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Methyl- and Ethyl Carbonates Derived from Vanillin and Vanillal in the Synthesis of Nitrogen-containing Compounds

E. A. Dikusar and N. G. Kozlov

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, ul. Surganova 13, Minsk, 220072 Belarus
e-mail: loc@ifoch.bas-net.by

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Abstract — Reactions of 4-hydroxy-3-methoxybenzaldehyde and 3-ethoxy-4-hydroxybenzaldehyde with methyl and ethyl chloroformates in the presence of pyridine gave the corresponding methyl and ethyl carbonates which were brought into condensation with biphenyl-4-amine, naphthalen-1- and -2-amines, and 3- and 4-aminobenzoic acids to obtain the corresponding Schiff bases. Alkyl 4-(9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-12-yl)-2-alkoxyphenyl carbonates were selectively synthesized by cascade heterocyclization of naphthalen-2-amine, 5,5-dimethylcyclohexane-1,3-dione, and 4-formyl-2-methoxy(or ethoxy)phenyl methyl(or ethyl) carbonates. Ammonium salts were obtained from the benzoacridine derivatives and Schiff bases derived from aminobenzoic acids.
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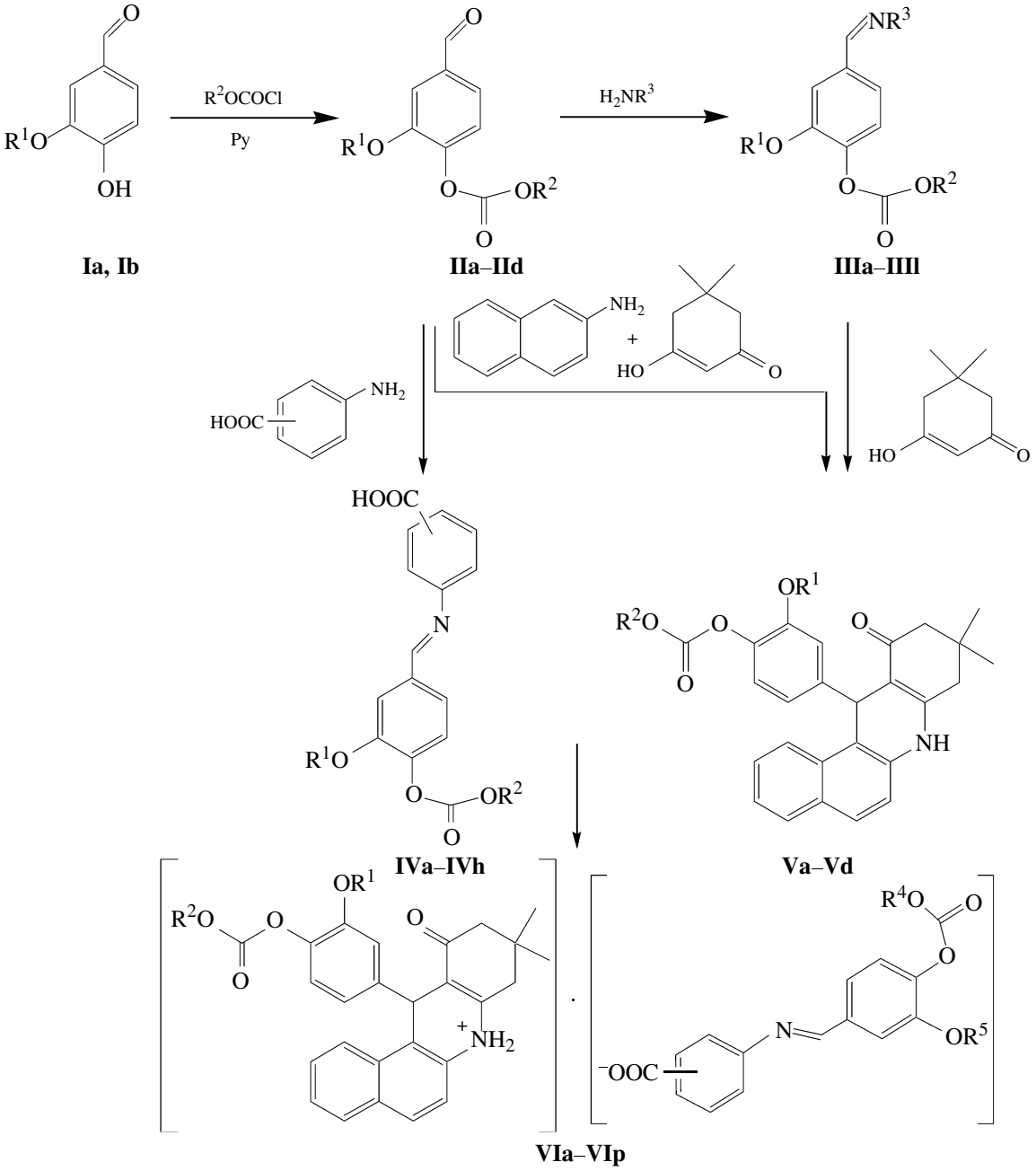
Vanillin (4-hydroxy-3-methoxybenzaldehyde) and vanillal (3-ethoxy-4-hydroxybenzaldehyde) are natural phytogenous aromatic hydroxy aldehydes. They are convenient synthons for the design of biologically active compounds and introduction of pharmacophoric fragments thereinto [1–3]. The presence of reactive hydroxy and formyl groups in their molecules ensures preparation of compounds having various pharmacophoric moieties and functional groups [4, 5].

