

# FORMYLATION OF 2-PHENYLBENZO[b]CYCLOPENTA[e]PYRAN

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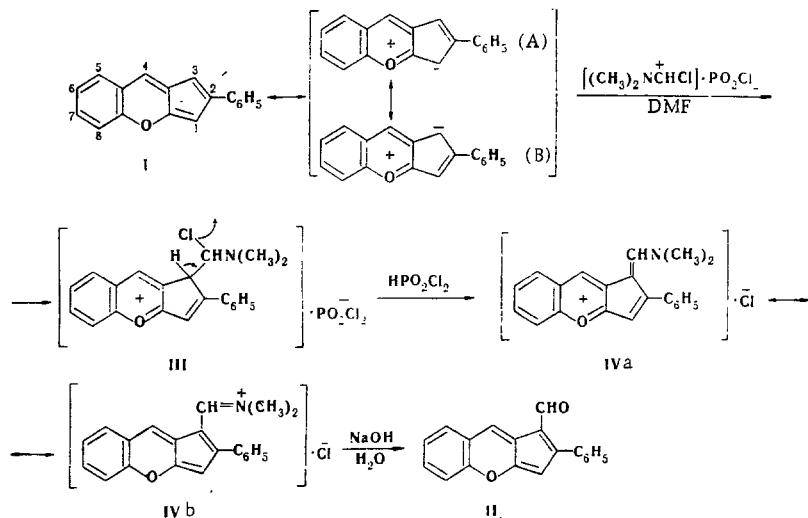
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The Vilsmeier formylation of 2-phenylbenzo[b]cyclopenta[e]pyran was realized. The structure of the resulting 2-phenyl-3-formylbenzo[b]cyclopenta[e]pyran was confirmed by the PMR spectral data.

The literature does not contain information regarding the reactivities of benzocyclopentapyrans, although one should expect a clearly expressed tendency to undergo electrophilic substitution reactions in the 1 and 3 positions in this series, inasmuch as this class of compounds is legitimately classified with oxygen heteroanalogs of azulene, in which the electron pair of the oxygen atom participates in the formation of a unified electronic system of the entire molecule.

We have observed that 2-phenylbenzo[b]cyclopenta[e]pyran (I) [1], like azulene [2], is readily formylated by the phosphorus oxychloride-dimethylformamide (DMF) complex at room temperature, during which the formyl group evidently enters the 3 position of the system to give 2-phenyl-3-formylbenzo[b]cyclopenta[e]pyran (II).

We propose that the partial positive charge in starting I is localized primarily in the benzopyran ring and that the negative charge of the five-membered ring is localized either on C-1 (intermediate state A) or on C-3 (intermediate state B) of the benzo[b]cyclopenta[e]pyran system. It might be assumed that the B state is more thermodynamically favorable, inasmuch as the phenyl group in this structure is conjugated with the oxonium cation of the benzopyrylium ring. In conformity with the mechanism adopted for the Vilsmeier reaction, attack on dipolar ion B by the carbonium ion complex leads to the formation of a benzopyrylium cation (III), which splits out hydrogen chloride under the reaction conditions to give a conjugated fulvene (IV). The hydrolysis of IV with aqueous alkali leads to aldehyde II in high yield. The structure of the chromatographically individual aldehyde II obtained in this way is confirmed by the PMR spectral data on comparison with the data for the starting compound.



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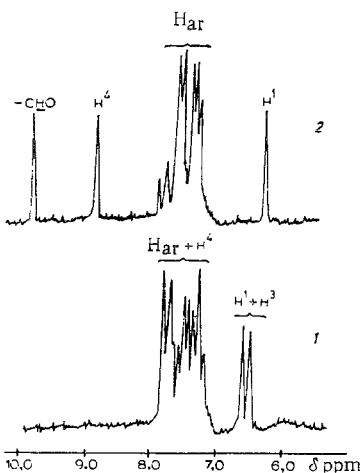


Fig. 1. PMR spectra (in dioxane): 1) 2-phenylbenzo[b]cyclopenta[e]pyran (I); 2) 2-phenyl-3-formylbenzo[b]cyclopenta[e]pyran (II).

A multiplet of aromatic protons of the benzene ring and the phenyl residue is observed in the PMR spectrum of I at 7.1-7.6 ppm. The signal of the 4-H proton is also present in this region and is not identified under these conditions. Singlets of 1-H and 3-H protons at  $\delta$  6.4 and 6.5 ppm are found at stronger field, as are the signals of the corresponding protons in the PMR spectrum of unsubstituted azulene [3].

