for 2-3 h. It was then poured into 100 ml of ether, and the precipitate was removed by filtration and washed with ether. The dyeswere purifiedby reprecipitation from acetic anhydride (Table 3).

8-Methyl-9-carbethoxyindolo-3,3'-trimethinecyanines. A mixture of 0.0004 mole of ethyl 3-(1'-methyl-2'-$R^1$-3-indolyl)crotonate IV, 0.0004 mole of 1-methyl-2-$R^2$-5(7)-$R^3$-3-formylindole, and 15 ml of acetic anhydride was stirred at room temperature until the solids had dissolved completely, after which 0.1 ml of 70% perchloric acid was added dropwise. After 2-3 h, the mixture was diluted with ether. The precipitate was removed by filtration and washed with ether. The dyes were purified by reprecipitation from nitroethane (Table 3).

## LITERATURE CITED


1. T. N. Galiullina, P. I. Abramenko, A. V. Kazymov, and V. M. Gorokhovskii, Khim. Geterotsikl. Soedin., No. 8, 1067 (1981).
2. T. N. Galiullina and P. I. Abramenko, Khim. Geterotsikl. Soedin., No. 12, 1652 (1983).
3. N. N. Suvorov, A. B. Kalinskii, and Yu. I. Smushkevich, Zh. Obshch. Khim., 13, 197 (1977).
4. M. Baron, P. Cointet, and G. Bauduin, Bull. Soc. Chim. France, Part II, Nos. 7-8, 369 (1977).
5. P. I. Abramenko, T. N. Galiullina, and A. N. Gusarov, Collection of Scientific Research of the Kazan Scientific-Research Technological and Planning Institute of the Photographic-Chemical Industry [in Russian], Moscow (1980), p. 126.


# REACTION OF 2-METHYLENE-2,3-DIHYDROINDOLES WITH ACRYLAMIDE


A. A. Shachkus and Yu. A. Degutis



UDC 547.828'753:543.422

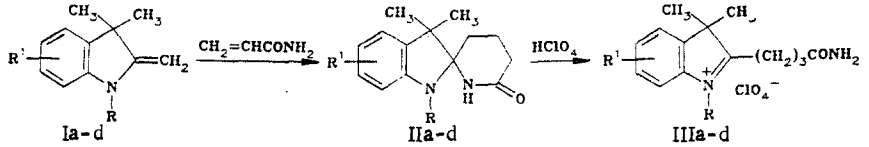


1,3-Dihydrospiro[2H-indolo-2,2'-piperidine] derivatives were obtained by the reaction of 2-methylene-2,3-dihydro-1H-indole derivatives with acrylamide in proton-containing solvents. 2-(3-Carbamoylpropyl)-3H-indolium perchlorates were formed when the 1,3-dihydrospiro[2H-indolo-2,2'-piperidine] derivatives were treated with perchloric acid.


Alkylation of enamines by induced addition is often used in the preparation of various heterocyclic compounds [1-3]. It is known that condensed heterocyclic systems containing a lactam ring are formed in the reaction of pyrrolidine-series endo-enamines with acrylamide [4, 5].

The purpose of the present paper is an investigation of the reaction of acrylamide with indoline enamines Ia-d.

1,3-Dihydrospiro[2H-indolo-2,2'-piperidine] derivative IIa is formed during heating of a mixture of 2-methylene-2,3-dihydro-1H-indole (Ia) with acrylamide in ethylene or diethylene glycol. We can assume that the first stage of this reaction is the addition of acrylamide to the β-carbon atom of the enamine group with the formation of a Michael adduct, which then undergoes ring closure to spiro compound IIa. The proton-containing solvent participates in the reaction during proton transfer. 1,3-Dihydrospiro[2H-indolo-2,2'-piperidines] IIb-d are obtained similarly to compound IIa.




Ia-d IIa-d IIIa-d

I—III a–b R=$CH_3$, d R=$C_2H_5$; a, d $R^1$=H, b $R^1$=5-$CH_3$, c $R^1$=7-$CH_3$


A. Snechkus Kaunas Polytechnic Institute, Kaunas 233006.

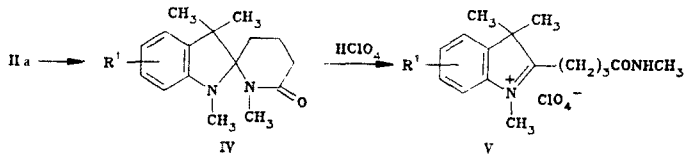

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 902-904, July, 1988. Original article submitted January 12, 1987.




