BENZOID–QUINOID TAUTOMERISM IN AZOMETHINES AND THEIR STRUCTURAL ANALOGS.

40.* SYNTHESIS AND STRUCTURE OF 2-(AMINOBENZYLIDENE)-3(2H)-BENZO[b]THIOPHENONES

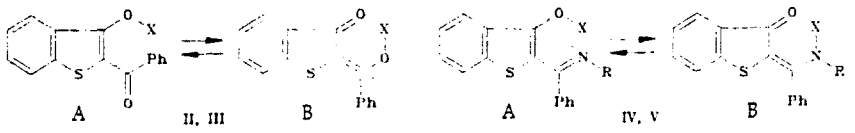
E. N. Shepelenko, V. A. Bren',
and G. E. Andreichkova

UDC 547.735:541.623:543.422

Some 2-benzoyl-3-alkoxybenzo[b]thiophenones, 2-[N-aryl(alkyl)aminobenzylidene]-3(2H)-benzo[b]thiophenones, and their N-formyl derivatives have been synthesized. According to their UV, IR, and PMR spectra, these have the aminobenzylidene-ketone structure.

Earlier work in this series has shown that O-acetyl derivatives of 3-hydroxybenzo[b]-thiophen-2-carboxaldehyde (I) exist in tautomeric equilibrium with the 2-acetoxyvinyl-3-ketone form, but in the condensation products of the aldehyde (I) with arylamines, as in the acetyl derivatives, the aminovinyl ketone tautomer is stable [2-4].

With a view to examining the effects of replacing the aldehyde group in (I) by benzoyl on the position of potential equilibria of the A ⇄ B type, we have synthesized 2-benzoyl-3-hydroxybenzo[b]thiophene (II), its acyl derivatives (III), the condensation products of aryl- and alkylamines with the ketone (II)-(IV), and their formyl derivatives (V).



II X=H; III X=Ac; IV X=H; V X=Ac

The structures of (II)-(V) in the solid phase and in solution have been examined by IR, PMR, and UV spectroscopy.

Irrespective of the conditions of acylation and the acylating agent (acid chlorides or anhydrides in the presence of triethylamine or pyridine in a variety of aprotic solvents), 2-benzoyl-3-hydroxybenzo[b]thiophene (II) gave 2-benzoyl-3-acyloxybenzo[b]thiophenes (III) only.

Direct reaction of 2-benzoyl-3-hydroxybenzo[b]thiophenes with amines does not occur, but in the presence of dialkyl- or diaryldichlorosilanes, which facilitate condensation, the condensation products, 2-[N-aryl(alkyl)aminobenzylidene]-3(2H)-benzo[b]thiophenones (IV), are formed (Table 1). These compounds (IV) cvan also be obtained by the reaction between (III) and highly basic amines, in which case the condensation is accompanied by deacylation. An alternative synthesis of the aminobenzylidene ketones (IV) could be by condensation of the ketone (II) with amines to give 3-(alkyl)arylamino-2-benzoylbenzo[b]thiophenes. However, the spectral characteristics of the latter [5] are not in accordance with the UV, IR, and PMR spectra of the compounds obtained by us (IV).

Treatment of (IV) with formic acetic anhydride gave the N-formyl derivative (V). Attempts to acetylate the aminobenzylidene ketones (IV) by standard methods [acid chlorides in the presence of bases, acid chlorides with the sodium salt of (IV) or in the presence of K_2CO_3, carboxylic anhydrides in the presence of strong acids or pyridine] were unsuccessful.

*For Communication 39, see [1].

Research Institute for Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1043-1046, August, 1987. Original article submitted March 19, 1986.

0009-3122/87/2308-0833$12.50

TABLE 1. Properties of (III)-(VI)

