

prior to the addition of 2 ml of a 10% solution of HCl. The mixture was stirred for 1 h. To the reaction mixture was added 5 ml of water. The precipitated residue was filtered off and washed with ethanol and hexane. The yield of (IX) was 0.8 g (75%). It had mp 243-244°C (from ethanol). The IR spectrum had (ν , cm^{-1}): 2186 (CN), 3236, 3348, and 3449 (NH_2). The PMR spectrum had (DMSO- d_6 , δ , ppm): 6.11 singlet (2H, NH_2), 5.44 singlet (1H, CH), 2.32 singlet (3H, CH_3), and 2.16 singlet (3H, COCH_3). Found: C 57.43, H 3.72, N 15.80, and S 9.18%. $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_3\text{S}$. Calculated: C 57.62, H 3.98, N 15.81, and S 9.05%.

The authors are grateful to B. M. Zolotarev for taking the mass spectra and helping in their interpretation.

CONCLUSIONS

1. A general method for the synthesis of substituted 4-aryl-3-cyano-2[1H]pyridinethiones and the corresponding selenones was developed. The method was based on the interaction of carbonyl compounds of the type $\text{R}^1\text{CH}_2\text{COR}^2$, where $\text{R}^1 = \text{H, Me, Ac, and COOEt}$; $\text{R}^2 = \text{Me and Ph or R}^1\text{-R}^2 = (\text{CH}_2)_3 \text{ and } (\text{CH}_2)_4$, and also of their enamines with the arylidene derivatives of cyanothio(seleno)acetamides.

2. The salts of the substituted 4-aryl-3-cyano-3,4-dihydro-2[1H]pyridinethiones with organic bases were obtained and characterized.

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VINYLIATION OF ALCOHOLS BY 10-VINYLPHENOTHIAZINE

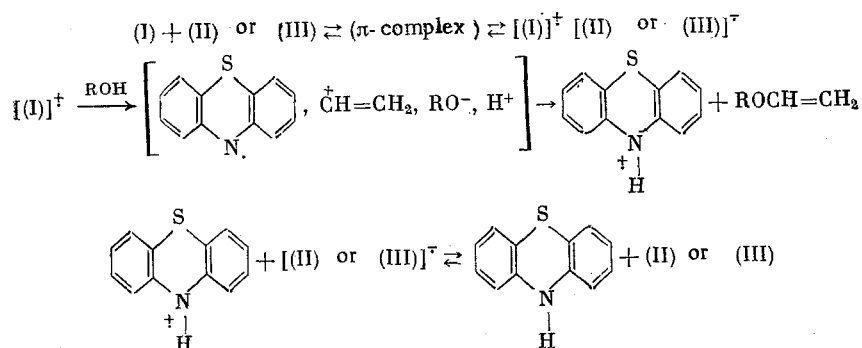
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UDC 542.91:547.262:547.869

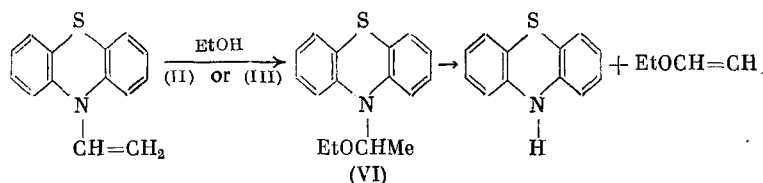
Previously we detected an unusual mechanism of hydrolytic cleavage of 10-vinylphenothiazine (I) in the presence of organic π -electron acceptors [1] occurring via a step of formation of a vinyl cation. It was also assumed that compound (I) reacts similarly with alcohols. The reaction occurs in the presence of p-benzoquinone (II), 2,4,7-trinitrofluorenone (III), p-chloranil (IV), and 7,7,8,8-tetracyanoquinodimethane (V) with formation of unsubstituted phenothiazine and vinyl alkyl ether. In addition, it was assumed that the formation of the final products was preceded by steps of formation and ionization of a donor-acceptor complex with subsequent solvolysis of the unstable radical cation of compound (I) into a vinyl cation and a phenothiazine radical.

*Deceased.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2108-2110, September, 1985. Original article submitted July 17, 1984.

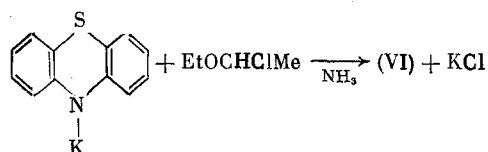


An alternate route for alcoholysis [2, 3] of substance (I) is possible, including addition of ethanol and then cleavage of the resulting aminal, 10-(α -ethoxyethyl)phenothiazine (VI), according to the scheme



The probability of formation of a compound of type (VI) under the conditions of the investigated reaction was shown in [4] for the case of addition of alcohols to 9-vinylcarbazole.

