
SYNTHESIS AND CYCLIZATION OF SOME 5-AMINOBENZIMIDAZOLE AND 5-AMINOBENZOTRIAZOLE DERIVATIVESVladimír BOBOŠÍK^a, Viktor MILATA^a, Dušan ILAVSKÝ^{a,*} and Igor GOLJER^b^a Department of Organic Chemistry, Slovak Technical University, 812 37 Bratislava^b Central Laboratory of Chemical Technique, Slovak Technical University, 812 37 Bratislava

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Dedicated to Dr Miroslav Protiva on the occasion of his 70th birthday.

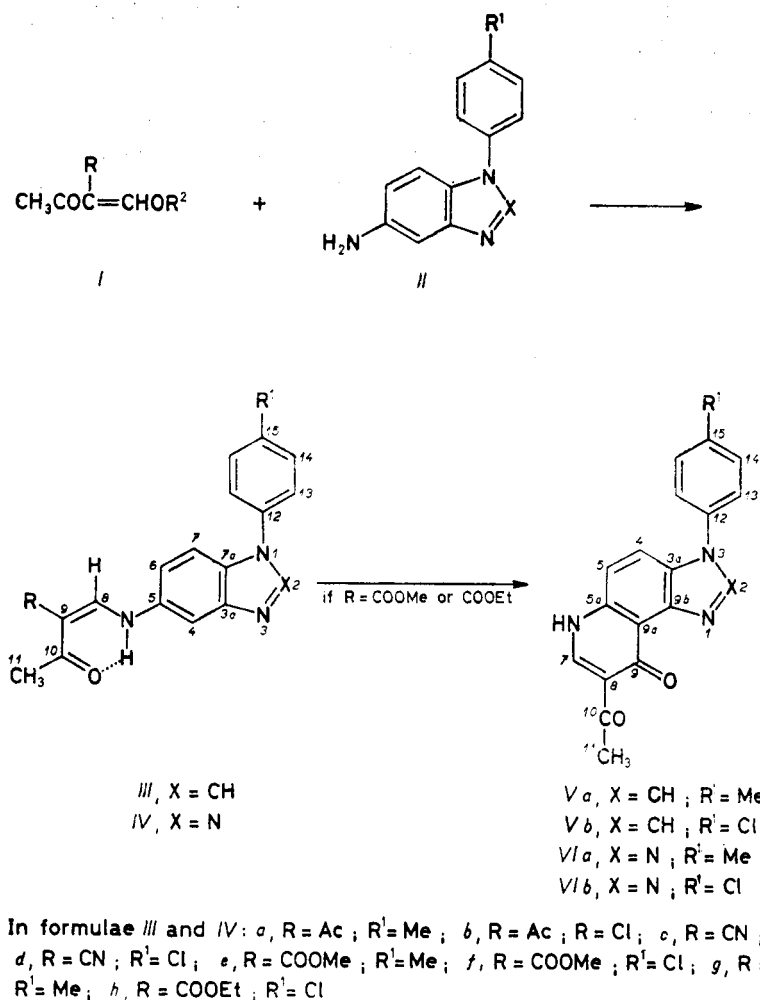
Alkoxyethylene derivatives *I* of 2,4-pentanedione, 3-oxobutanenitrile, and methyl and ethyl 3-oxobutanoates with substituted 1-phenyl-5-aminobenzimidazoles and -benzotriazoles *II* give the products of nucleophilic substitution *III* and *IV* which, bearing ester groups, undergo thermal cyclizations to the corresponding 8-acetyl-3-phenyl-6,9-dihydroazolo[4,5-*f*]quinolin-9(3*H*)-ones *V* and *VI*. IR, UV, ¹H and ¹³C NMR data are given.

Alkoxyethylene derivatives of β-dicarbonyl compounds, such as esters and nitriles of malonic, cyanoacetic and acetoacetic acids, and acetylacetone react with benzimidazoles and benzotriazoles bearing amino group in benzene ring to give products of nucleophilic substitution of the alkoxy groups with heterocyclic amine rests. Thermal cyclizations of the products formed from esters yield imidazo- and triazoloquinolinones¹⁻⁴. These compounds can serve as precursors in syntheses of the antibacterial nalidixic type compounds⁵.

