STRUCTURAL SPECIFICITY OF ELECTROPHILIC SUBSTITUTION OF REACTION OF 2-PHENYLBENZO[b]CYCLOPENTA[e]PYRAN

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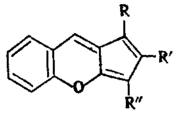
2-Phenyl- and 1,2-diphenylbenzo[b]cyclopenta[e]pyrans were subjected to formylation, nitration, and phenylsufonylation. It was shown by PMR spectroscopy that 2-phenylbenzo[b]cyclopenta[e]pyran undergoes substitution exclusively in the 1 position. The effect of the spatial orientation and the degree of electron-acceptor character of the introduced substituents on the chemical shift of the 9-H proton was studied.

It is known that dibenzo[b,f]cyclopentapyran [1], like azulene [2], readily undergoes formylation, nitration, and diazo coupling. We feel that reactions of this type can be readily accomplished with both 2-phenylbenzo[b]cyclopenta[e]pyran (I) [3] and 1,2-diphenylbenzo[b]cyclopenta[e]pyran (III) [4], but the site of incorporation of the first substituent must be accurately established in the first case, since the active 1 and 3 positions in I are nonequivalent both structurally and, probably, reactively.

The goal of the present research was to establish the orientation of the incorporation of substituents during electrophilic substitution in 2-phenylbenzo[b]cyclopenta[e]pyran I by PMR spectroscopy, as well as to study the effect of the spatial orientation and the degree of electron-acceptor character of the introduced substituents on the chemical shift of the 9-H proton in 2-phenyl- and 1,2-diphenylbenzo[b]cyclopenta[e]pyrans. The preferred incorporation of a formyl group in the 1 position of the benzocyclopentapyran system was indicated in [5] on the basis of the change in the chemical shift of the signal of the 9-H proton in the PMR spectra. The fact of the incorporation of the electrophilic particle in the 1 position of the 2-phenylbenzo[b]cyclopenta[e]pyran molecule (I) is not obvious, since it is not in agreement with the data on the

TABLE 1. Chemical Shifts of the Most Characteristic Protons in I-X



Compound	Structural formula			Chemical shifts, δ, ppm				
	R	R′	R″	1-H	3-H	9-H	CHO	aromatic H
I	H	C_6H_5	H	6,50	6,40	7,80	—	7,10—7,70
II	CHO	C_6H_5	H	—	6,22	8,80	9,75	7,10—7,90
III	C_6H_5	,, ,,	H	—	6,22	7,70	—	6,96—7,60
IV	C_6H_5	,, ,,	CHO	—	—	8,10	9,88	6,65—7,77
V	CHO	,, ,,	CHO	—	—	9,08	9,59 9,71	7,17—8,13
VI	NO_2	,, ,,	H	—	6,22	8,95	—	7,14—7,71
VII	$SO_2C_6H_5$	,, ,,	H	—	6,17	8,95	—	7,05—8,00
VIII	C_6H_5	,, ,,	NO_2	—	—	8,20	—	7,02—7,78
IX	C_6H_5	,, ,,	$SO_2C_6H_5$	—	—	8,13	—	6,66—7,78
X	C_6H_5	,, ,,	C_6H_5	—	—	7,77	—	6,80—7,42

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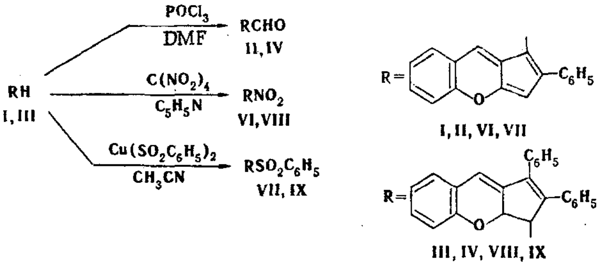
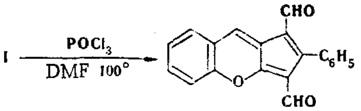
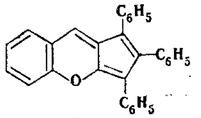
electron densities calculated for unsubstituted cyclopentapyran [6]. Since the rigorous establishment of the structural specificity of electrophilic substitution reactions in the benzocyclopentapyran system is of fundamental significance for an understanding of the electronic structure, the reactivities, and the reaction mechanisms for this class of nonbenzenoid aromatic compounds, we obtained a number of corresponding derivatives of I and III and investigated their PMR spectra; this confirmed the correctness of the initial assumption in a number of examples [5].





V



X

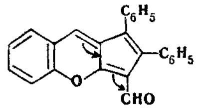
The formylation of I and III with the phosphorus oxychloride–dimethylformamide (DMF) complex at 20°C leads to the corresponding aldehydes II and IV in almost quantitative yield [5]. When I is heated with excess Vilsmeier reagent, 1,3-diformyl derivative V is obtained in high yield. The formation of the 3-formyl compound was not observed.

