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AZIRIDINYL KETONES AND THEIR CYCLIC ANILS.

11.* FLUORINE-CONTAINING PHOTOCHROMES

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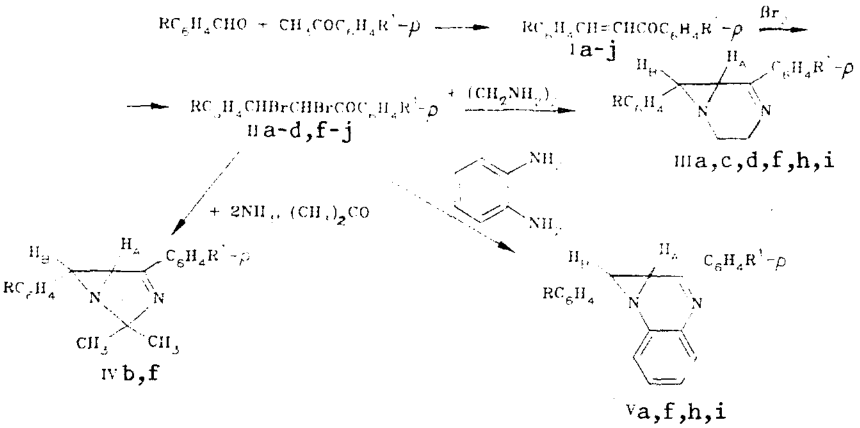
Chalcones with fluorine-containing groups were converted to α,β-dibromides and then to cyclic aziridinyl anils. The introduction of an electron-acceptor trifluoromethylsulfonyl group leads to a significant, although smaller as compared with the nitro group, bathochromic shift of the minimum of the reflection spectrum. Fluorine-containing substituents decrease appreciably the dark-decolorization time of the aziridinyl anils.

The photochromic properties of bicyclic compounds that contain an aziridine ring has been of interest to many researchers [1-3]. It has been noted [2] that a pronounced change in color (from light yellow to blue) occurs when there is an electron-acceptor p-nitrophenyl radical in the three-membered ring. It therefore seemed of interest to ascertain whether this is an effect of the manifestation of mesomeric activity of the nitro group or is characteristic for any strong electron acceptors. With this in mind, we accomplished the synthesis of cyclic aziridinyl anils with various fluorine-containing substituents and studied their structures and properties. We simultaneously studied the effect of these substituents on some spectral properties of intermediate compounds — chalcones and their dibromides.

The synthesis of III-V proceeds via the scheme



I—V a R=2-F, b R=4-F, c R=2-CF_3, d R=2-$SCHF_2$, e R=2-SO_2CHF_2, f R=4-SO_2CF_3, a-f R=H; g-i R=4-NO_2, g R^1=SO_2F, h R^1=SO_2CHF_2, i R^1=$SO_2C_3F_7$; j R=H, R^1=SO_2F

Crotonic condensation is realized in the case of acidic catalysis (in a mixture of glacial acetic acid and three to five drops of concentrated H_2SO_4). The progress of the reaction was monitored by TLC. o-Substituted benzaldehydes undergo this reaction with difficulty. To attain the yields of unsaturated ketones Ic-e indicated in Table 1 one must increase the H_2SO_4 concentration and the reaction time. For example, Id was obtained in a 13% solution of sulfuric acid in glacial acetic acid after 10 days at room temperature (heating caused resinification).

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*See [1] for Communication 10.

