2,6-Dimethyl-3,5-dimethoxycarbonyl-3,5-dichloro-4-phenyl-6-methoxy-3,4,5,6-tetrahydropyridine (IVa). A mixture of 3.01 g (0.01 mole) of 1,4-dihydropyridine Ia and 2.67 g (0.02 mole) of compound II in 200 ml of methanol was stirred for 2 h. A 110 ml portion of water was added, and the precipitate that separated out was crystallized from aqueous methanol (1:1) to yield 2.0 g (50%) of IVa in the form of crystals (Table 1).

Compounds IVc (by carrying out the reaction in ethanol), VIIa,b (with 4 moles of chlorosuccinimide II) and IXa (with 6 moles of chlorosuccinimide II) were obtained in a similar way (Table 1).

The formation of compounds Va, VIa and VIIIa was observed at 20°C in a DMSO-D_6 solution from compounds IVa (Va and VIa) and VIIa (VIIIa). The structure of compounds V, VI and VII was confirmed by the ^1H and ^{13}C NMR spectroscopy.

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REACTION OF 9-DIAZO-4-AZAFLUORENE WITH UNSATURATED COMPOUNDS AND CYCLIC KETONES

N. S. Prostakov, A. V. Varlamov,
A. Hussein, A. A. Fomichev,
N. A. Ryabova, and E. E. Stashenko

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Spiro[4-azafluorene-9,1'cyclopropanes] were obtained by the reaction of 9-diazo-4-azafluorene with various alkenes in the form of a mixture of geometrical isomers differentiated according to the position of the substituents in the cyclopropane ring and also also according to position relative to the pyridine ring. In the reaction of 9-diazo-4-azafluorene with cyclopentanone, di(4-azafluorene-9 nyl) oxide is formed, while from its reaction with cyclohexanone, 2'-oxo-spiro-[4-azafluorene-9,1'-cycloheptane] is obtained.

The availability of a 9-diazo-4-azafluorene (I) [1] made it possible to start a systematic study of this compound, particularly for obtaining previously unknown spiro compounds.

Spiro[4-azafluorene-9,1'-cyclopropanes] II-VII substituted in the cyclopropane ring were obtained in the reaction of the diazo compound I with ethyl cinnamate, cinnamaldehyde, trimethylvinylsilane, 2-methyl-4-penten-2-ol, maleic anhydride, and tetracyanoethylene.

The diacid VIII was obtained by hydrolysis of anhydride VI. The presence of two signals from each of the 1-H and 8-H protons in the PMR spectra (Table 1) of compounds II-VI shows that they are mixtures of Z- and E-isomers differentiated according to the disposition of the substituents in the cyclopropane ring relative to the pyridine fragment of azafluorene. The difference in the chemical shifts is especially great in compounds II and III, where the effect of the phenyl radical causes a strong-field shift (by 1.33-1.62 ppm of the 1-H proton

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P. Lumumba Peoples' Friendship University, Moscow, 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 495-501, April, 1990. Original article submitted April 5, 1988; revision submitted April 7, 1989.

TABLE 1. Chemical Shifts in the PMR Spectra of Spiro[4-azafluorene-cyclopropanes and Heptane] II-VII, IX and Azafluorenes X-XII

Compound	δ, ppm							
	1-H	2-H	3-H	5-H	6-H	7-H	8-H	9-H
Z-II	6,45	6,83	8,48	8,15	7,45	7,50	7,76	—
E-II	8,07	7,22	8,61	8,10	7,06	7,36	6,23	—
Z-III	6,46	6,86	8,50	8,06	6,90…7,80		6,90…7,80	—
E-III	6,90…7.80		8,61	8,06			6,31	—
IV	7,36 7,49	7,18 7,18	8,56 8,56	8,20 8,20	7,10…7,90			— —
V*	7,13…8,48		9,01 8,77	8,56 8,56	7,13…8,48			— —
VI**	8,55 8,57	7,0…7,88		7,95 7,95	7,0…7,88			— —
VII**	7,92	7,55	8,79	8,15	7,66…7,86			—
IX	7,79	7,18	8,58	7,79	7,46	7,41	7,58	—
X	7,78	7,17	8,52	8,09	7,30…7,70			3,95
XI*	7,3…8,8		9,05		7,30…8,80			4,25
XII	7,56	7,15 7,12	8,58	8,00	7,38…7,58		7,58 7,68	5,82 5,85

