INVESTIGATIONS IN THE FIELD OF 1-AZA BICYCLIC COMPOUNDS

VII. Cyanoethylation Reaction in the 1, 2-Dihydropyrrolizine Series*

A. A. Ponomarev and V. M. Levin

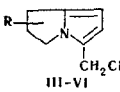
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 5, pp. 939–941, 1969

UDC 547.759.315+542.951.9

As the result of a study of the condensation of acrylonitrile and 1,2-dihydropyrrolizines in the presence of $AlCl_3$, 5-cyanoethyl-1,2-dihydropyrrolizines have been synthesized. Some of the properties of the compounds obtained have been studied and their IR spectra have been recorded.

Treibs and Michl [2] have shown that the cyanoethylation reaction takes place readily and with good yields in the case of pyrrole and its alkyl derivatives.

As our experiments have shown, 1,2-dihydropyrrolizines (I) also react readily with acrylonitrile (II). The reaction takes place at room temperature between equivalent amounts of I and II in the presence of anhydrous $AlCl_3$ in anhydrous dichloroethane. By this method we have synthesized the previously unknown 5-cyanoethyl-1,2-dihydropyrrolizine (III) and also its 3-methyl, 2-ethyl, and 2-methyl derivatives (IV–VI)



III–VI

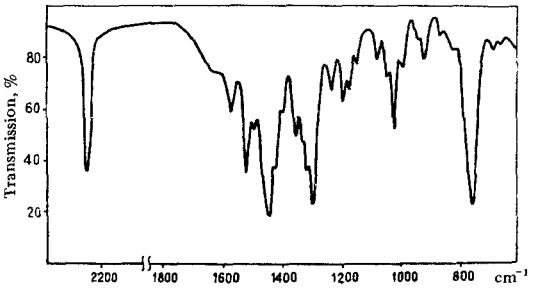
III R = H;
IV R = 3-CH_3;
V R = 2-C_2H_5;
VI R = 2-CH_3

The compounds obtained are colorless oily liquids readily soluble in organic solvents and insoluble in water. Their properties and analyses are given in the table.

In the IR spectra of compounds III–VI there are absorption bands characteristic for the 1,2-dihydropyrrolizine ring in the 1270–1300 cm^{-1} region (ν_{C-N}) and the 1500 cm^{-1} region ($\nu_{C=C}$). In addition, the spectra exhibited absorption bands at 2250 cm^{-1} corresponding to the stretching vibrations of the C≡N group (see figure).

EXPERIMENTAL

1,2-Dihydropyrrolizine and its 2-ethyl and 3-methyl derivatives (I) were obtained as described previously [3]. The previously-unreported **2-methyl-1,2-dihydropyrrolizine** was obtained by the dehydration of 1-amino-3-furyl-2-methylpropane over Al_2O_3 at 420–440° C with a yield of 41%, bp 69.5° C (12 mm); d_4^{20} 0.9680; n_D^{20} 1.5123. Found, %: C 79.08; 78.87; H 9.27; 9.50; N 11.39; 11.43. MR_D 37.75. Calculated for $C_8H_{11}N$, %: C 79.29; H 9.15; N 11.65. MR_D 37.58.



IR spectrum of 5-cyanoethyl-3-methyl-1,2-dihydropyrrolizine.

5-Cyanoethyl-1,2-dihydropyrrolizines (III–VI, table). A three-necked 0.5-liter flask fitted with a mechanical stirrer and reflux condenser with calcium chloride tube was charged with 0.1 mole each of the appropriate I and acrylonitrile and with 100 ml of absolute dichloroethane. With vigorous stirring and water cooling, 0.1 mole of anhydrous $AlCl_3$ was slowly added and then the mixture was stirred at room temperature for 30 min and at 50–60° C for 15 min, cooled to room temperature, and poured into 250–300 ml of water; the dichloroethane layer was separated off, and the aqueous layer was extracted with benzene (2 × 50 ml). The benzene extracts were combined with the dichloroethane solution and dried with Na_2CO_3 for 2 hr, after which

*For part VI, see [1].

