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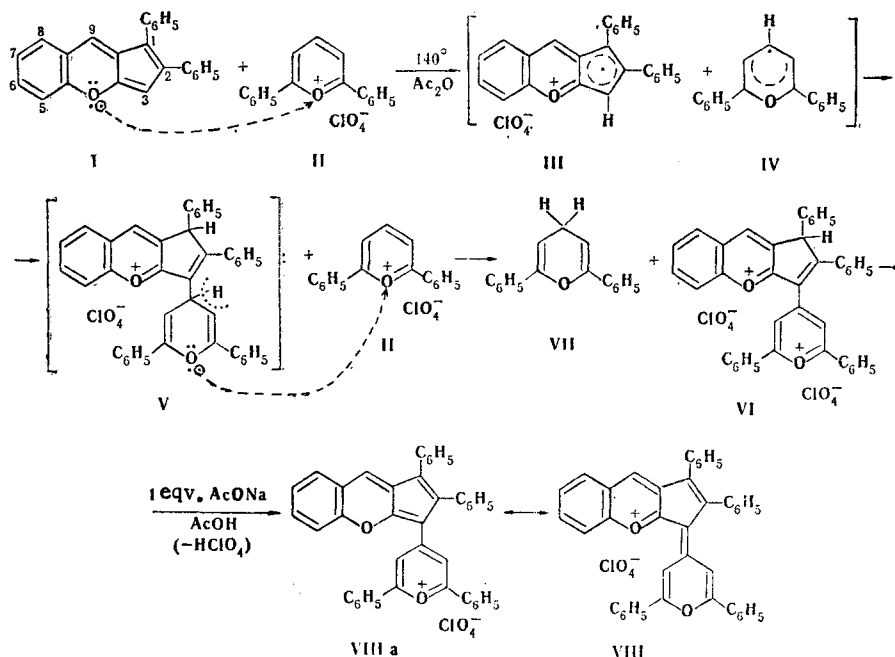
PYRYLATION OF 1,2-DIPHENYLBENZO[b]CYCLOPENTA[e]PYRAN

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1,2-Diphenylbenzo[b]cyclopenta[e]pyran was pyrylated with 2,6-diphenylpyrylium perchlorate. The structures of the singly and doubly charged 2,6-diphenyl-4-(1,2-diphenylbenzo[b]cyclopenta[e]-3-pyrania)pyrylium cations are confirmed by data from the electronic absorption spectra. A radical mechanism for the pyrylation is proposed on the basis of the ESR spectrum.

Radical substitution reactions in the benzo[b]cyclopenta[e]pyran series have not been studied at all, although it might be assumed *a priori* that, as in the case of azulenes, they would be directed to the 1 and 3 positions. An attempt to subject a substrate to substitution by cations that usually do not react at low temperatures but form radicals at temperatures that cause one-electron transfer, i.e., in the final analysis, to subject the substrate to radical substitution, would seem of great theoretical interest. The 2,6-diphenylpyrylium cation [1], for example, may serve as a one-electron oxidizing agent of this type. Organic compounds that either have increased electron density on at least one of the carbon atoms (N,N-dimethylaniline [2, 3], 1-methylindole [4], and 2-methylindole [5]) or are capable of easily undergoing oxidation to relatively stable cation radicals (ferrocene [6]) are usually substrates in this reaction.



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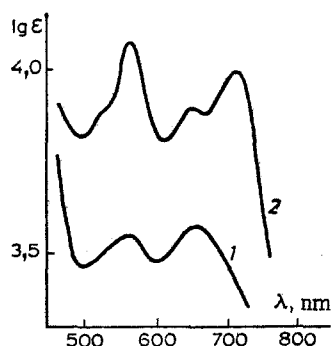


Fig. 1. Electronic absorption spectra of salts VI (1) and VII (2) in CHCl_3 .

We have established that 1,2-diphenylbenzo[b]cyclopenta[e]pyran (I) undergoes condensation with 2,6-diphenylpyrylium perchlorate (II) in refluxing acetic anhydride to give 2,6-diphenyl-4-(1,2-diphenylbenzo[b]cyclopenta[e]-3-pyrania)pyrylium diperchlorate in 75% yield. The first step in this reaction is evidently one-electron oxidation of substrate I by the 2,6-diphenylpyrylium cation of II, which leads to the hypothetical formation of the extremely reactive 1,2-diphenylbenzo[b]cyclopenta[e]pyranylium cation radical (III) and the 2,6-diphenyl-4H-pyran-4-yl radical (IV). Intermolecular recombination of these particles, which is simultaneously accompanied by allylic prototropic rearrangement in the benzocyclopentapyran portion of the molecule, gives a substituted benzocyclopentapyranylium cation (V) that is protonated at the 1-C atom.

The V cation is capable of undergoing reoxidation by 2,6-diphenylpyrylium perchlorate II at the 4H-pyran ring and is converted with the simultaneous loss of one hydrogen atom to double salt VI; in this case 2,6-diphenyl-4H-pyran (VII), which is isolated by chromatography of the benzene extract of the neutral portion of the filtrate on aluminum oxide (elution with n-heptane) [4], is formed. We were unable to detect the product of recombination of cation radical III, i.e., the dimer. It is possible that the electrostatic forces of repulsion of the positive charges of the benzopyrylium rings hinder its formation.