	δ, ppm
	Substituents at $C_{(9)}$
Z-II	CH_3 1,17; 2′-H 3,22; 3′-H, CH_2 4,1…4,2; C_6H_5 7,15…7,18
E-II	CH_3 1,21; 2′-H 3,21; 3′-H, CH_2 4,1…4,2; C_6H_5 7,27…7,29
Z-III	2′-H 4,27; 3′-H 3,43; CHO 9,92 C_6H_5 6,90…7,80
E-III	2′-H 4,27; 3′-H 3,31; CHO 9,92
IV	$Si(CH_3)_3$ 0,08; 3′-H 1,07; 2′-H 2,06 $Si(CH_2)_3$ 0,08; 3′-H 1,83; 2′-H 2,06
V*	CH_3 0,97 CH_3 1,10 CH_2, 2′-H, 3′-H 1,76…2,40
VI**	2′-H, 3′-H 3,25
VII**	—
IX	3′-H 3,10; 4′H 2,86; 5′H…7′H 0,2…2,29
X	CH_2OH 3,60; $(CH_2)_5$ 0,5…2,3
XI*	CH_2Cl 3,50; $(CH_2)_5$ 0,5…2,3
XII	—

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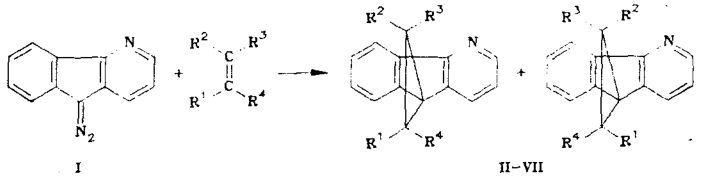
*Spectrum of hydrochloride.

**The spectrum was recorded in DMSO-D_6.



I

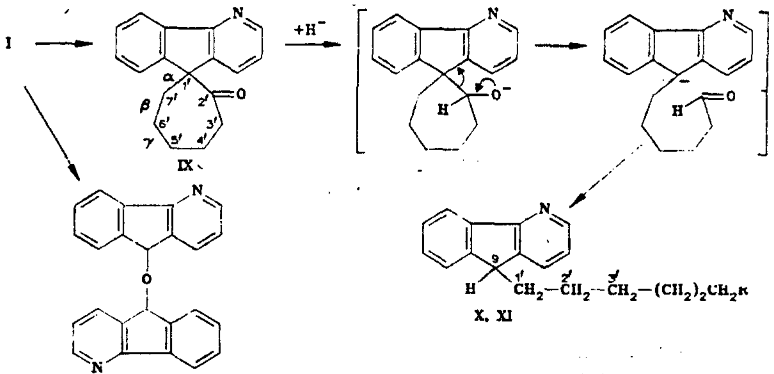
II–VII

II $R^1=C_6H_5$, $R^3=COOC_2H_5$; III $R^1=C_6H_5$, $R^3=CHO$; IV $R^1=Si(CH_3)_3$; V $R^1=CH_2-C(CH_3)_2OH$; VI $R^1+R^2=(CO)_2O$; VII $R^1=R^2=R^3=R^4=CN$; VIII $R^1=R^2=COOH$; II—V $R^2=H$; IV—VI, VIII $R^3=R^4=H$; II, III $R^4=H$

and by 1.53 ppm of the 8-H proton) of the aromatic proton in the cis-position to it. The ratio of the Z- and E-isomers in the case of compounds II and III is approximately 1:2, while for compounds IV-VII it is about 1:1. The values of the vicinal constants of the spin-spin interaction ($_{2',3'}$ = 7.0-7.5 Hz) of the cyclopropane ring protons in the spectra of compounds II and III show that on addition of the diazo compound I to ethyl cinnamate and cinnamaldehyde, the trans-disposition of the cyclopentanes is retained.

