HALOGEN DERIVATIVES OF 5-(1'KETOACENAPHTHYLIDENE)THIAZOLIDINE

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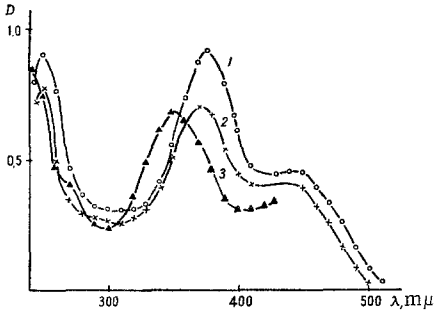
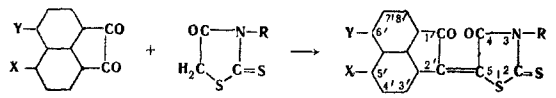
Acenaphthenequinone and its derivatives readily condense with 3-phenyl-, 3-p-tolyl-, 3-(4-methoxyphenyl)-, 3-(2-methoxyphenyl)-, 3-(4-ethoxyphenyl)rhodanines. The UV absorption spectra of these compounds in dioxane lie in the range 363–390 mμ. Replacement of oxygen by sulfur at position 2 in the thiazolidine ring gives rise to a 14 to 41 mμ bathochromic shift.

Continuing our research [1] into condensation of acenaphthenequinone and its halogen derivatives with



Ultraviolet absorption spectra (in dioxane): 1) 5-(5'6'-Dichloro-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one; 2) 5-5'-chloro-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one; 3) 5-(5'-chloro-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2,4-dione (C = $= 5 \cdot 10^{-4}$ g/cm^3).

thiazolidine derivatives, we have condensed the appropriate quinones with 3-phenyl-, 3-p-tolyl-, 3-(4-methoxyphenyl)-, 3-(2-methoxyphenyl)- and 3-(4-ethoxyphenyl)thiazolidine-2-thione-4-one. The reaction proceeds readily when acetic acid solutions are boiled in the presence of fused sodium acetate.



R=C_6H_5. I, X=Y=H. II–V, Y=H; X=F (II), Cl (III), Br (IV), I (V). VI, X=Y=Cl. VII, X=Y=Br. VIII, X=Y=I.

R=p-C_6H_4—CH_3. IX, X=Y=H. X — XIII, Y=H; X=F(X); Cl (XI); Br (XII), I (XIII). XIV, X=Y=Cl. XV, X=Y=Br. XVI, X=Y=I.

R=p-C_6H_4—OCH_3. XVII, X=Y=H. XVIII–XXI, Y=H; X=F (XVIII), Cl (XIX); Br (XX), I (XXI). XXII, X=Y=Cl. XXIII, X=Y=Br. XXIV, X=Y=I.

R=o-C_6H_4—OCH_3. XXV, X=Y=H. XXVI–XXIX, Y=H; X=F (XXVI), Cl (XXVII), Br (XXVIII), I (XXIX). XXX, X=Y=Cl. XXXI, X=Y=Br. XXXII, X=Y=I.

R=p-C_6H_4—OC_2H_5. XXXIII, X=Y=H. XXXIV–XXXVII, Y=H; X=F (XXXIV), Cl (XXXV), Br (XXXVI), I (XXXVII). XXXVIII, X=Y=Cl. XXXIX, X=Y=Br. XL, X=Y=I.

There are two possible structures in the cases of compounds II–V, X–XIII, XVIII–XXI, XVI–XXIX, XXIV–XXVII. However, we did not succeed in isolating the isomers, and their structures are assumed. Table 1 gives the properties of the compounds prepared. The UV absorption spectra maxima* in dioxane solution lie in the range 363–390 mμ. They are displaced towards the long wavelength region for the dihalogen compounds compared with the monohalogen ones (figure). Introduction of ethoxyl instead of methoxyl at position 4 leads to a bathochromic shift of up to 6 mμ. Replacement of an atom of sulfur by oxygen at position 2 gives rise to a bathochromic shift of up to 41 mμ (figure, Table 2).

EXPERIMENTAL

0.001 mole of acenaphthenequinone or its halogen derivative was dissolved in the minimum quantity of glacial AcOH, 0.0015 mole of the corresponding thiazolidine-2-thione-4-one and fused NaOAc (up to 20% on the AcOH) introduced, and the whole refluxed for 7–10 min. The crystals of condensation product which separated were filtered off, washed with (2 × 2 ml) hot AcOH, then with water, and dried. The products were recrystallized from chlorobenzene, nitrobenzene, and pyridine, to form red needles, insoluble in EtOH and ether, soluble in nitrobenzene, chlorobenzene, pyridine, dioxane, and aniline.

REFERENCE

1. A. P. Karishin, A. I. Timchenko, G. F. Dzhurka, Yu. V. Samusenko, T. F. Balkan, and G. M. Lysenko, KhGS [Chemistry of Heterocyclic Compounds], 704, 1965.

