The lower reactivity of 2- and 4-hydroxypyrimidines in condensations with aldehydes is probably caused by their predominant existence as carbonyl tautomers, in which the methyl protons possess a lower reactivity.

EXPERIMENTAL

NMR spectra were taken on an HA-100 instrument at 29° on 8-10% solutions in CD_3OD and $CDCl_3$, with hexamethyldisilane as internal standard. The accuracy of determination was $\delta \pm 0.02$.

Synthesis of 4(6)-styryl-5-hydroxypyrimidines. A mixture of 0.005 mole of (I), (II) or (III) and 0.01 mole of aldehyde was heated for 2 h on a boiling water bath with 10-20 ml of 5% HCl. The hot reaction mixture was evacuated to remove unreacted aldehyde (C_6H_5CHO). The mixture was then cooled and neutralized with Na_2CO_3. A solid precipitated. The solid was dried, dissolved by heating in a suitable solvent, filtered from inorganic salts, separated on a 40×100 μm silica gel (from Czechoslovakia) column, and eluted with acetone, ethyl acetate, and ether. Experimental data are given in Table 1.

CONCLUSIONS

1. 4,6-Dimethyl-5-hydroxypyrimidines with methyl or phenyl groups in the 2-position were condensed with aromatic aldehydes to give styrylpyrimidines.

2. A hydroxyl group in the 5-position of the pyrimidine ring did not prevent the condensation, in contrast to hydroxyl groups in the 2- or 4-position.

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PHOTOCHEMICAL TRANSFORMATIONS OF POLYFLUORO-SUBSTITUTED STILBENES

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We have already discovered a new type of photocyclization of fluoro-substituted N-alkyldiarylamines into carbazoles [1] and of anils of polyfluoroaromatic ketones into phenanthridines [2] with splitting of the aromatically bound fluorine. In the present work, we studied the possible realization of a similar photoreaction for 2,3,4,5,6-pentafluorostilbene. We know that during UV irradiation of their dilute solutions in organic solvents, stilbenes may undergo the photocyclization of an oxidative (with splitting of two H atoms) and nonoxidative type (with splitting of HX, where X = OMe, I) into derivatives of phenanthrene [3].

trans-2,3,4,5,6-Pentafluorostilbene (I) was synthesized by the Wittig reaction from pentafluorobenzaldehyde and benzylidenetriphenylphosphorane. An attempt to obtain (I) according to [4] by the reaction of pentafluorobenzaldehyde with $PhCH_2MgCl$ was unsuccessful.

It is known that the synthesis of the perfluorinated analog of (I) by the Wittig reaction leads to the formation of a mixture of cis- and trans-isomers [5]. For the stilbene (I) which we obtained, there are three signals in the ^{19}F NMR spectrum with an intensities ratio of 2:1:2, characteristic of the C_6F_5 group. The data of elemental analysis and the value of the molecular weight, determined mass spectrometrically, correspond to the empirical formula $C_{14}H_7F_5$. In the PMR spectrum, besides the signal of aromatic protons, an AB system with $J = 18$ Hz is also observed, corresponding to the trans-orientation of the vicinal olefinic protons [6]. The melt-

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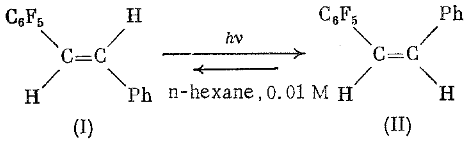
ing point of (I) is close to that of trans-2,3,4,5,6-pentafluorostilbene, obtained in [4]. In its UV spectrum, (I) is similar to a nonfluorinated analog [7] and has an intense band with λ_{max} 296 nm (log ε 4.48). We can therefore assume that the compound synthesized by us is trans-2,3,4,5,6-pentafluorostilbene.

During UV irradiation of a dilute solution of compound (I) in n-hexane (0.01 M), a practically complete transformation of the initial compound is observed after 5 h, with no splitting of ionic fluorine. From the data of elemental analysis, molecular weight (determined by mass spectrometry and vapor-phase osmometry methods) and spectral data, the product was identified as cis-2,3,4,5,6-pentafluorostilbene (II).

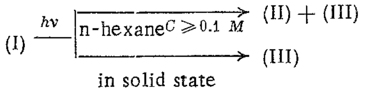


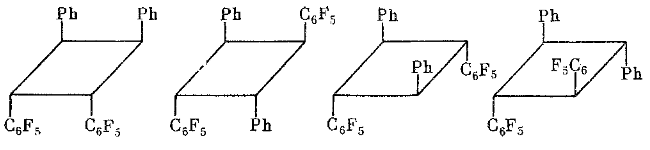
According to the PMR spectrum of (II), the spin–spin coupling constant (SSCC) of the olefinic protons is 12 Hz (comp. [6]). In the UV spectrum of (II), an intense absorption band at λ_{max} 256 nm (log ε 4.14), corresponding to the conjugated double bond, is shifted into the shortwave region by 14 nm, compared with the nonfluorinated analog [7], and by 40 nm compared with (I). This may be due to the weakening of the conjugation in (II) because of steric interaction of the phenyl and pentafluorophenyl rings.