Compound	X	R	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, % (method)
				C	H	S		C	H	S	
IIIa	CH_3CO	—	107—108	69.0	4.1	10.8	$C_{17}H_{12}O_3S$	68.9	4.0	10.5	98
IIIb	CHO	—	106—107	68.3	3.6	10.9	$C_{16}H_{10}O_3S$	68.1	3.5	11.3	85
IIIc	PhCO	—	113—114	73.0	3.9	9.5	$C_{22}H_{14}O_3S$	73.6	4.1	9.2	80
IVa	H	C_6H_5	186—187	76.5	4.6	10.3	$C_{21}H_{15}NOS$	76.6	4.6	9.8	80 (B)
IVb	H	p-$CH_3C_6H_4$	148—149	77.3	5.2	8.7	$C_{22}H_{17}NOS$	77.0	5.0	9.3	67 (A)
IVc	H	o-$CH_3C_6H_4$	145—146	77.1	5.1	8.9	$C_{22}H_{17}NOS$	77.0	5.0	9.3	70 (A)
IVd	H	p-$CH_3OC_6H_4$	163—164	73.8	4.8	9.4	$C_{22}H_{17}NO_2S$	73.5	4.8	8.9	80 (B)
IVe	H	p-$O_2NC_6H_4$	220—221 (dec.)	68.0	3.8	9.4	$C_{20}H_{14}N_2O_2S$	68.3	3.9	8.9	52 (B)
IVf	H	$C_6H_5CH_2$	139—140	76.5	5.1	9.7	$C_{22}H_{17}NOS$	76.4	5.0	9.3	65 (B)
IVg	H	$(CH_3)_2CH$	114—115	73.3	5.9	10.8	$C_{18}H_{17}NOS$	73.4	5.8	11.3	72 (C)
IVh	H	CH_3	112—113	71.0	4.7	11.4	$C_{16}H_{13}NOS$	70.7	5.0	11.9	49 (C)
Va	CHO	C_6H_5	181—182	73.9	4.3	8.4	$C_{22}H_{15}NO_2S$	74.0	4.2	9.0	85
Vf	CHO	$C_6H_5CH_2$	174—175	74.5	4.5	8.3	$C_{23}H_{17}NO_2S$	74.4	4.6	8.6	95
VI	CH_3	C_6H_5	133—134	77.3	5.1	8.8	$C_{22}H_{17}NOS$	76.4	5.0	9.3	55 (B)

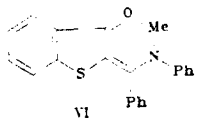
TABLE 2. Spectral Properties of (III)-(VI)

Compound	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) (in propanol)	IR spectrum, cm^{-1} (in Vaseline oil)
IIIa	255 (15.2), 305 (8,6), 335 (3.5)	1770, 1655, 1600, 1525
IIIb	255 (15.3), 305 (8,8), 335 (3,9)	1775, 1655, 1600, 1520
IIIc	260 (21.6), 315 (10,4), 338 (3,4)	1750, 1640, 1600, 1475
IVa	275 (12,6), 340 (14,2), 455 (25,8)	1615, 1595, 1570
IVb	280 (12.4), 330 (12,2), 440 (20,5)	1610, 1590, 1570
IVe	275 (9,5), 345 (13.5), 475 (19,2)	1635, 1585, 1510
IVf	285 (11,7), 340 (12.2), 440 (24.0)	1570, 1550, 1460
IVg	275 (12,8), 330 (11,5), 435 (10,5)	1575, 1550, 1500
Va	285 (9.5), 325 (13,5), 445 (4,5)	1700, 1650, 1575
Vf	300 (12.0), 345 (7,5), 455 (7,0)	1670, 1635, 1570
VI	265 (19,5), 328 (16,5), 470 (6,5)	1600, 1500, 1420

The absence of solvato- and thermochromism in the UV absorption spectra of the ketone (II) indicates the existence of 2-benzoyl-3-hydroxybenzo[b]thiophene in one of the tautomeric forms (IIA) or (IIB). A choice between these tautomeric structures was made on the basis of the IR spectra of (II), which showed maxima at 1580, 1550, and 1500 cm^{-1} corresponding to stretching vibrations of the conjugated carbonyl group and the aromatic fragment corresponding to structure (IIA). These facts, together with the presence in the UV spectra of absorption at 240, 310, and 375 nm, characteristic of structures of type A [3], enable the hydroxyketone structure (IIA) to be assigned to this compound.

In the UV spectra of the acetyl derivative of the hydroxyketone (IIIa), long wavelength absorption is seen with λ_{max} 304 and 335 nm (shoulder), similar to the absorption of 3-acetoxybenzo[b]thiophen-2-aldehyde, and markedly different from that of 2-acetoxymethylenebenzo-[b]thiophen-3(2H)-one (λ_{max} 405 nm) [4]. In the IR spectra of (III) (Table 2), characteristic absorption is present for the carbonyl acyloxy- (1770) and keto-groups (1655), but no absorption is present for an exocyclic C=C bond (1640 cm^{-1}) present in structure (IIIB). In the PMR spectrum of (IIIa), a singlet signal for the methyl protons of the acetyl group at 2.23 ppm and a multiplet for the aromatic protons in the region 7.3-7.9 ppm are present. Treatment of solutions of (III) with catalysts (CF_3COOH, saturated alcoholic HCl), heating to 120°C, and irradiation with sunlight or a mercury vapor lamp did not result in acyl transfer. Hence, replacement of the hydrogen in the CH group of the tautomeric fragment of (II) and (III) by phenyl increases the stability of the 3-hydroxy- and 3-acetoxy-tautomers (IIA) and (IIIA), respectively. This effect is apparently due to a decrease in the basicity and nucleophilicity of the oxygen atom on passing from the aldehydes (I) to the corresponding aromatic ketones (II) [6].

