UDC 547.78 + 547.678 + 542.95

CONDENSATION OF ACENAPHTHENEQUINONE AND ITS HALOGEN DERIVATIVES WITH 2-THIOHYDANTOIN AND THIAZOLIDINEDIONE-2, 4

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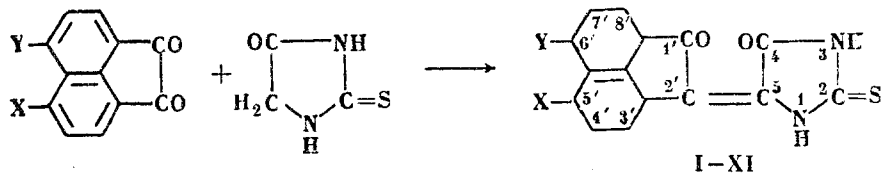
Acenaphthenequinone and its halogen derivatives readily undergo condensation with 2-thiohydantoin, thiazolidinedione-2, 4, and the N-phenyl and N-p-tolyl derivatives of the latter in acid medium, on boiling in the presence of anhydrous sodium acetate. Replacement of an oxygen atom in the thiazolodine ring by sulfur leads to bathochromic shift of UV absorption maxima both in solution in dioxane and in concentrated sulfuric acid. The large displacement of the spectral maxima in sulfuric acid as compared with dioxane is evidently due to salt formation.

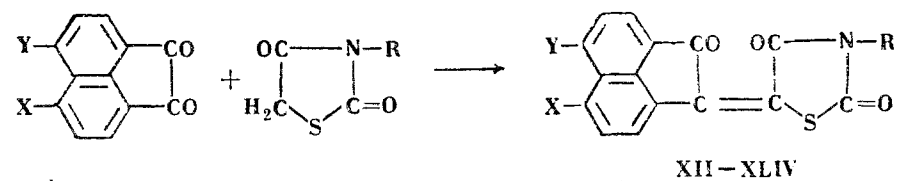
Continuing research on the properties of acenaphthenequinone and its halogen derivatives [1], they have now been condensed with 2-thiohydantoin, thiazolidinedione-2, 4, 3-phenyl- and 3-p-tolyl-thiazolidinedione-3, 4.

Condensation takes place readily when acetic acid solutions of the starting materials are boiled for 10-15 min in the presence of 15-20% anhydrous sodium acetate (from acetic acid). This gives 5-(1'-ketoacenaphthylidene) imidazolidinethione-2-one-4 and its 5'- and 6' halogen derivatives (I-XI), 5[1'-ketoacenaphthylidene] thiazolidinedione-2, 4, and its N-phenyl-, N-p-tolyl, and their 5' and 6 halogen derivatives (XII-XLIV).



I-XI

I x=y=H; II-V y=H; II x=F; III x=Cl; IV x=Br; V x=I; VI x=y=Cl; VII x=y=Br; VIII x=y=I; IX x=Cl, y=Br; X x=Cl, y=I; XI x=Br, y=I.



XII-XLIV

R=H

XII x=y=H; XIII-XVI y=H; XIII x=F; XIV x=Cl; XV x=Br; XVI x=I; XVII x=y=Cl; XVIII x=y=Br; XIX x=y=I; XX x=Cl, y=Br; XXI x=Cl, y=I; XXII x=Br, y=I.

R=C_6H_5

XXIII x=y=H; XXIV-XXVII y=H; XXIV x=F; XXV x=Cl; XXVI x=Br; XXVII x=I; XXVIII x=y=Cl; XXIX x=y=Br; XXX x=y=I; XXXI x=Cl, y=Br; XXXII x=Cl, y=I; XXXIII x=Br, y=I.

R=$C_6H_4CH_3(n)$

XXXIV x=y=H; XXXV-XXXVIII y=H; XXXV x=F; XXXVI x=Cl; XXXVII x=Br; XXXVIII x=I; XXXIX x=y=Cl; XL x=y=Br; XLI x=y=I; XLII x=Cl, y=Br; XLIII x=Cl, y=I; XLIV x=Br, y=I.

Two structures are possible for compounds II-V, IX-XI, XIII-XVI, XX-XXII, XXIV-XXVII, XXXI-XXXIII, XXXV-XXXVIII, XLII-XLIV, but it proved impossible to separate isomers.

The compounds obtained are slightly soluble in acetic acid, and insoluble in alcohol and ether. They crystallize from nitrobenzene, bromobenzene, pyridine, and dioxane. Their properties are given in Table 1.