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*A SF-4 spectrophotometer was used to measure the absorption spectra.

Table 1

Synthesized Derivatives of 5-(1'-Ketoacenaphthylidene)thiazolidine

Compound	Name	Mp, °C	λ_{max}, mμ (in dioxane)	Formula	S, %		Yield, %
					Found	Calculated	
1	2	3	4	5	6	7	8
I	5-(1'-Ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	298—299	363	$C_{21}H_{11}NO_2S_2$	17.23	17.17	80
II	5-(5'-Fluro-1'-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	311—313	370	$C_{21}H_{10}FNO_2S_2$	16.12	16.38	82
III	5-(5'-Chloro-1'-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	308—309	375	$C_{21}H_{10}ClNO_2S_2$	15.51	15.69	85
IV	5-(5'-Bromo-1'-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one.	314—315	372	$C_{21}H_{10}BrNO_2S_2$	14.32	14.17	92
V	5-(5'-Iodo-1'-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	326—328	374	$C_{21}H_{10}INO_2S_2$	12.69	12.84	77
VI	5-(5',6'-Dichloro-1-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	333—335	375	$C_{21}H_9Cl_2NO_2S_2$	14.38	14.52	61
VII	5-(5',6'-Dibromo-1'-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	364—365	375	$C_{21}H_9Br_2NO_2S_2$	12.24	12.07	84
VIII	5-(5',6'-Diiodo-1'-ketoacenaphthylidene)-3-phenylthiazolidine-2-thione-4-one	298—300 (decomp)	378	$C_{21}H_9I_2NO_2S_2$	10.39	10.25	64
IX	5-(1'-Ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one	312—315	368	$C_{22}H_{13}NO_2S_2$	16.37	16.55	70
X	5-(5'-Fluoro-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one	318—319	370	$C_{22}H_{12}FNO_2S_2$	15.68	15.81	72.5
XI	5-(5'-Chloro-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one	308—309	372	$C_{22}H_{12}ClNO_2S_2$	15.02	15.19	87.5
XII	5-(5'-Bromo-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one	309—310	369	$C_{22}H_{12}BrNO_2S_2$	13.62	13.74	84.7
XIII	5-(5'-Iodo-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one	304—305	372	$C_{22}H_{12}INO_2S_2$	12.32	12.48	69

Table 1
(cont'd)

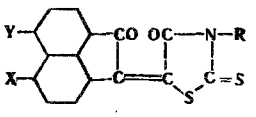
1	2	3	4	5	6	7	8
XIV	5-(5',6'-Dichloro-1'ketoacenaphthylidene)-3-p-tolylthiazolidine-2-thione-4-one	327—328	377	$C_{22}H_{11}Cl_2NO_2S_2$	14.27	14.05	62.2
XV	5-(5',6'-Dibromo-1'-ketoacenaphthylidene)-3-p-tolylthiazolidine)-2-thione-4-one	349—350 (decomp)	375	$C_{22}H_{11}Br_2NO_2S_2$	11.67	11.76	85.4
XVI	5-(5',6'-Diiodo-1'-ketoacenapthylidene)-3-p-tolylthiazolidine-2-thione-4-one	284—285 (decomp)	381	$C_{22}H_{11}I_2NO_2S_2$	9.81	10.03	62.5
XVII	5-(1'-Ketoacenaphthylidene)-3-(4-methoxyphenyl)thiazolidine-2-thione-4-one	314—315	370	$C_{22}H_{13}NO_3S_2$	16.12	15.86	87
XVIII	5-(5'-Fluoro-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)thiazolidine-2-thione-4-one	305—306	367	$C_{22}H_{12}FNO_3S_2$	15.02	15.19	50
XIX	5-(5'-Chloro-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)thiazolidine-2-thione-4-one	334—335	367	$C_{22}H_{12}ClNO_3S_2$	14.93	14.61	66
XX	5-(5'-Bromo-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)thiazolidine-2-thione-4-one	326—327	373	$C_{22}H_{12}BrNO_3S_2$	13.48	13.27	60
XXI	5-(5'-Iodo-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)thiazolidine-2-thione-4-one	318—319	372	$C_{22}H_{12}INO_3S_2$	12.22	12.09	51
XXII	5-(5',6'-Dichloro-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)-thiazolidine-2-thione-4-one	308—309	377	$C_{22}H_{11}Cl_2NO_3S_2$	13.63	13.55	73
XXIII	5-(5',6'-Dibromo-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)-thiazolidine-2-thione-4-one	334—335	380	$C_{22}H_{11}Br_2NO_3S_2$	11.50	11.39	60
XXIV	5-(5',6'-Diiodo-1'-ketoacenaphthylidene)-3-(4-methoxyphenyl)-thiazolidine-2-thione-4-one	296—297	388	$C_{22}H_{11}I_2NO_3S_2$	9.82	9.76	63
XXV	5-(1'-Ketoacenaphthylidene)-3-(2-methoxyphenyl)thiazolidine-2-thione-4-one	283—284	372	$C_{22}H_{13}NO_3S_2$	16.01	15.86	80
XXVI	5-(5'-Fluoro-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiazolidine-2-thione-4-one	292—293	368	$C_{22}H_{12}FNO_3S_2$	15.47	15.19	50
XXVII	5-(5'-Chloro-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiazolidine-2-thione-4-one	297—298	372	$C_{22}H_{12}ClNO_3S_2$	14.92	14.61	41