During the UV irradiation of a dilute solution of (I) in n-hexane, and also in benzene, alcohol, CCl_4, it isomerizes into the cis-isomer (II), as in the case of the nonfluorinated analog [8]. The photoisomerization is not accompanied by cyclization, which may be because the excited state of (II) has a lower polarity than polyfluorodiarylamines [1] or conjugated acids of polyfluoroaromatic anils [2].

It is known that during UV irradiation of a concentrated solution of trans-stilbene, photodimerization into tetraphenylcyclobutane is observed [9]; the cis-isomer is unable to undergo a similar transformation [10]. In the same way, during irradiation by visible or UV light of a concentrated solution of (I) in n-hexane or benzene, ($C \geq 0.1$ M), partial dimerization takes place together with the isomerization. In contrast to the nonfluorinated analog, which does not dimerize in the crystalline state [10], compound (I) gradually transforms into dimer (III) when left to stand in light in the solid state. By UV irradiation of finely ground stilbene (I) in a glass ampul, 3 mm in diameter, or between tightly compressed glass plates, we can attain complete transformation into the photodimer (III). Prolonged UV irradiation of cis-pentafluorostilbene (II) in the solid state leads, according to the ^{19}F NMR spectrum, to the formation of small amounts of the trans-isomer (I) and photodimer (III). It is also possible that the latter is obtained from the intermediate transisomer (I).

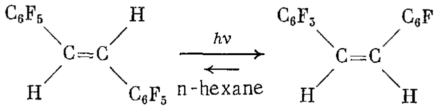
According to the data of the elemental analysis and the value of the molecular weight, found by the method of vapor-phase osmometry, the empirical formula of $C_{28}H_{14}F_{10}$ was found for compound (III). The cyclobutane structure of (III), assumed from the literature data, agrees with the character of its UV spectrum, in which the absorption in the long-wave region corresponding to conjugated C = C bond is absent. The ^{19}F NMR spectrum of dimer (III) contains three signals with an intensities ratio of 2:1:2, characteristic of the C_6F_5 group, which indicates the formation of one of the four possible isomers (III, a–d) during dimerization.




(IIIa) (IIIb) (IIIc) (IIId)

In the mass spectrum of (III) there is no peak of the molecular ion with a mass of 540. The peak with the maximal mass number 270 ($C_{14}H_7F_5$) corresponds to pentafluorostilbene. This characteristic of the dissociation agrees with the data for diphenylcyclobutane [11]. Due to the absence in the mass spectrum of (III) of a peak at 360 (the molecular weight of the decafluoro-substituted stilbene), we can assume that structures (IIIb) and (IIIc) are most probable. The PMR spectrum of (III) contains two broadened singlets with an intensities ratio of 2:5. The position of the signal of the methine protons at 4.87 ppm corresponds to the data for the nonfluorinated analog [9], and agrees with the structure (IIIb). By comparing the experimental value of the dipole moment of (III) (μ_{exp} = 0.76 D) with the calculated values [(IIIb) μ_{calc} = 0, (IIIc) μ_{calc} = 2.94 D], structure (IIIb) can be seen to be the most favorable.

trans-Decafluorostilbene (IV) synthesized in analogy with (I), during UV irradiation in n-hexane transforms into the cis-isomer, but much more slowly than (I)



(IV)

The irradiation of compound (IV) in concentrated solution in n-hexane or in the solid state does not lead to its dimerization.

EXPERIMENTAL

The UV spectra were recorded on the Specord UV-Vis apparatus in EtOH, the PMR spectra on the Varian A56/60A and Tesla BS-46C (60 MHz), and the ^{19}F NMR spectra on Varian A56/60A (56.4 MHz) in CCl_4, with $\Delta\delta$ for C_6F_6 and CCl_3F equal to 163.0 ppm. The molecular weights were determined by vapor-phase osmometry, and also on a high-resolution mass-spectrometer MC-3301. The dielectric constants of the benzene solutions of the compounds were determined at 25°C on the Tangens apparatus. The dipole moment was calculated from the Guggenheim equation [12]. The theoretical dipole moments were calculated by a vector-additive scheme using the following values of the bond moments: $m(C_{sp^3}-H) = 0.28$, $m(C_{sp^2}-H) = 0.70$, $m(C_{sp^3}-C_{sp^2}) = 0.78$ D [13]; $m(C_{sp^2}-F) = 0.76$ D was calculated from the experimental dipole moment of pentafluorobenzene. In the calculation, the geometry of 1,2,3,4-tetraphenylcyclobutane was used [14].