There are peaks of molecular ions of various intensities in the mass spectra of compounds II-VII, corresponding to their empirical formulas (Table 2). The fragmentation of these ions is characterized by splitting off of the substituents with the formation of $[M - R^1]^+$ fragments, and in the case of compounds II and III, also of the $[M - R^3]^+$ fragments, and cleavage of the cyclopropane ring. Thus, $[M - CR^2R^1]^+$ and $[M - CHR^3]^+$ ions are formed for compounds II and III. In the mass spectra of all the compounds, 166* and 167 fragments are observed which are formed as a result of the transfer of one or two hydrogen atoms, respectively, to the 4-azafluorene fragment. The fragmentation of ion M^+ of anhydride VI is characterized by a successive elimination of the CO and CO_2 particles. The appearance of the $[M - C_2H_5]^+$ ion 312 (5) in the mass spectrum of ester II should be noted. This ion was previously observed in the mass spectrum of 2-ethoxycarbonylspiro[4-azafluorene-9,1'-cyclopropane] [2].

In order to carry out the synthesis of acyclic spiroketones containing 4-azafluorene fragments, we studied the reaction of diazo compound I with cyclopentanone and cyclohexanone in the presence of boron trifluoride etherate. Using cyclohexanone, 2'-oxospiro[4-azafluorene-9,1'-cycloheptane] (IX) was obtained as a result of ring expansion.



XII

X R=OH; XI R=Cl

The spiro compound IX was characterized as an oxime. Reduction of the spiro compound IX with sodium borohydride is accompanied by cleavage of the cycloheptane ring at the $C_{(1')} - C_{(2')}$ bond, which, in analogy with the reductive splitting of α-substituted ketones [3], is due to the formation of a stable 4-azafluorenyl anion in the course of the reaction. Instead of the expected secondary alcohol, 9-(ω-hydroxyhexyl-4-azafluorene (X) was obtained in quantitative yield. It was converted by the action of thionyl chloride into 9-(ω-chlorohexyl)-4-azafluorene (XI). In the PMR spectra of azafluorenes X and XI (Table 1), in contrast to the spiro-compound IX, there are 9-H proton signals at δ 3.95 and 4.25 ppm, respectively, which are triplets with $J_{9,1'}$ = 8 Hz. Peaks of molecular ions are observed in the mass spectra of compounds IX-XI (Table 2), which correspond to their empirical formulas. The fragmentation of compound IX proceeds from the open form of ion M^+, formed as a result of cleavage of the cycloheptane ring at the $C_{(1')} - C_{(2')}$, bond. It is characterized by the elimination of a molecule of CO and cleavage of the α-, β and γ-bonds. The dissociation of the M^+ ions of azafluorenes X and XI involves a splitting off of an ω-substituted hexyl radical and its cleaveage at the $C_{(1')} - C_{(2')}$ bond. Thus, hydrogen migrates from the split hexyl radical to the 4-azafluorene fragment, which results in the appearance of the peak of the 167 ion.

The reaction of the diazo compound I with cyclopentane proceeds anonmalously. Instead of the expected spiroketone, di(4-azafluoren-9-yl) oxide XII was isolated from the reaction products in a 25% yield. It has been established mass spectrometrically that the neutral reaction products contain a considerable amount of 2-cyclopentylidenecyclopentanone, the product of a crotonic condensation of cyclopentanone. A peak of the molecular ion 348 (20) is observed in the mass spectrum of ester XII, which corresponds to its empirical for-

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*Here and below the m/z values (I_{rel}, %) are given for the ion peaks.