In the present article we report on the synthesis of previously unknown alkyl 2-alkoxy-4-formyl carbonates by reactions of vanillin (**Ia**) and vanillal (**Ib**) with methyl and ethyl chloroformate in anhydrous benzene in the presence of pyridine. The reactant ratio **I**–alkyl chloroformate–pyridine was equimolar, as in the procedure we developed previously for the synthesis of analogous carboxylic acid esters [6, 7]. The corresponding methyl and ethyl carbonates **IIa**–**IIe** were isolated in 90–93% yield.

By condensation of carbonates **IIa**–**IId** with biphenyl-4-amine, naphthalen-1- and -2-amines, and 3- and 4-aminobenzoic acids in boiling anhydrous methanol we obtained new Schiff bases **IIIa**–**IIIl** and **IVa**–**IVh** in 83– 92% yield. The reactions were complete in 15–20 min in the absence of a catalyst, which favored conservation of labile carbonate moeties [5, 8].

Schiff bases **IIIi**–**IIIl** smoothly reacted with an equimolar amount of dimedone (5,5-dimethylcyclohexane-1,3-dione) on heating in ethanol in the absence of a catalyst to give 70–75% of benzo[*a*]acridinones **Va**–**Vd**. Alkyl 4-(9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-12-yl)-2-alkoxyphenyl carbonates **Va**–**Vd** were also synthesized by another method, three-component condensation of the corresponding aldehydes with naphthalen-2-amine and dimedone. As shown in [9–12], such condensations provide effective and selective synthetic routes to fused nitrogen-containing heterocycles. The use in these condensations of aldehydes having an alkyl carbonate moiety could give rise to functionalized aza heterocycles containing a partially hydrogenated quinoline ring, which can be regarded as analogs of quinoline antibiotics, pesticides, and compounds exhibiting antitumor, bactericide, and antienzyme activity [13–17].

The condensation of aldehydes **IIa**–**IId** with naphthalen-2-amine and dimedone was performed with equimolar amounts of the reactants on heating in ethanol in the absence of a catalyst. The formation of fused heterocyclic product is the result of a series of transformations. Presumably, initial reaction of aldehyde **II** with naphthalen-2-amine gives Schiff base **III**, and addition of dimedone to the latter produces the corresponding amino diketone which undergoes hydramine fission in alcoholic medium. The exocyclic double bond in 2-arylmethylidenecyclohexane-1,3-dione thus formed is activated due to conjugation with the neighboring carbonyl group, and it takes up naphthalene-2-amine at the most electron-rich carbon