The present work deals with the nucleophilic substitution reaction of alkoxyethylene derivatives *I* of 2,4-pentanedione and of nitrile and esters of 3-oxobutanoic acid with substituted 1-phenyl-5-aminobenzimidazoles and -benzotriazoles *II*. It comprises also a study of regioselectivity in the subsequent thermal cyclocondensation of the substitution products *III* and *IV* (Scheme 1). Thermal catalytic cyclization with AlCl₃ through cyano group was studied on the malononitrile compounds⁶.

The nucleophilic substitution of alkoxyethylene derivatives *I* with amines *II*, carried out under mild conditions (short boiling of the methanolic solution), affords high yields of substitution products *III* and *IV* (Table I). The requisite alkoxyethylene derivatives *I* were prepared by the condensation of an alkyl orthoformate with an active methylene compound⁴. Amino derivatives *II* were prepared by the catalytic reduction of the corresponding nitro derivatives¹.

Substitution products *III* and *IV* bearing an alkoxy-carbonyl group cyclize upon boiling in an inert medium of Dowtherm at 250°C to give angularly annelated



SCHEME 1

8-acetyl-3-phenyl-6,9-dihydroimidazo[4,5-*f*]quinolin-9(3*H*)-ones and 8-acetyl-3-phenyl-6,9-dihydro[1,2,3]triazolo[4,5-*f*]quinolin-9(3*H*)-ones. The yields of the cyclization of methyl and ethyl esters were similar. The amount of Dowtherm used as well as the reaction time must be carefully chosen. Thus, the low ratio solvent/III or IV led to partially carbonized products, whilst the high ratio complicated the separation of the product which was formed in a gel-like, difficult to isolate form.

The IR spectra of the substitution products III and IV (Table II) show the characteristic vibrations of acetyl groups shifted to lower wavenumbers owing to the strong

TABLE I

Properties of substituted 1-phenyl-5-aminobenzimidazoles *III*, 1-phenyl-5-aminobenzotriazoles *IV*, and azolo[4,5-*f*]quinolinones *V* and *VI*

Compound	Formula (M. w.)	Calculated/Found				M.p. °C	Yield %
		% C	% H	% Cl	% N		
<i>IIIa</i>	C ₂₀ H ₁₉ N ₃ O ₂ (333.4)	72.05	5.74	—	14.40	128–129	78.9
		69.84	5.65		14.51		
<i>IIIb</i>	C ₁₉ H ₁₆ ClN ₃ O ₂ (353.8)	64.50	4.56	10.02	11.88	203–204	77.9
		64.38	4.48	10.21	11.93		
<i>IIIc</i>	C ₁₉ H ₁₆ N ₄ O (316.4)	73.06	5.16	—	17.94	235–237	82.1
		72.91	5.08		17.81		
<i>III d</i>	C ₁₈ H ₁₃ ClN ₄ O (336.8)	64.20	3.99	10.53	16.64	193–195	83.0
		64.11	3.99	10.38	16.49		
<i>IIIe</i>	C ₂₀ H ₁₉ N ₃ O ₃ (349.4)	68.75	5.48	—	12.03	144–145	66.8
		68.70	5.61		11.89		
<i>III f</i>	C ₁₉ H ₁₆ ClN ₃ O ₃ (369.8)	61.71	4.36	9.56	11.36	170–171	67.1
		61.52	4.20	9.46	11.21		
<i>III g</i>	C ₂₁ H ₂₁ N ₃ O ₃ (363.4)	69.41	5.82	—	11.56	140–141	67.4
		69.30	5.98		11.70		
<i>III h</i>	C ₂₀ H ₁₈ ClN ₃ O ₃ (383.8)	62.58	4.73	9.24	10.95	160–162	69.2
		62.41	4.84	9.11	10.72		
<i>IVa</i>	C ₁₉ H ₁₈ N ₄ O ₂ (334.4)	69.07	5.49	—	16.96	185–186	80.1
		69.14	5.60		16.85		
<i>IVb</i>	C ₁₈ H ₁₅ ClN ₄ O ₂ (354.9)	60.92	4.26	9.99	15.79	209–211	81.6
		60.84	4.36	9.81	15.65		
<i>IVc</i>	C ₁₈ H ₁₅ N ₅ O (317.4)	68.13	4.76	—	22.07	233–235	88.4
		68.05	4.91		22.00		
<i>IVd</i>	C ₁₇ H ₁₂ ClN ₅ O (337.8)	60.45	3.58	10.50	20.73	275–277	91.6
		60.33	3.70	10.39	20.50		
<i>IVe</i>	C ₁₉ H ₁₈ N ₄ O ₃ (250.4)	65.88	5.23	—	16.17	131–132	69.4
		65.82	5.11		16.02		
<i>IVf</i>	C ₁₈ H ₁₅ ClN ₄ O ₃ (370.9)	58.29	4.08	9.56	15.11	171–172	73.4
		58.12	4.19	9.42	15.24		
<i>IVg</i>	C ₂₀ H ₂₀ N ₄ O ₃ (364.4)	65.92	5.53	—	15.37	139–140	71.2
		65.74	5.62		15.44		
<i>IVh</i>	C ₁₉ H ₁₇ ClN ₄ O ₃ (384.8)	59.30	4.45	9.21	14.56	169–170	74.3
		59.14	4.58	9.10	14.36		