1,2,3-Triphenylbenzo[b]cyclopenta[e]pyran (X), which we obtained by heating 2,3,4-triphenyl-Δ^2-cyclopentenone [7] with excess salicylaldehyde in the presence of piperidine acetate, is not formylated by the Vilsmeier reagent even at 150°, and this constitutes evidence for the inertness of the 9 position or the benzene rings in this reaction.

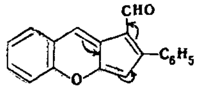
Electrophilic substitution in I and III by the action of cupric benzenesulfinate in acetonitrile leads to the formation of the corresponding phenylsulfones VII and IX. Nitration of I and III with tetranitromethane in pyridine gives the corresponding nitro derivatives VI and VIII, which are substituted in the same positions as the formylation and phenylsulfonylation products.

The data from the PMR spectra of the starting and final compounds confirm the structures of the substituted benzocyclopentapyrans obtained (Table 1) and show that 1,2-diphenyl derivative III is attacked exclusively in the 3 position, whereas 2-phenyl derivative I forms 1-substituted derivatives in the first step but under more severe conditions may also give 1,3-disubstitution products [for example, 2-phenyl-1,3-diformylbenzo-[b]cyclopenta[e]pyran (V)].

Whereas the introduction of a formyl group in the 1 position of I leads to a shift ($\Delta\delta$) of ~1.0 ppm to weak field of the 9-H signal, the shift for 3-formyl derivative IV is 0.4 ppm. In the first case the shift of the 9-H signal is explained by the powerful deshielding effect of the adjacent (in the peri position) electron-acceptor formyl group, whereas in IV (the amphi position) the latter shifts the 9-H signal to weak field only because of the electron-acceptor effect on the 9-C atom due to $\pi-\pi$ conjugation along the system of bonds, as depicted below:



IV



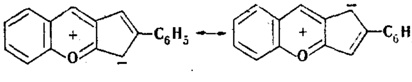
II

This sort of conjugation is also possible for aldehyde II, but in this case the deciding factor is spatial deshielding. The presence of two aldehyde groups in V leads to a still larger (1.28 ppm) shift of the 9-H signal to weak field.

The 9-H signals in the spectra of 1-phenylsulfonyl derivatives VI and VII are found at 8.95 ppm, i.e., they are shifted by 1.15 ppm to weak field as compared with starting I (7.80 ppm).

The 9-H signals in the spectra of VIII and IX, which have NO_2 and $C_6H_5SO_2$ groups in the 3 position, are found at, respectively, 8.20 and 8.13 ppm, i.e., they are shifted to weak field by only 0.50 and 0.4 ppm as compared with the spectrum of starting III.

One can explain the structural specificity of electrophilic attack in the 1 position of I if its molecule is depicted in the form of dipolar ion XI, which can exist formally in the form of limiting mesomeric states A and B. State B is thermodynamically more favorable, since the phenyl residue in this structure is conjugated through the double bond with the α position of the benzopyrylium cation, which has considerable positive charge; the same cannot be stated with regard to structure A, for a small negative charge should be concentrated in the β position of the benzopyrylium system. The electrophilic particle therefore attacks primarily the 1 position of the dipolar ion XI.



A XI B

EXPERIMENTAL

The PMR spectra of ~7 mole % solutions of the compounds in dioxane were recorded with a BS-487B spectrometer (operating frequency 80 MHz) at 41°. Dioxane and hexamethyldisiloxane were used as the internal standards. The accuracy in the measurements was ±0.02 ppm. The electronic spectra were recorded with an SF-14 spectrophotometer.

1,2-Diphenyl-3-formylbenzo[b]cyclopenta[e]pyran (IV). A 2.5-ml sample of phosphorus oxychloride was added dropwise with stirring and cooling to a solution of 0.64 g (2 mmole) of 1,2-diphenylbenzo[b]cyclopenta[e]pyran (III) in 75 ml of DMF. After 10 min, the mixture was treated with 400 ml of water containing 3 g of NaOH and extracted with 80 ml of benzene. The benzene extract was chromatographed on silica gel, the dark-red eluate was evaporated, and the residue was recrystallized from propyl alcohol to give 0.59 g (84.4%) of red-brown crystals of aldehyde IV with mp 245-246°. UV spectrum (THF): λ_{max} 490 nm (log ε 3.1). Found: C 86.2; H 4.7%. $C_{25}H_{16}O_2$. Calculated: C 86.1; H 4.6%.

2-Phenyl-1,3-diformylbenzo[b]cyclopenta[e]pyran (V). A 2.3-g sample of $POCl_3$ was added to a solution of 1.22 g (5 mmole) of I in 150 ml of DMF, and the mixture was heated to 100° and stirred at this temperature for 15 min. The red solution was then cooled and poured into water containing 8 g of sodium acetate. The reaction products were extracted with benzene, and the extract was chromatographed on silica gel. The bright-red zone of diformyl compound V was collected and worked up to give 1.05 g (70%) of bright-red plates with mp 238-239° (from benzene). UV spectrum (THF): λ_{max} 460 nm (log ε 3.4). Found: C 80.1; H 3.9%. $C_{20}H_{12}O_3$. Calculated: C 80.0; H 4.0%.

