and synthetic opportunities. The reactions of these compounds with various nucleophiles [1, 2] including amines [3, 4] have been widely studied. Recently we have performed reactions of β-aroylacrylic acids with phosphorus nucleophiles [5–7].

In continuation of these studies we obtained β-aroylvinyltriphenylphosphonium and 1-(β-aroylvinyl)-pyridinium bromides starting with β-aroylacrylic acids and compared the reactivity of the phosphorus and nitrogen atoms in the molecule.

The bromination of β-aroylacrylic acids afforded β-aroyl-α,β-dibromopropionic acids **Ia–Id** (Scheme 1, Tables 1, 2).

Scheme 1.



Ia–Id

Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**).

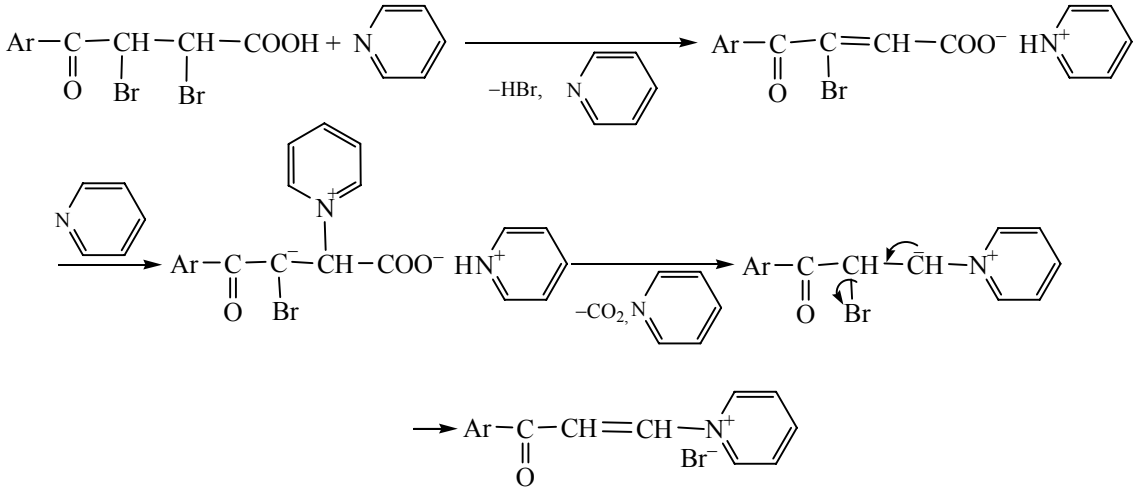
The latter reacted with pyridine in a ratio of 1 : 2 in boiling acetonitrile to give 1-(β-aroylvinyl)pyridinium bromides **IIa–IId** in good yields (Scheme 2, Tables 3, 4). The reaction is likely to occur through dehydrobromination and salt formation followed by addition of pyridine and decarboxylation of iminium salt due to the effect of the electron-acceptor pyridinium moiety.

Reactions of the obtained 1-(β-aroylvinyl)pyridinium bromides with an equimolar amount of triphenyl-

Table 1. Yields, melting points, and elemental analysis data of compounds **Ia–Id**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	Br		C	H	Br
Ia	40.64	148–149	36.02	2.58	47.56	$C_{10}H_8Br_2O_3$	35.71	2.38	47.62
Ib	61.27	158–159	37.54	2.09	46.07	$C_{11}H_{10}Br_2O_3$	37.71	2.86	45.71
Ic	62.59	142–143	32.24	3.05	–	$C_{10}H_7Br_2O_3Cl$	32.39	2.98	–
Id	86.23	152–153	28.66	1.74	57.76	$C_{10}H_7Br_3O_3$	28.92	1.69	57.83

Scheme 2.



IIa–IId

Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**).

phosphine resulted in β-aroylvinyltriphenylphosphonium bromides **IIIb–IIId** in high yields (Tables 5, 6). The formation of these compounds proceeds apparently through the nucleophilic addition of triphenylphosphine to the vinyl group followed by β-cleavage and elimination of pyridine. Nevertheless, a possibility of nucleophilic substitution cannot be excluded.

An effective method of the synthesis of β-aroylvinyltriphenylphosphonium and -pyridinium bromides **IIa–IId** and **IIIb–IIId** that we developed is a convenient alternative method for obtaining their analogs described in the literature.