TABLE I
(Continued)

Compound	Formula (M. w.)	Calculated/Found				M.p. °C	Yield %
		% C	% H	% Cl	% N		
<i>Va</i>	C ₁₉ H ₁₅ N ₃ O ₂ (317·4)	71·83	4·73	—	13·23	<360	54·2 ^a
		71·62	4·91		13·11		
<i>Vb</i>	C ₁₈ H ₁₂ ClN ₃ O ₂ (337·8)	63·94	3·55	10·49	12·43	<360	62·8 ^a
		63·72	3·70	10·31	12·34		
<i>VIa</i>	C ₁₈ H ₁₄ N ₄ O ₂ (318·4)	67·84	4·40	—	17·59	<360	64·8 ^a
		67·99	4·23		17·38		
<i>VIb</i>	C ₁₇ H ₁₁ ClN ₄ O ₂ (338·9)	60·19	3·25	10·46	16·52	<360	71·2 ^a
		60·05	3·40	10·32	16·40		

^a From the cyclization of ethyl esters.

TABLE II
UV and IR data of substituted 1-phenyl-5-aminobenzimidazoles *III*, 1-phenyl-5-aminobenzotriazoles *IV* and azolo[4,5-*f*]quinolinones *V* and *VI*

Compound	λ_{\max} , nm log ϵ	$\tilde{\nu}(\text{C}=\text{O})$ cm ⁻¹	$\tilde{\nu}(\text{C}=\text{N})$ and $\tilde{\nu}(\text{C}=\text{C})$ cm ⁻¹		
<i>IIIa</i>	—	258	342	1 652	1 589, 1 518
		3·30	3·39		
<i>IIIb</i>	—	259	342	1 630	1 591, 1 502
		3·38	3·43		
<i>IIIc</i>	227	243 ^a	345	1 651	1 612, 1 520
	3·35	3·28	3·43	2 199 ^b	
<i>III d</i>	224	253 ^a	347	1 655	1 610, 1 502
	3·31	3·23	3·55	2 205 ^b	
<i>IIIe</i>	—	244	341	1 684	1 595, 1 568, 1 518
		3·44	3·47	1 626	
<i>III f</i>	—	243	342	1 686	1 601, 1 574, 1 498
		3·38	3·43	1 628	
<i>III g</i>	—	244	342	1 686	1 599, 1 566, 1 518
		3·41	3·45	1 626	
<i>III h</i>	—	242	341	1 707	1 634, 1 612, 1 502
		3·37	3·42	1 684	

TABLE II
(Continued)