The insensitivity of the spectral characteristics of (IV) to changes in the solvent and variation of the substituent at nitrogen is also evidence for the predominating stability of one of the tautomeric forms. It is clear that this corresponds to the aminobenzylidene ketone structure (IVB), since the UV spectra of (IV) and the compound (VI), which is a model for structure B, are identical (Table 2).



VI

Proof of the aminobenzylidene ketone structure of (IVf) is provided by its PMR spectrum, in which coupling of the NH proton with those of the benzyl group is present (J = 8 Hz). The NH proton signals and the coupling disappear on deuteration of the sample, confirming the presence of the fragment $PhCH_2NH$ in (IVf). In the IR spectra of the aminobenzylidene ketones (IV), strong C=O absorption is present at 1600-1650, together with absorption at 1560-1590 cm^{-1} corresponding to the exocyclic C=C bond [7].

The formylation products (V) have UV spectra similar to those of the original compounds (IV) (Table 2). The PMR spectrum of N-benzyl-N-formylaminobenzylidene ketone (Vf) [8.40 (s, CHO), 7.3-7.6 (Ar), 4.50 ppm (s, CH_2)], together with the IR spectrum [absorption at 1700 (CHO), 1635 (CO), and 1570 cm^{-1} (C=C)] confirm structure (VB).

Heating solutions of (VB) to 150°C, treatment with trifluoroacetic acid, or irradiation by sunlight or a mercury vapor lamp had no effect on the UV spectra, indicating the absence of N → O formyl rearrangement under these conditions.

EXPERIMENTAL

UV spectra were obtained on a Specord M-40 spectrophotometer, IR spectra on a Specord UR-71 spectrometer, and PMR spectra on a Tesla BS 407-C (80 MHz) in $CDCl_3$ or DMSO-D_6, external standard HMDS.

Hydroxy-2-benzoylbenzo[b]thiophene (II) was obtained as described in [8, 9], from thiosalicylic acid and benzoylacetone or ω-bromoacetophenone.

3-Acyloxy-2-benzoylbenzo[b]thiophenes (III). To a solution of 0.254 g (1.0 mmole) of the ketone (II) in 2 ml of dry THF, cooled to 5°C, was added 1.1 mmole of the appropriate acid chloride and 0.15 g (0.2 ml, 1.5 mmole) of triethylamine. After 1 h, the mixture became paler in color, and colorless triethylamine hydrochloride crystals separated, which were filtered off and washed with THF. The filtrate was evaporated and the residue crystallized from 2-propanol, carbon tetrachloride, or toluene.

2-(N-Aryl(alkyl)aminobenzylidene]-3(2H)-benzo[b]thiophenones (IV). A. The ketone (II) (0.254 g, 1.0 mmole) was dissolved in 5 ml of dry THF, and 2.0 mmole of the amine, 1.55 mmole (0.1 ml, 0.15 g) of dimethyl- or diphenyldichlorosilane, and 1.5 mmole (0.2 ml, 0.15 g) of triethylamine added. The mixture was kept at 20°C for 5-7 days. Completion of the reaction was determined by TLC on Silufol, eluent chloroform, R_f 0.4-0.7. The reaction mixture was filtered through activated alumina, the filtrate evaporated, and the residual oil crystallized by treatment with pentane. The solid residue was recrystallized from 2-propanol, hexane, or acetonitrile.

B. To a solution of 0.254 g (1.0 mmole) of the ketone (II) in 3 ml of dry DMF was added 4 mmole of the amine and 1.5 mmole (0.1 ml, 0.15 g) of dimethyl- or diphenyldichlorosilane. After 30 min, the mixture was heated to 100°C for 15 min. Completion of the reaction was determined by TLC. The mixture was poured into 50 ml of cold water, acidified with concentrated HCl to pH 4, and extracted with chloroform (4 × 2.5 ml). The extract was evaporated, and the residue recrystallized from hexane, 2-propanol, or acetonitrile.

C. To a solution of 0.3 g (1.0 mmole) of the acyloxyketone (III) in 1 ml of dry DMF or acetonitrile was added a solution of 1.0 mmole of the amine in 1 ml of DMF or acetonitrile. The crystals which separated were filtered off and recrystallized from 2-propanol, hexane, or acetonitrile.

