SYNTHESIS OF 5-ARYLAZO-2-THIOHYDANTOINS

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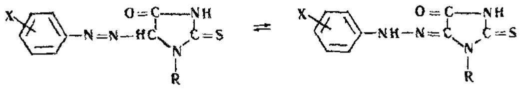
The methylene group of 2-thiohydantoin reacts with diazonium salts to give azothiohydantoins, whose longwave absorption maximum is shifted hypsochromically as compared with the corresponding azorhodanines, and bathchromically compared with azohydantoins.

Introduction of an acetyl group, particularly of benzoyl, at position 1 in the hydantoin ring causes considerable bathochromic displacement of the absorption maximum, while introducing a phenylsulfonyl group leaves the absorption maximum unaffected.

A number of publications [1–4] describe dyes containing the thiazolidine ring. It was of interest to investigate the possibility of synthesizing azo dyes containing a hydantoin ring, and to follow the effect of substituents on the colors of the compounds obtained.

Azo dyes of the following structure were obtained:



They are powders of various colors, of different colors, ranging from pale yellow to reddish orange, slightly soluble in alkalies, to give deeply colored solutions (see Table).

The compounds are capable of azo-hydrazone tautomerism. It is known [5] that introduction of electron-donating substituents into the diazo component shifts the equilibrium towards the azo structure, while introduction of electron-accepting substituents shifts it towards the hydrazone structure, which also shows up by a shift of the longwave absorption maximum. Thus, if in the case of I (Table) λ_{max} is at 415 mμ, for II it is at 416 mμ, and for III at 423 mμ, i. e. there is a bathochromic shift, evidenced by increase in the proportion of azo structure as we pass from I to II and then to III.

A bathochromic shift is also observed when electron-accepting substituents are introduced at position 1 in the hydantoin ring, and introduction of a benzoyl group gives rise to a larger bathochromic effect than does introduction of an acetyl one (cf. IV, VII, and IX, Table).

There the bathochromic shift must probably be ascribed not to shift the azo-hydrazone equilibrium, but most probably to equalization of electron density in the conjugated chain under the action of substituents and energy coupling of extreme structures in the azo dye [5].

Introduction of a sulfonyl group at position 1 does not affect the position of the absorption maximum, and this is in agreement wtih results of study of UV spectra in other sulfo derivatives [6]. Replacement of the thione group at position 2 by carbonyl gives rise to a large hypsochromic shift of the longwave absorption maximum (cf. I and XI, Table). When the >NH group at position 1 in the thiohydantoin ring is replaced by sulfur, i. e. on passing to azorhodanines, the absorption maximum is displaced by 10–20 mμ. Thus phenylazorhodanine has an absorption maximum at 425 mμ, n-tolylazorhodanine at 430 mμ, and p-methoxyphenylazorhodanine at 445 mμ.

These results agree with what has previously been found regarding regularities in other derivatives of the azolidine series [7, 8].

The table shows the azohydantoins synthesized, and some of their properties.

EXPERIMENTAL

1-Acetyl and 1-benzoyl-2-thiohydantoin were prepared by known methods [9, 10].

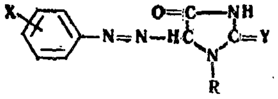
2-Thiohydantoin. 1-Acetyl-2-thiohydantoin was refluxed with 10% HCl for 1 hr, and after cooling the precipitate was filtered off and recrystallized from water, yield 70%, mp 226–228° (decomp), corresponding to the literature data [9, 10].

1-Phenylsulfanyl-2-thiohydantoin. A mixture of 2.1 g (0.01 mole) benzoylsulfoglycine, 1.2 g (0.015 mole) NaCNS, and 10 ml Ac_2O was heated for 30 min (until a homogeneous viscous yellow mass was formed). After cooling, 50 ml water was added. The precipitate was filtered off, washed with water, and dried, yield 35%. The product was recrystallized from dichloroethane, mp 210–212°. Found: N 11.33%. Calculated for $C_9H_8O_3N_2S_2$: N 10.92%.

5-Phenylazo-2-thiohydantoin (I). 1.16 g (0.01 mole) 2-thiohydantoin was dissolved in 10 ml pyridine, cooled to –2°, and a benzenediazonium chloride solution, made in the usual way from 0.93 g (0.01 mole) aniline, was added gradually, with stirring. The mixture immediately turned yellow, and a precipitate formed. The mixture was then left at 0° for 1 hr. The precipitate was filtered off, washed with water, and dried. After two recrystallizations from MeOH it formed rectangular yellow plates,

II, III, and IV were prepared from 2-thiohydantoin and the appropriate diazonium salts, while IX was prepared from 1-benzoyl-2-thiohydantoin and o–carboxylbenzenediazonium chloride.