Compound	λ_{\max} , nm	$\log \epsilon$	$\tilde{\nu}(\text{C}=\text{O})$ cm^{-1}	$\tilde{\nu}(\text{C}=\text{N})$ and $\tilde{\nu}(\text{C}=\text{C})$ cm^{-1}
<i>IVa</i>	—	260 3·27	342 3·45	1 616 1 595, 1 570, 1 518
<i>IVb</i>	—	261 3·29	339 3·42	1 626 1 589, 1 502
<i>IVc</i>	221 3·38	324 ^a 3·37	342 3·40	1 664 2 205 ^b 1 597, 1 522
<i>IVd</i>	223 3·34	259 3·20	341 3·39	1 662 2 204 ^b 1 622, 1 597, 1 508
<i>IVe</i>	—	235 3·31	340 3·40	1 715 1 703 1 635, 1 616, 1 570
<i>IVf</i>	—	234 3·32	337 3·41	1 695 1 608, 1 589, 1 568
<i>IVg</i>	—	235 3·31	340 3·39	1 713 1 693 1 635
<i>IVh</i>	—	235 3·31	338 3·39	1 682 1 664 1 630, 1 599
<i>Va</i>	236 —	277 —	347 ^a —	1 647 1 616, 1 568, 1 520
<i>Vb</i>	— —	282 —	351 ^c —	1 655 1 616, 1 574, 1 533
<i>VIa</i>	234 —	274 —	347 ^c —	1 664 1 612, 1 574, 1 533
<i>VIb</i>	— —	277 —	345 —	1 662 1 614, 1 576, 1 525

^a Inflex; ^b $\tilde{\nu}(\text{C}\equiv\text{N})$; ^c saturated solution.

conjugation. The electron-withdrawing effect of the nitrile group in *IIIc*, *IIIId*, *IVc* and *IVd* accounts for the higher values of $\tilde{\nu}(\text{C}=\text{O})$. In UV spectra of the substitution products (Table II) the longest-wavelength absorption maximum lies at 340 nm, i.e. by 7 nm higher than that of analogous derivatives of the benzazolylaminomethyl-enemalonic type¹. This bathochromic shift is a consequence of stronger intramolecular hydrogen bond between the acetyl carbonyl group and the NH proton as compared with that formed by carbonyl.

TABLE III
 ^1H NMR chemical shifts (δ , ppm; CD_3SOCD_3) and coupling constants (Hz) of substituted 1-phenyl-5-aminobenzimidazoles III and 1-phenyl-5-aminobenzotriazoles IV

Compound	H-2 ^a	H-4 ^b	H-6 ^c	H-7 ^b	H-8 ^b	NH ^b	Me ^d	H-13 ^b	H-14 ^b	R	R ^{1a}	$^3J(\text{8-NH})$
IIIa	8.51	7.97	7.38	7.57	8.49	12.72	2.40	7.43	7.54	2.35 s	2.30	12.9
IIIb	8.55	7.98	7.36	7.56	8.43	12.67	2.41	7.61	7.66	2.32 s	—	12.6
IIIc	8.47	7.87	7.36	7.49	8.33	12.21	2.41	7.34	7.46	—	2.22	13.8
IIId	8.48	7.80	—	—	8.43	10.75	2.31	—	—	—	2.21	13.8
IIIe	8.59	7.95	7.45	7.62	8.49	12.29	2.50	7.67	7.72	—	—	13.2
IIIe	8.51	7.92	7.33	7.54	8.41	10.75	2.31	7.59	7.64	2.72 s	2.32	13.8
IIIe	8.51	7.92	7.33	7.54	8.40	12.64	2.41	7.59	7.64	2.72 s	2.32	12.9
IIIe	8.51	7.92	7.33	7.54	8.40	12.64	2.31	—	—	3.81 t	—	—
IIIe	8.43	8.39	7.23	7.50	8.50	12.59	2.41	7.60	7.60	3.63 s	—	12.3
IIIe	8.44	7.71	7.24	7.49	8.42	10.58	2.34	7.33	7.44	3.72 s	2.35	13.2
IIIe	8.42	7.60	7.25	7.85	8.39	10.72	2.35	7.55	7.60	4.09 q	—	—
IIIe	8.42	7.60	7.25	7.85	8.40	12.55	2.41	7.55	7.60	4.11 q	—	13.2
IIIe	8.42	7.60	7.25	7.85	8.39	10.65	2.35	7.55	7.60	4.11 q	—	13.2
IVa	—	8.24	7.72	7.49	8.44	12.62	2.41	7.33	7.44	2.34 s	2.32	13.2
IVb	—	8.29	7.80	7.65	8.44	12.55	2.41	7.40	7.50	2.33 s	—	12.3
IVc	—	8.27	7.90	7.79	8.52	12.23	2.50	7.49	7.75	—	2.35	13.2
IVd ^d	—	8.16	8.08	7.74	8.57	10.92	2.44	7.68	7.87	—	2.32	13.8
IVe	—	8.18	7.66	7.89	8.43	10.10	2.45	7.68	7.87	—	—	—
IVe	—	8.12	7.66	7.87	8.56	12.65	2.40	7.48	7.71	3.73 s	2.40	13.2
IVf	—	8.21	7.67	7.87	8.54	10.80	2.39	7.66	7.84	3.82 s	—	13.2
IVf	—	8.13	7.67	7.87	8.50	12.58	2.41	7.66	7.84	3.63 s	—	13.5
IVg	—	8.10	7.59	7.78	8.47	10.68	2.38	7.38	7.63	3.72 s	2.34	13.2
IVg	—	8.05	7.59	7.78	8.45	12.55	2.41	7.38	7.63	4.10 q	2.34	13.2
IVh	—	8.21	7.66	7.87	8.48	10.72	2.34	7.66	7.84	1.21 t	—	—
IVh	—	8.14	7.66	7.87	8.48	12.56	2.41	7.66	7.84	4.10 q	—	13.2
IVh	—	8.14	7.66	7.87	8.42	10.80	2.35	7.66	7.84	4.10 q	—	13.2

