BENZYLIDENE DERIVATIVES OF 5-NITRO- AND 5-AMINOBENZO[b]-3(2H)-THIOPHENONE

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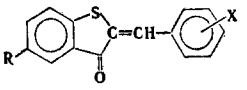
Continuing our investigations of photochromic compounds obtained from benzo[b]-3(2H)-thiophenone [1,2], we have synthesized a number of previously undescribed substances (III-XIII). Compounds III-VII were obtained by the condensation of 5-nitro-3-acetoxybenzo[b]thiophene (I) with various benzaldehydes, while 5-acetamido-3-acetoxybenzo[b]thiophene (II) was used for the synthesis of VIII-XIII. Although the condensation of aldehydes with I and II proceeds more slowly and gives lower yields than in the case of non-acetylated benzo[b]-3(2H)-thiophenones, the use of the latter is complicated by their lability. The conditions used for the condensation – heating I or II with aldehydes in acetic acid containing water and hydrochloric acid to 80-100°C – led to resinification of I and II during the reaction. Some characteristics of the compounds obtained are presented in Table 1. It is apparent from Table 1 that the absorption maxima of the 5-amino derivatives are shifted bathochromically as compared with the heteroring-unsubstituted thioindogenides; the maxima of the 5-nitro derivatives experience a hypsochromic shift. This is apparently associated with modification of the electron-donor capacity of sulfur.



III-VII R=NO_2
VIII-XIII R=NH_2

It was demonstrated that the introduction of an amino group into the 5 position of the heteroring generally leads to a sharp deterioration in the photoisomerization capacity of the compounds.

TABLE 1. Characteristics of 5-Nitro- and 5-Amino-2-benzylidene-benzo[b]-3(2H)-thiophenones (III-XIII)

Comp.	R	X	mp, °C	Empirical formula	Found, %				Calc., %			
					C	H	N	S	C	H	N	S
III	NO_2	4-CH_3	276—277	$C_{16}H_{11}NO_3S$	64,5	3,8	4,8	10,6	64,6	3,7	4,7	10,8
IV	NO_2	4-OH	255—256	$C_{15}H_9NO_4S$	60,4	3,2	4,7	10,6	60,2	3,0	4,7	10,7
V	NO_2	4-NH_2	Above 300	$C_{15}H_{10}N_2O_3S$	60,6	3,4	9,4	10,6	60,4	3,4	9,4	10,8
VI	NO_2	2-F	223—224	$C_{15}H_8FNO_3S$	60,1	2,7	4,7	10,5	59,8	2,6	4,6	10,6
VII	NO_2	3-NO_2	261—262	$C_{15}H_8N_2O_5S$	54,9	2,4	8,8	9,6	54,9	2,4	8,5	9,8
VIII	NH_2	H	279—280	$C_{15}H_{11}NOS$	71,0	4,2	5,6	12,4	71,1	4,3	5,5	12,7
IX	NH_2	4-CH_3	291—292	$C_{16}H_{13}NOS$	70,9	4,9	5,3	11,7	70,9	4,9	5,2	12,0
X	NH_2	4-OH	Above 300	$C_{15}H_{11}NO_2S$	67,0	4,1	5,2	11,8	66,9	4,1	5,2	11,9
XI	NH_2	4-F	Above 300	$C_{15}H_{10}FNOS$	66,3	3,6	5,2	11,8	66,4	3,7	5,2	11,8
XII	NH_2	4-Cl	293—294	$C_{15}H_{10}ClNOS$	62,4	3,5	4,9	11,0	62,6	3,5	4,9	11,1
XIII	NH_2	2-NO_2	238—239	$C_{15}H_{10}N_2O_3S$	60,4	3,4	9,2	10,7	60,4	3,4	9,4	10,8

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TABLE 1 (continued)

Comp.	Spectra in alcohol						Yield, %
	before irradiation		after irradiation*		isosbestic point		
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ, nm	$\varepsilon \cdot 10^{-4}$	
III	438	1,88	440	1,34	451	1,06	88
IV	450†	2,32	450 †	2,32	—	—	92
V	450	2,88	451	2,24	465	1,78	92
VI	432	1,66	Decomposes				90
VII	424‡	—	426 ‡	—	446 ‡	—	93
VIII	451	0,73	453	0,67	480	0,36	57
IX	453	0,92	455	0,77	477	0,53	58
X	460	1,36	460	1,32	490	0,56	53
XI	450	0,71	452	0,62	475	0,42	55
XII	453	0,76	455	0,69	478	0,45	53
XIII	452‡	—	455 ‡	—	499 ‡	—	74

*Illuminated with a 1000-watt incandescent lamp for 20 min.

† This compound did not isomerize.

‡ These compounds are only slightly soluble in alcohol.

LITERATURE CITED

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