I, R^1 = Me (**a**), Et (**b**); **II**, $R^1 = R^2$ = Me (**a**), R = Me, R^2 = Et (**b**), R = Et, R^2 = Me (**c**), R = R^2 = Et (**d**); **III**, $R^1 = R^2$ = Me, R^3 = 4- PhC_6H_4 (**a**), R^1 = Me, R^2 = Et, R^3 = 4-PhC_6H_4 (**b**), R^1 = Et, R^2 = Me, R^3 = 4-PhC_6H_4 (**c**), $R^1 = R^2$ = Et, R^3 = 4-PhC_6H_4 (**d**); $R^1 = R^2$ = Me, R^3 = 1-$C_{10}H_7$ (**e**), R^1 = Me, R^2 = Et, R^3 = 1-$C_{10}H_7$ (**f**), R^1 = Et, R^2 = Me, R^3 = 1-$C_{10}H_7$ (**g**), $R^1 = R^2$ = Et, R^3 = 1-$C_{10}H_7$ (**h**), $R^1 = R^2$ = Me, R^2 = 2-$C_{10}H_7$ (**i**), R^1 = Me, R^2 = Et, R^3 = 2-$C_{10}H_7$ (**j**), R^1 = Et, R^2 = Me, R^3 = 2-$C_{10}H_7$ (**k**), $R^1 = R^2$ = Et, R^3 = 2-$C_{10}H_7$ (**l**); **IV**, 3-COOH, $R^1 = R^2$ = Me (**a**), R^1 = Me, R^2 = Et (**b**), R^1 = Et, R^2 = Me (**c**), $R^1 = R^2$ = Et (**d**), 4-HOCO, $R^1 = R^2$ = Me (**e**), R^1 = Me, R^2 = Et (**f**), R^1 = Et, R^2 = Me (**g**), $R^1 = R^2$ = Et (**h**); **V**, $R^1 = R^2$ = Me (**a**), R^1 = Me, R^2 = Et (**b**), R^1 = Et, R^2 = Me (**c**), $R^1 = R^2$ = Et (**d**); **VI**, 3-COOH, $R^1 = R^2 = R^3 = R^4$ = Me (**a**), 3-COOH, $R^1 = R^2 = R^4$ = Me, R^3 = Et (**b**), 4-COOH, $R^1 = R^2 = R^3$ = Me, R^4 = Et (**c**), 4-COOH, $R^1 = R^2$ = Me, $R^3 = R^4$ = Et (**d**), 3-COOH, $R^1 = R^3 = R^4$ = Me, R^2 = Et (**e**), 3-COOH, $R^1 = R^4$ = Me, $R^2 = R^3$ = Et (**f**), 4-COOH, $R^1 = R^3$ = Me, $R^2 = R^4$ = Et (**g**), 4-COOH, R^1 = Me, $R^2 = R^3 = R^4$ = Et (**h**), 3-COOH, R^1 = Et, $R^2 = R^3 = R^4$ = Me (**i**), 3-COOH, $R^1 = R^3$ = Et, $R^2 = R^4$ = Me (**j**), 4-COOH, $R^1 = R^4$ = Et, $R^2 = R^3$ = Me (**k**), 4-COOH, $R^1 = R^3 = R^4$ = Et, R^2 = Me (**l**), 3-COOH, $R^1 = R^2$ = Et, $R^3 = R^4$ = Me (**m**), 3-COOH, $R^1 = R^2 = R^3$ = Et, R^4 = Me (**n**), 4-COOH, $R^1 = R^2 = R^4$ = Et, R^3 = Me (**o**), 4-COOH, $R^1 = R^2 = R^3 = R^4$ = Et (**p**).

atom in the α position with respect to the amino group. Dehydrocyclization of the adduct leads to selective formation of alkyl 4-(9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-12-yl)-2-alkoxyphenyl carbonates **V** in 79–89% yield. It should be noted that, by analogy with the data of [18], the above transformation of one amino diketone into another can be regarded as a version of the Hofmann–Martius rearrangement (migration of alkyl groups in *N*-alkylanilines to the aromatic ring [19]).

