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SYNTHESIS OF 9-DIAZO-4-AZAFLUORENES

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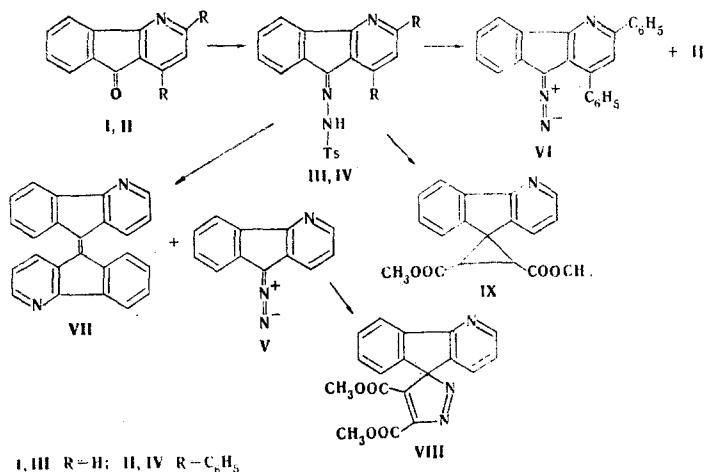
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Stable diazo compounds of the azafluorene series, viz., 9-diazo-4-azafluorenone and 1,3-diphenyl-4-azafluorene, were obtained from 4-azafluorenone and 1,3-diphenyl-4-azafluorene tosylhydrazones. 1',2'-Dicarbomethoxyspiro(4-azafluorene-9,3'-cyclopropane) was obtained from 4-azafluorenone tosylhydrazone, and 4',5'-dicarbomethoxyspiro(4-azafluorene-9,3'-pyrazolenine) was obtained from 9-diazo-4-azafluorene. It is assumed that the product in the latter case is obtained as a result of reaction of a carbene, viz., 4-azafluorenylidene carbene, which is formed from 9-diazo-4-fluorene, with dimethyl acetylenedicarboxylate.

2,4,7-Trinitrodiazazafluorene has proved to be a very stable compound [1], and this fact constitutes an exception in the diazo series. Its stability is evidently due to the electron-acceptor effect of the nitro groups. Proceeding from the presence in the azafluorene molecule of a pyridine ring, the effect of which is similar to the effect of a nitro group, one may assume that diazo compounds of azafluorenes will also be stable. The synthesis of compounds of this type is of theoretical interest and also opens up a pathway for the preparation of new azafluorene derivatives that possibly have practically useful properties.

To prepare the diazo compounds of the azafluorene series we used the accessible 4-azafluorenone (I) and 1,3-diphenyl-4-azafluorenone (II) [3], from which we obtained their tosylhydrazones III and IV. Treatment of tosylhydrazone III with sodium isopropoxide in benzene gave the stable 9-diazo-4-azafluorene (V) (in higher than 60% yield) in the form of slightly red crystals with mp 68-69°C (mp 55-59°C [4]), the isolation of which was accomplished by a chromatographic method. In this experiment bis(4-aza-9-fluorenylidene) (VII) was also isolated in ~10% yield in the form of dark-red crystals with mp 284-286°C; this compound is evidently obtained from diazo compound V through a step involving the formation of a carbene, viz., 4-aza-9-fluorenylidene carbene. Compound VII was previously synthesized from 9-bromo-4-azafluorene by treatment with potassium hydroxide. 9-Diazo-1,3-diphenyl-4-azafluorene (VI), which is also a stable substance and was obtained in the form of light-pinkish crystals with mp 140-141°C, was obtained in considerably lower yield (8%) from tosylhydrazone IV and UV irradiation of a solution in tetrahydrofuran (THF) in the presence of sodium hydride. Azafluorenone II, which is evidently formed from diazo compound VI, was also obtained during the chromatographic separation of diazo compound VI.

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The structure of diazo compounds V and VI was proved by their analytical and spectral characteristics. Molecular-ion peaks with m/e 193 (8.9%) and 345 (8.2%), which correspond to their molecular weights, are observed in the mass spectra of V and VI. The intense (100%) peaks of $[M - N_2]^+$ fragments that are observed in the spectra of both compounds confirm the presence of a diazo group in them.

