ABSORPTION SPECTRA OF 3-OXO-2,3-DIHYDROTHIONAPHTHENE AND ITS DERIVATIVES

IX. Benzylidene Derivatives of 3-Oxo-5-Methyl-2,3-Dihydrothionaphthene and 5-Methylcoumaranone*

M. A. Mostoslavskii and M. D. Kravchenko

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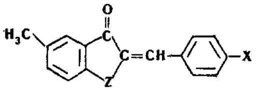
The absorption spectra of a number of aurones and thioindogenides specially synthesized for this purpose have been measured. It has been shown that aurones are phototropic in solution. The side reaction of irreversible photochemical decomposition takes place more rapidly with the aurones than with the thioindogenides. The shifts caused by the introduction of substituents into the 4' position are dissimilar in the aurones and the analogous thioindogenides, which is explained by the greater basicity of the thionaphthene system as compared with the benzofuran system.

The absorption spectra of the aurones (2-benzylidenecoumaranones) have been subjected to a special investigation [2], and have been measured repeatedly with the object of characterizing or identifying particular substances (for example [3–5]). There is, however, no information in the literature on the phototropy of solutions of aurones.

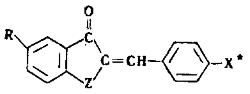


I Z = O, II Z = S

We have synthesized several aurones (I) and several thioindogenides (II) and have measured their absorption spectra before and after the action of light. Table 1 shows that in solution aurones possess phototropic properties similar to those of the thioindogenides and indogenides [13,14], for which it has been shown [15] that the phototropy is caused by a photochemical cis-trans isomerization. When a solution of 2-(4-dimethylaminobenzylidene)-3(2H)-benzofuranone prepared in the dark is irradiated with daylight, the intensities of the maxima at 412 and 437 nm decrease (figure). At the same time a new well-defined maximum appears at 462 nm, which corresponds to the second stereoisomeric form of the substance. When a solution irradiated with daylight for 30 min

Table 2

λ_{max}(nm) of Substances of the General Formula Relative to the Compounds in which X = H



Z	R	X N(CH₃)₂	 OCH₃	 H	 C	 NO₂
S	H	34; 46	−1; 7	0; 0	1; 3	10; 15
S	CH_3	31; 42	2; 8	0; 0	0; 2	14
O	CH_3	67; 66	20; 17	0; 0	−1; 1	7
S	NO_2	50; 65	1; 12	0; 0	2; 2	10;9

*All the λ_{max} figures were determined for solutions in benzene; since the long-wave absorption band of the majority of substances has two maxima (see figure), data for both maxima are given.

Table 1

Phototropic Properties of Solutions of Aurones and Thioindogenides (I and II) in n-Hexane

Z	X	Mp, °C	Spectrum of a solution prepared in the dark λ^{I}_{max}, nm	 $\varepsilon^{I}_{max} \cdot 10^{-4}$	Spectrum of an irradiated solution* λ_{max}, nm	 $\varepsilon_{max} \cdot 10^{-4}$	Isobestic point λ, nm	 $\varepsilon \cdot 10^{-4}$
S	$N(CH_3)_2$	197^6	464, 438	5.0; 3.4	496	1.2	475	2.2
O	$N(CH_3)_2$	190	437, 412	4.8; 3.8	462	2.6	446	2.6
S	OCH_3	156^6	438, 420	2.09; 1.5	465	0.79	448	0.9
O	OCH_3	154^7	393, 372	3.3; 2.6	414	1.9	400	1.6
S	H	147^8	434, 424	1.18; 1.13	452	0.76	445	0.72
O	H	$120^{7,9-11}$	376, 363	1.6; 1.2	392	0.83	387	0.78
S	Cl	176.5^6	437, 425	1.24; 1.17	455	0.73	450	0.73
O	Cl	176	379, 366	2.03; 1.58	395	1.06	390	1.04
S	2^1-Cl	178	438, 426	0.92; 0.96	455	0.4	452	0.4
O	2^1-Cl	130	377, 363	1.66; 1.4	398	0.65	392	0.65
S	NO_2	262^6	447, 435	—; —	460	—	465	—
O	NO_2	208^{12}	383, —	—; —	398	—	400	—

*Only the new maximum appearing on irradiation is given: the intensity of the maxima present before irradiation fall markedly (see figure).

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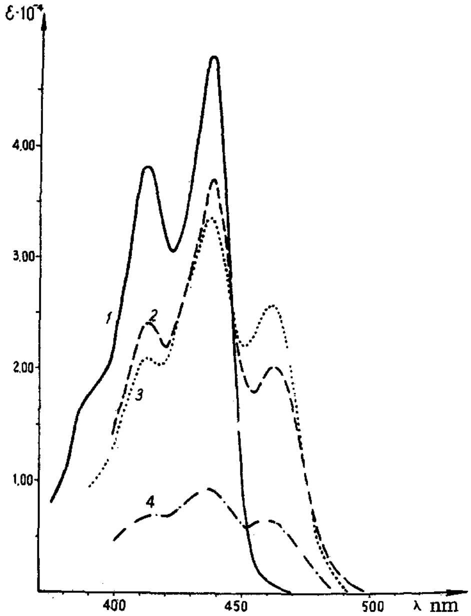
*For part VIII, see [1].

is stored in the dark, the spectrum resumes its original form. With a longer time of irradiation, however, a secondary photochemical decomposition of the substance accompanying the photoisomerization becomes appreciable. The aurones I decompose more rapidly than the thioindogenides II. The difference is particularly great in the case of the dimethylamino derivatives. o-Chloro derivatives are less stable than p-chloro derivatives, as has been recorded previously for the thioindogenides [16].