Benzo[*a*]acridinones **Va**–**Vd** reacted with carboxylic acids **IVa**–**IVh** in anhydrous chloroform to give the corresponding ammonium salts **VIa**–**VIp** in 92–96% yield. Previously unknown salts **VIa**–**VIh** were obtained by reaction of acids **IVa**–**IVh** with benzo[*a*]acridinones **Va**–**Vd** at a ratio of 1 : 1. The reaction was complete in 10–15 min under reflux. It is known that ammonium salts derived from pharmacophoric acids and bases exhibit a high biological activity [20–23].

The structure of compounds **IIa**–**IId**, **IIIa**–**IIIl**, **IVa**–**IVh**, **Va**–**Vd**, and **VIa**–**VIp** was confirmed by elemental analysis, molecular weight determination (by cryoscopy or alkalimetry; see table), and IR, UV, and ^{1}H NMR spectroscopy.

The IR spectra of **IIa**–**IId**, **IIIa**–**IIIl**, **IVa**–**IVh**, **Va**–**Vd**, and **VIa**–**VIp** contained the following absorption bands, ν, cm^{-1}: 3100–3000 (C–H_{arom}), 2990–2700 (C–H_{aliph}), 1770–1758 (C=O, carbonate), 1600–1367 (C–C_{arom}), 1280–1027 (C–O), 900–583 (C–H_{arom}). Compounds **IIa**–**IId** showed absorption bands due to aldehyde carbonyl group at 1700–1685 cm^{-1}, and stretching vibrations of the C=N bond in Schiff bases **IIIa**–**IIIl** and **IVa**–**IVh** appeared at 1630–1625 cm^{-1}. The carboxy group in **IVa**–**IVh** gave rise to absorption at 1700–1680 (C=O) and 2100–3650 cm^{-1} (several bands, OH). In the IR spectra of **Va**–**Vd**, absorption bands corresponding to stretching and bending vibrations of the NH group in the dihydropyridine ring were located at 3270–3260 and 1635–1630 cm^{-1}, respectively. Stretching vibrations of the carbonyl group conjugated with the enamine fragment had a frequency of 1645–1640 cm^{-1}. The spectra of ammonium salts **VIa**–**VIp** contained absorption bands typical of both initial carboxylic acids **IVa**–**IVh** and heterocyclic bases **Va**–**Vd** with the difference that the intensities of the acid C=O and NH bands were lower as the result of salt formation.

The UV spectra of the isolated compounds were characterized by the presence of the following absorption maxima, λ_{max}, nm (ε, l mol^{-1} cm^{-1}): carbonates **IIa**–**IId**: 206 (9000), 225 (15 000), 260 (8000), 310 (3000); Schiff bases **IIIa**–**IIIl** and **IVa**–**IVh**: 206 (48 000), 273 (29 000), 331 (24 000) (**IIIa**–**IIId**); 207 (27 000), 227 (26 000), 260 (8000), 290 (5000), 305 (6000), 340 (3000) (**IIIe**–**IIIh**); 225 (28 000), 270 (17 000), 325 (10 000), 357 (7000) (**IIIi**–**IIIl**); 204 (17 000), 221 (29 000), 250 (10 000), 306 (3000) (**IVa**–**IVd**); 205 (23 000), 220 (18 000), 280 (22 000), 295 (22 000), 315 (12 000) (**IVe**–**IVh**); benzo[*a*]acridinones **Va**–**Vd**: 217 (29 000), 232 (35 000), 270 (10 000), 281 (14 000), 292 (15 000), 326 (3000), 339 (13 000), 370 (8000); salts **VIa, VIb, VIe, VIf, VIi, VIj, VIm**, and **VIn** derived from 3-aminobenzoic acid: 217 (58 000), 231 (61 000), 265 (25 000), 280 (27 000), 292 (27 000), 325 (15 000), 338 (15 000), 370 (15 000); salts **VIc, VId, VIg, VIh, VIk, VIl, VIo**, and **VIp** derived from 4-aminobenzoic acid: 207 (76 000), 216 (80 000), 231 (80 000), 281 (58 000), 292 (62 000), 326 (21 000), 336 (22 000), 375 (18 000).