Table 1

Properties of Compounds Synthesized

Compound No.	Compound	Mp, °C	λ_{max}* mμ in dioxane	Formula	S, %		Yield, %
					Found	Calculated	
I	5-[1'-ketoacenaphthylidene] imidazolidinethione-2-one-4	316—317	305	$C_{15}H_8N_2O_2S$	11.23	11.41	77.7
II	5-[5'-fluoro-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	321—322	310	$C_{15}H_7FN_2O_2S$	10.58	10.72	94.0
III	5-[5'-chloro-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	318—320	312	$C_{15}H_7ClN_2O_2S$	10.01	10.16	81.2
IV	5-[5'-bromo-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	311—312	312	$C_{15}H_7BrN_2O_2S$	8.82	8.91	90.5
V	5-[5'-iodo-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	304—306	317	$C_{15}H_7IN_2O_2S$	7.62	7.87	78.8
VI	5-[5', 6'-dichloro-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	Does not melt at 365	314	$C_{15}H_6Cl_2N_2O_2S$	9.03	9.16	85.9
VII	5-[5', 6'-dibromo-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	„	313	$C_{15}H_6Br_2N_2O_2S$	7.01	7.30	86.7
VIII	5-[5', 6'-diiodo-1'-ketoacenaphthylidene] imidazolidine-thione-2-one-4	„	322	$C_{15}H_6I_2N_2O_2S$	5.87	6.01	85.3
IX	5-[5'-chloro-6'-bromo-1'-ketoacenaphthylidene] imidazolidinethione-2-one-4	„	315	$C_{15}H_6BrClN_2O_2S$	7.92	8.13	81.4
X	5-[5'-chloro-6'-iodo-1'-ketoacenaphthylidene] imidazolidinethione-2-one-4	„	313	$C_{15}H_6ClIN_2O_2S$	7.32	7.26	75.0
XI	5-[5'-bromo-6'-iodo-1'-ketoacenaphthylidene] imidazolidinethione-2-one-4	„	319	$C_{15}H_6BrIN_2O_2S$	6.43	6.59	62.0
XII	5-[1'-ketoacenaphthylidene] thiazolidinedione-2, 4	287—288	336	$C_{15}H_7NO_3S$	11.21	11.40	78.5
XIII	5-[5'-fluoro-1'-ketoacenaphthylidene] thiazolidinedione-2, 4	309—310	336	$C_{15}H_6FNO_3S$	11.28	11.04	76.4
XIV	5-[5'-chloro-1'-ketoacenaphthylidene] thiazolidinedione-2, 4	313—314	336	$C_{15}H_6ClNO_3S$	10.32	10.18	80.1
XV	5-[5'-bromo-1'-ketoacenaphthylidene] thiazolidinedione-2, 4	343—344	342	$C_{15}H_6BrNO_3S$	8.78	8.90	67.2

* Absorption spectra determined by V. I. Ponochovnyi.

Table 1 (continued)

XVI	5-[5'-iodo-1'-ketoacenaphthylidene] thiazolidinedione-2, 4	Does not melt at 365	346	$C_{15}H_6INO_3S$	7.96	7.87	73.2
XVII	5-[5', 6'-dichloro-1'-ketoacenaphthylidene] thiazolidine-dione-2, 4	333—334	344	$C_{15}H_5Cl_2NO_3S$	9.36	9.15	69.7
XVIII	5-[5', 6'-dibromo-1'-ketoacenaphthylidene] thiazolidine-dione-2, 4	Does not melt at 365	341	$C_{15}H_5Br_2NO_3S$	7.49	7.30	66.8
XIX	5-[5', 6'-diiodo-1'-ketoacenaphthylidene] thiazolidine-dione-2, 4	„	370	$C_{15}H_5I_2NO_3S$	6.29	6.14	64.9
XX	5-[5'-chloro-6'-bromo-1'-ketoacenaphthylidene] thiazo-lidinedione-2, 4	341—342	351	$C_{15}H_6ClBrNO_3S$	7.92	8.10	62.3
XXI	5-[5'-chloro-6'-iodo-1'-ketoacenaphthylidene] thiazo-lidinedione-2, 4	Does not melt at 365	357	$C_{15}H_6ClINO_3S$	7.06	7.24	68.7
XXII	5-[5'-bromo-6'-iodo-1'-ketoacenaphthylidene] thiazo-lidinedione-2, 4	„	367	$C_{15}H_6BrINO_3S$	6.71	6.59	60.2
XXIII	5-[1'-ketoacenaphthylidene]-3-phenylthiazolidinedione-2, 4	280	329	$C_{21}H_{11}NO_3S$	8.82	8.97	48.4
XXIV	5-[5'-fluoro-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	265—266	332	$C_{21}H_{10}FNO_3S$	8.87	8.54	37.6
XXV	5-[5'-chloro-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	313—314	335	$C_{21}H_{10}ClNO_3S$	8.43	8.18	38.2
XXVI	5-[5'-bromo-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	318—319	336	$C_{21}H_{10}BrNO_3S$	7.51	7.34	52.7
XXVII	5-[5'-iodo-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	344—345	340	$C_{21}H_{10}INO_3S$	6.76	6.63	56.2
XXVIII	5-[5', 6'-dichloro-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	299—300	341	$C_{21}H_9Cl_2NO_3S$	7.49	7.52	58.3
XXIX	5-[5', 6'-dibromo-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	335—336	334	$C_{21}H_9Br_2NO_3S$	6.48	6.22	49.9
XXX	5-[5', 6'-diiodo-1'-ketoacenaphthylidene]-3-phenylthiazo-lidinedione-2, 4	298—300	364	$C_{21}H_9I_2NO_3S$	5.12	5.26	59.8
XXXI	5-[5'-chloro-6'-bromo-1'-ketoacenaphthylidene]-3-phenyl-thiazolidinedione-2, 4	308—310	343	$C_{21}H_9ClBrNO_3S$	6.70	6.81	42.5