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TABLE 1. Characteristics of Fluorine-Containing Chalcones Ia-j and Their α,β-Dibromides IIa-j

Compound	mp, °C	UV spectrum λ, nm (ε·10^{-3})	IR spectrum, ν, cm^{-1}			PMR spectrum δ, ppm		SSCC, J, Hz	Yield, %
			C=O	C=C	NO_2	α-H	β-H		
Ia	36	302 (19,8)	1668	1610	—				86
Ib	75	311 (17,0); 252 (7,5)	1672	1601	—	7,38	7,75	15,4	68
Ic	69...70	292 (23,2)	1667	1615	—	7,17	7,87	15,6	60
Id	—*	308 (20,8); 236 (13,2)	1664	1602	—				48
Ie	83...84	291 (15,6)	1672	1601	—	7,08	8,23	15,5	40
If	120	297 (22,0); 250 (6,0)	1666	1608	—	7,68	7,81	15,5	65
Ig	188	319 (25,8); 251 (13,2)	1660	1612	1506, 1334	7,57	7,87	16,2	59
Ih	182	319 (24,4); 254 (13,3)	1668	1615	1516, 1342	7,57	7,86	16,3	55
Ii	174	324 (27,8); 225 (15,1)	1661	1612	1538, 1354	7,60	7,86	16,3	64
Ij	131	321 (19,3); 245 (17,4)	1657	1600	—	7,46	7,82	15,4	65
IIa	146	258 (16,9)	1680	—	—	5,75	5,57	11,0	51
IIb	150	258 (16,8)	1679	—	—	5,77	5,04	12,0	76
IIc	150	258 (13,4)	1691	—	—	5,83	5,58	11,5	70
IId	70	255 (18,1)	1665	—	—				88
IIf	170...172	252 (16,8)	1686	—	—	5,76	5,68	11,3	82
IIg	172	282sh (9,5); 253 (16,8)	1685	—	1534, 1355	6,13	6,13	—	90
IIh	180...181	279 sh, 255 (20,9)	1692	—	1528, 1355	5,74	5,67	11,3	66
IIi	134	275 (19,5); 247 sh	1695	—	1525, 1348	5,74	5,67	11,5	57
IIj	176	292 (3,1); 247 (19,9)	1685	—	—	6,13	6,05	12,0	84

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*For a reliable identification of the α and β protons in the dibromides we synthesized β-D-1-(4-Br-phenyl)-3-phenyl-2,3-dibromo-1-propanone; the signal at δ 5.57 ppm vanishes in the PMR spectrum of this compound.

In the IR spectra of ketones Ia-j (see Table 1) we unequivocally identified bands of stretching vibrations of C=O and C=C groups; the ratio of their intensities (the $\nu_{C=C}$ band is characterized by the higher intensity in all cases) indicates the preferableness of the s-cis conformation of the enone fragment [4]. When we recorded the IR spectra of the chalcones in solutions in CCl_4 or $CHCl_3$ at 1630-1650 cm^{-1} we observed a second substantially less intense $\nu_{C=O}$ band, which should be ascribed to the s-trans conformer [4]. The spin-spin coupling constant (SSCC) of 15.4-16.3 Hz found in an analysis of the PMR spectra of these ketones constitutes evidence for a trans geometry of the I molecules. It is known [5] that the $\nu_{C=O}$ values of chalcones are sensitive to the electronic effects of the substituents introduced into the aromatic rings, particularly in positions closest to the C=O group. This is also observed in the IR spectra of ketones Ia-j (for comparison, the $\nu_{C=O}$ band of chalcone is 1677 cm^{-1} in KBr). In the UV absorption spectra of chalcones Ia-j the effect of the introduced groups on the λ_{max} value of the long-wave absorption band is also manifested in complete conformity with their electronic character [6, 7].

Chalcone α,β-dibromides II were obtained by the action of bromine on ketones I in CCl_4, $CHCl_3$, or acetic acid. It is known [8, 9] that the presence of electron-acceptor substituents, as well as carrying out the bromination in low-polarity media, promotes the formation of erythro isomers. A comparison of the properties of II (see Table 1) with the properties of the chalcone dibromides previously described in [10] makes it possible to unequivocally assign them to the erythro series.

Compounds III were synthesized by the method in [3] by the reaction of dibromides II with ethylenediamine in the presence of triethylamine. The reaction of dibromides IIg-i (R = NO_2) proceeds in 30 min, while compounds with ortho substituents react with ethylenediamine slowly, and, in the case of IId, the reaction does not take place at all.