The signals of the aromatic protons of the benzene ring and the phenyl residue are observed in approximately the same region (7.1-7.8 ppm) in the PMR spectrum of aldehyde II. The 1-H signal (singlet at  $\delta$  6.2 ppm) is shifted somewhat to the strong-field region, and this is in agreement with the shift of this proton when there is an acetyl group in the 3 position of azulene [4]. The signal of the proton of an aldehyde group is observed at  $\delta$  9.8 ppm, and the 4-H signal undergoes an extremely significant shift to the weak-field region ( $\delta$  8.8 ppm). This can be explained by the strong deshielding effect on the 4-H proton of the aldehyde group in the 3 position, i.e., the peri position. An aldehyde group in the 4 position is excluded, inasmuch as our attempt to formylate, under the conditions of the Vilsmeier reaction, the previously undescribed 1,2,3-triphenylbenzo[b]cyclopenta[e]pyran, which one of us obtained by high-temperature condensation (200°) of 2,3,4-triphenylcyclopenten-2-one [5] with salicyaldehyde, was unsuccessful even at 150°; this should be explained by the inertness of the benzo-pyrylium cation to electrophilic agents.

#### EXPERIMENTAL

The PMR spectra of 5% solutions of the compounds in dioxane, which was also used as the internal standard, were recorded with a BS-487B spectrometer (operating frequency 80 MHz) at 43°. The chemical shifts are expressed on the  $\delta$  scale with respect to tetramethylsilane. The accuracy in the measurement of the chemical shifts was  $\pm 0.03$  ppm.

**2-Phenyl-3-formylbenzo[b]cyclopenta[e]pyran (II).** Phosphorus oxychloride (4 ml) was added dropwise with vigorous stirring and cooling to a solution of 1.22 g (5 mmole) of I in 100 ml of DMF. After 10 min, the mixture was treated with a fivefold volume of water containing 4 g of NaOH and extracted with 100 ml of benzene. The benzene extract was chromatographed with a column filled with silicon oxide. The dark-red eluate was evaporated, and the residue was crystallized from acetic acid to give 1.25 g (92%) of red needles of aldehyde II with mp 204-205° and  $R_f$  0.27 (in benzene on a Silufol UV-254 plate). Electronic spectrum,  $\lambda_{\text{max}}$ : 306, 356 (inflection), 370 and 480 nm (in benzene). Found: C 84.2; H 4.5%.  $C_{19}H_{12}O_2$ . Calculated: C 83.8; H 4.4%.

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## AMINOLYSIS OF DIPHENYLDICHLOROSILANE AND HETEROCYCLIC CHLOROSILANES

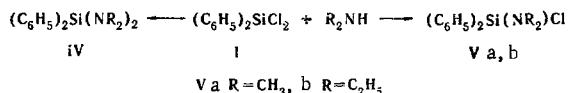
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Reaction of diphenyldichlorosilane, dichlorosilafluorene, and dichlorosiloxarophenanthrene with amines in mono- or disubstituted organoaminosilanes gave mono- or disubstituted organoaminosilanes.

In the present paper we report the results of aminolysis of diphenyldichlorosilane, dichlorosilafluorene, and dichlorosiloxarophenanthrene in connection with the possibility of transformation of organosilicon heterocyclic derivatives. Diorganochlorosilanes react with amines to give chlorine-substitution products [1]: thus diphenyldichlorosilane reacts with primary amines to give the corresponding disubstituted derivatives [2].

The reaction of diphenyldichlorosilane (I) with secondary amines differs from its reaction with primary amines: the degree of substitution of the chlorine atoms depends not only on the component ratio but also on the structure of the amine. One or both chlorine atoms can be replaced by an amine residue in the case of dimethylamine; the formation of a total substitution product occurs only as a result of prolonged contact of the incomplete substitution product with excess amine. In the case of diethylamine, only N,N'-diethylaminodiphenylchlorosilane (IV) is obtained, regardless of the reaction conditions.



Heterocyclic chlorosilanes — dichlorosilafluorene (II) and dichlorosiloxarophenanthrene (III) — react readily with primary and secondary amines to give the corresponding organoaminosilanes (VI, VII).

The difference in the amination reactions of I, II and III can be explained by shielding of the chlorine atom in the partially aminated product (V) by phenyl groups as compared with II and III, which have a planar orientation of the fluorene and phenanthrene fragments.

The isolated organoaminosilanes are readily hydrolyzed. After 30-min contact of VIa with moist air, the absorption bands at 1000, 1290  $\text{cm}^{-1}$  (Si—N), and 2800  $\text{cm}^{-1}$  (methylamino group) vanish completely, and a band appears at 1050  $\text{cm}^{-1}$ ; this indicates hydrolysis of N,N'-bis(dimethylamino)silafluorene (VIa) at the Si—N bond to give an Si—O—Si bond.

### EXPERIMENTAL

The purity of the chlorosilanes used in this research was no less than 99.9% according to gas-liquid chromatography; the organic amines (chemically pure grade) were additionally purified by fractionation over sodium metal.

Reaction of Diphenyldichlorosilane with Dimethylamine. Dimethylamine [90 g (2 moles)] was added with vigorous stirring at 15–20° to a solution of 25.3 g (0.1 mole) of diphenyldichlorosilane in 200 ml of toluene.

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