^a Singlets; ^b doublets; ^c doublets of doublets; ^d not observed due to low solubility.

The presence of the condensed 4-pyridone skeleton in the cyclization products is manifested by a slightly bathochromically shifted and significantly less intense longest-wavelength band in the UV spectra.

In the ^1H NMR spectra of compounds *III* and *IV* (Table III), it is possible to observe signals of protons with the expected multiplicities. The value of the interaction constant 3J between the hydrogen of the amino group and H-8 (about 13 Hz) confirms the antiperiplanar conformation of the enamine group stabilized by an intramolecular hydrogen bond. The multiplicities of the signals of the enamine substituent and the benzene ring of the benzazole skeleton prove the existence of geometric isomerism in unequally substituted derivatives *IIIc–IIIh* and *IVc–IVh*. Similar isomerism is missing in 2,4-pentanedione derivatives *IIIa*, *IIIb*, *IVa* and *IVb*. The greater electron-withdrawing effect of 1-phenyltriazole in comparison with that of 1-phenylimidazole manifests itself especially in the shifts of the H-4, H-6 and H-7 signals. Out of 1-phenyl, 1-methyl³ and unsubstituted² benzimidazole derivatives only the 1-phenylbenzimidazole derivatives have the H-2 signal shifted to lower field by about 0.2 to 0.3 ppm.

The angular annelation of products of thermal cyclization is evidenced by the *ortho* position of protons of the benzene ring, which is evident from the high value of the interaction constant $^3J(4, 5)$ of over 9.0 Hz (Table IV).

The ^{13}C NMR spectra of compounds *III* and *IV* (Table V) confirm the geometric isomerism due to the enamine double bond by showing doublets of signals of the substituent R and the benzene ring of the benzazole skeleton. It is evident that the greater electron-accepting effect of 1-phenyltriazole versus 1-phenylimidazole affects especially the chemical shift of C-6. The shift of signals of carbon atoms of the phenyl substituent in position 12 is affected mainly by the azole ring, and to a lesser extent also by the substituent in the *para* position. The electron-accepting effect of the substituent R on enamine double bond decreases in the order $\text{CN} < \text{COOMe}$

TABLE IV

^1H NMR chemical shifts (δ , ppm; CF_3COOD) and coupling constants (Hz) of 8-acetyl-3-phenyl-6,9-dihydroazolo[4,5-*f*]quinolin-9(3*H*)-ones *V* and *VI*

Compound	H-2	H-4	H-5	H-7	H-11	H-13	H-14	R ¹	$J(4, 5)$	$J(13, 14)$
<i>Va</i>	9.33	8.08 d	8.15 d	9.27 s	2.60 s	7.18 d	7.22 d	2.17 s	9.3	8.7
<i>Vb</i>	9.17	7.92 d	8.01 d	9.14 s	2.43 s	7.13 d	7.23 d	—	9.0	9.0
<i>Vla</i>	—	7.92 d	8.01 d	9.08 s	2.40 s	7.02 d	7.10 d	1.97 s	9.3	7.5
<i>Vlb</i>	—	7.98 d	8.08 d	9.14 s	2.46 s	7.25 d	7.29 d	—	9.3	9.0