The synthesis of 2,2-dimethyl-4,6-diaryl-1,3-diazabicyclo[3.1.0]hex-3-enes was previously [2] accomplished on the basis of aziridinyl ketones, ammonia, and acetone. We have found [1] that by maintaining alcohol solutions

TABLE 2. Characteristics of Fluorine-Containing Cyclic Aziridinyl Anils III-V

Compound	mp, °C	UV spectrum, λ, nm (ε·10⁻¹)		IR spectrum, $\nu_{C=N}$,* cm⁻¹	PMR spectrum, δ, ppm*2		SSCC, J_{AB}, Hz	Yield, %
		molecular form	bipolar form		H_A	H_B		
IIIa	66	244 (17,8)	—*3	1621				42
IIIc	66	243 (16,6)	352, 480	1627				45
IIId	69...70	246 (18,8)	452	1613				47
IIIf	136	250 (25,0)	412, 544	1623				39
IIIh	174	249 (21,3), 280 sh	408, 608	1622	3,00	3,58	1,9	55
IIIi	156	249 sh, 272 (21,3)	412, 592	1620	3,01	3,58	1,9	65
IVb	110...112	245 (18,3), 273 sh	356, 482	1605	3,56	2,54	2,0	50
IVf*4	157	252 (17,8), 280 sh	414, 528	1607	3,55	2,51	1,7	25
Va	120	250 (30,0), 298 (15,1), 348 sh,	380, 508	1602				31
Vf	140 dec.	235 (34,0), 261 (23,8) 293 sh (15,5), 360 (7,5)	400, 578	1602	3,50	3,01	3,0	72
Vh	151...152	267 (45,5), 338 (23,4)	416, 606	1605				21
Vi	129...130	267 (25,2), 306 sh (18,0), 382 sh (6,5)	420, 600	1605	3,47	3,07	3,0	24

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*The $\nu_{NO}{}^{as}$ and $\nu_{NO_2}{}^{s}$ bands show up in the spectra of IIIh, IIIi, Vh, and Vi at 1519-1522 and 1350-1355 cm⁻¹, respectively.

*2Protons of the aziridine ring, δ_{CH_3}: 1.50 (IVb) and 1.53 ppm (IVf).

*3A photochromic effect was not discovered.

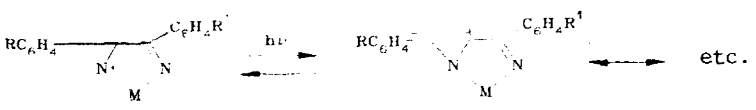
*4Mass spectrum of IVf, m/z (I_{rel}, %): 395 (21), 394 (75), 380 (21), 379 (79), 261 (15), 246 (58), 205 (40), 204 (49), 186 (17), 185 (86), 159 (18), 158 (93), 157 (56), 145 (25), 144 (23), 143 (37), 116 (29), 115 (16), 104 (100), 103 (32), 102 (53), 89 (31), 77 (40), 76 (23), 63 (23), 51 (39), 50 (31). The peaks of ion with m/z ≥ 50 and I_{rel} > 15% are presented.

of dibromides IIb, f, saturated with ammonia (saturation was carried out up to the point at which the dibromides dissolved completely), and by pouring acetone into them, one can obtain the desired IVb, f in high yields; the addition of catalytic amounts of ammonium salts facilitates the reaction. The dibromides (IIa, c-e) of chalcones with o-fluoro-containing groups do not undergo this reaction; this is probably due not so much to the electronic properties of these groups as it is to their steric effects.

Compounds Va, f, h, i were obtained by the reaction of dibromides II with o-phenylenediamine as in [3].

