Perchlorate Salts of 1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4-(4-methoxyphenyl)-6-phenylpyridine (IIIb), 1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4-phenyl-6-(4-methoxyphenyl)pyridine (IIIc), 1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4,6-di(4-methoxyphenyl)pyridine (IIId), 1-Methyl-2-[3-(1,3,3-trimethyl-5-nitroindolinylidene-2)-1-propenyl]-4,6-diphenylpyridine (IIIe), and 1-Methyl-2-[3-(1,3,3-trimethyl-5-nitroindolinylidene-2)-1-propenyl]-4,6-di(4-methoxyphenyl)pyridine (IIIf). These were obtained in an analogous manner to IIIa from the dyes IIb-f, respectively.

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CHEMISTRY OF HETEROCYCLIC QUINONIMINES.

6.* DIRECT AMINATION OF BENZO[a]PHENOTHIAZIN-5-ONE WITH AROMATIC AMINES

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UDC 547.869.2:542.953

The reaction of benzo[a]phenothiazin-5-one with aromatic amines proceeds under mineral acid activation of the substrate to generate 6-arylamino derivatives exclusively. N-Alkylanilines give, in addition to the corresponding 6-N-alkyl-N-arylaminobenzo[a]phenothiazin-5-ones, the dealkylation product, namely 6-anilinobenzo[a]phenothiazin-5-one.

The potential utilization of aryl(alkyl)aminobenzo[a]phenothiazin-5-ones as laser agents [2], dyes [3], or biologically active compounds [4] has stimulated a need for the development of straightforward methods for their synthesis. At the present time they are synthesized via difficult multistep cyclization procedures based on the initial introduction of appropriate substituents into the synthons [5, 6]. The direct amination of heterocyclic quinonimines (HQI) which are benzoannelated on the quinonimine fragment has not been described in the literature. The simple introduction of O- and S-nucleophilic residues into benzo[a]phenothizain-5-one (I) has recently been reported [1].

In the present paper we describe the nucleophilic amination of benzo[a]phenothiazin-5-one with the following aromatic and aliphatic-aromatic amines: aniline, p-chloro-, p-bromo-, p-methyl-, p-methoxy-, N-methyl-, and N-ethylaniline.

It has previously been demonstrated [7] that the method of activation of the reagents significantly influences the ease of nucleophilic substitution of hydrogen in HQI. Without prior activation benzo[a]phenothiazin-5-one does not react, even at reflux, with any of the amines

*For Communication No. 5, see [1].

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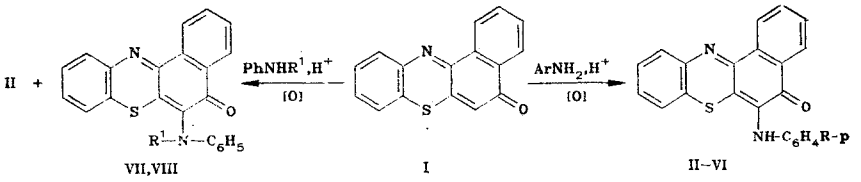
mentioned above, regardless of the polar or nonpolar nature of the solvent (DMF, ethanol, benzene). Activation of the substrate with mineral acid (HCl) is effective only at temperatures above 80°C in dipolar aprotic solvents (DMF, DMSO). In the presence of acid, or their own hydrochloride salts, aromatic amines react with the substrate to give the intensely colored products II-VI after prolonged reflux. The reaction of the substrate with aliphatic-aromatic amines gave, in addition to the corresponding N-alkyl-N-phenylaminobenzo[a]phenothiazin-5-ones, small amounts of the anilino derivative (II), identical with that obtained upon treatment of the substrate with aniline itself.



II R=H; III R=Cl; IV R=Br; V R=OCH_3; VI R=CH_3; VII R^1=CH_3; VIII R^1=C_2H_5

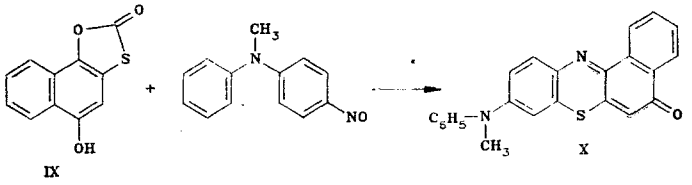
Examples of dealkylation accompanying the reaction of aliphatic amines with quinones are well known [8].

The amino derivatives II-VIII of benzo[a]phenothiazin-5-one are characterized by their intense colors; the maximum absorbances of the compounds II-VI exhibit bathochromic shifts of up to 100 nm relative to the unsubstituted substrate (see Table 1). The deep coloration of the products, as has been shown in the case of phenothiazin-3-one and other HQI [9], is evidence that the N-containing nucleophile has been introduced at the para position to the nitrogen atom in the aromatic portion of the substrate.

