PHOTOSTIMULATED AND DARK REACTIONS OF ARYL HALIDES

# WITH 2- AND 4-PYRIDINETHIOLATES

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The nonactivated aryl halides are characterized by very low reactivity in regard to nucleophilic reagents, in particular to thiyl anions. Therefore, drastic conditions are applied in order to accomplish the nucleophilic substitution of the halogen in them. One of the methods of the nucleophilic thiylation of aryl halides is the heating in aprotic solvents in the presence [1-3] and in the absence [4-7] of a catalyst. The last works [5-7] are devoted to the isolation of alkylthio- and poly(alkylthio)benzenes; the low reactivity of thiophenolate is noted even in regard to the activated aryl halides. Communications on the application of interphase catalysis for the isolation of alkyl aryl sulfides have appeared [8-10]. The mild nucleophilic substitution in aryl halides occurs in the photostimulated thiylation by thiophenolate of the iodo- and dihalogenobenzenes in liquid NH<sub>3</sub> [11]. We previously [12] applied the catalyst tetrabutylammonium hydroxide (TBAH), which rendered possible the photochemical substitution of the nonactivated bromine and chlorine in the nucleus by the thiophenolate in liquid NH<sub>3</sub>.

In the present work, pyridinethiolates were utilized as the thiylating agents in both the dark reaction and the photostimulated reaction with aryl halides; the possible synthesis of biologically active aryl pyridyl sulfides [13], some of which were previously obtained by another method [1, 14], was investigated. The reaction proceeds according to the scheme

$$Y \longrightarrow X + RSNa \longrightarrow Y \longrightarrow SR + NaX$$
$$X = I, Br, Cl; Y = H, NO_2; R = -\langle N \rangle (I); -\langle N \rangle (II).$$

It follows from the results obtained (Table 1) that the utilization of the catalyst TBAH leads to an increase in the yield of the aryl pyridyl sulfides in almost all cases. The formation of sulfides is not observed under analogous conditions in the dark reactions, even in the presence of a catalyst. The optimal amount of the catalyst comprises 2 mole % of the initial aryl halide. An increase in the amount of TBAH leads to resinification and a decrease in the yield of the aryl pyridyl sulfide. Thus, the data presented in Table 2 were obtained in the reaction of o-chloronitrobenzene (o-CNB) with 2-pyridinethiolate after 1 h of irradiation.

The equimolar amount of TBAH, which significantly accelerates the process of the formation of the sulfide (20%, 0.5 h) in the given case, simultaneously increases the formation of resin (up to 40\%). An increase in the light intensity lowers the effectiveness of the thiylation, causing the marked formation of resin.

It can be seen from Table 1 that the reactivity of the nonactivated aryl halides in regard to the thiopyridyl nucleophile decreases in the order: ArI > ArBr > ArCl. Such an order is characteristic of reactions proceeding by the SRN1-mechanism [15].

The presence of the electron-acceptor nitro group in the o- and p-positions in the aryl halide molecule activates the nucleus, and permits the substitution of the Cl atom, albeit with a low yield. The formation of the aryl pyridyl sulfide is not observed in the case of m-CNB. The substitution of the I atom in m-iodonitrobenzene (m-INB) can evidently be explained by the ease of the breaking of the C-I bond in the anion-radical  $[m-IC_6H_4NO_2]$ . [15].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 833-837, April, 1987. Original article submitted October 8, 1985. TABLE 1. Photostimulated Reaction of Aryl Halides with 2- and 4-Pyridinethiolates in Liquid Ammonia

YC₀H₄X			Time of ir-	Yield of sulfide, %*		
Y	x	Nucleophile	radiation, h	with TBAH	without TBAH	
H H m-NO <sub>2</sub> m-NO <sub>2</sub> H H o-NO <sub>2</sub> o-NO <sub>2</sub> p-NO <sub>2</sub> m-NO <sub>2</sub>	I I Br Cl Cl Cl Cl Cl	(I) (II) (I) (I) (I) (I) (I) (I) (I) (I)	3 6 0.5 6 6 6 6 6 6 6 6 6	$\begin{array}{c} 68(70)\\ 47(71)\\ 44(71)\\ 32(100)\\ 9\\ 3\\ 25(76)\\ 32(59)\\ 12(100)\\ 0\end{array}$	$ \begin{bmatrix} 59(70) \\ 27(49) \\ 20(76) \\ 23(100) \\ 0 \\ 13 \\ 7(34) \\ 0 \\ 0 \end{bmatrix} $	

\*Based on the aryl halide taken or (in brackets) converted.