The formation of the desired III-V is confirmed by the results of elementary analysis and the spectral characteristics (Table 2). Thus the characteristic bands in the IR spectra of III are fully subject to the principles previously noted [11] for the spectra of 5-aryl-7-(4-nitrophenyl)-1,4-diazabicyclo[4.1.0]hept-4-enes. In particular, the observed low-frequency shift of $\nu_{C=N}$ as compared with linear azomethines (for example, benzalmethylamine with $\nu_{C=N}$ 1645 cm⁻¹ [12]) is also characteristic for the other aziridinyl anils IV and V. This was previously explained by flattening of the azastyryl fragment in the rings and found confirmation in the x-ray diffraction analysis of 2,2-dimethyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene [1]. Doublet signals of protons of the aziridine ring with spin-spin coupling constants 1.7-3.0 Hz, which attest to a trans orientation of these protons, were reliably identified in the PMR spectra of III-V. The protons of the methyl groups of IVb, f show up in the PMR spectra in the form of a singlet with δ 1.50 and 1.53 ppm, respectively. The structure of IVf was also confirmed by the mass spectrum (see Table 2). The π-electron fragments are unconjugated in the III-V molecules, and their electronic absorption spectra therefore are satisfactorily modeled via an additive pathway on the basis of the data in [13, 14] on the absorption of such fragments, which also confirms the structure of the aziridinyl anils.

Most III-V in the crystalline state have photochromic properties: under the influence of UV light their colorless crystals are red, green or blue. The observed changes in the color can be evaluated quantitatively by means of the reflection spectra (see Table 2). As already noted [1, 15], the photochromism of cyclic aziridinyl anils is due to opening, under the influence of UV light, of the three-membered ring to give ylids:



Substituent R plays the deciding role in stabilization of the ylid and redistribution of the electron density in it, and it is therefore natural that the introduction of R = 4-NO_2 group, which has a significant electron-acceptor effect, deepens the color of the ylid forms of IIIg-i and IVg-i, shifting the absorption maximum to 592-608 nm. As regards fluorine-containing groups, their effect on the reflection spectra of the ylids is substantially smaller. Thus the introduction of 2- or 4-F and 2-CF_3 has virtually no effect on the reflection spectra as compared with the ylids of unsubstituted compounds, the wavelength of the reflection minimum for which is 498-500 nm, whereas the introduction of a 2-$SCHF_2$ group is even accompanied by a hypsochromic shift, probably because of the increased steric hindrance. The R = 4-SO_2CF_3 group (σ_n = 1.04 [16]) has the most pronounced electron-acceptor character, but even its introduction is less effective as compared with the nitro group (σ_n =0.78). In our opinion, this may be explained by the shorter (as compared with the nitro group) conjugation chain of the chromophore. As demonstrated in [16], the terminal oxygen atoms participate in conjugation in the case of the nitro group, whereas in the case of the CF_3SO_2 group the conjugation chain is broken at the sulfur atom. A comparison of the spectral characteristics of ylids IIIf, IVf, and Vf makes it possible to reveal the role of the bridge group, which is leveled out in the spectra of the other substituted compounds. The ylid of aziridinoquinoxaline derivative Vf has the deepest color; in our opinion, this is due to its lengthier π system, in which the bridge grouping is included.

The R^1 substituents have no effect on the color of the ylid forms. Moreover, it was noted that the introduction of fluorine-containing R^1 substituents decrease the time of dark decolorization of IIIh, i and Vh, i crystals to 1.5-2 h. This time ranges from 7 h to 24 h for the analogous compounds with R^1 = H.

EXPERIMENTAL

The IR spectra of KBr pellets of I-V were recorded with a Specord IR-75 spectrometer. The electronic absorption spectra of solutions in methanol [(2-4)$\cdot 10^{-5}$ mole/liter] were recorded with a Specord UV-vis spectrometer. The electronic reflection spectra of the ylid forms were recorded with a Hitachi-330 spectrometer; the samples were prepared by applying the ground (into powders) III-V to chromatographic paper with subsequent irradiation with the UV light of a PRK-2 lamp. The PMR spectra of solutions in $CDCl_3$ were recorded with a Tesla 487-BS (100 MHz) spectrometer with tetramethylsilane as the internal standard. The mass spectrum of IVf was obtained with a Varian MAT CH-6 spectrometer with direct introduction of the sample into the ion source; the ionization-chamber temperature was 180°C, the ionizing-electron-energy was 70 eV, and the emission current was 100 μA.

