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BISINDOLES

34.* PREPARATION AND REACTIONS OF DEHYDRAZIDES OF THE BENZO[e]PYRROLO[3,8-g]-INDOLE AND INDOLO[4,5-e]INDOLE SERIES

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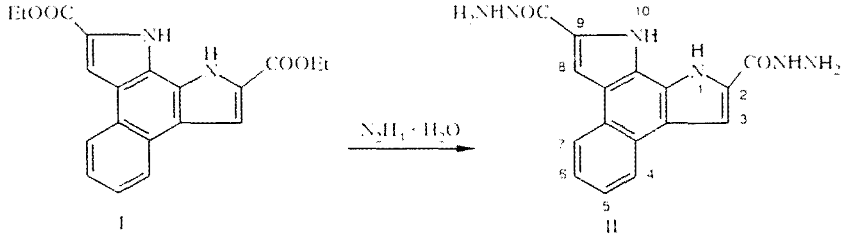
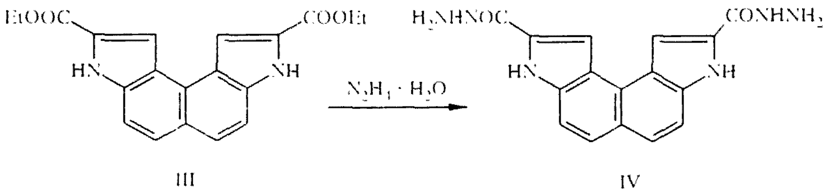
2,9-Di(carbohydrazide)-1H,10H-benzo[e]pyrrolo[3,2-g]indole and 2,9-di(carbohydrazide)-3H,8H-indolo[4,5-e]indole have been prepared. Nitrosation of the dihydrazides has been effected. The acyl azides do not undergo the curtius rearrangment.

In the present article, we report the preparation of the dihydrazides of the di-acids of 1H,10H-benzo[e]pyrrolo[3,2-g]indole [2] and 3H,8H-indolo[4,5-e]indole [3] which we prepared earlier. 2,9-Di(carbohydrazide)-1H,10H-benzo[e]pyrrolo-[3,2-g]indole (II) and 2,9-di(carbohydrazide)-3H,8H-indolo[4,5-e]indole (IV) were prepared from 2,9-diethoxycarbonyl-1H,10H-benzo[e]pyrrolo[3,2-g]indole (I) and 2,9-diethoxycarbonyl-3H,8H-indolo[4,5-e]indole (III) by heating with hydrazine hydrate at boiling point in isopropanol.





In the PMR spectra of compounds II and IV there are proton signals for the indole NH group at 11.65 and 11.78 ppm respectively. In the spectrum of compound II, signals in the form of a doublet of doublets at 8.10 and 7.45 ppm belong to the 4H, 7H and 5H, 6H protons ($J_{4,5}$ = 6,21, $J_{4,6}$ = 3.29 Hz respectively) and in the spectrum of compound IV the protons of the naphthalene nucleus appear as doublets at 7.52 ppm (4H, 7H) and 7.69 ppm (5H, 6H) $J_{4,5}$ = 8.77 Hz. The protons of the hydrazide group appears as broad signals, NH at 9.45 ppm (compound II) and 9.49 ppm (compound IV), and NH_2 at 4.41 ppm (compound II) and 4.45 ppm (compound IV).

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*Communication 33, see [1].

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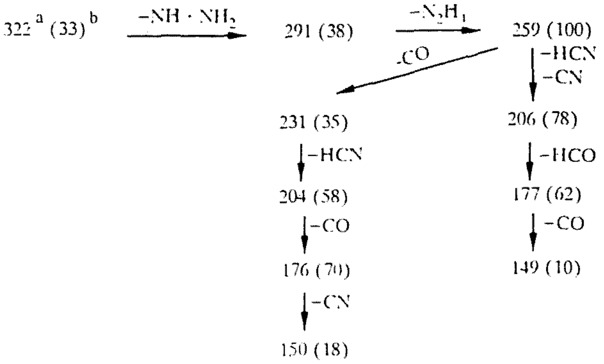
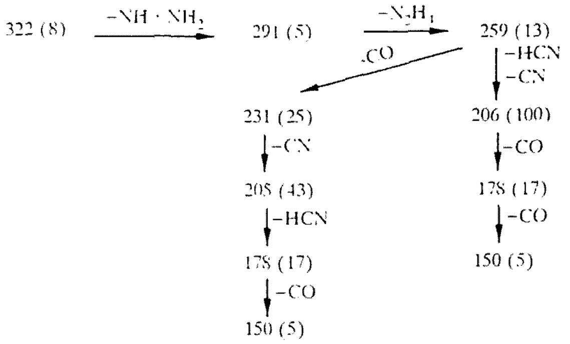
In the mass spectra of compounds II and IV in the early stages of fragmentation, rupture at the carbonyl group and detachment of the $NHNH_2$ groups are observed, followed by elimination of a molecule of hydrazine. The fragment ion formed with *m/z* 259 gives the maximum intensity peak in the spectrum of compound II while in the spectrum of compound IV the maximum is observed for the ion with m/z 206 the formation of which is possibly by simultaneous splitting off of HCN from the ion with *m/z* 259.