Table 1 (concluded)

Compound No.	Compound	Mp, °C	λ_{max}*mμ in dioxane	Formula	S, %		Yield, %
					Found	Calculated	
XXXII	5-[5'-chloro-6'-iodo-1'-ketoacenaphthylidene]-3-phenylthiazolidinedione-2,4	308—309	351	$C_{21}H_9ClINO_3S$	6.35	6.19	51.7
XXXIII	5-[5'-bromo-6'-iodo-1'-ketoacenaphthylidene]-3-phenylthiazolidinedione-2,4	334—335	353	$C_{21}H_9BrINO_3S$	5.89	5.70	61.1
XXXIV	5-[1'-bromo-6'-iodo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	280—281	338	$C_{22}H_{13}NO_3S$	8.76	8.63	59.0
XXXV	5-[5'-fluoro-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	279—280	340	$C_{22}H_{12}FNO_3S$	8.42	8.23	64.4
XXXVI	5-[5'-chloro-1'-ketoacenaphthylidene] 3-p-tolythiazolidinedione-2,4	304—305	348	$C_{22}H_{12}ClNO_3S$	7.72	7.90	49.0
XXXVII	5-[5'-bromo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	298—299	352	$C_{22}H_{12}BrNO_3S$	7.39	7.12	44.5
XXXVIII	5-[5'-iodo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	286—287	351	$C_{22}H_{12}INO_3S$	6.32	6.42	48.7
XXXIX	5-[5',6'-dichloro-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	354	357	$C_{22}H_{11}Cl_2NO_3S$	7.08	7.28	54.7
XL	5-[5',6'-dibromo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	332	355	$C_{22}H_{11}Br_2NO_3S$	6.32	6.05	40.0
XLI	5-[5',6'-diiodo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	320—322	366	$C_{22}H_{11}I_2NO_3S$	5.02	5.13	58.0
XLII	5-[5'-chloro-6'-bromo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	318	349	$C_{22}H_{11}ClBrNO_3S$	6.87	6.61	41.0
XLIII	5-[5'-chloro-6'-iodo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	309—310	357	$C_{22}H_{11}ClINO_3S$	5.92	6.02	54.0
XLIV	5-[5'-bromo-6'-iodo-1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2,4	325—326	356	$C_{22}H_{11}BrINO_3S$	5.44	5.56	42.4

The maxima of the absorption spectra of 5' and 6' halogen derivatives of 5-[1'-ketoacenaphthylidene] imidazolidinethione-2-one-4 lies in the UV region inside the limits 305-322 mμ. With the series of F, Cl, Br, and I monohalogen derivatives, the absorption maxima are shifted towards the long-wave region in dioxane solution. In concentrated sulfuric acid solution the absorption spectra maxima are also displaced towards the long-wave region by 45-80 mμ as compared with the maxima in dioxane, and lie in the 355-400 mμ region (Fig. 1, Table 2).

