REACTION OF 2-DIALKYL-5-FORMYLFURANS, -THIOPHENES, AND -SELENOPHENES WITH AROMATIC DIAZONIUM SALTS

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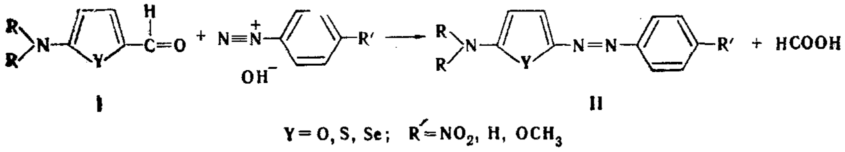
The reaction of 2-dialkylamino-5-formylfurans, -thiophenes, and -selenophenes with diazonium salts gives azo dyes with elimination of the aldehyde group.

2-Dialkylamino-5-formylfurans (I, Y = O) react readily with arenediazonium salts:



In aldehydes I and thiophene and selenophene derivatives the tendency to undergo diazo coupling decreases. Thus dimethyl- and diethylaminoformyl-thiophenes and dimethylaminoformylselenophenes react only with p-nitrobenzenediazonium salts, while morpholino- and piperidinoformylthiophenes form only traces of azo dyes under similar conditions. p-Dimethylaminobenzaldehyde, the analogs of which are aldehydes I, react with the p-nitrobenzenediazonium salt only on prolonged reaction [1].

The formic acid formed during diazo coupling was determined in the case of azo dye II (R = CH_3, R = NO_2, and Y = O) via the method described in [1]. According to the quantitative absorption spectrum in ethanol, azo dye II (R = CH_3, R = NO_2, and Y = S) proved to be identical to the dye of the same structure obtained by coupling 2-dimethylaminothiophene with the p-nitrobenzenediazonium salt [2].

As seen from Table 1, azo dyes II, in contrast to their well-known benzene analogs, have higher color in acid solutions. The reason for this difference in the change in color during protonation was examined in [2] for azo dyes II (thiophene derivatives) and can also be used for azo dyes II (furan and selenophene derivatives).

EXPERIMENTAL

2-Diethylamino-5-formylthiophene (I, Y = S, R = C_2H_5). A solution of 3.8 g (0.02 mole) of 2-bromo-5-formylthiophene, 2.9 g (0.04 mole) of diethylamine, and 3.1 g (0.02 mole) of diethylamine hydrobromide in 10 ml of absolute alcohol was heated in a sealed ampule at 110° for 3 h. After decomposition with excess 30% sodium hydroxide solution, the resulting oil was extracted with ether, and the ether layer was dried with sodium sulfate. The ether was removed, and the residue was vacuum distilled to give 2.6 g (69%) of a product with bp 122° (0.1 mm) and mp 24°. Found: S 17.4%. $C_9H_{13}NOS$. Calculated: S 17.5%.

Azo Dyes II. These dyes were obtained by the addition of an equimolar amount of aqueous diazonium salt solution to a solution of the appropriate aldehyde (I) in a small

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TABLE 1. Properties of the Azo Dyes

Y	R	R′	Dec. temp., °C	Empirical formula	N, %		λ_{max} of the salt in CH_3OH, nm ($\varepsilon \cdot 10^{-4}$)	λ_{max} of the base in $CHCl_3$, nm	Yield, %
					found	calc.			
O	CH_3	NO_2[a]	236	$C_{12}H_{13}ClN_4O_7$	15,6	15,5	442 (4,0)	538[b]	72
O	CH_3	H[a]	230	$C_{12}H_{14}ClN_3O_5$	13,1	13,3	450 (2,3)	472[b]	45
O	CH_3	OCH_3[a]	199	$C_{13}H_{16}ClN_3O_6$	11,9	12,2	470 (2,5)	476[b]	48
O	Piperidino-	NO_2[a]	239	$C_{15}H_{17}ClN_4O_7$	14,1	14,0	446 (4,3)	544[b]	55
O	Morpholino-	NO_2[a]	238	$C_{14}H_{15}ClN_4O_8$	14,0	13,8	452 (4,3)	526[b]	22
O	Piperidino-	OCH_3[a]	206	$C_{16}H_{20}ClN_3O_6$	11,1	10,9	484 (2,9)	476[b]	57
S	CH_3	NO_2	198[c]	$C_{12}H_{12}N_4O_2S$	20,0	20,3	460 (5,0)[d]	546	38
S	C_2H_5	NO_2	113[e]	$C_{14}H_{16}N_4O_2S$	18,5	18,4	462 (4,8)[d]	548	52
Se	CH_3	NO_2	207[c]	$C_{12}H_{12}N_4O_2Se$	17,1	17,3	464 (4,8)[d]	564	50

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a) Perchlorate. b) For the preparation of a solution of the base, the salt was suspended in dry chloroform, triethylamine was added, and the solution was filtered to remove impurities. c) From toluene. d) Methanol acidified with hydrochloric acid. e) From heptane.

amount of 50% acetic acid at –5 to 0°. After 15 min at this temperature, furanazo dyes II were precipitated as the perchlorates by the addition of excess 42% perchloric acid, and the resulting salts were crystallized from 95% acetic acid. The bases of azo dyes II (Y = O) are unstable in proton-donor solvents. The bases of azo dyes II (Y = S, Se) were isolated by means of ammonia from the acid solutions after diazo coupling and were crystallized from a suitable solvent. The yields, melting points, and analytical and spectral characteristics of azo dyes II are presented in Table 1.

LITERATURE CITED

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