UV spectra of solutions of 2-(4'-dimethylaminobenzylidene)-5-methyl-3(2H)-benzofuranone in n-hexane: 1) solution prepared in the dark; 2) solution 1 after irradiation with daylight for 5 min; 3) solution 2 after irradiation for 10 min; 4) solution 3 after irradiation for 8 hr.

It is known that the unstable stereoisomeric form of oxindigo [17] absorbs light in the shorter-wave region than the stable form. The same is true for stilbene and its derivatives [18]. The aurones (I), the molecules of which may be regarded schematically as a combination of half the molecule of 5,5'-dimethyloxindigo and half the molecule of stilbene have the opposite properties. It can be seen from Table 1 that the unstable stereoisomeric form produced by the irradiation of solutions of the aurones absorbs light in the region of longer waves than the initial stable form. This may indicate that the steric hindrance arising in the unstable isomer leads to the deformation of the "essential" double bond, which is accompanied by a deepening of the color [19].

It is also of interest to compare the absorption spectra of thioindogenides and aurones of similar structure. As the data of Table 1 show, compounds of the 5-methyl-3-oxo-2,3-dihydrothionaphthene series absorb light in the region of longer wavelengths but less strongly than the corresponding 5-methylcoumaranone derivatives. If one considers how the replacement of the hydrogen in position 4' affects the position of λ_{max}, it is found that the aurones respond considerably more strongly to the introduction of electron-donating substituents [$-OCH_3$, $-N(CH_3)_2$] and less strongly to the introduction of electron-accepting substituents ($-NO_2$). Table 2 gives the magnitudes of the shifts in λ_{max} of the long-wave absorption band of the benzylidene derivatives of 3-oxo-2,3-dihydrothionaphthene [14], 5-methyl-3-oxo-2,3-dihydrothionaphthene, 5-methylcoumaranone, and 5-nitro-3-oxo-2,3-dihydrothionaphthene [20] on the introduction of a substituent into position 4'. It can be seen that the figures in column 3 are closer to the figures in column 4 than to the figures in column 2, i. e., the behavior of substances of the 5-methylcoumaranone series is closer to that of derivatives of 5-nitro-3-oxo-2,3-dihydrothionaphthene than to that of derivatives of 5-methyl-3-oxo-2,3-dihydrothionapthene. This is apparently connected with the lower basicity of the benzofuranone nucleus as compared with the benzothiophene nucleus. The introduction of a nitro group lowers the basicity of the thionaphthene nucleus and brings its capacity for reacting with the substituent in the benzylidene part of the molecule closer to the corresponding properties of 5-methylcoumaranone.

EXPERIMENTAL

2-(4'-Chlorobenzylidene)-5-methyl-3(2H)-benzofuranone. A mixture of 0.50 g (0.0034 mole) of 5-methyl-3(2H)-benzofuranone, 0.48 g (0.0034 mole) of p-chlorobenzaldehyde, and 0.8 ml of water in 8 ml of acetic acid was heated to 60° C, 0.5 ml of concentrated HCl was added, and the mixture was kept at 80° C for 2 hr. Then it was cooled and filtered, and the precipitate was washed with cold petroleum ether. This gave 0.68 g (73.1%), mp 178° C (from petroleum ether). Found, %: Cl 13.29, 13.18. Calculated for $C_{16}H_{11}ClO_2$, %: Cl 13.10. The following compounds were obtained similarly: **2-(2'-Chlorobenzylidene)-5-methyl-3(2H)-benzofuranone.** Yield 64%, mp 130° C (from petroleum ether). Found, %: Cl 13.18, 13.18. Calculated for $C_{16}H_{11}ClO_2$, %: Cl 13.10. **2-(4'-Dimethylaminobenzylidene)-5-methyl-3(2H)-benzofuranone.** Yield 63%, mp 190° C (from 50% aqueous acetic acid). Found, %: N 5.0, 5.05. Calculated for $C_{18}H_{17}O_2$, %: N 5.01. **2-(2'-Chlorobenzylidene)-5-methyl-3(2H)-benzothiophenone.** Yield 48%, mp 178° C (from hexane). Found, %: N 11.16, 11.21. Calculated for $C_{16}H_{11}ClO$, %: N 11.17.

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Rubezhnoe Branch, Scientific
Research Institute for Organic
Intermediates and Dyes