9-Diazo-4-azafluorenene (V) undergoes 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate at room temperature, and 4',5'-dicarbomethoxyspiro(4-azafluorene-9,3'-pyrazolenine) (VIII) is formed in high yield. The two singlets at 4.03 (3M) and 3.55 ppm (3H) in the PMR spectrum of VIII correspond to the protons of two methoxy groups. The signals at 6.96–8.66 ppm are due to the protons of the azafluorenene ring. 1',2'-Dicarbomethoxyspiro(4-azafluorene-9,3'-cyclopropane) (IX) is formed by treatment of a mixture of tosylhydrazone III and dimethyl fumarate with sodium isopropoxide. The reaction evidently proceeds through a step involving the formation of diazo compound V and subsequently through 4-azafluorenene carbene [5, 6]. Signals of the protons of the cyclopropane ring [a singlet at 3.4 ppm (2H)] and of the protons of the carbomethoxy groups [a singlet at 3.58 ppm (6H)] are observed in the PMR spectrum of spiro compound IX. It has been shown [6, 7] that equivalence of the signals of the protons of the cyclopropane ring and the protons of carbomethoxy groups is observed in the spectra of such compounds for both the trans and cis isomers. The trans configuration of the starting fumarate is evidently retained in spiro compound IX.

EXPERIMENTAL

The PMR spectra of the compounds were measured with a BS 487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR 71 spectrometer. The UV spectra of ethanol solutions were measured with a Specord UV-vis spectrophotometer. The mass spectra were obtained with an MKh-1303 spectrometer equipped with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and an admission temperature of 60°C. Thin-layer chromatography (TLC) was carried out on activity II aluminum oxide.

4-Azafluorenone Tosylhydrazone (III). A 1.23-g (7 mmole) sample of tosylhydrazine in 5 ml of ethanol was added with vigorous stirring to a solution of 1.1 g (6 mmole) of ketone I in 30 ml of ethanol, and the mixture was refluxed for 10 min. The next day, the precipitate was removed by filtration to give 1.7 g of yellowish cottony crystals of tosylhydrazone III. Workup of the mother liquor after 2 days gave another 0.3 g of III for an overall yield of 94% of a substance with mp 128–130°C (from benzene). IR spectrum: 3120 (N–H), 1590, 1570 (N–NH), 1330, 1170 (–SO₂), 750, 690 cm^{–1} (aromatic C–H). UV spectrum (in alcohol), λ_{max} (log ε): 228 (4.88), 314 (4.48), and 386 nm (4.34). Found: C 65.1; H 4.5; N 12.3%. C₁₉H₁₅N₃O₂S. Calculated: C 65.3; H 4.3; N 12.0%.

1,3-Diphenyl-4-azafluorenone Tosylhydrazone (IV). A 1-g (5.3 mmole) sample of tosylhydrazine in 30 ml of benzene was added to 0.95 g (2.8 mmole) of ketone II in 25 ml of benzene, and the mixture was refluxed for 3 h in the presence of a catalytic amount of concentrated HCl. Tosylhydrazone IV separated in the form of a yellow precipitate. Workup of the reaction mixture yielded a total of 0.91 g (63.8%) of tosylhydrazone IV as yellow crystals with mp 179–181°C (from ethanol). IR spectrum: 3205 (–H–H), 1570, 1560 (–N–NH), 1300, 1160 (–SO₂), 750, 690 cm^{–1} (aromatic C–H). PMR spectrum (in CF₃COOH), δ: 8.44 (s, 1H, NH), 7.15 (s, 4H,

protons of the tosyl fragment), and 2.45 ppm (s, 3H, CH_3). UV spectrum (in alcohol), λ_{max} (log ϵ): 212 (4.50), 227 (4.49), 258 (4.40), 320 (4.00), 390 nm (3.86). Found: C 74.4; H 4.7; N 8.6%. $\text{C}_{31}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$. Calculated: C 74.2; H 4.6; N 8.3%.