In the ^{1}H NMR spectra of **IIa**–**IId**, **IIIa**–**IIIl**, **IVa**–**IVh**, **Va**–**Vd**, and **VIa**–**VIp** we observed the following signals that unambiguously confirm their structure, δ, ppm: 3.93–3.99 s (MeO), 1.20–1.70 t (CH_2CH_3), 3.90– 4.50 q (CH_2CH_3); **IIa**–**IId**: 7.15–7.55 m (C_6N_3), 9.91 s (CHO); **IIIa**–**IIIl**, **IVa**–**IVh**: 8.40–8.60 s (HC=N), 9.98–10.20 s (COOH); 6.65–7.60 m (C_6H_3, C_6H_4, C_6H_5, **IIIa**–**IIId**), 7.00–8.05 m (C_6H_3, $C_{10}H_7$, **IIIe**–**IIIl**), 6.90–8.05 m (C_6H_3, C_6H_4, **IVa**–**IVd)**, 6.40–8.10 m (C_6H_3, C_6H_4, **IVe**–**IVh**). The ^{1}H NMR spectra of benzo[*a*]acridinones **Va**–**Vd** were identical to those reported in [9, 10, 12], δ, ppm: 0.89–0.90 s and 1.04–1.05 s (Me_2C), 2.10–2.20 d and 2.45–2.60 d (CH_2), 5.80–5.85 s (CH), 6.45–8.20 m (C_6H_3, $C_{10}H_6$), 9.69–9.75 s (NH). Salts **VIa**–**VIp** showed in the spectra signals from both acid and base components. The NH_2^+ signal was a broadened singlet at δ 8.90–9.30 ppm [22].

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protege-460 spectrometer with Fourier transform. The UV spectra were measured on a Specord UV-Vis spectrophotometer from 1×10^{-4} M solutions in methanol. The ^{1}H NMR spectra were obtained on a Tesla BS-587A instrument (100 MHz) from 5% solutions in DMSO-d_6 using tetramethylsilane as internal reference. The elemental compositions were determined on a Vario EL-III Elementar C,H,N,O,S-analyzer with an accuracy of ±0.1%. The molecular weights of **IIa**–**IId**, **IIIa**–**IIIl**, and **Va**–**Vd** were determined by cryoscopy in benzene, and those of **IVa**–**IVh** and **VIa**–**VIp**, by alkalimetric titration of carboxy groups with a 0.1 N solution of NaOH in the presence of phenolphthalein as indicator.

Yields, melting points, elemental analyses, and molecular weights of compounds **IIa–IId, IIIa–IIIl, IVa–IVh, Va–Vd**, and **VIa–VIp**

