SYNTHESIS OF 5-ARYLAZO-2,4-DITHIOHYDANTOINS

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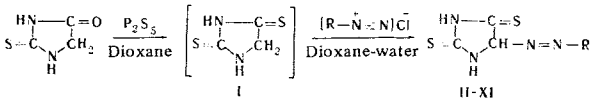
It was shown that during the interaction between 2-thiohydantoin and P_2S_5 in dioxane 2,4-dithiohydantoin (I) is formed, and without isolation from the reaction solution this compound forms 5-arylazo-2,4-dithiohydantoins (II–XI) with salts of diazone. The structure of two of these compounds has been determined by countersynthesis. When 5-arylazo-2,4-dithiohydantoins interact with amines the corresponding 4-substituted derivatives are formed.

Previously it has been shown [1] that 2-thiohydantoin combines with diazonium salts in pyridine to form the 5-substitutes.

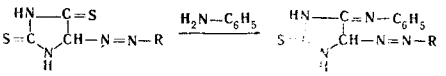
As substitution of the C=O group by the C=S group in pyrrolidones-4 and their derivatives strongly activates position 5 [2] and leads to an increase in color intensity [3], we studied the possibility of synthesizing dithiohydantoin dyes. Although individual derivatives of compound I were obtained and examined as medicinal remedies [4], there is no description of the unsubstituted compound I in the literature. Attempts to obtain compound I from 2-thiohydantoin in dioxane [2] showed that a good yield of this substance is formed under the given conditions although it cannot be isolated. However, on account of the high activity of compound I it is possible to conduct azo-combination with isolation of the substance. One should note that under the given conditions 2-thiohydantoin does not combine.



I II-XI

Compounds II–XI are highly colored and readily soluble in organic solvents. Their structures were determined by countersynthesis involving the interaction between arylazo-2-thiohydantoins and P_2S_5 in dioxane. This transformation was only achieved in the case of o-carboxyphenyl- and n-ethoxyphenylazo-2-thiohydantoin.

In compounds II–XI the C=S group in position 4 is distinguished by its distinct thioketone nature, which has been found for unsubstituted 4-thionpyrrolidones [2]. On interaction with aniline, hydrogen sulfide is evolved and the corresponding 4-phenylimino-5-arylazosubstitutes of compound I were formed according to the reaction:



EXPERIMENTAL

2,4-Dithiohydantoin (I). A 2.32 g quantity (0.02 mole) of 2-thiohydantoin, 2.5 g P_2S_5, and 25 ml of anhydrous freshly distilled dioxane were boiled for 50 min with a reflux condenser, after which the hot solution was filtered, cooled, and immediately used for the synthesis of 5-arylazo-2,4-dithiohydantoins.

5-(o-Carboxyphenylazo)-2,4-dithiohydantoin (V). a) A 0.02 mole quantity of diazotized anthranilic acid was added to a dioxane solution of compound I, cooled to 0° C by the addition of 10 g of ice. The resulting red solution was held at 0° and then diluted with acidified water. The precipitate was removed by filtration and washed with water. Yield, 2.1 g (37%). It was crystallized from methanol.

b) A 0.01 mole quantity of 5-(o-carboxyphenylazo)-2-thiohydantoin [1] was dissolved by heating in 50 ml dioxane. To the hot solution was added 1.0 g of sublimated P_2S_5. The mixture was boiled in a reflux condenser for 45 min, after which the hot dark-red solution was filtered and cooled. The precipitated crystals were separated and washed with dioxane. The yield was 2.2 g (78%). The compound ob-

5-Arylazo-2,4-dithiohydantoins (II–XI)

Compound	R	Color	Mp,* °C (decomp.)	Empirical formula	Found, %		Calculated, %		Yield, %
					N	S	N	S	
II	C_6H_5	Dark-red	208—209	$C_9H_8N_4S_2$	23.17	27.49	23.70	27.23	12
III	*n*-HO-C_6H_4	Black	209—210	$C_9H_8ON_4S_2$	21.84	25.76	22.20	25.42	22
IV	*n*-C_2H_5O-C_6H_4	Greenish-black	203—204	$C_{11}H_{12}ON_4S_2$	19.48	22.56	19.98	22.88	22.4
V	*o*-HOOC-C_6H_4	Light-red	255—256	$C_{10}H_8O_2N_4S_2$	20.13	22.63	19.98	20.80	36
VI	*n*-HOOC-C_6H_4	Dark-red	above 350	$C_{10}H_8O_2N_4S_2$	19.59	22.50	19.98	22.80	24
VII	*m*-HOOC-C_6H_4	Red	259—260	$C_{10}H_8O_2N_4S_2$	19.54	22.37	19.98	22.80	11
VIII	*o*-H_2O_3As-C_6H_4	Yellow	209—210	$C_9H_9O_3N_4S_2As$	15.83	—	15.53	—	42
IX	*n*-H_2O_3As-C_6H_4	Red-orange	above 350	$C_9H_9O_3N_4S_2As$	15.07	—	15.55	—	20
X	*n*-C_6H_5-N-N-C_6H_4	Dark-brown	235—236	$C_{15}H_{12}N_6S_2$	27.49	22.07	27.97	21.34	12
XI	β-$C_{10}H_7$	Red-brown	214—215	$C_{13}H_{10}N_4S_2$	19.23	22.44	19.56	22.39	26

*II, III, from dichlorethane; IV, from butanol; V, VI, from methanol; VIII, IX, from ethanol; VII, X, XI, two-fold reprecipitation with water from dimethylformamide.

tained was found to be identical to compound V obtained by method (a).

Compounds II-IV and VI-XI were obtained in an analogous manner.

4-Phenylimido-5-phenylazo-2-thiohydantoin. A 2.3 g quantity (0.01 mole) of compound II, 1.2 g (0.013 mole) of aniline, and 20 ml of methanol were boiled in a reflux condenser for 2 hr 30 min. After the evolution of hydrogen sulfide a clear red-orange crystalline precipitate was formed Yield = 1.7 g (58%). Recrystallization from methanol produces fine yellow needles, mp 259°-260° C (decomp.). Found, %: N 23.56; S 11.12. Calculated for $C_{15}H_{13}N_5S$, %: N 23.71; S 10.85.

In an analogous manner 4-phenylimino-5-(n-carboxyphenylazo)-2-thiohydantoin was obtained from compound VI and aniline. Yield, 65%. Small red-orange needles, mp 263°-265° C (decomp., methanol). Found, %: N 20.99; S 8.96. Calculated for $C_{16}H_{13}O_2N_5S$, %: N 20.63; S 9.44.

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