TABLE 2. Influence of the Amount of TBAH on the Reaction of o-Chloronitrobenzene with 2-Pyridinethio-late ( $NH_3$ , -40°C, 1 h of irradiation)

Amount of TBAH, mole, %	Yield of sulfide, % on the convert- ed o-CNB taken		Resini- fication	Recovery of o-CNB, %	
2	100	8		92	
10	34	9		75	

TABLE 3. Dark Reaction of the Aryl Halides with 2-Pyridinethiolate\*

YC6H4X		Solvent		Designation	Yield of	
Y	x		T., °C	time, h	sulfide, %†	
H H m-NO <sub>2</sub> m-NO <sub>2</sub> H H do-NO <sub>2</sub> o-NO <sub>2</sub> o-NO <sub>2</sub> p-NO <sub>2</sub> p-NO <sub>2</sub> m-NO <sub>2</sub>	I I I Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl	NH. <sup>4</sup> DMF DMF DMF DMF DMF DMF DMF HMPA HMPA DMF DMF DMF	-40 100 $\sim 20$ $\sim 20$ 100 100 100 $\sim 20$ 100 $\sim 20$ 100 $\sim 20$ 100 $\sim 20$ 100 $\sim 20$ 100	$\begin{array}{c} 4\\ 15\\ 45\\ 48\\ 5\\ 18\\ 16\\ 1\\ 40\\ 1\\ 2,5\\ 0,5\\ 30\\ 15\end{array}$	0 0 0 25 (61) 0 72 (87) 45 (83) 74 (87) 78 (85) 68 (72) 61 (82) 0	

\*The reaction of sodium 2-pyridinethiolate with 2,4-(dinitro)chlorobenzene in DMF proceeds quantitatively at 20°C in 15 min. +The yield of the aryl pyridyl sulfide, given in brackets, is the percentage based on the converted

aryl halide.

These facts indicate the more complex character of the photostimulated catalytic pyridylthiylation, and require kinetic and spectral investigation. The dark process of the thiylation was also carried out in the aprotic solvents DMF and HMPA (Table 3). In contrast to the photostimulated reaction, the nonactivated aryl halides (PhI, PhBr, PhC1) do not undergo substitution in the dark conditions, even with the prolonged heating in DMF.

TABLE 4. Aryl Pyridyl Sulfides

Calculated, %	s	17,11	17,11	13,79	13,79	13,79	13,79	13,79	11,55
	N	7,49	7,49	12,07	12,07	12,07	12,07	12.07	15,16
	н	4,81	4,81	3.45	3,45	3,45	3,45	3,45	2,53
	c	70.59	70.59	56.90	56,90	56,90	56,90	56,90	47.65
Empirical	formula	C <sub>11</sub> H <sub>9</sub> NS	*	$C_{11}H_8N_2O_2S$	*	*	*	*	C <sub>41</sub> H <sub>7</sub> N <sub>3</sub> O <sub>4</sub> S
	S2	16,50	16,84	13,26	13,95	13,50	13,46	13,46	11,54
Found, %	z	7,65	7.37	12,16	12,03	12,14	11,86	11,83	14,89
	н	5,06	5,35	3,74	3,81	3,48	3,67	3,63	2,27
	σ	70,79	70.77	56,76	56,74	56,62	57,15	56,77	47,27
bp, °C (p, nm of	Hg); mp, °C	156–158 (6) 107–110 (3) [1]	$\begin{array}{c} 168{-}169 \ (15) \\ 126{-}127 \ (1,2) \ [14] \end{array}$	72–73	71-72 72-73 [13]	83-84 82-83 [13]	185 - 187 (0, 15)	119-120	115-116 115-116 [13]
	Formula	S-S-		S-S-			N S-C	NO <sup>2</sup> S	$NO_2 NO_2 O_2 N - O_2 O_2 N - O_2 O_2 N - O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2$

The presence of one nitro group in the o- and p-position in the aryl halide molecule significantly facilitates the process of the substitution of the halogen. The reaction may proceed at ~20°C, and heating accelerates it significantly (see Table 3). When two nitro groups are present in the o- and p-positions, the thiylation proceeds very rapidly with quantitative yield under the mild conditions.