TABLE V
¹³C NMR chemical shifts (ppm; CD₃SOCD₃) of substituted 1-phenyl-5-aminobenzimidazoles III and 1-phenyl-5-aminobenzotriazoles IV

Carbon	IIIa	IIIb	IIIc	IIId	IIIe	IIIf	IIIg	IIIh	IVa	IVb	IVc	IVd	IVe	IVf	IVg	IVh
C-2	143.9	144.6	144.3 144.4	144.5	144.3	144.4	144.4	144.3	—	—	—	—	—	—	—	—
C-3a	144.4	144.4	144.6 144.8	144.3	144.5	144.6 144.5	144.5	144.2 144.1	146.4	146.5	146.3 146.2	146.1	146.1	146.5	146.2	146.5
C-4	108.8	109.0	109.4 109.1	109.0	108.9	108.9	108.9	108.8	107.2	107.3	107.5	107.5	107.2	107.5	107.1	107.4
C-5	134.5	134.7	135.4 134.0	134.5	134.5	134.5	134.4	134.5	136.6	126.8	135.9 137.1	135.8 135.0	136.3 136.2	135.0	136.3	135.0
C-6	115.4	116.0	115.5 115.3	115.3	115.0	115.0	115.0	115.0	121.9	122.2	121.4 121.6	121.5	121.7	121.7	121.2	121.8
C-7	111.2	111.5	111.5 111.3	111.3	111.5	111.4	111.5	111.3	112.0	112.0	111.9 112.0	111.4	111.9	112.2	112.0	112.3
C-7a	133.1	132.2	133.3 133.8	132.0	133.1	132.0	133.1	132.0	133.8	133.3 133.2	133.7	133.1	133.6	133.3	133.7	133.3
C-8	153.0	153.6	153.3 153.1	153.1	152.4	152.1	152.3	152.1	153.3	153.3	153.1	153.0	152.2	152.5	152.1	152.4
						152.0	152.0	151.5			152.7	152.3	152.0			

C-9	112.3	112.3	83.3	83.3	101.4	101.5	101.7	101.8	112.9	113.0	84.2	84.6	102.3	102.3	102.3	102.6	102.6
			85.9	101.6		102.4					87.3	87.3	102.6	102.5			
C-10	199.1	199.3	195.8	195.5	197.9	197.8	197.9	197.8	199.6	199.6	195.8	195.5	198.1	198.4	198.4	198.2	198.4
			191.7	191.2		194.8					191.8	191.2					
C-11	31.0	31.6	28.1	27.8	30.3	29.8	30.3	29.9	31.6	31.6	28.3	27.9	30.3	30.7	30.4	30.4	30.8
			26.2		30.1							30.2					
C-12	137.3	135.0	137.5	134.0	137.4	134.4	137.3	135.8	138.7	136.8	138.7	137.0	138.5	136.7	138.5	136.7	136.7
			137.6	134.4							138.8						
C-13	123.3	125.4	123.5	125.1	123.4	124.9	123.3	125.0	122.6	124.4	122.6	124.0	122.3	124.4	122.4	122.4	124.4
			125.2									123.9					
C-14	130.2	130.1	130.5	129.8	130.3	129.6	130.3	129.8	130.5	130.1	130.5	129.7	130.2	130.1	130.3	130.3	130.1
C-15	131.1	132.2	131.4	130.6	131.2	131.3	130.3	130.9	129.7	129.6	129.5	129.6	129.7	129.7	129.7	129.7	129.7
			130.9	131.0							129.9						
R	194.8	195.3	120.4	120.0	166.6	166.4	166.2	166.0	195.5	195.5	120.1	119.7	166.4	166.7	166.7	166.1	166.3
			117.1	116.8	166.2	167.7	167.7				116.7	116.4	166.0				
	27.2	27.6	—	—	50.7	50.4	59.2	59.0	27.6	27.6	—	—	50.8	51.1	59.4	59.4	59.6
							59.4	59.3					50.7				
							14.2	13.9	—	—	—	—	—	—	—	—	—
							14.1										
R ¹	20.4	—	20.6	—	20.4	—	20.4	—	20.7	—	20.7	—	20.5	—	20.5	—	—
													20.4				

-(COOEt) < COCH₃ as shown by the increase in shifts of the respective signals of the carbon atom C-9 (from 82 to 112 ppm).