0009-3122/88/2407-0740$12.50

Absorption bands characteristic of six-membered lactams are observed in the IR spectrum of spiroindolo-2,2'-piperidine IIa at 3210 (N–H) and 1655 cm$^{-1}$ (C=O) [6]. In the $^{13}C$ NMR spectrum, the signal of the α-carbon spiro atom of the indole ring system is at 86.5 ppm, and that of the carbon atom of the carbonyl group is at 172.6 ppm (δ-lactam) [7].

Strong protic acids promote cleavage of the piperidine ring of compounds IIa-d. Thus, 2-(3-carbamoylpropyl)-3H-indolium perchlorates IIIa-d are obtained when an alcoholic solution of compounds IIa-d is treated with perchloric acid. In the proton NMR spectra (in $CF_3COOH$) the chemical shift of the protons of the 1-$CH_3$ group of perchlorates IIIa-c (3.85-4.03 ppm) is close in value to the chemical shift of the protons of the corresponding methyl group of 1,2,3,3-tetramethyl-3H-indolium iodide (3.78 ppm).




Alkylation of spiro compound IIa by methyl iodide in dimethylformamide (DMFA) in the presence of potassium hydroxide occurs at the nitrogen atom of the lactam ring, and 1'-methylspiro[indolo-2,2'-piperidine] IV is formed, which is converted to perchlorate V in the presence of perchlroic acid.

The IR spectrum of salt V contains absorption bands at 3410 (N–H), 1665 (C=O), and 1540 cm$^{-1}$ (amide II) characteristic of secondary amides [6]. In the proton NMR spectrum (in $CD_3CN$) the signal of the protons of the methyl group at the amide nitrogen atom is split into a doublet with a center at 2.72 ppm ($^3J_{CH_3,NH}$ = 4.5 Hz). In the case of recording of the proton NMR spectrum of salt V in $CF_3COOH$, the signal of the same protons is observed in the form of a singlet at 2.69 ppm, which is apparently related to exchange processes because of protonation in the acid medium of the O atom of the carbamoyl group [8].

## EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 325 instrument with KBr tablets. The proton NMR spectra of compounds IIa-c were obtained on a Varian XL-200 spectrometer, and those of the remaining compounds were obtained on Varian XL-100 and Tesla BS-487C spectrometers (80 MHz) with a hexamethyldisilazane (HMDS) internal standard. The $^{13}C$ NMR spectra were recorded on a Tesla BS-567 spectrometer (25.14 MHz). The signals were assigned on the basis of the results of using various pulsed spectrum-recording methods [9] and the data of [7], [10], and [11]. The mass spectra were recorded on an LKB-9000 instrument (40 eV) with direct injection of the substance into the ion source. The course of the reactions and the purity of the compounds were monitored by thin-layer chromatography on aluminum oxide of activity grade II in the acetone–hexane (3:5) system with development by iodine vapor.

6'-Oxo-1,3,3-trimethyl-1,3-dihydrospiro[2H-indolo-2,2'-piperidine] (IIa). A. A mixture of 6.93 g (40 mmoles) of 2-methylene-1,3,3-trimethyl-2,3-dihydro-1H-indole (Ia) and 4.26 g (60 mmoles) of acrylamide in 20 ml of ethylene glycol was heated for 6 h at 110°C. The mixture was poured into 150 ml of water and extracted with ether (2 × 25 ml). The extract was washed with 20 ml of water and dried with calcium chloride, the solvent was driven off, and the residue was crystallized from acetone. Yield: 5.6 g (57%), mp 140-141°C. Proton NMR spectrum ($CDCl_3$): 1.21 (3H, s, 3-$CH_3$); 1.30 (3H, s, 3-$CH_3$); 1.85-2.42 (6H, m, $CH_2CH_2CH_2$); 2.73 (3H, s, 1-$CH_3$); 5.74 (1H, broadened singlet, NH); 6.44 (1H, doublet doublet doublet, J = 0.6; 1.0; 7.6 Hz, 4-H); 6.76 (1H, doublet triplet, J = 1.0; 7.4 Hz, 6-H); 7.01 (1H, doublet doublet doublet, J = 0.6; 1.3; 7.3 Hz, 7-H) 7.11 ppm (1H, doublet triplet, J = 1.3; 7.5 Hz, 5-H). Carbon-13 NMR spectrum ($CDCl_3$): 18.3 ($CH_3$); 21.7 ($C_{(4')}$); 25.2 ($C_{(3')}$); 25.4 ($CH_3$); 28.5 ($C_{(5')}$); 31.2 ($CH_3$); 48.4 ($C_{(3)}$); 86.5 ($C_{(2)}$); 107.2 ($C_{(7)}$); 118.9; 121.8 ($C_{(4)}$, $C_{(5)}$); 127.9 ($C_{(6)}$); 135.8 ($C_{(3a)}$); 148.1 ($C_{(7a)}$); 172.6 ppm (CO). Found: C 73.9; H 8.2; N 11.6%; $M^+$ 244. $C_{15}H_{20}N_2O$. Calculated: C 73.7; H 8.2; N 11.5%; M 244.