TABLE 2. Mass Spectra of Compounds II-VII, IX-XI (10 of the most intense peaks are given)

Compound	m/z (relative intensity, %)
II	134 (11), 165 (17), 166 (29), 167 (20), 190 (13), 253 (10), 266 (19), 267 (21), 268 (100), 341 (M^+, 15)
III	91 (7), 181 (7), 218 (8), 219 (11), 256 (8), 267 (12), 268 (100), 269 (60), 296 (7), 297 (M^+, 12)
IV	73 (50), 166 (5), 179 (3), 191 (9), 192 (7), 220 (5), 234 (5), 250 (13), 264 (13), 265 (M^+, 100)
V	77 (10), 91 (8), 167 (11), 179 (27), 192 (20), 206 (14), 247 (50), 250 (10), 264 (5), 265 (M^+, 100)
VI	65 (5), 77 (6), 91 (5), 105 (7), 166 (16), 183 (18), 191 (18), 219 (100), 262 (8), 263 (M^+, 60)
VII	65 (5), 77 (6), 91 (6), 166 (25), 192 (4), 229 (100), 266 (7), 267 (6), 292 (3), 293 (M^+, 15)
IX	75 (23), 96 (29), 152 (29), 166 (50), 167 (56), 179 (100), 192 (78), 206 (46), 235 (20), 263 (M^+, 75)
X	139 (11), 140 (8), 152 (10), 153 (4), 166 (43), 167 (34), 180 (100), 236 (10), 249 (6), 267 (M^+, 21)
XI	152 (7), 153 (5), 166 (15), 167 (32), 180 (15), 236 (8), 249 (11), 250 (6), 285 (M^+, 100), 287 (M^+, 33)

mula. The fragmentary ions 182 (100) and 166 (55) are formed as a result of splitting off of ion M^+ at the $C_{(9)} - O$ bond. This cleavage is accompanied by the migration of hydrogen, which causes the appearance of an intense peak of the 167 (78) ion, corresponding to the molecular ion of 4-azafluorene. The presence of two singlet signals of the 9-H proton with a ratio of 1.0:2.5 in the PMR spectrum of compound XII indicates that it is a mixture of two diastereomers.

Ether XII was obtained in 44% yield in the reaction under the same conditions of the diazo compound I with 4-azafluoren-9-ol. Ether XII is formed in the same yield when a catalytic amount of water is added to an ether solution of the diazo compound I and boron trifluoride etherate. When a threefold amount of water was used in the reaction, then only 4-azafluoren-9-ol was obtained. From these experimental data it can be assumed that in the reaction of the diazo compound I with water, which separates out during the crotonic condensation of cyclopentanone, 4-azafluoren-9-ol is first formed. The reaction of this alcohol with the next molecule of diazo compound I results in the formation of ether XII.

It is known [4] that in the reaction of α- and α,α'-disubstituted cyclopentanone with ethyl diazoacetate in the presence of boron trifluoride etherate, the spiroketone ring expands with a high regioselectivity. This indicates that the transition state formed as a result of the nucleophilic attack of the diazo compound I on the carbonyl carbon atom of cyclopentanone from sp^2 to sp^3 leads to the occurrence of four screened interactions [5]. Therefore, the reaction of the diazo compound with water, formed as a result of the crotonic condensation becomes more favorable. However, in the case of cyclohexanone, the transition from sp^2 – hybridization of the carbonyl carbon atom to sp^3 – hybridization is accompanied by the elimination of two screened interactions, which possibly stabilizes the transition state. As a result, the expansion of the cyclohexane ring proceeds much more rapidly than the crotonic condensation, and ether XII is not formed.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets. The PMR spectra were run on a WP-80 spectrometer, and for the compounds II and XII on a Bruker WM-400 spectrometer in $CDCl_3$, using TMS as internal standard. The mass spectra were obtained on a MX-1303 mass spectrometer, equipped with a direct introduction system, at an ionization energy of 70 eV, and at admission temperatures of 60...150°C. For column and thin layer chromatography, Al_2O_3 grade II of activity and Alufol plates with a stationary Al_2O_3 layer, as well as silica gel brands L 100/160 and Silufol UV-254 were used. The development was carried out with iodine vapors.

The data of the elementary analysis of C, H, N correspond to the calculated values.