1-Nitro-2-phenylbenzo[b]cyclopenta[e]pyran (VI). A 0.4-g sample of tetranitromethane was added to a solution of 0.24 g of I in 20 ml of pyridine, and the mixture was stirred for 10 min, after which it was poured into 100 ml of water. The resulting crystals were removed by filtration to give 0.26 g (91%) of nitro compound VI with mp 246-248° (from benzene). UV spectrum (dioxane): λ_{max} 500 nm (log ε 3.6). Found: C 74.7; H 4.0; N 4.6%. $C_{18}H_{11}NO_3$. Calculated: C 74.7; H 3.8; N 4.8%.

1,2-Diphenyl-3-nitrobenzo[b]cyclopenta[e]pyran (VIII). The procedure of the preceding experiment was used to obtain this compound, with mp 275-276° (from propyl alcohol), in 89% yield. UV spectrum (THF): λ_{max} 460 nm (log ε 2.8). Found: C 78.7; H 4.3; N 4.0%. $C_{24}H_{15}NO_3$. Calculated: C 78.9; H 4.1; N 3.8%.

1-Phenylsulfonyl-2-phenylbenzo[b]cyclopenta[e]pyran (VII). A mixture of 0.49 g (2 mmole) of I, 1.5 g of cupric benzenesulfinate, and 150 ml of acetonitrile was refluxed with stirring, after which the solvent was evaporated, and the residue was chromatographed on silica gel (elution with benzene) to give bright-red sulfone VII, which was obtained as fine red needles with mp 164-165° (from heptane). The yield was 0.51 g (66%). UV spectrum (THF): λ_{max} 470 nm (log ε 3.4). Found: C 75.1; H 4.4; S 8.1%. $C_{24}H_{16}O_3S$. Calculated: C 75.0; H 4.2; S 8.3%.

1,2-Diphenyl-3-phenylsulfonylbenzo[b]cyclopenta[e]pyran (IX). The method of the preceding experiment was used to obtain this compound, with mp 197-198° (from propyl alcohol), in 77% yield. UV spectrum (THF): λ_{max} 470 nm (log ε 2.8). Found: C 78.4; H 4.6; S 6.9%. $C_{30}H_{20}O_3S$. Calculated: C 78.2; H 4.4; S 7.0%.

1,2,3-Triphenylbenzo[b]cyclopenta[e]pyran (X). A 3.1-g (10 mmole) sample of 2,3,4-triphenylcyclopenten-2-one was refluxed in 2 ml of salicylaldehyde in the presence of 1 g of piperidine acetate for 5 min, after which the mixture was cooled and dissolved in 50 ml of benzene. The benzene solution was washed with 5% aqueous KOH solution and water, dried with Na_2SO_4, and chromatographed on silica gel. The violet zone of X was eluted with benzene–hexane (1 : 1), and the eluate was evaporated to give 0.83 g (21%) of X in the form of violet-black needles with mp 178-179° (from benzene). UV spectrum (dioxane): λ_{max} 540 nm (log ε 3.2). Found: C 90.5; H 5.0%. $C_{30}H_{20}O$. Calculated: C 90.9; H 5.1%.

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INVESTIGATION OF THE CONDUCTIVITY OF ELECTRONIC EFFECTS BY THE AZIRIDINE RING

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Different degrees of conductivity of electronic effects through the aziridine ring in the direction of the C–C, C–N, and N–C bonds were observed for 1,2-diarylaziridines by ^1H and ^{19}F NMR spectroscopy.

Various researchers have shown [1-3] that a pronounced decrease in the algebraic value of the geminal spin–spin coupling constant (SSCC) occurs in aziridines as the electronegativity of the substituent in the 1 position increases. In order to study the relative effect of substituents in the 1 and 2 positions on $^2J_{HH}$ we synthesized two series of 1,2-disubstituted aziridines and studied their PMR spectra (Table 1).

The signs of the SSCC between the protons of the heteroring were determined by the INDOR method [4] (Fig. 1). The signs were found to be identical for the geminal and both vicinal SSCC, and they should therefore be considered to be positive ($^3J_{HH} > 0$ [5]).

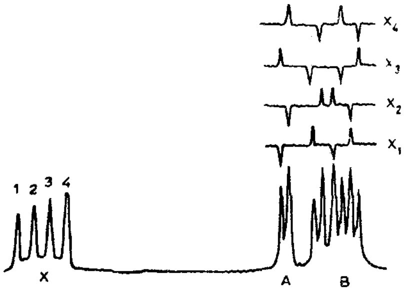

Fig. 1. INDOR spectra of the protons of the aziridine ring of 1,2-diphenylaziridine.

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