It is interesting that the nitro group in the m-position, which does not activate the aromatic nucleus in the case of Cl, nevertheless causes the weakening of the C-I bond. Thus, the sulfide is obtained in 25% yield as a result of the dark reaction on heating for the thiylation of m-INB (in contrast to m-CNB, where the substitution does not generally occur). The preferableness of the photostimulated process of the substitution of m-INB should be noted in view of the higher yield of the sulfide. No influence on the dark process of the thiylation is exerted by TBAH.

The favorable influence of an electron-acceptor substituent on the nucleophilic substitution, as well as the insignificant differences in the reactivity of the aryl halides (PhI ~ PhBr ~ PhC1), indicates that the given dark reaction of thiylation evidently proceeds by the SN2-mechanism.

## EXPERIMENTAL

The irradiation was carried out in the medium of Ar in a photochemical unit with available light sources (DRT-230 lamps) in a reactor of "Pyrex" with a mechanical stirrer [16] in liquid  $NH_3$  at -40°C.

The 2- and 4-pyridinethiolates were obtained by the reaction of a 10 mole % excess of pyridinethiol with EtONa in alcohol; the solution was evaporated after 1 h, and the residue was dried in vacuo. We obtained TBAH by the method of [17].

The yields of the aryl pyridyl sulfides were determined by the method of GLC on an LKhM-8MD chromtograph with a  $1.5 \times 3$  mm stainless steel column with SE-30 (5%) on silanized HMDS Chromaton N-AW. The gas carrier was Ar (20 cm<sup>3</sup>/min); the temperatures of 150-250°C were programmed at 25°C/min. The preparative separation of the products was performed on a 20 m  $\times$  400 mm column with SiO<sub>2</sub> having the granulation of 40/100  $\mu$ m. The constants are presented in Table 4.

Photostimulated Thiylation in Liquid Ammonia. The mixture of 2.5 mmole of the aryl halide, 2.5 mmole of sodium pyridinethiolate, 0.05 mmole of TBAH, and 60 ml of liquid  $NH_{a}$ was irradiated at -40°C with stirring. After the irradiation, the mixture was evaporated; the residue was extracted with ether and concentrated in vacuo. The sulfide was isolated by chromatography on a column with silica gel in the 12:4 mixture of benzene and ether.

Dark Thiylation in DMF. The mixture of 2.5 mmole of the aryl halide, 2.5 mmole of sodium pyridinethiolate, and 30 ml of DMF was stirred at 100°C in an atmosphere of Ar. After cooling, the reaction mixture was diluted with water and extracted with ether; the extract was dried with MgSO<sub>4</sub> and concentrated in vacuo. The sulfide was isolated analogous-1y.

Biological tests showed that some of the synthesized nitrophenyl pyridyl sulfides possess fungicidal activity. Herbicidal activity was shown by 3-nitrophenyl 2-pyridyl sulfide at the level of the standard of pentachlorophenolate.

## CONCLUSIONS

Tetrabutylammonium hydroxide is a catalyst in the photostimulated reaction of the thiylation of aryl halides by pyridinethiolates.

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### INTRAMOLECULAR ACID-CATALYZED REACTIONS

### OF ο-CARBOMETHOXY-ω-DIAZOACETOPHENONES

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 $\omega$ -Diazoacetophenones (DAP) are broadly applied as model compounds in studying the correlation between structure and reactivity of diazoketones in their acid-catalyzed decomposition reactions [1, 2].

In order to elucidate the intramolecular (anchimeric) effect of the  $o-CO_2CH_3$  group on the rate and mechanism of acid-catalyzed DAP decomposition, we studied the decomposition kinetics of o-carbomethoxy- $\omega$ -diazoacetophenones (CMDAP) (Ia-h) and DAP (IIIa-f) in methanol on exposure to  $H_2SO_4$ .



The synthesis of (Ia-h) and (IIIa-f) was performed according to [3, 4] by acylation of diazomethane with the appropriate carbonic acid chloranhydrides. Thin layer chromatographic analysis of the CMDAP (Ia-h) acid conversion products showed that isochromane-1,4-diones (IIa-h) were formed exclusively. The structure of compounds (Ia-h) and (IIa-h) was confirmed by physicochemical methods (Tables 1 and 2). The properties of compounds (IIIa-f) correspond to the literature data [4].

The kinetics of the acid-catalyzed decomposition of (Ia-h) and (IIIa-f) were followed spectrophotometrically by the disappearance of the characteristic absorption bands of the diazocarbonyl group (Table 3). The reactions are of the first order with respect to diazo-ketone and acid. The kef values (kef =  $kobs/[H^+]$ ) are shown in Table 3.

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765