Comp. no.	Yield, %	mp, °C	Found, %			Fomula	Calculated, %			*M*	
			C	H	N		C	H	N	found	calculated
IIa	93	77–78	57.39	5.02	–	$C_{10}H_{10}O_5$	57.14	4.80	–	202.1	210.2
IIb	92	63–64	59.14	5.41	–	$C_{11}H_{12}O_5$	58.93	5.39	–	211.8	224.2
IIc	90	35–36	59.09	5.48	–	$C_{11}H_{12}O_5$	58.93	5.39	–	216.6	224.2
IId	91	34–35	60.67	6.13	–	$C_{12}H_{14}O_5$	60.50	5.92	–	229.4	238.2
IIIa	90	133–134	73.36	5.38	3.60	$C_{22}H_{19}NO_4$	73.12	5.30	3.88	355.0	361.4
IIIb	90	96–97	73.72	5.83	3.51	$C_{23}H_{21}NO_4$	73.58	5.64	3.73	361.7	375.4
IIIc	91	82–83	73.66	5.80	3.62	$C_{23}H_{21}NO_4$	73.58	5.64	3.73	364.5	375.4
IIId	93	84–85	74.23	6.12	3.40	$C_{24}H_{23}NO_4$	74.02	5.95	3.60	378.2	389.5
IIIe	85	72–73	71.84	5.25	3.89	$C_{20}H_{17}NO_4$	71.63	5.11	4.18	322.6	335.4
IIIf	90	95–96	72.37	5.59	3.84	$C_{21}H_{19}NO_4$	72.19	5.48	4.01	332.7	349.4
IIIg	87	62–63	72.50	5.63	3.80	$C_{21}H_{19}NO_4$	72.19	5.48	4.01	337.9	349.4
IIIh	84	60–61	72.95	5.97	3.56	$C_{22}H_{21}NO_4$	72.71	5.82	3.85	352.0	363.4
IIIi	87	55–56	71.88	5.14	4.02	$C_{20}H_{17}NO_4$	71.63	5.11	4.18	328.1	335.4
IIIj	86	86–87	72.25	5.64	3.75	$C_{21}H_{19}NO_4$	72.19	5.48	4.01	330.3	349.4
IIIk	85	52–53	72.37	5.70	3.78	$C_{21}H_{19}NO_4$	72.19	5.48	4.01	339.4	349.4
IIIl	85	61–62	73.05	6.05	3.49	$C_{22}H_{21}NO_4$	72.71	5.82	3.85	352.7	363.4
IVa	84	135–136	62.21	4.68	3.90	$C_{17}H_{15}NO_6$	62.04	4.59	4.25	328.8	329.3
IVb	86	66–67	63.23	5.17	3.82	$C_{18}H_{17}NO_6$	62.97	4.99	4.08	341.6	343.3
IVc	88	118–119	63.17	5.09	3.91	$C_{18}H_{17}NO_6$	62.97	4.99	4.08	341.0	343.3
IVd	83	125–126	64.00	5.46	3.73	$C_{19}H_{19}NO_6$	63.86	5.36	3.92	357.1	357.4
IVe	92	198–199	62.32	4.70	3.98	$C_{17}H_{15}NO_6$	62.04	4.59	4.25	327.6	329.3
IVf	91	186–187	63.19	5.18	3.87	$C_{18}H_{17}NO_6$	62.97	4.99	4.08	342.0	343.3
IVg	92	145–146	63.22	5.12	3.90	$C_{18}H_{17}NO_6$	62.97	4.99	4.08	342.5	343.3
IVh	91	137–138	63.98	5.38	3.85	$C_{19}H_{19}NO_6$	63.86	5.36	3.92	355.8	357.4
Va	81	284–285	73.84	6.08	2.86	$C_{28}H_{27}NO_5$	73.51	5.95	3.06	440.2	457.5
Vb	89	252–253	74.04	6.33	2.78	$C_{29}H_{29}NO_5$	73.87	6.20	2.97	450.7	471.6
Vc	87	254–255	73.98	6.29	2.80	$C_{29}H_{29}NO_5$	73.87	6.20	2.97	455.4	471.6
Vd	79	262–263	74.56	6.43	2.62	$C_{30}H_{31}NO_5$	74.21	6.43	2.88	467.3	485.6
VIa	94	140–141	68.82	5.51	3.40	$C_{45}H_{42}N_2O_{11}$	68.69	5.38	3.56	775.0	786.8
VIb	96	154–155	69.22	5.68	3.21	$C_{46}H_{44}N_2O_{11}$	68.99	5.54	3.50	791.6	800.9
VIc	95	183–184	69.15	5.61	3.32	$C_{46}H_{44}N_2O_{11}$	68.99	5.54	3.50	796.5	800.9
VId	92	149–150	69.38	5.80	3.25	$C_{47}H_{46}N_2O_{11}$	69.28	5.69	3.44	810.7	814.9
VIe	93	138–139	69.24	5.65	3.38	$C_{46}H_{44}N_2O_{11}$	68.99	5.54	3.50	794.7	800.9
VIf	94	122–123	69.43	5.81	3.27	$C_{47}H_{46}N_2O_{11}$	69.28	5.69	3.44	811.9	814.9
VIg	96	180–181	69.39	5.70	3.20	$C_{47}H_{46}N_2O_{11}$	69.28	5.69	3.44	812.1	814.9
VIh	95	139–140	69.84	6.03	3.05	$C_{48}H_{48}N_2O_{11}$	69.55	5.84	3.38	822.3	828.9
VIi	93	138–139	69.15	5.62	3.30	$C_{46}H_{44}N_2O_{11}$	68.99	5.54	3.50	796.2	800.9
VIj	95	123–124	69.44	5.80	3.19	$C_{47}H_{46}N_2O_{11}$	69.28	5.69	3.44	810.0	814.9
VIk	94	182–183	69.50	5.77	3.21	$C_{47}H_{46}N_2O_{11}$	69.28	5.69	3.44	811.4	814.9
VIl	94	144–145	69.83	5.92	3.12	$C_{48}H_{48}N_2O_{11}$	69.55	5.84	3.38	828.0	828.9
VIm	95	146–147	69.42	5.82	3.33	$C_{47}H_{46}N_2O_{11}$	69.28	5.69	3.44	812.5	814.9
VIn	96	140–141	69.70	6.00	3.14	$C_{48}H_{48}N_2O_{11}$	69.55	5.84	3.38	825.7	828.9
VIo	94	184–185	69.76	5.90	3.07	$C_{48}H_{48}N_2O_{11}$	69.55	5.84	3.38	826.3	828.9
VIp	93	154–155	70.05	6.15	3.18	$C_{49}H_{50}N_2O_{11}$	69.82	5.98	3.32	839.8	842.9

