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SYNTHESIS OF STYRYL-SUBSTITUTED 2-PHENYL- AND 1,2-DIPHENYLCYCLOPENTA[b]-CHROMENES

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A number of styryl derivatives that are capable of undergoing formylation and acylation at the side CH=CH group were obtained from 1,2-diphenyl-3-formyl- and 2-phenyl-1,3-diformylcyclopenta[b]chromene by means of the Wittig reaction. It was observed that the Wittig reaction is structurally selective for 2-phenyl-1,3-diformylcyclopenta[b]chromene; the reaction proceeds only at the aldehyde group in the 3 position. Sulfuration of 2-phenyl-1,3-distyrylcyclopenta[b]chromene with sulfur leads to the formation of a new system — benzo[2',3']thiepino[4',5':4,5]cyclopenta[b]chromene. A significant bathochromic effect of the styryl groups on the electronic spectra of the cyclopentachromenes was noted.

We have obtained a number of styryl-substituted pseudoazulenes (III-IX) from 1,2-diphenyl-3-formyl- and 2-phenyl-1,3-diformylcyclopenta[b]chromenes (I and II) by means of the Wittig reaction.

It was shown that aldehyde I reacts with cinnamylidenephosphorane to give the virtually individual trans isomer (V), whereas cis (III) and trans (IV) isomers are formed in 24 and 52% yields, respectively, with benzylidenephosphorane. The structures of cis and trans isomers III and IV are confirmed by the presence in the IR spectra of bands of out-of-plane deformation vibrations of the hydrogen atoms in disubstituted cis- and trans-ethylenes [1] at 730 and 965 cm^{-1}; the alternative bands were absent in each case. Bands with λ_{max} 542 and 570 nm, respectively, are present in the electronic spectra of cis and trans isomers III and IV; this can be explained by partial deviation of the cisoid styryl group from the plane of the cyclopentachromene ring. In addition, cis isomer III was converted quantitatively to the trans isomer by the action of catalytic amounts of iodine in analogy with the isomerization of cis-1-styrylazulene [2]. Compound IV is capable of undergoing electrophilic substitution at the side CH=CH group, i.e., in the α position of the styryl residue farthest from the cyclopentachromene ring and simultaneously conjugated with it. A hypsochromic shift of 30 nm (40 nm in the case of XI) as compared with the spectrum of IV is observed in the spectrum of aldehyde X (as in the case of trifluoroacetyl derivative XI) (see Table 1).

The fact that stilbene does not undergo Vilsmeier formylation and the fact that approximately the same hypsochromic effect is also characteristic for β-(1-azulenyl)acrolein [3,