Recently the research in the field of the synthesis of relatively simple compounds having structural similarity

Table 2. ^{1}H NMR (DMSO-d_6 + CCl_4, 1 : 3) data for compounds **Ia–Id**

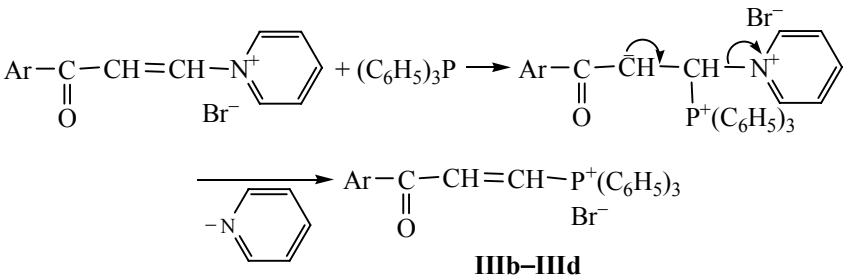
Comp. no.	δ, ppm
Ia	4.72 d (1H, CH, *J* 10.1 Hz); 5.67 d (1H, CH, *J* 10.1 Hz), 7.50–7.56 m (2H, *m*-C_6H_5), 7.62–7.68 m (1H, *p*-C_6H_5), 8.02–8.07 m (2H, *m*-, *o*-C_6H_5), br.s (COOH)
Ib	2.45 s (3H, CH_3), 4.69 d (1H, CH, *J* 10.1 Hz), 5.59 d (1H, CH, *J* 10.1 Hz), 7.29–7.34 m (2H, C_6H_4) and 7.90–7.94 m (2H, C_6H_4), br.s (COOH)
Ic	4.71 d (1H, CH, *J* 10.1 Hz), 5.70 d (1H, CH, *J* 10.1 Hz), 7.50–7.54 m (2H, C_6H_4), 8.04–8.08 m (2H, C_6H_4), 13.31 br.s (1H, COOH)
Id[a]	4.70 d (1H, CH, *J* 10.1 Hz), 5.71 d (1H, CH, *J* 10.1 Hz), 7.66–7.71 m (2H, C_6H_4), 7.96–8.01 m (2H, C_6H_4), 9.72 br.s (1H, COOH)

[a] ^{13}C NMR spectrum, δ_C, ppm: 47.3 (CH), 47.6 (CH), 128.5 (C^i), 130.4 and 131.6 ($CH^{o,m}$), 132.0 (C^p), 168.6 (COOH), 191.1 (CO).

Table 3. Yields, melting points, and elemental analysis data of compounds **IIa–IId**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	Br	N		C	H	Br	N
Ia	31.77	160–161	58.01	4.02	27.63	4.89	$C_{14}H_{12}BrNO$	57.93	4.14	27.59	4.83
Ib	41.59	227–228	58.96	4.64	26.42	4.67	$C_{15}H_{14}BrNO$	59.21	4.60	26.32	4.60
Ic	79.32	231–232	50.98	3.42	–	4.37	$C_{14}H_{11}BrClNO$	51.77	3.39	–	4.31
Id	97.98	235–236	45.66	3.02	43.54	3.81	$C_{14}H_{11}Br_2NO$	45.53	2.98	43.36	3.79

Scheme 3.



IIIb–IIId

Ar = 4-$CH_3C_6H_4$ (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**).

to natural antibiotics is extensively developed. It is presumed that the antibacterial activity of penicilloic acid and clavicin is due to the presence in their structure of the fragment –CH=CH–C=O [8, 9]. We believe that obtained compounds **IIa–IId** and **IIIb–IIId** containing various functional groups are potential physiologically active compounds.

EXPERIMENTAL

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury-300 spectrometer operating at 300 MHz relative to internal TMS.

Bromination of β-aroylacrylic acids. A solution of 0.05 mol of bromine in 10 mL of chloroform was