To determine the reliability of the two considered mechanisms for vinylation of alcohols by compound (I), we synthesized substance (VI) by the reaction of α -chlorodiethyl ether with potassium phenothiazine in a medium of liquid ammonia



The composition and structure of the isolated product were confirmed by the data of elemental analysis and IR, proton NMR, and mass spectrometry. The IR spectra of compound (VI) contained bands of stretching vibrations of the phenothiazine ring (760, 1440, 1570, and 1595 cm^{-1}), C-O-C bonds (1160 and 1180 cm^{-1}), CH (2870 cm^{-1}), and CH_3 (2980 cm^{-1}). The proton NMR spectra contained a complex multiplet in the region of 6.8-7.2 ppm belonging to protons of the phenothiazine ring. The signals of aliphatic protons of CH, CH_2 , and CH_3 groups were in the regions of 4.67 (quartet), 3.84 (multiplet), 1.39 (doublet), and 1.09 ppm (multiplet), respectively. The mass spectra of (VI) contained a molecular ion with m/z 271 and also masses of fragment ions of the following molecular fragments with m/z : 226 [$\text{S}(\text{C}_6\text{H}_4)\text{NC}_2\text{H}_4$] † , 198 [$\text{S}(\text{C}_6\text{H}_4)_2\text{N}$] † , 73 [$\text{C}_2\text{H}_5\text{OC}_2\text{H}_4$] † and 45 [$\text{C}_2\text{H}_5\text{O}$] † .

It was found that compound (VI) was very stable in the presence of (IV). From the reaction medium, we isolated only 10% of the unsubstituted phenothiazine and 85% of unreacted product (VI). Under the same conditions, conversion of (I) to unsubstituted phenothiazine and of alcohol to vinyl ethyl ether in the presence of (IV) and (V) went to 94 and 47% completion, respectively. The effective values of the rate constants (k) of the investigated reaction depended symbatically on the electron-affinity energies (E_A) of the acceptors that were used (Table 1), which confirms the probability of the electron-transfer step in the mechanism of vinylation of alcohols by compound (I). This is also indicated by the observed increase of the rate constant of the process ($4.2 \cdot 10^{-5} \text{ sec}^{-1}$) with photolytic excitation of the system in the charge-transfer band of the donor-acceptor complex of compounds (I) and (II) in comparison with the dark reaction (see Table 1).

TABLE 1. Relation of the Initial Rates of the Reaction of (I) with (II)-(V) to the Electron-Affinity Energy of the Acceptors (A)
 $[(I)]=0,0667,$
 $[A]=2,4 \cdot 10^{-4} \text{ M}, 40^\circ$

Electron acceptor	$E_A, \text{ eV}$	$k \cdot 10^5, \text{ sec}^{-1}$
(II)	1,85	$1,0 \pm 0,1$
(III)	2,05	$7,9 \pm 0,2$
(IV)	2,45	$11,5 \pm 0,4$
(V)	2,8	$18,5 \pm 0,5$

It is of interest to note that the reaction of 9-vinylcarbazole (VII) with alcohol in the presence of (III) and (IV) did not lead to formation of vinyl alkyl ether and carbazole, which was probably due to the greater stability of the intermediate radical cation formed from (VII) and to its inability to decay in the presence of alcohol.

Thus, the obtained experimental data indicate that the vinyl cation was the main vinylating species in the reaction of alcohols with 10-vinylphenothiazine.

As was shown in [5, 6], transfer of vinyl derivatives to the radical-cation state significantly facilitated generation of a vinyl cation.

EXPERIMENTAL

The investigated compounds were obtained and purified by the following procedures: (I) and (VII) by the procedure of [7]; α -chlorodiethyl ether by the procedure of [2]; (II), mp 115°C , by twofold sublimation; (IV), mp 294°C , by the procedure of [8]; and (III), mp 175°C , and (V), mp 296°C , were recrystallized twice from chlorobenzene. The solvents were dehydrated by the familiar methods. The IR, proton NMR, and mass spectra of (VI) were recorded on UR-20 (in mineral oil), Tesla BS-487 C (in CDCl_3 , internal standard HMDS), and Varian MAT-212 (energy of ionizing electrons of 70 eV) instruments. The kinetics was studied by the procedure of [1]. Photoirradiation of a mixture of (I) with alcohol in the presence of (II) was carried out at $\sim 20^\circ\text{C}$ with a DKSSh-1000 Xe lamp. The spectral irradiation region (350-600 nm) was isolated with a water filter and an SZS27 filter.