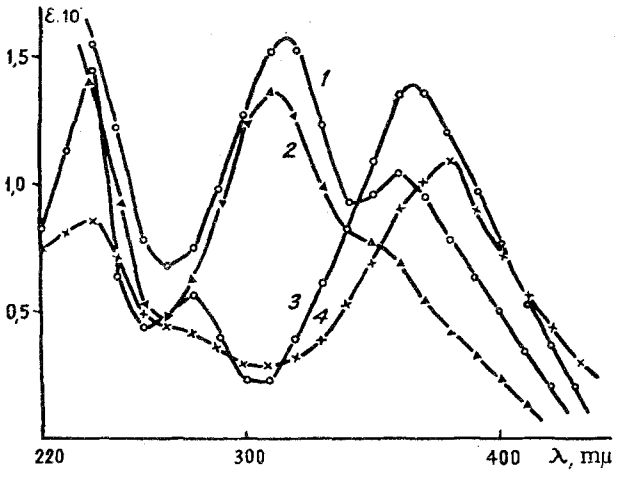


Fig. 1. Absorption spectra of halogen derivatives of 5-[1'-keto-acenaphthylidene] imidazolidinethione-2-one-4: 1) 5'-iodo- in dioxane; 2) 5'-fluoro- in dioxane; 3) 5'-fluoro- in sulfuric acid; 4) 5'-iodo- in sulfuric acid.

Table 2

Comparison of the Absorption Spectra Maxima for 5-[1'-Ketoacenaphthylidene] imidazolidinethione-2-one-4 and its 5' and 6' Halogen Derivatives

Compound No.	λ_{max}, mμ in dioxane	λ_{max}, mμ in H_2SO_4	λ_{max}, mμ in shift
I	305	365	60
II	310	355	45
III	312	364	52
IV	313	370	57
V	317	380	63
VI	314	373	59
VII	313	376	63
VIII	322	398	76
IX	315	377	62
X	313	392	79
XI	319	389	70

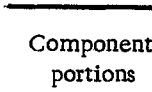
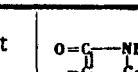
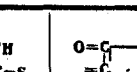
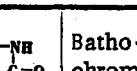
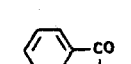
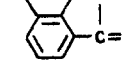
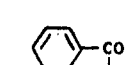
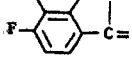
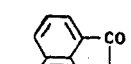
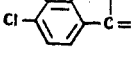
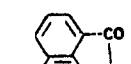
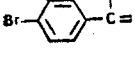
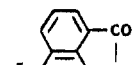
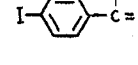
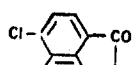
The compounds are not decomposed by solution in concentrated sulfuric acid, as they are recovered unchanged by diluting with water.

The absorption spectra maxima for 5-[1'-ketoacenaphthylidene]-thiazolidinedione-2, 4, 5-[1'-ketoacenaphthylidine]-3-p-tolyl-thiazolidinedione-2, 4, and their 5' and 6' halogen derivatives in dioxane solution lie in the region 329-370 mμ (Fig. 2). Substitution of hydrogen at position 3 by a phenyl group causes the absorption spectra maxima to be shifted towards the shortwave region by about 14 mμ. Introduction of a methyl group in the para position in the phenyl group makes the absorption spectra maxima shift to the longwave region, by 2-21 mμ (Fig. 2).

As compared with absorption in dioxane, in concentrated sulfuric acid solution the absorption spectra maxima of these compounds are shifted towards the longwave region, for N-phenyl derivatives by 17-40 mμ, for those not substituted at the nitrogen atom by 10-20 mμ and by 9-17 mμ for the N-p-tolyl-substituted ones (Fig. 3). The absorption spectra of 5-[1'-ketoacenaphthylidene) thiazolidinethione-2-one-4, and its 5' and 6' halogen derivatives [2] were also measured in dioxane and concentrated sulfuric acid solutions. It was found that the absorption maxima in dioxane

Table 3

Comparison of the Absorption Spectra Maximum for 5-[1'-Ketoacenaphthylidene] thiazolidinethione-2-one-4 and 5-[1'-Ketoacenaphthylidene] thiazolidinedione-2, 4 and their 5' and 6' Halogen Derivatives.

Component portions of compounds			Batho-chromic shift, mμ			Batho-chromic shift, mμ
	λ_{max}, mμ in dioxane			λ_{max}, mμ in H_2SO_4		
	369	336	33	380	346	34
	372	336	36	381	352	29
	373	336	37	389	356	33
	372	343	28	388	360	28
	376	346	30	396	366	30
	373	344	29	393	362	31
	376	341	35	386	356	30
	384	370	18	415	386	29
	379	351	28	403	371	32
	387	357	30	416	377	39
	386	367	19	421	387	34

solution lie in the limits 369-387 mμ, in sulfuric acid solution in the 380-421 mμ region (Fig. 4). Comparing the absorption spectra maxima of 5-(1'-ketoacenaphthylidene) thiazolidinethione-2-one-4 and 5-(1'-ketoacenaphthylidene) thiazolidinedione-2, 4 and their 5' and 6' halogen derivatives, it is found that for 5-(1'-ketoacenaphthylidene)-thiazolidinethione-2-one-4 in dioxane they are displaced 19-37 mμ towards the longwave region, and in sulfuric acid by 28-39 mμ (Table 3).