2'Phenyl-3'-ethoxycarbonylspiro[4-azafluorene-9',1-cyclopropane (II, $C_{23}H_{19}NO_2$). A mixture of 0.36 g (1.8 mmole) of diazo compound I and 1.5 g (8.5 mmole) of ethyl cinnamate was held for 30 min at 120...125°C. The mixture was cooled and chromatographed on aluminum oxide (h = 45 cm, d = 2 cm), eluting with a 10:1 heptane-ethyl acetate mixture. First, 1.2 g of ethyl cinnamate was eluted, and then 0.15 g (25%) of the spiro-compound II (ratio of Z:E isomers = 1.0:1.7). Colorless crystals, mp 118...120°C (from heptane). R_f 0.44 (Al_2O_3) heptane – ethyl acetate, 3:1). IR spectrum: 1730 cm^{-1} (CO).

2'Phenyl-3'-formylspiro[4-azafluorene-9,1-cyclopropane] (III, $C_{21}H_{15}NO$) . A mixture of 0.3 g (1.5 mmole) of the diazo compound I and 0.26 g (8.1 mmole) of cinnamaldehyde was held for 30 min at 120...125°C in a nitrogen current. The reaction products were isolated chromatographically on aluminum oxide (h = 40 cm, d = 1 cm) and eluted with a 10:1 heptane-ethyl acetate mixture. First 1 g of the initial cinnamaldehyde was eluted, and then 0.1 g (33%) of the spiro compound III (ratio of Z:E isomers = 1:2). Colorless crystals, mp 164...166°C (from heptane). R_f 0.23 (Silufol, heptane- ethyl acetate, 3:1). IR spectrum: 1718 cm^{-1} (CO).

2'-Trimethylsilylspiro[4-azafluorene-9',1-cyclopropane (IV, $C_{17}H_{19}NSi$). A mixture of 0.3 g (1.5 mmole) of the diazo compound I and 10 g (0.1 mole) of trimethylvinylsilane was held for 6 h at 70...80°C in a nitrogen current. The residue (0.35 g) remaining after distillation of excess trimethylvinylsilane was chromatographed on silica gel (h = 45 cm, d = 1 cm) and eluted with a 10:1 heptane-ethyl acetate mixture. Yield, 0.3 g (75%) of spiro compound IV (ratio of Z:E isomers = 1:1). A yellowish oil substance, R_f 0.71 (Silufol, hexane-ethyl acetate, 1:1). IR spectrum: 830 and 1255 cm^{-1} ($SiCH_3$).

2'-(2"-Hydroxy-2"-methylpropyl)spiro[4-azafluorene-9',1-cyclopropanel] (V, $C_{18}H_{19}NO$). A mixture of 0.2 g (1 mmole) of the diazo compound I and 0.5 g (5.7 mmoles) of dimethylallylcarbinol was held for 1 h at 120...125°C in a nitrogen current. The mixture was cooled and acidified with 18% hydrochloric acid to pH 1. The neutral reaction products were extracted with ether (3 × 35 ml). The residue of salts of the organic bases was extracted with ether (3 × 80 ml), and the extact was dried over magnesium sulfate. The residue (0.2 g) remaining after the evaporation of ether was chromatographed on silica gel (h = 40 cm, d = 1 cm) and eluted with a 10:1 heptane-ethyl acetate mixture. Yield 0.15 g (56%) of compound V (ratio of Z:E isomers ≈1:1). R_f 0.15 (Silufol, hexane-ethyl acetate, 1:1).

Hydrochloride of compound V ($C_{18}H_{19}NO \cdot HCl$), mp 160...162° (from absolute acetone) IR spectrum: 2580 ($\overset{+}{N}H$), 3425 cm^{-1} (OH).