On the basis of elemental and IR spectroscopic analysis the compounds II-VI have been identified as monoarylamine-substituted benzo[a]phenothiazin-5-ones; the IR spectra contain characteristic N–H absorption bands for the amino functions at 3260 cm^{-1}. The absence of these bands in the IR spectra of VII and VIII also attests to the formation of arylamine derivatives substituted exclusively at the amine nitrogen, characteristic of quinoid compounds.

The PMR spectra of the compounds II-VIII do not allow an unequivocal assignment for the position of attachment of the arylamino group, inasmuch as the 6.5-7.5 ppm region contains signals for the aromatic protons of the substituent which may mask the characteristic singlet for the 6-H proton of the quinonimine fragment; in the unsubstituted substrate this proton appears at ca. 6.0 ppm. The structures of the compounds II-VIII were therefore confirmed via chemical methods, namely via the independent synthesis of the two possible substitution products, the 9- and 6-arylamino derivatives of the starting material.

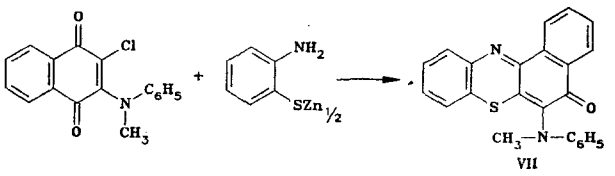
9-N-Methyl-N-phenylaminobenzo[a]phenothiazin-5-one (X) was obtained via the condensation reaction of 5-hydroxynaphtho-[2,1-d]-1,3-oxathiol-2-one (IX) with 4-nitroso-N-methyl-N,N-diphenylamine according to the method described in [10]:



The compound X exhibits a beautiful fluorescent reaction in most organic solvents. The electronic spectrum of this material differs significantly from those of compounds II-VIII; the molar extinction coefficient of the maximum absorbance band is much larger than for II-VIII and precludes the possibility of a 9-orientation for the arylamino groups introduced via nucleophilic substitution.

6-N-Methyl-N-phenylaminobenzo[a]phenothiazin-5-one (VII) was prepared via the condensation of 2-chloro-3-N-methyl-N-phenylamino-1,4-naphthoquinone with the zinc salt of 2-aminothiophenol according to [5]; its IR, PMR, and electronic spectra were identical with those

obtained for the compound generated via the direct nucleophilic displacement of hydrogen in I. In an analogous manner other 6-arylaminobenzo[*a*]phenothiazin-5-ones, prepared via the directions in [5], proved to be identical with the corresponding derivatives II-VI:



VII

The reaction of N-, as well as O- and S-containing nucleophiles [1], with I demonstrates that the 6-position in benzo[*a*]phenothiazin-5-one is a highly reactive electrophilic center which permits the utilization of the nucleophilic substitution reaction as a method for the selective synthesis of 6-substituted derivatives. In this context, it is worth noting that nonbenzoannelated HQI (phenothiazin-3-one, phenoxazin-3-one) react with arylamines under significantly milder conditions to give two amination products, i.e., substitution occurs on both the quinoid and benzenoid nuclei; these results suggest that these quinonimines are less electrophilic than the aryl fragments in the 1,2-benzoannelated analogs.

EXPERIMENTAL

PMR spectra were recorded on a Perkin-Elmer R12B spectrometer at 60 MHz in chloroform solutions with HMDS as internal standard. Electronic spectra were obtained on a Specord UV-VIS spectrophotometer in ethanol solutions; IR spectra were taken on a UR-20 spectrophotometer on vaseline oils. The purity of the products was monitored by TLC on Silufol UV-254 plates with chloroform eluent.

Arylaminobenzo[*a*]phenothiazin-5-ones (II-VIII) (see Table 1). A. To a solution of 0.5 g (ca. 2 mmole) of benzo[*a*]phenothiazin-5-one in 50 ml of DMF was added 5 drops of concentrated HCl; the mixture was heated to 100°C, and a fivefold excess of the corresponding amine was added. The reaction mixture was maintained at this temperature for 30 h, and the extent of the reaction was monitored by TLC. At the completion of the reaction the mixture was added to 100 ml of water, and the resulting precipitate was filtered, dried, dissolved in a minimum amount of chloroform, and chromatographed on a silica gel (100-250 μ) column with chloroform eluent. The first zone (blue-violet) was collected; evaporation of the eluent yielded the corresponding 6-arylaminobenzo[*a*]phenothiazin-5-one. The second zone (red) yielded up to 0.1 g of unreacted benzo[*a*]phenothiazin-5-one after solvent evaporation.