Table 4. ^1H NMR (DMSO-d_6 + CCl_4, 1 : 3) data for compounds **IIa–IId**

Comp. no.	δ, ppm
IIa	7.55–7.62 m (2H, H^m, C_6H_5), 7.65–7.71 m (1H, H^n, C_6H_5), 8.32–8.40 m (4H, H^o, C_6H_5 and H^β, Py), 8.58 d (1H, =CH, *J* 13.8 Hz), 8.79 d (1H, =CH, *J* 13.8 Hz), 8.83–8.90 m (1H, H^γ, Py), 9.96–10.00 m (2H, H^α, Py)
IIb	2.44 s (3H, CH_3), 7.44–7.48 m (2H) and 8.11–8.16 m (2H, C_6H_4), 8.30–8.37 m (2H, H^β, Py), 8.41 d (1H) and 8.45 d (1H, *J* 13.9, CH=CH), 8.77–8.84 m (1H, H^γ, Py), 9.58–9.62 m (2H, H^α, Py)
IIc	7.60–7.65 m (2H) and 8.58–8.60 m (2H, C_6H_4), 8.30–8.36 m (2H, H^β, Py), 8.45 d (1H, =CH, *J* 13.8 Hz), 8.61 d (1H, =CH, *J* 13.8 Hz), 8.80–8.90 m (1H, H^γ, Py), 9.58–9.62 m (2H, H^α, Py)
IId	7.84–7.89 m (2H) and 8.13–8.18 m (2H, C_6H_4), 8.31–8.37 m (2H, H^β, Py), 8.41 d (1H, =CH, *J* 13.8 Hz), 8.49 d (1H, =CH, *J* 13.8 Hz), 8.78–8.85 m (1H, H^γ, Py), 9.58–9.63 m (2H, H^α, Py)

Table 5. Yields, melting points, and elemental analysis data of compounds **IIIb–IIId**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	Br	P		C	H	Br	P
IIIb	87.56	79–80	68.94	5.02	16.02	6.50	$C_{28}H_{24}BrOP$	69.00	4.93	16.43	6.36
IIIc	49.78	82–83	64.01	4.12	–	5.98	$C_{27}H_{21}BrOPCl$	63.84	4.14	–	6.10
IIId	95.73	149–150	58.81	3.37	28.97	5.56	$C_{27}H_{21}Br_2OP$	58.70	3.80	29.00	5.62

Table 6. ^1H (DMSO-d_6 + CCl_4, 1 : 3) and ^{31}P NMR data for compounds **IIIb–IIId**

Comp. no.	δ_H, ppm	δ_P, ppm
IIIb[a]	2.46 s (3H, CH_3), 7.32–7.36 m (2H, C_6H_4), 7.77–7.99 m (18H, Ar), 8.25 d.d (1H, =CH, J_1 21.2, J_2 16.7 Hz)	25.24
IIIc	7.02–7.78 m (2H) and 7.83–7.87 m (2H, C_6H_4), 7.80–8.00 m (16H, Ar), 8.22 d.d (1H, =CH, J_1 20.8, J_2 16.7 Hz)	25.15
IIId	7.69–7.73 m (2H) and 7.97–8.02 m (2H, C_6H_4), 7.78–7.97 m (16H, Ar), 8.25 d.d (1H,=CH, J_1 20.9, J_2 16.7 Hz)	25.15

[a] ^{13}C NMR spectrum, δ_C, ppm (assignment was made by DEPT experiment): 116.86 d (J_{CP} 90.9, C^i, PPh_3), 121.81 d (J_{CP} 82.8, P<u>CH</u>=CH), 130.06 d (*J* 13.2), 132.77 d (*J* 2.3), 134.0 d (*J* 10.9), 135.08 (J_{CP} 3.0), 148.27 d (J_{CP} 3.3, PCH=<u>CH</u>), 185.56 d (J_{CP} 19.2, CO).

added to a solution of 0.05 mol of β-aroylacrylic acid in 25–30 mL of chloroform within 3 h under vigorous stirring at room temperature. The crystals formed were filtered off, washed with chloroform, and dried in a vacuum. Characteristics of the obtained compounds **Ia–Id** are given in Tables 1 and 2.

1-(β-Aroylvinyl)pyridinium bromides (IIa–IId). A mixture of 0.005 mol of β-aroyl-α,β-dibromopropionic acid **Ia–Id** and 0.01 mol of pyridine in 5–7 mL of acetonitrile was heated for 2 h. The resulting crystals were filtered off, washed with acetonitrile, and dried in a vacuum. Characteristics of the obtained compounds **IIa–IId** are given in Tables 3 and 4.

1-(β-Aroylvinyl)triphenylphosphonium bromides (IIIb–IIId). A mixture of 0.001 mol of 1-(β-aroylvinyl)pyridinium bromide **IIa–IId** and 0.001 mol of triphenylphosphine was refluxed in 10 mL of acetonitrile for 4 h. The acetonitrile filtrate was poured into diethyl ether. The resulting crystals were filtered off, washed with ether, and dried in a vacuum. Characteristics of the obtained compounds **IIIb–IIId** are given in Tables 5 and 6.

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