Spiro[4-azafluorene-9'1-cyclopropane]2',3'-dicarboxylic acid anhydride (VI, $C_{16}H_9NO_3$). A mixture of 0.2 g (1 mmole) of diazo compound I and 0.2 g (2 mmoles) maleic anhdride was boiled for 20 min at 10 ml of absolute toluene. The residue remaining after the evaporation of toluene was crystallized from ethyl acetate. Yield, 0.15 g (55%) of anhydride VI (ratio of Z:E isomers ≈1:2). Colorless crystals, mp 123...125°C, R_f 0.25 (Silufol, heptane-ethyl acetate, 1:1). IR spectrum: 1735, 1795, 1873 cm^{-1} (CO).

2',2',3',3'-Tetracyanospiro[4-azafluorene-9',1-cyclopropane] (VII, $C_{18}H_7N_5$). A solution of 0.7 g (3.63 mmoles) of diazo compound I and 0.7 g (5.14 mmoles) of tetracyanotheylene in 25 ml of absolute tetrahydrofuran was held for 7 days at 20°C. The residue (1.2 g) remaining after the evaporation of tetrahydrofuran was chromatographed on silica gel (H = 50 cm, d = 1 cm) and eluted with a 10:1 heptane-ethyl acetate mixture. First, 0.2 g of tetracyanoethylene was eluted, and then 0.8 g (75%) of compound VII. Yellow crystals, mp 217...219°C (dec, from heptane) R_f 0.64 (Silufol, hexane-ethyl acetate, 1:1). IR spectrum: 2250 cm^{-1} (CN).

2',3'-Dicarboxyspiro[4-azafluorene-9',1'-cyclopropane] (VIII, $C_{16}H_{11}NO_4$). A 0.42 g portion (1.6 mmole) of anhydride VI was dissolved in 10 ml of 20% aqueous solution of sodium hydroxide. After 1 h, the reaction mixture was neutralized with a 2 N solution of hydrochloric acid to pH 7. Yield, 0.3 g (70%) of diacid VIII. Colorless crystals, mp 243...245°C (dec., from alcohol).

2'-Oxospiro[4-azafluorene-9',1-cyclopropane] (IX, $C_{18}H_{17}NO$) A 0.2 g portion (1.4 mmole) of boron trifluoride etherate was added to a solution of 0.6 g (3.1 mmoles) of diazo compound I in 2 g (20 mmoles) of cyclohexanone, cooled to 0°C. The mixture was stirred at 0°C for 3 h, and then made alkaline to pH 11 with a 20% aqueous solution of sodium hydroxide. The reaction products were extracted with ether (4 × 35 ml) and 10 ml of 10% hydrochloric acid was added to the extract. The ether layer was separated, washed with a 5% aqueous solution of sodium carbonate, and dried over magnesium sulfate. The residue remaining after the evaporation of ether was chromatographed on a column with silica gel, and eluted with hexane. First, 0.5 g of cyclohexanone was eluted, and then 0.4 g of 2-cyclohexylidenecyclohexanone. A colorless liquid, R_f 0.7 (Silufol, hexane-ethyl acetate, 2:1). Found: M^+ 178. $C_{12}H_{18}O$. Calculated: M 178.

The residue of salts of the organic bases was made alkaline to pH 10 with a 20% solution of sodium hydroxide. The organic bases were extracted with ether (3 × 30 ml) and the extract was dried over magnesium sulfate. The residue (0.9 g) remaining after the evaporation of ether was chromatographed on a column (h = 40 cm, d = 1.5 cm) with aluminum oxide and eluted with a 10:1 heptane-ethyl acetate mixture, to yield 0.6 g (73%) of spiroketone IX. Yellow crystals. mp 106...108°C (from heptane), R_f 0.23 (Silufol, hexane-ethyl acetate, 3:1). IR spectrum: 1700 cm^{-1} (CO).