B. The reaction of 3.47 g (20 mmoles) of compound Ia with 2.13 g (30 mmoles) of acrylamide was carried out similarly to the above-described example, but 10 ml of diethylene glycol was used as the solvent. The yield of compound IIa was 2.0 g (41%).

6'-Oxo-1,3,3,5-tetramethyl-1,3-dihydrospiro[2H-indolo-2,2'-piperidine] (IIb) was obtained from 7.49 g (40 mmoles) of methylene base Ib similarly to compound IIa (method A). Yield:

6.09 g (59%), mp 166-167°C (from acetone). IR spectrum: 3180 (N–H), 1650 $cm^{-1}$ (C=O). Proton NMR spectrum ($CDCl_3$): 1.20 (3H, s, 3-$CH_3$); 1.28 (3H, s, 3-$CH_3$); 1.87-2.49 (6H, m, $CH_2CH_2CH_2$); 2.26 (3H, br. s, 5-$CH_3$); 2.70 (3H, s, 1-$CH_3$); 6.35 (1H, d, J = 7.8 Hz, 7-H); 6.83 (1H, d.q. J = 0.6; 2.5 Hz, 4-H); 6.91 ppm (1H, d.d.q, J = 0.8; 2.5; 7.8 Hz, 6-H). Found: C 74.4; H 8.6; N 10.7%. $M^+$ 258. $C_{16}H_{22}N_2O$. Calculated: C 74.4; H 8.6; N 10.8%; M 258.

6'-Oxo-1,3,3,7-tetramethyl-1,3-dihydrospiro[2H-indolo-2,2'-piperidine] (IIc) was obtained from 7.49 g (40 mmoles) of methylene base Ic similarly to compound IIa. Yield: 5.27 g (51%), mp 106-107°C (from acetone). IR spectrum: 3220 (N–H), 1660 $cm^{-1}$ (C=O). Proton NMR spectrum ($CDCl_3$): 1.17 (3H, s, 3-$CH_3$); 1.26 (3H, s, 3-$CH_3$); 1.82-2.41 (6H, m, $CH_2CH_2CH_2$); 2.41 (3H, br. s. 7-$CH_3$); 2.99 (3H, s, 1-$CH_3$); 5.87 (1H, br. s. NH); 6.67 (1H, d.d. J = 6.8; 8.0 Hz, 5-H): 6.85 ppm (2H, multiplet, 4-H, 6-H). Found: C 74.5; H 8.7; N 10.8%. $C_{16}H_{22}N_2O$. Calculated: C 74.4; H 8.6; N 10.8%.

3,3-Dimethyl-6'-oxo-1-ethyl-1,3-dihydrospiro[2H-indolo-2,2'-piperidine] (IId) was obtained from 7.49 g (40 mmoles) of methylene base Id similarly to compound IIa. Yield: 4.55 g (44%), mp 79-80°C (from petroleum ether). IR spectrum: 3180 (N–H), 1660 $cm^{-1}$ (C=O). Proton NMR spectrum ($CDCl_3$): 1.20 (3H, s, 3-$CH_3$); 1.20 (3H, t, J = 7 Hz, $CH_2\underline{CH_3}$); 1.30 (3H, s, 3-$CH_3$); 1.68-2.56 (6H, m, $CH_2CH_2CH_2$); 2.86-3.46 (2H, m, $\underline{CH_2}CH_3$); 5.85 (1H, br.s., NH); 6.36-7.31 ppm (4H, m, ArH). Found: C 74.6; H 8.5; 10.6%. $C_{16}H_{22}N_2O$. Calculated: C 74.4; H 8.6; N 10.8%.

2-(3-Carbamoylpropyl)-1,3,3-trimethyl-3H-indolium Perchlorate (IIIa). A solution of 1.22 g (5 mmoles) of compound IIa in 6 ml of alcohol was neutralized with 60% perchloric acid. The mixture was kept at −5°C for 12 h, and the crystalline material was filtered off and recrystallized from alcohol. Yield: 1.10 g (63%), mp 195-196°C. IR spectrum: 3440 (N–H), 3200 (N–H), 1680 $cm^{-1}$ (C=O). Proton NMR spectrum ($CF_3COOH$): 1.31 (6H, s, 3,3-$CH_3$); 1.68-3.16 (6H, m, $CH_2CH_2CH_2$); 3.85 (3H, s, 1-$CH_3$); 7.21-7.51 ppm (4H, m, ArH). Found: C 52.1; H 6.2; Cl 10.4; N 8.1%. $C_{15}H_{21}ClN_2O_5$. Calculated: C 52.3; H 6.1; Cl 10.3; N 8.1%.