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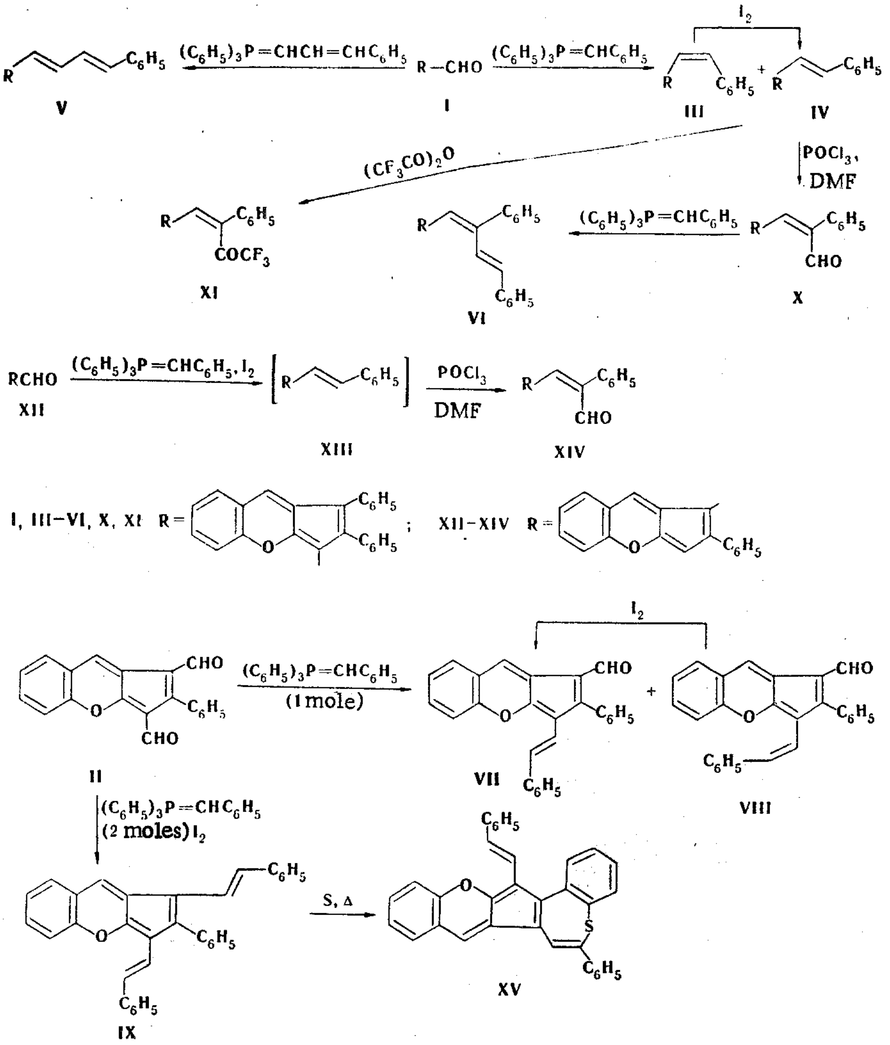
TABLE 1. Electronic Spectra of Cyclopenta[b]chromene Derivatives (in tetrahydrofuran)

Compound	λ_{max}, nm	lg ε	Compound	λ_{max}, nm	lg ε
I	490	3,10	X	540	2,97
II	460	3,40	XI	530	3,08
III	542	2,85	XII	480	3,39
IV	570	3,06	XIII	560	—
V	580	2,65	XIV	550	2,92
VI	550	2,84	XV	565, 434	2,79, 4,11
VII	570	3,43	XVI*	470	2,70
VIII	536	3,44	XVII*	512	2,91
IX	610	2,87	—	—	—

*Compounds XVI and XVII are 2-phenyl- and 1,2-diphenylcyclopenta[b]chromenes, respectively.

4] (as compared with 1-vinylazulene [2]) serve as conformation for our assigned X and XI structures. Successive alternation of the formylation steps in the Wittig reaction can serve as a method for lengthening the aryl-substituted polyene chains for ethylene or polyenes that contain at least one ring electron-donor aromatic substituent. By means of this method using the Wittig reaction we obtained conjugated diene VI, in the spectrum of which the position of the absorption band (550 nm) differs little from the position for cis-styryl derivative III (542 nm), since diene VI is the cis isomer (the cyclopentachromene ring and the trans-styryl group are regarded as the major substituents). trans Isomer V, which does not have steric hindrance to conjugation, absorbs at 580 nm, i.e., 30 nm in the longer-wave region than in the case of VI. The introduction of an additional trans-styryl



group in 1,2-diphenylcyclopenta[b]chromene (XVII) consequently leads to a bathochromic shift (∿60 nm) of the absorption band in the visible region, whereas 1,3-distyryl-2-phenylcyclopenta[b]chromene (IX) has a maximum at 610 nm, which is 140 nm higher than the value for starting XVI.