9-Diazo-4-azafluorene (V). Sodium isopropoxide was obtained from 0.1 g (0.004 mole) of sodium in 10 ml of absolute isopropyl alcohol, after which the excess alcohol was removed by distillation, and the residue was dissolved in 30 ml of benzene. The solution of sodium isopropoxide was added slowly with heating and stirring in a nitrogen atmosphere to 12 g (2.9 mmole) of tosylhydrazone III in 180 ml of benzene, after which the mixture was refluxed for 3 h, cooled, and poured into 200 ml of water. The organic layer was extracted with ether (three 150-ml portions), and the extract was dried with magnesium sulfate. The solvent was removed by distillation to give 0.85 g of residue, which was then chromatographed on aluminum oxide [successive elution with heptane and heptane-ethyl acetate (8:1 and 5:1)] to give initially 0.35 g (63%) of V in the form of reddish crystals with mp 68-69°C (from heptane) and R_f 0.62 [ethyl acetate-heptane (1:2)]. IR spectrum: 2080 (--N_2) and 750 cm^{-1} (aromatic C-H). UV spectrum (in alcohol), λ_{max} (log ϵ): 218 (4.64), 254 (4.30), 286 (4.36), 356 nm (3.38). Found: C 74.4; H 3.9; N 21.7%; M^+ 193. $\text{C}_{12}\text{H}_7\text{N}_3$. Calculated: C 74.6; H 3.5; N 21.8%; M^+ 193.

Subsequent elution yielded 0.09 g (9.5%) of VII in the form of dark-red crystals with mp 284-286°C and R_f 0.5 (chloroform).

9-Diazo-1,3-diphenyl-4-azafluorene (VI). A 0.03-g (1.2 mmole) sample of sodium hydride was added to a solution of 0.45 g (0.86 mmole) of tosylhydrazone IV in 50 ml of dry THF, and stirring was continued until hydrogen evolution ceased. The flask was then purged with dry nitrogen and irradiated with UV light for 4 h. The formation of diazo compound VI was monitored by TLC until a spot with R_f 0.75 [heptane-ethyl acetate (2:1)] appeared. The solvent was removed by distillation, ether was added to the residue, and the resulting precipitate was removed by filtration. The ether was removed by distillation, and the residue (0.2 g) was chromatographed [successive elution with heptane and heptane-ethyl acetate (5:1)] to give 0.025 g (8.3%) of diazo compound VI in the form of pinkish crystals with mp 140-141°C (from heptane) and R_f 0.75 [heptane-ethyl acetate (2:1)]. IR spectrum: 2020 (--N_2), 740, and 680 cm^{-1} (aromatic C-H), UV spectrum (in alcohol), λ_{max} (log ϵ): 212 (4.08), 248 (4.20), 267 (4.23), 330 nm (3.97). Found: N 11.5%; M^+ 345. $\text{C}_{24}\text{H}_{15}\text{N}_3$. Calculated: N 12.2%; M^+ 345. Subsequent elution gave 0.08 g (36.5%) of ketone II in the form of yellow crystals with mp 163-164°C and R_f 0.69 [heptane-ethyl acetate (2:1)].

4',5'-Dicarbomethoxyspiro(4-azafluorene-9,3'-pyrazolene) (VIII). A 0.23-g (1.4 mmole) sample of dimethyl acetylenedicarboxylate was added to 0.2 g (1.0 mmole) of diazo compound V in 1.5 ml of absolute ether. After 3 h, the precipitate was removed by filtration and washed with ether to give 0.27 g (77.1%) of golden crystals of VIII that decomposed at 120-121°C. IR spectrum: 1725 (CO), 1280 (--CO--OCH_3), and 760 cm^{-1} (aromatic C-H). PMR spectrum (in acetone), δ : 8.66 (J_1 = 5.0, J_2 = 1.0 Hz, 1H, 3-H), 8.10 (doublet with additional splitting, 1H, 5-H), 7.66 (J_1 = 7.0, J_2 = 1.0 Hz, 1H, 1-H), 7.25 (J_1 = 7.0, J_2 = 5.0 Hz, 1H, 2-H), 6.95 (doublet with additional splitting, 1H, 8-H), 4.04 (s, 3H, --OCH_3), and 3.55 ppm (s, 3H, --OCH_3). UV spectrum (in alcohol), λ_{max} (log ϵ): 208 (4.78), 285 (4.35), 295 (4.33), 308 (4.32), 445 (3.17), 606 nm (2.62). Found: C 64.3; H 4.0; N 12.5%; M^+ 335. $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_4$. Calculated: C 64.5; H 3.9; N 12.5%; M^+ 335.