2-(3-Carbamoylpropyl)-1,3,3,5-tetramethyl-3H-indolium perchlorate (IIIb) was obtained from 1.29 g (5 mmoles) of compound IIIb similarly to perchlorate IIIa. Yield: 0.80 g (45%), mp 179-180°C (from alcohol). Proton NMR spectrum ($CF_3COOH$): 1.30 (6H, s, 3,3-$CH_3$); 1.73-3.13 (6H, m, $CH_2CH_2CH_2$); 2.17 (3H, s, 5-$CH_3$); 3.86 (3H, s, 1-$CH_3$); 7.03-7.31 ppm (3H, m, ArH). Found: Cl 10.0%. $C_{16}H_{23}ClN_2O_5$. Calculated: Cl 9.9%.

2-(3-Carbamoylpropyl)-1,3,3,7-tetramethyl-3H-indolium perchlorate (IIIc) was obtained from 1.29 g (5 mmoles) of compound IIc similarly to perchlorate IIIa. Yield: 0.90 g (50%), mp 174-175°C (from alcohol). Proton NMR spectrum ($CF_3COOH$): 1.28 (6H, s, 3,3-$CH_3$); 1.73-3.11 (6H, m, $CH_2CH_2CH_2$); 2.47 (3H, s, 7-$CH_3$); 4.03 (3H, s, 1-$CH_3$); 7.00-7.26 ppm (3H, m, ArH). Found: Cl 9.9%. $C_{16}H_{23}ClN_2O_5$. Calculated: 9.9%.

3,3-Dimethyl-2-(3-carbamoylpropyl)-1-ethyl-3H-indolium perchlorate (IIId) was obtained from 1.29 g (5 mmoles) of compound IId similarly to perchlorate IIIa. Yield: 1.22 g (68%), mp 169-170°C (from alcohol). Proton NMR spectrum ($CF_3COOH$): 1.34 (6H, s, 3,3-$CH_3$); 1.35 (3H, t, J = 7.0 Hz, $CH_2\underline{CH_3}$); 1.68-3.13 (6H, m, $CH_2CH_2CH_2$); 4.33 (2H, q, J = 7.0 Hz, $\underline{CH_2}CH_3$); 7.26-7.48 ppm (4H, multiplet, ArH). Found: Cl 9.7%. $C_{16}H_{23}ClN_2O_5$. Calculated: Cl 9.9%.

6'-Oxo-1,1',3,3-tetramethyl-1,3-dihydrospiro[2H-indolo-2,2'-piperidine] (IV). To a solution of 2.44 g (10 mmoles) of compound IIa in 20 ml of DMFA was added 1.40 g (25 mmoles) of finely ground potassium hydroxide, and 2.84 g (1.25 ml, 20 mmoles) of methyl iodide as added dropwise. The mixture was kept at 20°C for 1 h, poured into 150 ml of water, and extracted with ether (3 × 20 ml). The extract was washed with water (2 × 20 ml) and dried with $CaCl_2$, the solvent was driven off, and the residue was crystallized from an acetone–hexane mixture. The yield of compound IV was 1.45 g (56%), mp 111-112°C. IR spectrum: 1640 $cm^{-1}$ (C=O). Proton NMR spectrum ($CDCl_3$): 1.21 (3H, s, 3-$CH_3$); 1.31 (3H, s, 3-$CH_3$); 1.68-2.68 (6H, m, $CH_2CH_2CH_2$); 2.39 (3H, s, 1'-$CH_3$); 2.75 (3H, s, 1-$CH_3$); 6.29-7.26 ppm (4H, m, ArH). Found: C 74.3; H 8.5; N 10.7%; $M^+$ 258. $C_{16}H_{22}N_2O$. Calculated: C 74.4; H 8.6; N 10.8%; M 258.