1-Styryl-2-phenylcyclopenta[b]chromene (XIII), which was obtained from aldehyde XII by the Wittig reaction, is stable only in solutions in low-polarity solvents (for example, in heptane or toluene). This compound completely unexpectedly underwent formylation at the CH=CH group (we were unable to detect the expected 3-formyl derivative). The reactivity of the α position of the styryl group in the 1 position of the cyclopentachromene ring with respect to electrophilic agents is probably higher (because of the vinylogous effect) than the reactivity of the unsubstituted 3 position. The unusually increased electron density in the 1 position affects even the structural selectivity of the Wittig reaction for dialdehyde II, which reacts with one equivalent of benzylidenetriphenylphosphorane to give only isomeric 3-styryl aldehydes VII and VIII in a ratio of 2:1. cis Isomer VIII is converted completely to trans isomer VII when it is heated with a catalytic amount of iodine in toluene for 10 min. The structures of aldehydes XIV, VII, and VIII are in agreement with both the electronic absorption spectra and the PMR spectra. The absorption maxima in the visible region for aldehydes XIV, VII, and VIII are found at 536, 570, and 550 nm, respectively, in agreement with the maximum value of the electromagnetic oscillator for structure VII. Formally speaking, the longest-wave absorption should have been expected for structure XIV; however, steric hindrance, which prevents complete coplanarity and, consequently, conjugation of the α,β-unsaturated aldehyde group with the remainder of the molecule, should inevitably be manifested here. The decrease in the molar extinction coefficient is also possibly associated with this (see Table 1).

The signals of the 9-H protons in the PMR spectra of XIV, VII, and VIII have chemical shifts of δ 8.90, 9.18, and 9.13 ppm, respectively. The minimum shift in the spectrum of aldehyde XIV is evidently associated with the remoteness of the formyl group from the 9-H proton and with partial disruption of the coplanarity in view of steric factors.

1,3-Distyryl derivative IX displays high reactivity in reactions with electrophilic reagents. For example, a new heterocyclic system — 6-phenyl-14-styrylbenzo[2',3']thiepino-[4',5':4,5]cyclopenta[b]chromene (XV) — is formed in 40% yield when it is heated with sulfur in quinoline. The XV structure was assumed on the basis of its mass spectrum and the fact that 3-monostyryl derivative IX does not undergo this sort of reaction with sulfur. Since the 1 position in XVI is more reactive, it is natural to also assume, in accordance with the principle of vinylogy, that the α position of the 1-styryl residue in distyryl derivative IX is more reactive than in the case of the 3-styryl residue. Attempts to close a second thiepine ring in XV were unsuccessful. The absorption band in the spectrum of XV (565 nm) is shifted 45 nm hypsochromically as compared with the spectrum of IX (610 nm), evidently because of the electron-acceptor effect of the sulfur atom. It should be noted that our attempts to close a thiepine ring in 2-phenyl-1,3-distyrylazulene were also unsuccessful.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in tetrahydrofuran (THF) were recorded with a Unicam SP-500 spectrophotometer. The PMR spectra of ∿7 mole % solutions of the compounds in dioxane were obtained with a Tesla BS-467 spectrometer. Thin-layer chromatography was carried out on Silufol; unless stated otherwise, the eluent was heptane—benzene (1:1).

1,2-Diphenyl-3-styrylcyclopenta[b]chromenes (III and IV). A 1.74-g (5 mmole) sample of 1,2-diphenyl-3-formylcyclopenta [b]chromene [5] was dissolved in 40 ml of boiling toluene, the solution was cooled to 20°C, 3 g (7.5 mmole) of triphenylbenzylphosphonium chloride and 5 ml of absolute alcohol containing 0.23 g of dissolved sodium were added successively, and the mixture was heated to the boiling point, during which the color changed from red to blue. The mixture was then cooled and treated with 40 ml of heptane and 80 ml of 70% aqueous methanol, and the mixture was shaken in a separatory funnel. The hydrocarbon layer was washed successively with aqueous methanol (three times) and water, dried with Na_2SO_4, and chromatographed on silica gel (elution with heptane). The first (violet) zone eluted contained cis isomer III, and the second (blue) zone contained trans isomer IV. The eluates were evaporated, and the residue was recrystallized from heptane to give 0.53 (24%) of III in the form of fine black crystals, with mp 187-188°C and R_f 0.56, and 1.15 g (52%) of IV as black-blue plates with mp 156-157°C and R_f 0.54. Found for III: C 90.6; H 5.3%. $C_{32}H_{22}O$. Calculated: C 91.0; H 5.2%. Found for IV: C 90.8; H 5.3%. $C_{32}H_{22}O$. Calculated: C 91.0; H 5.2%. Treatment of cis isomer III with traces of iodine in refluxing toluene for 30 min converted it quantitatively to trans isomer IV.