B. 6-N-Methyl-N-phenylaminobenzo[*a*]phenothiazin-5-one (VII) was prepared from 2-chloro-3-N-methyl-N-phenylamino-1,4-naphthoquinone and the zinc salt of o-aminothiophenol according to [5]. Violet crystals were obtained; these were identical in all respects (mp, R_f, and spectral properties) with that obtained according to method A above.

N-Nitroso-N-methyl-N,N-diphenylamine was obtained via the nitrosation of N-methyl-N,N-diphenylamine according to [11]. Bright green crystals, mp 44°C (44°C [11]).

TABLE 1. Properties of 6-Arylaminobenzo[*a*]phenothiazin-5-ones

Compound	mp, °C (from acetone)	R_f*	λmax, nm (log ε), (in DMF)	Found, %				Molecular formula	Calc., %				Yield (g/g of compound I)
				C	H	N	S		C	H	N	S	
II	245—247	0,75	552 (3,79)	73,0	3,8	8,0	8,8	$C_{22}H_{14}N_2OS$	72,9	4,4	7,7	8,8	1,0—1,2
III	266—268	0,5	538 (3,81)	68,4	3,4	7,2	8,2	$C_{22}H_{13}ClN_2O$	67,9	3,4	7,2	8,2	1,0—1,2
IV	264—265	0,5	540 (3,82)	60,6	3,1	6,6	7,6	$C_{22}H_{13}BrN_2O$	60,9	3,0	6,5	7,4	1,0—1,2
V	200—202	0,3	574 (3,81)	71,5	4,1	7,3	8,4	$C_{21}H_{16}N_2O_2S$	71,8	4,2	7,3	8,3	1,0—1,2
VI	259—261	0,6	561 (3,84)	74,5	4,5	7,6	8,6	$C_{23}H_{16}N_2OS$	74,9	4,4	7,6	8,7	1,0—1,2
VII	212—214	0,7	471 (3,93)	74,4	3,0	—	8,4	$C_{23}H_{16}N_2OS$	74,9	4,4	7,6	8,7	0,6—0,8
VIII	234—236	0,72	477 (3,92)	74,1	4,8	7,7	—	$C_{24}H_{18}N_2OS$	73,7	5,0	7,8	8,9	0,6—0,8

*On Silufol UV-254 plates, chloroform eluent.

5-Hydroxynaphtho[2,1-d]-1,3-oxathiolone-2 (IX) was obtained according to [10] from 1,4-naphthoquinone and thiourea. Light gray crystals, mp 178-180°C (178-180°C [10]).

9-N-Methyl-N-phenylaminobenzo[a]phenothiazin-5-one (X). A mixture of 0.2 g (ca. 1 mmole) of 5-hydroxynaphtho[2,1-d]-1,3-oxathiolone-2 and 0.2 g (ca. 1 mmole) of 4-nitroso-N-methyl-N,N'-diphenylamine in 10 ml of glacial acetic acid was heated to boiling for 10 min, cooled, and the resulting precipitate was removed by filtration. Recrystallization from acetone afforded 0.2 g (60%) of compound X, red-violet crystals, λ_{max} 450 nm (log ε 4.28); mp 110-112°C. Found: N 7.3; S 8.4%. $C_{23}H_{16}N_2OS$. Calculated: N 7.6; S 8.7.

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REACTION OF AZIRINES WITH SULFUR NUCLEOPHILES.

1. TREATMENT OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH β-SUBSTITUTED ETHANETHIOLS

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The reaction of 2,2-dimethyl-3-phenylazirine with β-substituted ethanethiols results in the formation of a previously unknown series of 2-substituted aziridines, namely aziridinylalkylsulfides. Their three-dimensional structures were investigated by x-ray crystallography.

The high reactivity of the C=N bond in 2H-azirines with nucleophilic reagents opens up a wide range of possibilities for the synthesis of diverse nitrogen-containing acyclic and heterocyclic compounds [1]. Up to this time, however, of the large selection of nucleophilic reagents with lone electron pairs, only N-, O-, and P-containing nucleophiles have been reacted with 2H-azirines. Studies of the addition of sulfur-containing nucleophiles, for instance thiols, to the C=N bond in 2H-azirines have not been reported in the literature.

In order to exploit the reactivity of 2,2-dimethyl-3-phenylazirine (I) with functionally substituted thiols, we have investigated its reaction with β-substituted ethanethiols. These reactions lead to the formation of 2-sulfur-containing aziridines, as well as products resulting from their fragmentation and rearrangement.

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