Preparation of Polyfluoro-Substituted Stilbenes. A 4.68 g portion of benzyltriphenylphosphonium chloride [15], or 6.28 g of 2,3,4,5,6-pentafluorobenzyltriphenylphosphonium bromide [16] was added at ≤ 20°C in an argon current to a solution of phenyllithium (prepared from 0.25 g of Li and 1.76 ml of bromobenzene in 30-40 ml of absolute ether). The reaction mixture was then stirred for 30 min, and a solution of 1.8 g of pentafluorobenzaldehyde in 20 ml of ether was added dropwise at ≤ 20°C. The reaction mixture was stirred for 2-3 h at 20°C, poured onto ice with HCl, and extracted with ether. The ether solution was washed with water, dried over $CaCl_2$, and evaporated. The residue was washed with alcohol.

trans-2,3,4,5,6-Pentafluorostilbene (I), yield 70%, mp 136-138°C (from EtOH). UV spectrum (λ_{max}, nm (log ε)): 214 sh (4.10), 220 (4.18), 225 sh (4.17), 232 sh (4.03), 296 (4.48), 315 sh (4.27). ^{19}F NMR spectrum, ppm: 144.0, 157.9, 164.1 (2 : 1 : 2). PMR spectrum (CCl_3D, δ, ppm): 6.67 d, 7.57 d (CH=CH, system AB, J = 18 Hz,* 7.37 (Ph). Found: C 62.70; H 2.85; F 35.44%; mol. wt. 270 (mass spectrometrically). $C_{11}H_7F_5$. Calculated: C 62.23; H 2.61; F 35.16%; mol. wt. 270.

trans-2,2',3,3',4,4',5,5',6,6'-Decafluorostilbene (IV), yield 47%. mp 100-102°C (comp. [17]). ^{19}F NMR spectrum, ppm: 139.2, 154.5, 163.0 (2:1:2).

UV Irradiation of trans-2,3,4,5,6-Pentafluorostilbene (I). Experiment 1. A 0.01M solution of (I) in n-hexane was placed in a quartz test tube, 30 mm in diameter, and irradiated for 5 h with a DRS-500 Hg lamp at a distance of 25 cm at ~ 20°C. The data of the ^{19}F NMR spectrum showed that the product isolated after evaporation of the solution contains 95% of cis-2,3,4,5,6-pentafluorostilbene (II) and 5% of the trans-isomer (I). The pure cis-isomer (II) was isolated by sublimation at 60°C (bath temperature), mp 53.5°-54.5°C (from EtOH). UV spectrum (λ_{max}, nm (log ε)): 214 sh (4.39), 256 (4.14). PMR spectrum (δ, ppm): 6.16 d, 6.89 d (CH=CH, system AB, J = 12 Hz),* 7.12 (Ph). ^{19}F NMR spectrum, ppm: 139.2, 157.0, 163.5 (2:1:2). Found: C 61.98; H 2.55; F 35.44%; mol. wt. 270 (mass spectrometrically), 276 (vapor-phase osmometry). $C_{14}H_7F_5$. Calculated: C 62.63; H 2.55; F 35.14%; mol. wt. 270.

Experiment 2. A 0.2 g portion of stilbene (I) was placed between tightly compressed glass plates at a distance of 30 cm from a UV light source, and irradiated for 10 h. In the ^{19}F NMR spectrum of the product there are signals at 142.4, 156.8, 163.5 ppm. (2:1:2). Pure dimer (III) was isolated by recrystallization from EtOH, mp 119-120.5°C. PMR spectrum (δ, ppm): 4.87, 7.14 (2:5). μ_{exp} = 0.76 D. Found: C 62.18; H 2.65; F 34.65%; mol. wt. 533 (vapor-phase osmometry). $C_{28}H_{14}F_{10}$. Calculated: C 62.63; H 2.61; F 35.16%; mol. wt. 540.

Experiment 3. A 0.2 g portion of stilbene (I) in 2 ml of benzene was irradiated in a glass test tube for 23 h. The product isolated by evaporation of the solution contains, as shown by the ^{19}F NMR spectrum, 74% of the cis-isomer, 18% of photodimer (III) and 8% of initial (I).

UV Irradiation of cis-2,3,4,5,6-Pentafluorostilbene (II). A 0.2 g portion of compound (II) was placed n-hexane was irradiated by UV light for 30 h under the conditions. The data of ^{19}F NMR spectrum showed that the product obtained contained the initial compound (IV) and cis-decafluorostilbene (V) in a trans-stilbene (I).

UV Irradiation of trans-Decafluorostilbene (IV). Experiment 1. A 0.01 M solution of compound (IV) in n-hexane was irradiated by UV light for 30 h under the above described conditions. The data of ^{19}F NMR spectrum showed that the product obtained contained the initial compound (IV) and cis-decafluorostilbene (V) in a ratio of 1:4. The PMR spectrum of (V) is identical with that described in [17].

Experiment 2. A 0.2 g portion of solid decafluorostilbene (IV) was placed in a glass ampul, 3 mm in diameter, and irradiated for 40 h with UV light. The data of the ^{19}F NMR spectrum showed that the product isolated is identical with the initial compound (IV).

CONCLUSIONS

1. When their dilute solutions in organic solvents are irradiated with UV light, polyfluoro-substituted trans-stilbene undergo, in the same way as the nonfluorinated analog, a transformation into the cis-isomer, but not photocyclization.

2. Irradiation of a concentrated solution of trans-2,3,4,5,6-pentafluorostilbene in a hydrocarbon solvent with visible or UV light leads to its partial dimerization into the derivatives of cyclobutane. In contrast to the nonfluorinated analog, pentafluorostilbene undergoes photodimerization in the solid phase.

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