3-(4-Phenyl-1,3-butadien-1-yl)-1,2-diphenylcyclopenta[b]chromene (V). This compound was similarly obtained in 82% yield from aldehyde I and triphenylcinnamylphosphonium chloride as a dark-green powder with mp 163-165°C (from propyl alcohol) and R_f 0.51. Found: C 91.5; H 5.3%. $C_{34}H_{24}O$. Calculated: C 91.0; H 5.4%. Treatment with iodine produced no changes.

3-(2,4-Diphenyl-1,3-butadien-1-yl)-1,2-diphenylcyclopenta[b]chromene (VI). This compound was similarly obtained in 75% yield from aldehyde X and triphenylbenzylphosphonium chloride as a black crystalline powder with mp 117-118°C [from toluene—propyl alcohol (1:1)] and R_f 0.48. Found: C 91.1; H 5.6%. $C_{40}H_{28}O$. Calculated: C 91.5; H 5.4%.

1-Formyl-2-phenyl-3-styrylcyclopenta[b]chromenes (VII and VIII). Absolute alcohol (3 ml) containing 0.12 g of dissolved sodium was added rapidly to a suspension of 1.94 g (5 mmole) of triphenylbenzylphosphonium chloride in 20 ml of dry toluene, after which a solution of 1.50 g (5 mmole) of dialdehyde II was added, and the mixture was heated to the boiling point. It was then cooled and worked up as in the preparation of III. The hydrocarbon extract was filtered through a thick layer of silica gel and evaporated to a volume of 10 ml. A 2-ml sample of the solution was evaporated, and the overall yield of the mixture of styryl aldehydes (73%) was determined from the weight of the residue. A 2-ml sample of the concentrated solution of aldehydes VII and VIII was separated on large Silufol plates to give 180 mg (49% based on the total amount of starting material) of trans-styryl aldehyde VII and 90 mg (24%) of cis-styryl aldehyde VIII. Aldehyde VII had mp 231-232°C (from toluene) and R_f 0.29 [toluene—ether (9:1)]. Found: C 86.3; H 4.9%. $C_{27}H_{18}O_2$. Calculated: C 86.6; H 4.8%. Aldehyde VIII had mp 155-156°C (from toluene) and R_f 0.37 [toluene—ether (9:1)]. Found: C 86.2; H 4.9%. $C_{27}H_{18}O_2$. Calculated: C 86.6; H 4.8%. When cis-isomer VIII was refluxed in toluene with iodine for 10 min, it was converted quantitatively to trans-isomer VII.

2-Phenyl-1,3-distyrylcyclopenta[b]chromene (IX). A 10-ml sample of absolute alcohol containing 0.35 g of dissolved sodium was added to a suspension of 5.8 g (15 mmole) of triphenylbenzylphosphonium chloride in 50 ml of toluene, after which 1.5 g (5 mmole) of 2-phenyl-1,3-diformylcyclopenta[b]chromene [5] was added rapidly, and the mixture was heated to the boiling point. It was then cooled and treated with 50 ml of heptane, and the mixture was washed three times with 50-ml portions of 70% aqueous methanol and once with water. The solution was dried with Na_2SO_4 and treated with 10 ml of a toluene solution of iodine to bring about isomerization of the cis,cis and cis,trans isomers to trans,trans-isomer IX (this process was monitored by TLC). The solution was chromatographed with a column filled with silica gel; the green eluate was evaporated, and the residue was recrystallized from propyl alcohol to give 1.77 g (79%) of distyryl derivative IX in the form of dark-green needles with mp 175-176°C and R_f 0.50. Found: C 90.7; H 5.2%. $C_{34}H_{24}O$. Calculated: C 91.0; H 5.4%.