Oxime of ketone IX ($C_{17}H_{18}N_2O$). A mixture of 0.6 g (2.2 mmoles) of spiro-ketone IX and 0.7 g (10 mmoles) of hydroxylamine hydrochloride in 15 ml of pyridine was boiled for 5 h, then poured into 50 ml of water, and 0.55 g (87%) of oxime was filtered. Pale yellow crystals, mp 227...229°C (heptane-ethyl acetate), R_f 0.3 (Silufol, hexane-ethyl acetate, 1:1). IR spectrum 3200 (OH), 930 cm^{-1} (NO). PMR spectrum: 0.9...2.1 (8H, m, 4'-...7-CH_2); 3.00 (2H, m, 3'-CH_2); 7.15 (1H, d.d, 2-H, $J_{2,3}$ = 4.8 Hz, $J_{2.1}$ = 8 Hz); 7.38 (1H, t.d, 7-H, $J_{7,5}$ = 1.7 Hz, $J_{7.8}$ = 8 Hz); 7.42 (1H, t.d, 6-H, $J_{6.7}$ = 8 Hz, $J_{6.8}$ = 1.7 Hz); 7.55 (1H d.d, 8-H); 7.78 (1H, d.d, 1-H, $J_{1,3}$ = 1.7 Hz); 7.99 (1H, d.d, 5-Hm, $J_{5.4}$ = 8 Hz); 8.52 (1H, d.d, 3-H), 11.34 ppm (1H, s, N-OH).

9-(ω-Hydroxyhexyl)-4-azafluorene (X, $C_{18}H_{21}NO$). A solution of 0.4 g (1.5 mmole) of ketone IX in 30 ml of ethanol was added in the course of 10 min to a suspension of 0.4 g of sodium borohydride (0.01 mmole) in 30 ml of ethanol, and the mixture was boiled for 4 h. A 100 ml portion of water was added, the reaction products were extracted with ether (3 × 30 ml), and the extract was dried over magnesium sulfate. After the evaporation of ether, a yellowish viscous mass remained (0.38 g 95%). R_f 0.1 (Al_2O_3, hexane-ethyl acetate , 3:1). Found: M^+ 267. Calculated: M 267. This residue was converted into a hydrochloride. Yields, 0.42 g of hydrochloride of compound X ($C_{18}H_{21}NO \cdot HCl$). Colorless crystals mp 140...142°C (from absolute acetone). IR spectrum: 2380...2710 (NH), 3400 cm^{-1} (OH).

9-(ω-Chlorohexyl)-4-azafluorene hydrochloride (XI, $C_{18}H_{20}ClN \cdot HCl$). A solution of 0.2 g (0.8 mmole) of alcohol X in 10 ml of thionyl chloride was boiled for 3 h. The residue (0.18 g) remaining after the evaporation of thionyl chloride was crystallized from absolute acetone. Yield, 0.13 g (55%) of a hydrochloride of compound XI. Colorless crystals, mp 134...135°C, R_f 0.52, (Al_2O_3, hexane-ethyl acetate, 3:1).

Di(4-azafluorene-9-yl) oxide (XII, $C_{24}H_{16}N_2O$). A. A 0.2 g portion (1.4 mmole) of boron trifluoride etherate was added to a solution of 0.4 g (2 mmoles) of diazo compound I in 1.4 g (0.18 mole) of cyclopentanone, cooled to 0°C. The mixture was stirred for 3 h at 0°C (the course of the reaction was monitored by TLC). The mixture was made alkaline with a 15% solution of sodium hydroxide to pH 10...11. The reaction products were extracted with ether (3 × 50 ml). The extract was treated with 20 ml of 10% hydrochloric acid. The ether layer was separated, washed with a 5% solution of sodium carbonate, and dried over magnesium sulfate. The residue remaining after the evaporation of ether was chromatographed on a column with silica gel (h = 50 cm, d = 1 cm) and eluted with hexane. Yield, 0.12 g of 2-cyclopentylidene-cyclopentanone. Colorless oil, R_f 150. $C_{10}H_{14}O$). Calculated: M 150.

The residue of salts of the organic bases was treated with a 15% solution of sodium hydroxide to pH 10. The bases were extracted with ether (4 × 25 ml). The extract was dried over magnesium sulfate. The residue remaining after the evaporation of ether was chromatographed on a column (h = 50 cm, d = 2 cm) with aluminum oxide, and eluted with a 10:1 heptane-ethyl acetate mixture. First, 40 mg of 4-azafluorenone was separated. Yellowish crystals mp 138...140°C (from heptane). Then 0.16 g (25%) of ether XII was eluted. Yellowish crystals, mp 162...164°C (from a mixture of heptane with ethyl acetate), R_f 0.2 (Silufol, hexane-ethyl acetate, 1:1).