The course of the reaction and the purity of the I-V obtained were monitored by TLC on Silufol UV-254 plates by elution with chloroform.

1-Phenyl-3-(4-trifluoromethylsulfonylphenyl)propen-1-one (If). A 2.38-g (10 mole) sample of 4-trifluoromethylsulfonylbenzaldehyde [17] and 1.2 g (10 mmole) of acetophenone were dissolved in 10 ml of glacial acetic acid, 1.5 ml of concentrated H_2SO_4 was added, and the mixture was allowed to stand in a dark place for 3 days. The precipitated crystals were removed by filtration, washed with water until the wash waters were neutral, and crystallized from methanol to give 2.21 g (65%) of light-yellow crystals of ketone If with mp 120°C.

Compounds Ia-e, g-j. These compounds were similarly obtained.

1-Phenyl-3-(4-trifluoromethylsulfonylphenyl)-2,3-dibromo-1-propanone (IIf). A solution of 0.48 g (3 mmole) of bromine in 2 ml of acetic acid was added in portions with stirring to a solution of 1.0 g (2.9 mmole) of If in 4 ml of acetic acid; each subsequent portion was added after complete decolorization of the preceding portion. The resulting precipitate was removed by filtration, washed successively with water and methanol, and crystallized from CCl_4 to give 1.2 g (82%) of IIf.

Compounds IIa-d, g-j. The compounds were similarly obtained. Dibromides IIa-c, g-j were crystallized from chloroform.

5-Phenyl-7-(4-trifluoromethylsulfonylphenyl)-1,4-diazabicyclo[4.1.0]hept-4-ene (IIIf). a 0.5-ml (7.5 mmole) sample of dried and distilled (over KOH) ethylenediamine and 1.0 ml (7 mmole) of triethylamine were added to 1.0 1 g (2 mmole) of 1-phenyl-3-(4-trifluoromethylsulfonylphenyl)-2,3-dibromopropan-1-one (IIf) in 20 ml of methanol, and the mixture was heated cautiously until the chalcone dibromide had dissolved completely, after which it was allowed to stand at room temperature for 2 days. The solvent was removed by distillation with a rotary evaporator, and IIIf was extracted from the residual oil with warm hexane. The hexane extract was concentrated until crystals began to develop. Cooling yield 0.3 g of IIIf.

Compounds IIIa, c, d. These compounds were similarly obtained.

Compounds IIIh, i. These compounds precipitated spontaneously without requiring addition concentration of the reaction mixtures. The precipitate was removed by filtration, washed with aqueous methanol, and crystallized from chloroform—methanol (1:3).

2,2-Dimethyl-4-phenyl-6-(4-trifluoromethylsulfonylphenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (IVf). Dry ammonia was passed for 2 h through a suspension of 1.0 g (2 mmole) of dibromide IIf in 10 ml of methanol and 1.0 ml of acetone, after which the reaction mixture was allowed to stand for 2 days in a refrigerator. The resulting precipitate was removed by filtration, washed with aqueous methanol (1:1) and alcohol, and crystallized successively from methanol—acetone (3:2) and ethanol. The yield was 0.2 g.

Compound IVb. This compound was similarly obtained.

1-(Trifluoromethylsulfonylphenyl)-2-phenyl-1,1*a*-dihydroazirino[1,2-*a*]quinoxaline (Vf). A mixture of 1.0 g (2 mmole) of IIf, 0.42 g (4 mmole) of 1,2-phenylenediamine, and 0.7 ml (5 mmole) of triethylamine in 10 ml of methanol was refluxed for 30 min, after which it was allowed to stand in the dark at room temperature for 2 days. The resulting violet precipitate was removed by filtration, washed on the filter with water and aqueous methanol (1:1), dried, and crystallized from methanol—acetone (3:1) to give 0.62 g of Vf with R_f 0.64 (chloroform).

Compounds Va, h, i. These compounds were similarly obtained.

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