Table 1
(cont'd)

1	2	3	4	5	6	7	8
XXVIII	5-5'-Bromo-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiazol-idene-2-thione-4-one	266—267	374	$C_{22}H_{12}BrNO_3S_2$	13.47	13.27	43
XXIX	5-5'-Iodo-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiazol-idene-2-thione-4-one	272—273	374	$C_{22}H_{12}INO_3S_2$	12.17	12.09	35
XXX	5-5',6'-Dichloro-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiazol-idine-2-thione-4-one	239—240	381	$C_{22}H_{11}Cl_2NO_3S_2$	13.64	13.55	41
XXXI	5-(5',6'-Dibromo-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiaz-olidine-2-thione-4-one	339—340	384	$C_{22}H_{11}Br_2NO_3S_2$	11.56	11.39	80
XXXII	5-(5',6'-Diiodo-1'-ketoacenaphthylidene)-3-(2-methoxyphenyl)thiaz-olidine-2-thione-4-one	259—260	387	$C_{22}H_{11}I_2NO_3S_2$	9.79	9.76	30
XXXIII	5-(1'-Ketoacenaphthylidene)-3-(4-ethoxyphenyl-thiazolidine-2-thione-4-one	315—316	370	$C_{23}H_{15}NO_3S_2$	15.28	15.33	63
XXXIV	5-(5'-Fluoro-1'-ketoacenaphthylidene)-3-(4-ethoxyphenyl)thiazol-idene-2-thione-4-one	305—306	371	$C_{23}H_{14}FNO_3O_2$	15.02	14.70	65
XXXV	5-(5'-Chloro-1'-ketoacenaphthylidene)-3-(4-ethoxyphenyl)thiazol-idene-2-thione-4-one	282—283	372	$C_{23}H_{14}ClNO_3S_2$	14.41	14.16	51
XXXVI	5-(5'-Brome-1-ketoacenaphthylidene)-3-(4-ethoxyphenyl)thiazol-idene-2-thione-4-one	280—282	376	$C_{23}H_{14}BrNO_3S_2$	13.25	12.81	50
XXXVII	5-(5'-Iodo-1'-ketoacenaphthylidene)-3-(4-ethoxyphenyl)thiazol-idene-2-thione-4-one	296—298	378	$C_{23}H_{14}INO_3S_2$	11.91	11.78	43
XXXVIII	5-(5',6'-Dichloro-1'-ketoacenaphthylidene)-3-(4-ethoxyphenyl) thiazolidine-2-thione-4-one	304—305	381	$C_{23}H_{13}Cl_2NO_3S_2$	13.45	13.16	90
XXXIX	5-(5',6'-Dibromo-1'-ketoacenaphthylidene)-3-(4-ethoxyphenyl)thiaz-olidene-2-thione-4-one	333—334	381	$C_{23}H_{13}Br_2NO_3S_2$	11.43	11.12	40
XL	5-(5',6'-Diiodo-1'-ketoacenaphthylidene)-3-(4-ethoxyphenyl)thiazol-idene-2-thione-4-one	285—286	390	$C_{23}H_{13}I_2NO_3S_2$	9.68	9.56	43

Table 2

Maxima of Absorption Spectra of Halogen Derivatives of 5-(1'-ketoacenaphthylidene)-3-phenyl- and 3-p-tolylthiazolidines



Compound	λ_{max}, mμ in dioxane		Bathochromic shift λ_{max}, mμ
	Z=S	Z=O	
R=C_6H_5			
X=Y=H	363	329	34
X=F, Y=H	370	332	38
X=Cl, Y=H	375	335	40
X=Br, Y=H	372	336	36
X=I, Y=H	375	340	35
X=Y=Cl	375	341	34
X=Y=Br	375	334	41
X=Y=I	378	364	14
R=*p*-$C_6H_4CH_3$			
X=Y=H	368	338	30
X=F, Y=H	370	340	30
X=Cl, Y=H	372	348	24
X=Br, Y=H	369	352	17
X=I, Y=H	372	351	21
X=Y=Cl	377	357	20
X=Y=Br	375	355	20
X=Y=I	381	366	15