B. A solution of 0.11 g (0.5 mmole) of the diazo compound I in 10 ml of absolute ether was added dropwise in the course of 20 min, in a nitrogen current, to an emulsion of 0.1 g (0.55 mmole) of 4-azafluoren-9-ol and 0.2 g (1.4 mmole) of boron trifluoride etherate in 25 ml of absolute ether, cooled to 0°C. After 3 h (the course of reaction was monitored by TLC), the reaction mixture was heated to 20°C, and made alkaline with a 20% solution of sodium hydroxide to pH 11. The reaction products were extracted with ether (3 × 20 ml) and the extract was dried over magnesium sulfate. The residue remaining after the evaporation of ether was chromatographed on aluminum oxide (h = 40 cm, d = 2 cm), and eluted with a 5:1 hexane-ethyl acetate mixture. Yield, 0.08 (44%) of ether XII, mp 164...166°C (heptane). A sample mixed with the compound obtained by method A, did not give a depression of the melting point.

C. A drop of water was added to an emulsion of 0.1 g (0.5 mmole) of the diazo compound I and 0.2 g (1.4 mmole) of boron trifluoride etherate in 25 ml of absolute ether, purged with a current of nitrogen and cooled to 0°C. The mixture was stirred for 3 h at 0°C, and then treated as indicated in procedure B. Yield, 40 mg (44%) of ether XII, mp, 164...166°C (heptane).

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HETEROARYLATION BY N-METHOXYCARBONYL- AND N,N-DIALKYL(ARYL)-CARBAMOYLBENZOPYRIDINIUM SALTS IN SITU

A. K. Sheinkman, E. V. Fedash,
T. S. Chmilenko, and S. I. Orlov

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The conditions for the heteroarylation of indole and malononitrile by quinoline and isoquinoline in the presence of methyl chloroformate and N,N-dialkyl(aryl)carbamoyl chlorides were studied. Aromatization of the obtained compounds by 2,2,6,6-tetramethyl-1-oxopiperidinium and triphenylcarbenium perchlorates gave for the first time α-substituted and unsubstituted stable N-methoxycarbonyl- and N,N-dialkyl(aryl)carbamoylbenzopyridinium perchlorates.

Heteroarylation of N-heteroaromatic bases in the presence of acyl halides includes three stages, i.e., the formation of the salts of the N-acylheteroaromatic cations, nucleophilic addition of the organic compounds to them, and aromatization of the obtained N-acyl-1,2-dihydro derivatives [1-3]. Nucleophilic addition takes place more readily the stronger the electron-withdrawing effect of the N-acyl residues, and the heteroaromatic cations are consequently stronger electrophiles. The aromatization stage, on the other hand, is facilitated with decrease in the electron-withdrawing characteristics of the N-acyl residues of the respective N-acyl-1,2-dihydro compounds [3]. In this connection it seemed of interest to study the effect of chloroformates and carbamoyl chlorides, which are acid chlorides containing electron-donating substituents and therefore possessing the lowest electron-withdrawing power of all the possible acyl halides, on the two stages of the heteroarylation processs.

It is known that chloroformates are used to activate the pyridine [4] and phenanthridine [5] rings in reactions with potassium cyanide (the Reissert reaction) and of pyridine in reaction with Grignard reagents [6]. Diphenylcarbamoyl chloride was used to active isoquinoline during heteroarylation of N-methylpyrrole [7], where the authors noticed that the heteroarylating agent in this case was significantly less active than normal N-acylpyridinium salts. The use of carbamoyl chlorides in heteroarylation reaction has been restricted to these few examples (see also [8]), although there is significantly more information on the formation of the corresponding N-acylpyridinium salts with various substituents [2].

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