5-(3'-Bromophenylazo)-2-thiohydantoin (V) was synthesized from 2.32 g (0.02 mole) 2-thiohydantoin in 40 ml 3% NaOH and m-bromobenzenediazonium

Properties of 5-Arylazo-2-thiohydantoins  synthesized

Compound	X	Y	R	Mp, °C	Color	λ_{max}, mμ	Formula	Found, %		Calculated, %		Yield, %
								N	S	N	S	
I	C_6H_5	S	H	257—258*	Yellow	415	$C_9H_8ON_4S$	25.38	14.67	25.39	14.56	75.3
II	p-H_3C—C_6H_4	S	H	254—255*	Yellowish-orange	416	$C_{10}H_{10}ON_4S$	23.76	13.16	23.92	13.69	83.6
III	p-H_3CO—C_6H_4	S	H	230—231*	Yellowish-orange	423	$C_{10}H_{10}O_2N_4S$	22.28	12.40	22.38	12.81	96
IV	o-HOOC—C_6H_4	S	H	243—244*	Bright yellow	415	$C_{10}H_8O_3N_4S$	20.75	—	21.19	—	65.3
V	m-Br—C_6H_4	S	H	231—232**	Yellow	409.5	$C_9H_7ON_4SBr$	18.76	—	18.72	—	74.6
VI	C_6H_5	S	H_3C—CO	238—239***	Yellowish-orange	423	$C_{11}H_{10}O_2N_4S$	21.19	—	21.36	—	99.2
VII	p-H_3CO—C_6H_4	S	H_3C—CO	228—229***	Yellowish-orange	425	$C_{12}H_{12}O_3N_4S$	18.77	11.51	19.16	10.99	42.4
VIII	o-HOOC—C_6H_4	S	H_3C—CO	221—222****	Yellowish-orange	420	$C_{12}H_{10}O_4N_4S$	18.12	—	18.28	—	50.8
IX	o-HOOC—C_6H_4	S	H_5C_6—CO	191—192*	Bright yellow	430	$C_{17}H_{12}O_4N_4S$	15.04	—	15.18	—	100.0
X	o-HOOC—C_6H_4	S	H_5C_6—O_2S	173—174*	Lemon-yellow	415	$C_{16}H_{12}O_5N_4S_2$	13.45	—	13.85	—	83.3
XI	C_6H_5	O	H	248—249****	Pale yellow	367	$C_9H_8O_2N_4$	27.02	—	27.43	—	78.6

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*Crystallized from MeOH.

**EtOH solution chromatographed on Al_2O_3, with subsequent precipitation with water.

***Crystallized ex 80% EtOH and glacial AcOH.

****Crystallized ex 80% EtOH.

chloride, prepared in the usual way from 3.42 g (0.02 mole) m-bromoaniline. The initial green color changed to brown, then a precipitate formed. The solution was left at 0°, and after half an hour the precipitate filtered off. The dye was reprecipitated with hydrochloric acid (1:1), to remove tar. A MeOH solution of the dye was chromatographed on alumina. V was isolated from the alcoholic solution by means of water.

VI and VII were prepared similarly from 1-acetyl-2-thiohydantoin and the appropriate diazonium salts, and X was obtained from 1-phenylsulfanyl-2-thiohydantoin and o-carboxylbenzenediazonium chloride in 3% aqueous EtOH (1:1.5) NaOH.

5-Phenylazo-1-acetyl-2-thiohydantoin (VI). 1.53 g (0.005 mole) 5-(o-carboxylphenylazo)-1-acetyl-2-thiohydantoin was refluxed for 1 hr with 30 ml glacial AcOH. On cooling, yellowish-orange needles separated down. They were filtered off, washed, and dried.

5-Phenylazohydantoin (XI). 35 ml 50% monochloroacetic acid and 10 ml EtOH were added to 0.6 g (0.003 mole) I, and the whole refluxed for 4 hr. There was a slight evolution of H_2S, and the solid slowly dissolved. At the end of the heating solution of the solid was complete. The solution was evaporated to 10 ml, then cooled, the precipitate formed was filtered off, treated with water, and $NaHCO_3$. It was recrystallized from EtOH, pale yellow needles, mp 248–249°.

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