It is possible to infer the site of protonation of the azole ring in compounds *V* and *VI* from the change of chemical shifts of 1-phenyl substituent (C-12) by measuring in trifluoroacetic acid (Table VI).

EXPERIMENTAL

The melting points were measured on a Kofler micro hot-stage. The IR spectra (0.5 mg of the substance per 300 mg KBr) and UV spectra ($1 \cdot 10^{-4}$ mol/l or saturated solution in methanol, cell width 2 mm) were recorded with a Specord M 80 and a Specord M 40 (Zeiss, Jena) spectrometers, respectively. The ¹H and ¹³C NMR spectra were measured with a Varian VXR-300 instrument at 298 K, the chemical shifts are related to hexamethyldisiloxane for ¹H NMR spectra and to CD₃SOCD₃ ($\delta = 39.5$) or the CF₃COOD carbonyl ($\delta = 164.2$) for ¹³C NMR spectra. Saturated solutions were measured in a 5 mm multinuclear probe. The ¹H NMR spectra were recorded at the spectral width of 4 kHz, number of points 16 000. The ¹³C NMR spectra were measured at 75 kHz, spectral width 16 kHz and 64 k per spectrum. The number of accumulations of proton-decoupled ¹³C NMR spectra varied between 250 and 1 000. The pulse repetition time 3 s, flip angle 45°.

TABLE VI
¹³C NMR chemical shifts (ppm; CF₃COOD) of 8-acetyl-6,9-dihydro[4,5-*f*]quinolin-9(3*H*)-ones *V* and *VI*

Carbon	<i>Va</i>	<i>Vb</i>	<i>Vla</i>	<i>Vlb</i>
C-2	141.0	139.3	—	—
C-3a	128.1	130.9	132.8	133.0
C-4	120.4	120.8	122.6	122.4
C-5	123.2	123.0	122.7	122.4
C-5a	139.2	139.5	140.6	138.8
C-7	146.9	147.2	146.4	146.2
C-8	109.7	109.9	111.2	112.7
C-9	172.1	172.3	172.2	172.9
C-9a	112.4	112.6	113.7	114.1
C-9b	130.9	129.2	134.7	137.6
C-10	203.6	203.7	203.4	203.9
C-11	24.5	24.6	25.3	25.3
C-12	144.0	141.4	143.7	140.6
C-13	124.0	125.9	123.9	125.4
C-14	131.0	131.0	131.1	130.9
C-15	124.8	125.0	130.8	132.9
R ¹	19.1	—	19.7	—

1-Phenyl-5-aminobenzimidazole and 1-Phenyl-5-aminobenzotriazole Derivates *III* and *IV*

A solution of 10 mmol 1-phenyl-5-nitrobenzazole derivative in 100 ml methanol was hydrogenated at 120 kPa with 200 mg Raney nickel catalyst until 660 ml hydrogen was consumed. The catalyst was filtered off, a solution of 10 mmol alkoxymethylene compound *I* in 20 ml methanol was added and the mixture was refluxed 30 min. The mixture was shortly boiled with charcoal, filtered, and most of the solvent was evaporated; the separated product was filtered off and washed with cold methanol. Recrystallization from methanol gave analytically pure products. The yields and other data are presented in Table I.

8-Acetyl-3-phenyl-6,9-dihydroazolo[4,5-*f*]quinolin-9(3*H*)-ones *V* and *VI*

A mixture of 2 g ester *IIIe*—*IIIh* (or *IVe*—*IVh*) and 100 ml Dowtherm was boiled 1 h. The esters dissolved and after few minutes the product precipitated from the reaction mixture. After cooling the product was filtered off and the residual Dowtherm was removed by washing with toluene and ether. For analysis a sample was prepared by recrystallization from aqueous dimethylformamide. The products are rather insoluble substances with meltig points over 360°C. Yield and other data are presented in Table I.

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