2-[3-(N-Methylcarbamoyl)propyl]-1,3,3-trimethyl-3H-indolium perchlorate (V) was obtained from 1.29 g (5 mmoles) of compound IV similarly to perchlorate IIa. Yield: 0.65 g (36%), mp 173-174°C (from alcohol). Proton NMR spectrum ($CD_3CN$): 1.59 (6H, s, 3,3-$CH_3$); 1.81-2.18 (2H, m, $CH_2$); 2.46 (2H, t, J = 7 Hz, $CH_2$); 2.72 (3H, d, J = 4.5 Hz, $CONH\underline{CH_3}$); 2.97-3.24 (2H, m, $CH_2$); 4.07 (3H, s, 1-$CH_3$); 6.62 (1H, br. s., NH); 7.56-7.87 ppm (4H, m, ArH). Found: C 53.8; H 6.5; Cl 10.1; N 7.8%. $C_{16}H_{23}ClN_2O_5$. Calculated: C 53.6; H 6.5; Cl 9.9; N 7.8%.

LITERATURE CITED

1. G. A. Cook (editor), Enamines: Synthesis, Structure and Reactions, Marcel Dekker, New York, London (1969).
2. P. W. Hickmott, Tetrahedron, 38, 3362 (1982).
3. V. G. Granik, Usp. Khim., 53, 651 (1984).
4. I. Ninomiya, T. Naito, S. Higuchi, and T. Mori, Chem. Commun., No. 8, 457 (1971).
5. A. A. El-Barbary, S. Carlsson, and S.-O. Lawesson, Tetrahedron, 38, 405 (1982).
6. G. Sokrates, Infrared Characteristic Group Frequencies, Wiley, Chichester, New York (1980), p. 74.
7. K. L. Williamson and J. D. Roberts, J. Am. Chem. Soc., 98, 5082 (1976).
8. Ch. L. Perrin and G. M. L. Arrhenius, J. Am. Chem. Soc., 104, 6693 (1982).
9. P. Trška, V. Sklenař, and M. Hajek, Chem. Listy, 77, 874 (1983).
10. H.-I. Teuber, J. Hohn, and A. Gholami, Chem. Ber., 116, 1309 (1983).
11. J. R. Fehlner, P. I. Borowski, P. L. Pettinato, and A. J. Freyer, J. Org. Chem., 49, 170 (1984).

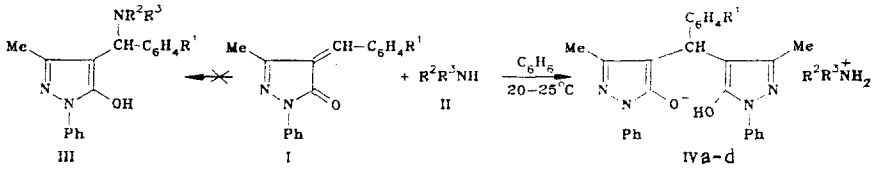
# REACTION OF 4-ARYLIDENE-3-METHYL-1-PHENYL-5-PYRAZOLONES WITH AMINES

G. Mann, D. Bendler, L. Hennig, M. A. Kuznetsov, and V. N. Belov

UDC 547.233'775:543.422.25

The reaction of primary and secondary amines with 4-arylidenepyrazolones gives the corresponding ammonium salts of 4,4'-benzylidenebis-5-pyrazolone derivatives but not adducts on the exocyclic C=C bond as was previously believed.

The reactions of 4-arylidene-5-pyrazolones with nucleophiles have been the subject of numerous studies [1]. In particular, it has been reported [2] that with secondary amines (piperidine, morpholine) addition products (III) are formed on the exocyclic C=C bond. Compounds of this type are of interest to us as intermediates in the synthesis of dyes, therefore we have studied the reaction of two 4-arylidene-3-methyl-1-phenyl-5-pyrazolones (I) with primary and secondary amines (II).




IV a $R^1=R^2=H$, $R^3=i$-Bu; b $R^1=H$, $R^2=R^3=Et$; c $R^1=H$, $R^2+R^3=(CH_2)_5$; d $R^1=p$-MeO, $R^2=H$, $R^3=i$-Bu

In accordance with the findings of [2], the reaction proceeds readily even at room temperature and in all cases white crystalline addition products IVa-d are obtained (Table 1). However, their composition and PMR spectra do not correspond to the previously proposed structure of III. As can be seen from Table 2, for adducts IVa, b, d the ratio of intensities of the signals from the methyl groups in the pyrazoline ring and in the amine fragment is not 1:2 as in structure III, but 1:1. Moreover, there is a signal from only one arylidene proton in the spectra, while for compound IVd there is a signal from only one methoxyl group, in other words, the addition products have a symmetrical structure that contains two pyrazoline fragments, a CH group with an aryl substituent, and one amine molecule.

Karl Marx University, Leipzig, GDR 7010. A. A. Zhdanov Leningrad State University, Leningad 199004. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 905-908, July, 1988. Original article submitted February 4, 1987; revision submitted January 26, 1988.

0009-3122/88/2407-0743$12.50 