2-(N-Methylanilinobenzylidene)-3(2H)-benzo[b]thiophenone (VI) was obtained by methods A and B. The amine used was N-methylaniline.

2-[N-Formyl-N-phenyl(benzyl)aminobenzylidene]-3(2H)-benzo[b]thiophenones (V). A solution of 1.0 mmole of (IV) in 2 ml of freshly prepared formic acetic anhydride was boiled for 15 min, then cooled. The solid which separated (V) was filtered off, washed with hexane, and crystallized from a mixture of equal volumes of hexane and propanol.

LITERATURE CITED

1. A. D. Dubonosov, L. M. Sitkina, A. É. Lyubarskaya, V. I. Minkin, and V. A. Bren', Zh. Org. Khim., 23 (1987) (in press).
2. L. M. Sitkina, A. D. Dubonosov, V. A. Bren', S. M. Aldoshin, V. I. Minkin, and L. O. Atovmyan, Zh. Org. Khim., 23, 803 (1987).
3. V. A. Bren', V. I. Usacheva, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 7, 920 (1972).
4. V. A. Bren', G. E. Andreichkova, V. V. Krikov, V. I. Minkin, S. M. Aldoshin, and L. O. Atovmyan, Zh. Org. Khim., 21, 862 (1985).
5. G. D. Pauli, A. E. Lyubarskaya, B. Ya. Simkin, V. A. Bren', Yu. A. Zhdanov, V. I. Minkin, M. I. Knyazhanskii, and L. P. Olekhnovich, Zh. Org. Khim., 15, 1348 (1979).
6. A. Albert and E. Sergent, Ionization Constants of Acids and Bases [Russian translation], Khimiya, Moscow–Leningrad (1964), p. 179.
7. L. Bellamy, The Infra-Red Spectra of Complex Molecules [Russian translation], IL, Leningrad (1963).
8. V. M. Rodionov and B. M. Bogoslovskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 586 (1948).
9. Organic Syntheses [Russian translation], IL, Vol. 2 (1949), p. 455.

BORON FLUORIDES OF cis- AND trans-2-ARYL-3-AROYLAZIRIDINES

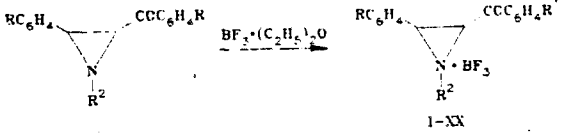
O. N. Bubel', V. A. Konovalov, and I. G. Tishchenko

UDC 547.717.07:541.634

The reaction of boron trifluoride etherate with cis- and trans-2-aryl-3-aroylaziridines yields the respective complexes in high yield. According to PMR spectral data the methyl group of boron trifluoride trans-1-methyl-3-aroylaziridines is located in syn-position, and in the cis-aziridine complexes in anti-position, to the carbonyl group.

With certain acids ($HClO_4$, $HFSO_3$) aziridine derivatives form quite stable salts [1-3] that show increased reactivity toward nucleophiles [4, 5]. We have shown [6, 7] that complexes of 3-aroylaziridines with boron trifluoride also react quite easily with acetone and acetonitrile. But no data have been published on the synthesis and structure of these complexes.

In the present work we establish that the boron fluoride trans-2-aryl-3-aroylaziridines (I-XII) (Table 1) can be obtained in high yield (85-90%) by treatment of trans-2-aryl-3-aroylaziridines in methanol at −20° to −30° with an equimolar amount of boron trifluoride etherate.



I, XI, XIV R=*p*-Cl, II, XII, XIII R=*p*-Br, III, XV R=*m*-NO_2, IV R=*p*-NO_2, V, X, XVI R=*p*-CH_3, VI—IX, XVII—XX R=H; I—VI, IX—XVII R^1=H, VII, XVIII R^1=*p*-Br, VIII, XIX R^1=*p*-Cl, XX R^1=OCH_3; I—VIII, XIII—XX R^2=CH_3, IX—XII R^2=H

When compounds I-XII are treated with aqueous salt solution the respective free aziridines separate; this confirms [2] the retention of the aziridine ring in the complex.

Similarly cis-1-methyl-2-aryl-3-aroylaziridines also react with boron trifluoride etherate to form complexes. The yield of complexes XIII-XX is also high, 85-90% (Table 1).

A. N. Sevchenko Scientific-Research Institute for Applied Physics Problems, Minsk 220106.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1047-1049, August, 1987. Original article submitted March 26, 1986.

 0009-3122/87/2308-0836$12.50