1,2-Diphenyl-3-(α-formylstyryl)cyclopenta[b]chromene (X). Dimethylformamide (10 ml) containing 1 ml of $POCl_3$ was added to a solution of 1.05 g (2.5 mmole) of IV in 100 ml of toluene, and the mixture was stirred for 30 min. A solution of 6 g of NaOH in 300 ml of water was added, and the mixture was shaken in a separatory funnel. The organic layer was dried with Na_2SO_4 and chromatographed on silica gel [elution with a mixture of toluene and ether (20:1)]. The violet eluate was evaporated, and the residue was recrystallized from propyl alcohol to give 0.99 g (88%) of dark-brown needles with mp 263-265°C. Found: C 87.5; H 5.0%. $C_{33}H_{22}O_2$. Calculated: C 88.0; H 4.9%.

1,2-Diphenyl-3-(α-trifluoroacetylstyryl)cyclopenta[b]chromene (XI). Trifluoroacetic anhydride (2 ml) was added to a solution of 2.11 g (5 mmole) of IV in 100 ml of benzene, and the mixture was refluxed for 30 min. The color of the solution changed from dark-blue to red. The mixture was cooled, and the benzene solution was washed with water, dried with Na_2SO_4, and chromatographed on silica gel to give 1.68 g (65%) of ketone XI with mp 184-186°C (from propyl alcohol) and R_f 0.19. Found: C 79.1; H 4.3; F 10.7%. $C_{34}H_{21}F_3O_2$. Calculated: C 78.8; H 4.1; F 11.0%.

1-(α-Formylstyryl)-2-phenylcyclopenta[b]chromene (XIV). trans-1-Styryl-2-phenylcyclopenta[b]chromene (XIII) was obtained (after isomerization with iodine in toluene) in the form of a solution in toluene containing heptane from 1-formyl-2-phenylcyclopenta[b]chromene (XII) [6] and triphenylbenzylphosphonium chloride by a method similar to the procedure used to obtain IV. Compound XIII is unstable in pure form (it is decolorized in a solution in toluene containing heptane after a few hours and is evidently oxidized by air oxygen during evaporation), and we therefore were able to measure only the R_f value [0.71, toluene–heptane (1:1)] and λ_{max} (560 nm). After chromatography, on silica gel, the eluate was treated with a solution of $POCl_3$ in DMF, and stable styryl adlehyde XIV was isolated in the usual way. Aldehyde XIV, with mp 210-211°C (from propyl alcohol) and R_f 0.60 [ether–benzene (1:2)], was obtained in 63% yield. Found: C 86.2; H 5.0%. $C_{27}H_{18}O_2$. Calculated: C 86.6; H 4.8%.

6-Phenyl-14-styrylbenzo[2',3']thiepino[4',5':4,5]cyclopenta[b]chromene (XV). A mixture of 1.12 g (2.5 mmole) of distyryl derivative IX, 0.16 g (5 mmole) of powdered sulfur, and 40 ml of freshly distilled quinoline was heated at 240°C for 30 min, after which it was cooled and dissolved in 100 ml of toluene. The toluene solution was washed with 5% hydrochloric acid until the odor of quinoline vanished, after which it was dried with Na_2SO_4 and chromatographed with a column filled with silica gel. The greenish-yellow eluate was evaporated, and the residue was recrystallized from propyl alcohol to give 0.48 g (40%) of brown needles with mp 235-236°C and R_f 0.61. The product sublimed in vacuo without decomposition. Mass spectrum: M^+ 478. Found: C 84.9; H 4.8; S 6.6%. $C_{34}H_{22}OS$. Calculated: C 85.3; H 4.6; S 6.7%.

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