A conjectural scheme for the breakdown can be presented as follows:

Compound II



Compound IV

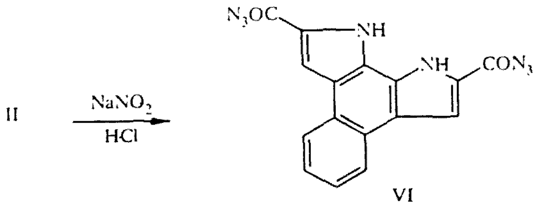


Here and later: a) m/z, b) intensity in % for maximum peak.

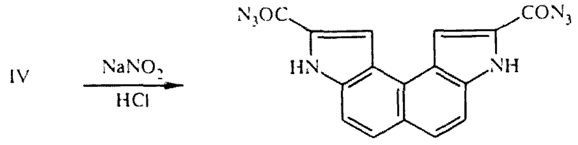
Nitrosation of the dihydrazides II and IV was carried out under different conditions. Under conditions previously reported [4] for hydrazides of 3-indolcarboxylic acids (nitrosation of the dihydrazide II in acetic acid) acetylation of the hydrazide NH_2 takes place with the formation of 2,9-di(N-acetylcarbohydrazide)-1H, 10H-benzo[e]pyrrolo[3,2-g]indole (V) which undergoes no further nitrosation on account of its low solubility.

Hence, with the object of preparing the azides, nitrosation of compounds II and IV was carried out using conc. HCl. 2,9-Di(acylazide)-1H,10H-benzo[e]pyrrolo[3,2-g]indole (VI) and 2,9-di(acylazide)-3H,8H-indolo[4,5-e]indole (VII) were prepared.

Curtus rearrangement of compounds VI and VII, carried out in different solvents in an atmosphere of inert gas, yielded unidentified products.



VI



VII

EXPERIMENTAL

The progress of the reactions was monitored and the purity of the compounds assessed by TLC on Silufol UV-254 plates. Silica gel with particle size 100-250 μm was used as adsorbent. Infrared spectra were run on a UR-20 instrument as mulls in mineral oil and UV spectra on a Specord spectrophotometer in ethanol. PMR spectra were recorded on a Varian CFT-20 spectrometer (80 MHz) and a WP-20 SI (200 MHz) with TMS as internal standard. A MERMAG'S R-10-10B gas chromatograph mass spectrometer was used to obtain mass spectra with an ionization energy of 70 eV.

The results of elemental analyses were in agreement with those calculated.

2,9-Di(carbohydrazide)-1H,10H-benzo[e]pyrrolo[3,2-g]indole (II, $C_{16}H_{14}N_6O_2$). A suspenion of 0.2 g (0.6 mmole) 2,9-diethoxycarbonyl-1H,10H-benzo[e]pyrrolo[3,2-g]indole (I) in 20 ml isopropanol was warmed and 10 ml hydrazine hydrate added and heated 3 h at bp. The mixture was then cooled, and the precipitate filtered off, washed with isopropanol and ether, and dried. The yield was 0.17 g (85%) cream-colored crystals with mp 403°C (decomp.), R_f 0.66 (10:1 ethanol–ammonia). IR spectrum (cm^{-1}): 3430 (NH_2), 3250-3280 (hydrazide NH), 3330 (indole NH), 1610, 1670 (C=O, amide band I), 1510, 1580 (C=O, amide band II). UV spectrum (λ_{max} nm (log ε)): 227 (3.16), 238 (3.25), 255 (3.21), 270 (3.32), 282 (3.31), 345 (3.25), 355 nm (3.24). PMR spectrum in DMSO-D_6 (δ ppm): 11.66 (2H, br.s, 1- and 10-H), 9.55 (2H, br.s, hydrazide NH), 8.10 (2H, d.d, 4- and 7-H), 7.68 (2H, s, 3- and 8-H), 7.45 (2H, d.d, 5- and 6-H), 4.41 (4H, br.s, NH_2), $J_{4,5}$ = 6.21, $J_{4,6}$ = 3.29 Hz. M^+ 322.