10-(α -Ethoxyethyl)phenothiazine (VI). Sublimed phenothiazine (mp 182°C) (10 g) was dissolved in 500 ml of liquid NH_3 . With constant stirring, 2 g of metallic K was added to the solution until its complete dissolution. The NH_3 was evaporated in an intense stream of Ar, and 80 ml of abs. toluene was added. Then 5 ml of freshly distilled α -chlorodiethyl ether was added dropwise to the reaction mixtures at $\sim 20^\circ\text{C}$ with stirring. After 2 h, the resulting precipitate was filtered, the filtrate was evaporated, and the residue was extracted with boiling hexane. The hexane solution was passed through a column with Al_2O_3 , and the solvent was evaporated. Obtained: 4 g of (VI) as a viscous yellow liquid, bp $123-126^\circ\text{C}$ (6.6 Pa), n_D^{20} 1.6270. Found: C 71.5; H 6.4; S 11.4%. $\text{C}_{16}\text{H}_{17}\text{ONS}$. Calculated: C 70.9; H 6.37; S 11.8%.

Reaction of 10-Vinylphenothiazine (I) with Alcohol. A solution of 2.25 g of (I) and 0.005 mole of (IV) or (V) in 20 ml of ethanol was placed in a glass ampul, Ar was blown through it, and the ampul was sealed. After 10 h at 60°C , 2.05 g (94%) of phenothiazine was separated from the reaction products by filtration. The quantitative content (47%) of vinyl ethyl ether in the filtrate was determined by GLC (2.5-m \times 3-mm column with 5% silicone DS-550 on Chromaton N-AW-DMS, 45°C , He carrier gas, and velocity 25 ml/sec). Under similar conditions, 0.221 g (10%) of phenothiazine and 2.3 g (85%) of (VI) were isolated from the reaction mixture of (VI) and (IV). The concentrations of the starting compounds were: $[(I)] = [(VI)] = 0.5$, $[(IV)] = [(V)] = 5 \cdot 10^{-3}$ mole/liter.

CONCLUSIONS

The mechanism of vinylation of alcohols by 10-vinylphenothiazine in the presence of organic π -electron acceptors was investigated. The main vinylating species was the vinyl cation, the decay product of the 10-vinylphenothiazine radical cation.

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REACTIONS OF BROMONIUM SALTS OF THE CARBOBORANE SERIES
WITH NUCLEOPHILES

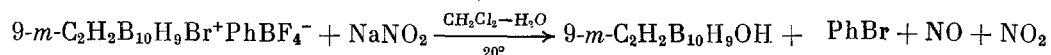
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UDC 542.91:547.1'127

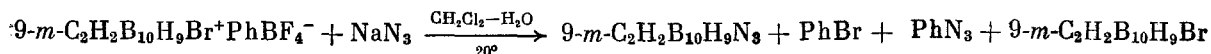
We recently reported the synthesis of the first bromonium compounds of the carborane series, viz., bis(9-*m*-carboranyl)bromonium and phenyl-(9-*m*-carboranyl)bromonium salts [1]. The present work is devoted to the reactions of these compounds with nucleophilic reagents.

As is known, there is a strong similarity in chemical behavior between aromatic iodonium and bromonium salts; both are excellent arylating agents [2-4]. But bromonium compounds usually react with nucleophiles under milder conditions than do iodonium compounds and their reactions are far more rarely accompanied by radical side reactions. In this connection it was of interest to study the chemical behavior of carboranyl bromonium salts and to compare it with its analogs the phenyl-(*B*-carboranyl)iodonium salts [5-9].

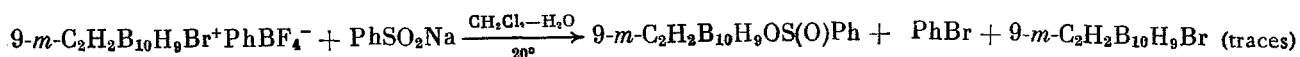
It has been found that phenyl-(9-*m*-carboranyl)bromonium borofluoride (I) reacts with nucleophiles entirely like the iodonium analog [5-9], but there are a number of basic differences in its behavior. Thus, as expected, (I) reacts with azide, nitrite, and benzenesulfinate ions more readily than phenyl-(9-*m*-carboranyl)iodonium borofluoride (II) [5], to give mainly bromobenzene and the respective boron-substituted carborane, for example,



It is very much more important to note, however, that these reactions are no longer regio-specific. For example, azide ion reacts with (II) exclusively with scission of the B-I⁺ bond and the C-I⁺ bond is practically unaffected, whereas under the same conditions I undergoes C-Br⁺ scission (although slight). The reaction with NaN₃ forms, besides 97% of bromobenzene and 9-*m*-carboranyl azide, 3% of 9-bromo-*m*-carborane (III) and phenyl azide*:



We also found (III)* in trace amounts in the reaction of (I) with sodium benzenesulfinate. In this reaction the formation of diphenyl sulfone could not be demonstrated, due to the similarity of its chromatographic properties to those of the main product 9-*m*-carboranylbenzenesulfinate (61%):



This difference between (I) and (II) can apparently be explained by the fact that the bromonium atom, being a stronger electron acceptor than the iodonium atom, increases the posi-

*Identified by TLC with a reference spot.

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