Methyl or ethyl 2-alkoxy-4-formylphenyl carbonates IIa–IId *(general procedure).* A solution of 0.02 mol of pyridine in 10 ml of benzene was added under shaking to a solution of 0.02 mol of hydroxy aldehyde **Ia** or **Ib** and 0.02 mol of methyl or ethyl chloroformate in 100 ml of anhydrous benzene. The reaction flask was tightly capped and left to stand for 10–12 h at 20–23°C with intermittent careful shaking. The mixture was then transferred into a separatory funnel, thoroughly washed with water, a 20% solution of NaCl (to avoid emulsification), and 2–3 portions of a 5% solution of $NaHCO_3$, and the organic phase was separated and filtered through a filter paper. The solvent was removed under reduced pressure, and the residue was recrystallized from a benzene–hexane mixture.

Schiff bases IIIa–IIIl and IVa–IVh *(general procedure).* Compound **IIa–IId**, 0.01 mol, was dissolved in 30 ml of anhydrous methanol, 0.01 mol of biphenyl-4-amine, naphthalen-1- or -2-amine, or 3- or 4-aminobenzoic acid was added, and the mixture was heated for 15–20 min under reflux and left to stand for 15–20 h at 5°C. The precipitate was filtered off through a glass filter, washed with a small amount of methanol, and dried under reduced pressure. Schiff bases **IIIa–IIIl** and **IVa–IVh** thus obtained were sufficiently pure, and no additional recrystallization was necessary.

Alkyl 2-alkoxy-4-(9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-12-yl)phenyl carbonates Va–Vd *(general procedure). a.* A mixture of 0.005 mol of Schiff base **IIIi–IIIl** and 0.005 mol of dimedone in 20 ml of ethanol was heated for 3–4 h under reflux. After cooling, the precipitate was filtered off, washed on a filter with two portions of diethyl ether to remove unreacted initial compounds, and dried under reduced pressure. Compounds **Va–Vd** thus obtained were pure, and no additional recrystallization was necessary.

b. A mixture of 0.005 mol of aldehyde **IIa–IId**, 0.005 mol of naphthalen-2-amine, and 0.005 mol of dimedone in 20 ml of ethanol was heated for 3–4 h under reflux. After cooling, the precipitate was filtered off, washed on a filter with two portions of diethyl ether to remove unreacted initial compounds, and dried under reduced pressure. Compounds **Va–Vd** thus obtained were pure, and no additional recrystallization was necessary.

12-(3-Alkoxy-4-alkoxycarbonyloxyphenyl)-9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*a*]-acridin-7-ium 3(4)-(3-alkoxy-4-alkoxycarbonyloxybenzylideneamino)benzoates VIa–VIp *(general procedure).* A mixture of 0.01 mol of carboxylic acid **IVa**, **IVc**, **IVf**, or **IVh** and 0.01 mol of benzo[*a*]-acridinone **Va–Vd** was thoroughly ground in an agate mortar until a homogeneous powder-like material was obtained. To complete the complex formation process, the mixture was heated for 10–15 min in 30 ml of boiling anhydrous chloroform until it became homogeneous. The solvent was removed under reduced pressure to leave salt **VIa–VIp** as a brittle porous material.

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