1',2'-Dicarbomethoxyspiro(4-azafluorene-9,3'-cyclopropane (IX). A 0.33 N solution of sodium isopropoxide in 22 ml of benzene was added with stirring in a nitrogen atmosphere to a mixture of 2.2 g (5.7 mmole) of tosylhydrazone III and 5 g (34.8 mmole) of dimethyl fumarate in 170 ml of dry benzene, and the mixture was refluxed for 5 h. It was then cooled, 100 ml of water was added, and the aqueous mixture was extracted with ether (four 100-ml portions). The ether extracts were washed with water and dried with magnesium sulfate, the ether was removed by distillation, and the residue (1.5 g) was chromatographed [elution with heptane-ethyl acetate (5:1)] to give 0.82 g (46.3%) of colorless crystals of IX with mp 157-158°C. IR spectrum: 1725 (CO) and 1200 cm^{-1} (--CO--OCH_3). PMR spectrum (in CDCl_3), δ : 3.58 (s, 6H, 2'- CH_3 , 1'- CH_3) and 3.40 ppm (s, 2H, 1'-H, 2'-H). UV spectrum (in alcohol), λ_{max} (log ϵ): 208 (4.90), 245 (4.24), 297 (4.44), 310 nm (4.39). Found: C 70.2; H 4.7; N 4.7%; M^+ 309. $\text{C}_{18}\text{H}_{15}\text{NO}_4$. Calculated: C 69.9; H 4.9; N 4.5%; M^+ 309.

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INVESTIGATION OF LACTAMS

33.* SYNTHESIS OF 2-OXO-1H,2,3,4,5-TETRAHYDROAZEPINO-[4,5-b]INDOLE DERIVATIVES

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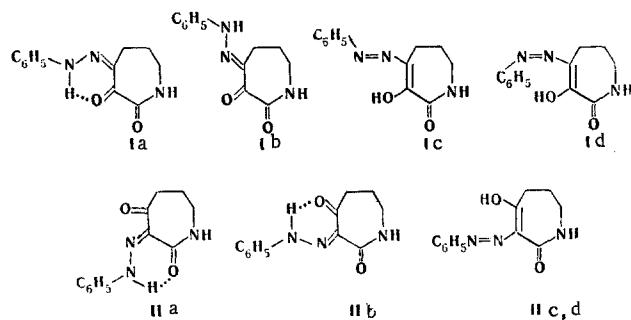
2,3,4-Trioxohexahydroazepine 4-phenylhydrazone with a ¹⁵N-labeled atom bonded to the phenyl fragment was obtained in order to establish its structure. It was established by means of the PMR spectra that this substance is a mixture of syn and anti isomers of the hydrazone form. 2,3,4-Trioxohexahydroazepine 3-phenylhydrazone was isolated when an attempt was made to indolize the 4-phenylhydrazone. Both hydrazones react with phenylhydrazine to give the same 2,3,4-trioxohexahydroazepine 3,4-bis(phenylhydrazone). Derivatives involving the carbonyl group were obtained for both hydrazones, and the conditions for their indolization were studied, as a result of which a number of azepino[4,5-b]indole derivatives were synthesized.

Continuing our research on the synthesis of condensed heterocyclic compounds from enamines of α -oxolactams, in the present communication we report the development of a new synthesis of the azepino[4,5-b]indole system.

The starting compound in this synthesis was 2,3,4-trioxohexahydroazepine 4-phenylhydrazone (I), which was obtained by reaction of the enamine of α -oxocaprolactam with benzenediazonium chloride [2].

We have studied the structure of I with allowance for the fact that the arylhydrazones of 1,2-dicarbonyl compounds can exist in two tautomeric forms, viz., the azo and hydrazone forms [3], and that two geometrical isomers (Ia, b and Ic, d) are possible for each of these forms.

The limited solubility of I in organic solvents hindered the use of IR and UV spectroscopy for the solution of our problem. The IR spectrum of I in the solid state did not enable us to draw an unambiguous conclusion regarding its structure, since the absorption bands in the literature (3300, 3080, 1675, 1620, and 1600 cm^{-1}) could have been assigned equally satisfactorily to any of the forms.



The following signals are present in the PMR spectrum of I (in solution in d_6 -DMSO + CCl_4): 1.85 (6- CH_2 , q), 2.66 and 2.86 (5- CH_2 , t), 3.18 (7- CH_2 , m), 6.80-7.40 (aromatic protons, m), and 8.33 and 8.44 ppm (1-NH, t);

*See [1] for communication 32.

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