2,9-Di(carbohydrazide)-3H,8H-indolo[4,5-e]indole (IV, $C_{16}H_{14}N_6O_2$) was prepared in a similar manner to compound II from 1 g (3 mmole) 2,9-diethoxycarbonyl-3H,8H-indolo[4,5-e]indole (III) and 20 ml hydrazine hydrate in 50 ml isopropanol. The product was filtered hot, washed with isopropanol and ether, and dried. Yield 0.9 g (85%), mp 330°C (decomp.). IR spectrum (cm^{-1}): 3100-3300 (indole and hydrazide NH), 3430 (NH_2), 1610, 1640 (C=O, amide band I), 1530, 1570 (C=O, amide band II). PMR spectrum in DMSO-d_6 (δ ppm): 11.78 (2H, br.s, 3- and 8-H), 9.49 (2H, br.s, hydrazide NH), 8.00 (2H, s, 1- and 10-H), 7.69 (2H, d, 5- and 6-H), 7.52 (2H, d, 4- and 7-H), 4.45 (4H, br.s, NH_2), $J_{4,5}$ = 6.77 Hz. M^+ 322.

2,9-Di(N-acetylcarbohydrazide)-1H,10H-benzo[e]pyrrolo[3,2-g]indole (V, $C_{20}H_{18}N_6O_4$) was prepared by heating 0.1 g (0.3 mmole) compound II in acetic acid for 2 h at bp. The residue was filtered off, washed with water to pH 7, and dried. Yield 0.1 g (77%), mp 365°C (decomp.), R_f 0.67 (ethanol). IR spectrum (cm^{-1}): 3335, 3265 (N–H), 1660 (C=O), 1540 (amide band II). UV spectrum (λ_{max} nm (log ε)): 207 (4.03), 238 (4.04), 270 (4.06), 282 (4.09), 357 (4.09), 397 (4.02). PMR spectrum in DMSO-D_6 (δ ppm): 11.7 (2H, br.s, 1- and 10-H), 10.13 (2H, br.s, NHα), 9/76 (2H, br.s, NHβ), 8.13 (2H, d.d, 4- and 7-H), 7.49 (2H, d.d, 5- and 6-H), 1.96 (6H, s, CH_3), $J_{4,5}$ = 5.84, $J_{4,6}$ = 2.93 Hz. M^+ 406. Fragmentation scheme:

$$M^+\ 406\ (100) \xrightarrow{-COCH_2} 364\ (10) \xrightarrow{-N_2H_4} 332\ (70) \xrightarrow{-COCH_3} 289\ (30) \longrightarrow$$

$$\xrightarrow{-N_2H_4} 259\ (10) \xrightarrow{-CO} 231\ (35) \xrightarrow{-CO} 203\ (9) \xrightarrow{-HCN} 175\ (7) \xrightarrow{-HCN} 149\ (11)$$

2,9-Di-(acylazide)-1H,10H-benzo[e]pyrrolo[3,2-g]indole (VI, $C_{16}H_8N_8O_2$). A mixture of 20 ml conc. HCl and 5 ml water was slowly added to 0.2 g (0.6 mmole) compound II, the mixture stirred for 15 min and then cooled to 0 to 5°C and a solution of 0.2 g (3 mmole) $NaNO_2$ in 2 ml water added dropwise after which the mixture was vigorously stirred for 1 h. The precipitate was quickly filtered off, washed with water to pH 7, and dried *in vacuo*. Yield 0.16 g (82%) compound VI which was chromatographed on a column using benzene as eluent. Compound VI was obtained in the form of yellow crystals, mp 146-7°C (with explosive decomp.), R_f 0.60 (7:1 benzene–acetone). IR spectrum (cm^{-1}): 3310, 3290 (sh) (N–H), 2140

($-C\equiv N$), 1660, 1700 ($C=O$). PMR spectrum in $CDCl_3$ (δ ppm): 10.83 (2H, br.s, 1- and 10-H), 8.05 (2H, br.s, 4- and 7-H), 7.65 (2H, br.s, 5- and 6-H), 7.48 (2H, br.s, 3- and 8-H).

2,9-Di(acylazide)-3H,8H-indolo[4,5-e]indole (VII, $C_{16}H_8N_8O_2$) was prepared in a similar manner to compound VI from 0.1 g (0.3 mmole) compound IV and a mixture of 10 ml conc. HCl and 1 ml H_2O, adding 0.1 g (1.5 mmole) $NaNO_2$ in 1 ml H_2O. Yield 0.1 g (60%), mp 180°C (with explosive decomp.). IR spectrum (cm^{-1}): 3300 (NH), 1600, 1650 ($C=O$), 2130 ($-C\equiv N$).

REFERENCES

1. Sh. A. Samsoniya, N. N. Ovsyannikov, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 1, 40 (1994).
2. Sh. A. Samsoniya, M. V. Trapaidze, N. A. Kuprashvili, A. M. Kolesnikov, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 9, 1222 (1985).
3. Sh. A. Samsoniya, M. V. Trapaidze, S. V. Dolidze, N. A. Ésakiya, N. N. Suvorov, A. M. Kolesnikov, and F. A. Mikhailenko, Khim. Geterotsikl. Soedin., No. 3, 352 (1984).
4. N. N. Suvorov, V. S. Velezheva, A. N. Yarosh, Yu. V. Erofeev, and T. N. Kozik, Khim. Geterotsikl. Soedin., No. 8, 1099 (1975).