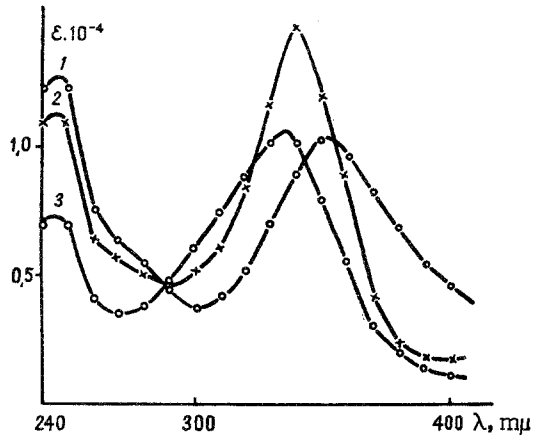


Fig. 2. Absorption spectra of 5'-bromo derivatives: 1) 5-[1'-ketoacenaphthylidene] thiazolidinedione-2, 4; 2) 5-[1'-ketoacenaphthylidene] -3-p-tolythiazolidinedione-2, 4; 3) 5-[1'-ketoacenaphthylidine]-3-phenylthiazolidinedione-2, 4. All in dioxane.

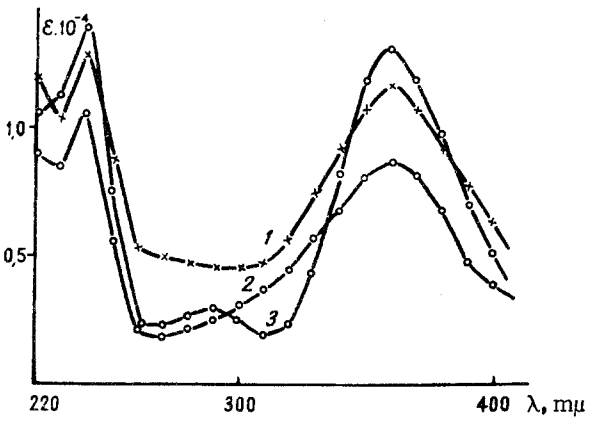


Fig. 3. Absorption spectra of 5'-bromo derivatives: 1) 5-[1'-ketoacenaphthylidene] thiazolidine-2, 4; 2) 5-[1'-ketoacenaphthylidene] - 3-phenylthiazolidinedione-2, 4; 3) 5-[1'-ketoacenaphthylidene]-3-p-tolythiazolidinedione-2, 4.

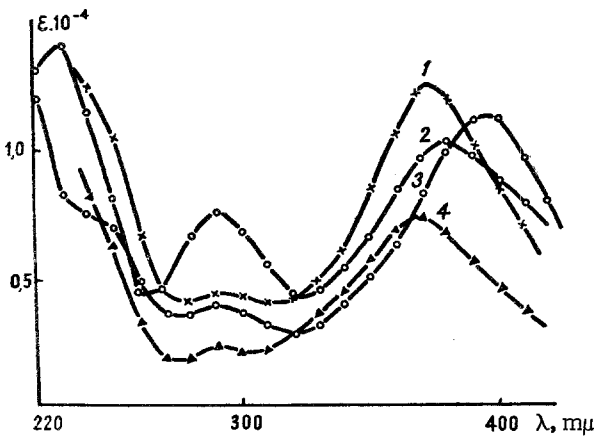


Fig. 4. Absorption spectra of halogen derivatives of 5-[1'-ketoacenaphthylidene] thiazolidinethion-2-one-4: 1) 5'-iodo compound in dioxane; 2) 5'-fluoro compound in sulfuric acid; 3) 5'-iodo compound in sulfuric acid; 4) 5'-fluoro compound in dioxane.

Experimental

0.002 mole acenaphthequinone or its halogen derivative was dissolved with refluxing in the minimum amount of glacial acetic acid, and 0.003 mole 2-thiohydantoin or thiazolidinedione-2, 4, or the N-phenyl- or N-p-tolyl derivative of the latter, together with the appropriate amount (15-20% of the acetic acid) of anhydrous sodium acetate added, after which refluxing was continued for 10. 15 min, the crystals of condensation product which separated were filtered off, washed twice with a small amount of acetic acid, then with water, and dried. Recrystallized from benzene or bromobenzene.

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