Data from the ESR spectrum of the reaction mixture after it was first heated to 140°C and then cooled rapidly to 77°K (liquid nitrogen) provide evidence in favor of our proposed mechanism. A poorly resolved ESR signal, which is related to the paramagnetic particles formed during the reaction, appears at a field strength of 3320 G.

When salt VI is treated with one equivalent of sodium acetate in glacial acetic acid, one molecule of HClO_4 is split out, and a monobasic salt — 2,6-diphenyl-4-(1,2-diphenylbenzo[b]cyclopenta[e]-3-pyrania)pyrylium perchlorate (VIII) — is formed. In contrast to salt VI, in which the styryl grouping is crossconjugated simultaneously with two cations (pyrylium and benzopyrylium), salt VIII contains one fully conjugated cation, the structure of which is best conveyed by limiting resonance structures VIIIA and VIIIB. The different degrees of delocalization of the positive charges in the cations of VI and VIII affect the patterns of their electronic absorption spectra (Fig. 1).

The higher degree of delocalization of the only positive charge in the cation of VIII leads not only to the appearance of a rather intense new absorption band at 714 nm (the bathochromic shift of the long-wave λ_{max} is 60 nm) but also to an increase in $\log \epsilon$ (at 500–750 nm) of 0.4 (average value) as compared with $\log \epsilon$ of the cation of VI.

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EXPERIMENTAL

The electronic spectra of the compounds were recorded with a Specord UV-vis spectrophotometer. The ESR spectra were recorded with a Rubin spectrometer.

2,6-Diphenyl-4-(1H-1,2-diphenylbenzo[b]cyclopenta[e]-3-pyrania)pyrylium Diperchlorate (VI). A mixture of 1.65 g (5 mmole) of 2,6-diphenylpyrylium perchlorate, 0.8 g (2.5 mmole) of 1,2-diphenylbenzo[b]cyclopenta[e]pyran (I), and 20 ml of acetic anhydride was refluxed

for 20 min, after which it was cooled and diluted with 20 ml of absolute ether, and the crystalline precipitate was removed by filtration and recrystallized from 15 ml of glacial acetic acid to give 1.4 g (75%) of double salt VI in the form of black crystals with mp 225-226°C. UV spectrum (chloroform), λ_{\max} (log ϵ): 565 (3.54) and 655 nm (3.57). Found: C 65.1; H 4.0; Cl 9.4%. $C_{41}H_{28}Cl_2O_{10}$. Calculated: C 65.5; H 3.8; Cl 9.4%.

2,6-Diphenyl-4H-pyran (VII). This compound was isolated by the method in [4] in the form of colorless crystals with mp 89-90°C.

2,6-Diphenyl-4-(1,2-diphenylbenzo[b]cyclopenta[e]-3-pyran)pyrylium Perchlorate (VIII). A mixture of 0.75 g (1 mmole) of double salt VI, 0.08 g (1 mmole) of sodium acetate, and 10 ml of glacial acetic acid was heated to the boiling point, after which it was cooled, diluted with 10 ml of absolute ether, and worked up to give 0.59 g (91%) of perchlorate VIII in the form of black crystals with mp 204-205°C. UV spectrum (chloroform), λ_{\max} (log ϵ): 532 (3.89), 566 (4.07), 653 (3.87), and 714 nm (3.98). Found: C 75.3; H 4.4; Cl 5.6%. $C_{41}H_{27}ClO_6$. Calculated: C 75.6; H 4.2; Cl 5.5%.

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NEW METHOD FOR THE SYNTHESIS OF cis-2-THIAHYDRINDANE DERIVATIVES*

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A new method was worked out for the stereospecific synthesis of derivatives of cis-1,3-disubstituted cis-2-thiahydrindanes; the method is based on the reaction of sulfur dichloride with cis-1,2-divinylcyclohexane and is distinguished by its simplicity and high yields. It was established that two stereoisomeric sulfoxides that differ only with respect to the orientation of the sulfoxide oxygen atom are formed in the oxidation of cis-1,3-dichloromethyl-2-thiahydrindane. The structures of cis-1,3-dichloromethyl-cis-2-thiahydrindane and its oxidation products were studied by 1H NMR spectroscopy, 1H NMR spectroscopy with the addition of a shift reagent [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium], and ^{13}C NMR spectroscopy.

Thiahydrindane derivatives are difficult to obtain [2, 3]. The available literature data make it possible to arrive at the judgement that the methods for the synthesis of thiahydrindanes are extremely laborious and inadequate.

We have developed a new method for the synthesis of 1,3-disubstituted cis-2-thiahydrindane that is distinguished by its simplicity, high yields, and stereospecificity. The method is based on the reaction of SCl_2 with cis-1,2-divinylcyclohexane, which is a completely

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