5-Cyanoethyl-1,2-dihydropyrrolizines (III–VI)

Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Empirical formula	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N	Yield, %
III	128—129 (2)	1.0715	1.5354	46.6	46.8	$C_{10}H_{12}N_2$	74.79 74.56	7.28 7.62	17.31 17.25	75.02	7.54	17.44	62.9
IV	149—150 (4)	1.0470	1.5280	51.2	51.4	$C_{11}H_{14}N_2$	75.50 75.30	8.18 8.26	15.83 15.70	75.83	8.09	16.07	57.0
V	129—130 (1)	1.0223	1.5196	55.9	56.0	$C_{12}H_{16}N_2$	76.31 76.70	8.51 8.78	14.70 14.91	76.57	8.56	14.86	48.0
VI	150 (4)	1.0367	1.5250	51.4	51.4	$C_{11}H_{14}N_2$	75.93 75.73	8.57 8.37	16.18 16.25	75.83	8.09	16.07	61.1

the solvent was distilled off under reduced pressure and the residue was distilled in vacuum.

The IR spectra were recorded by I. Ya. Evtushenko on a UR-10 double-beam spectrophotometer in the 670–2400 cm^{-1} region with NaCl and LiF prisms in the form of the pure liquids.

REFERENCES

1. I. M. Skvortsov, I. V. Antipova, and A. A. Ponomarev, DAN (in press).

2. A. Treibs and K. H. Michl, Ann., **589**, 163, 1954.

3. A. A. Ponomarev and I. M. Skvortsov, ZhOKh, **32**, 97, 1962.

18 December 1967

Chernyshevskii Saratov State University

INVESTIGATIONS IN THE FIELD OF 1-AZA BICYCLIC COMPOUNDS

VIII. The Catalytic Reduction of 5-(β-Cyanoethyl)-1,2-dihydropyrrolizines*

A. A. Ponomarev and V. M. Levin

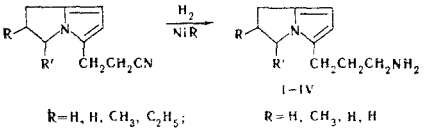
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 5, pp. 941–943, 1969

UDC 547.759:542.961

1,2-Dihydropyrrolizin-5-ylpropylamines have been obtained by the reduction of 5-(β-cyanoethyl)-1,2-dihydropyrrolizines on Raney nickel. Some properties of the amines obtained and of their acetyl derivatives have been studied and their IR spectra have been recorded.

One of the well-studied methods of obtaining primary amines is the reduction of nitriles on Raney nickel catalysts [2–4].

We have performed the reduction of 5-(β-cyanoethyl)-1,2-dihydropyrrolizines on Raney nickel in methanol saturated with ammonia at 80–90° C with a hydrogen pressure of 100–120 atm. The yields of amines amounted to 80–85%.



In this way we have obtained: 1,2-dihydropyrrolizin-5-ylpropylamine (I), (3-methyl-1,2-dihydropyrrolizin-5-yl)propylamine (II), (2-methyl-1,2-dihydropyrrolizin-5-yl)propylamine (III), and (2-ethyl-1,2-dihydropyrrolizin-5-yl)propylamine (IV).

The acetyl derivatives of compounds I–IV were obtained: N-(1,2-dihydropyrrolizin-5-ylpropyl)acet-

*For part VII, see [1].

1,2-Dihydropyrrolizin-5-ylpropylamines and Their Acetyl Derivatives

Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Empirical formula	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N	Yield, %
I	124—125 (3)	1.0218	1.5385	50.32	50.41	$C_{10}H_{16}N_2$	73.41 73.36	10.19 10.29	16.85 16.89	73.13	9.81	17.05	80
II	110—111 (1)	1.0030	1.5308	54.97	55.03	$C_{11}H_{18}N_2$	74.10 74.20	10.19 9.73	15.38 15.46	74.16	10.12	15.71	81
III	120—121 (2)	0.9946	1.5273	55.13	55.03	$C_{11}H_{18}N_2$	74.16 74.15	10.34 10.33	15.61 15.80	74.16	10.12	15.71	83
IV	132—133 (2)	0.9847	1.5225	59.61	59.64	$C_{12}H_{20}N_2$	75.16 74.92	10.62 10.73	14.30 14.48	74.95	10.48	14.56	85
V	196—197 (3)	1.0883	1.5410	59.59	59.83	$C_{12}H_{18}N_2O$	69.38 69.38	8.74 8.38	13.46 13.52	69.87	8.79	13.58	50
VI	178—179 (3)	1.0569	1.5330	64.67	64.45	$C_{13}H_{20}N_2O$	70.59 70.62	9.15 9.32	12.63 12.75	70.88	9.15	12.72	58
VII	194—195 (3)	1.0572	1.5305	64.62	64.45	$C_{13}H_{20}N_2O$	70.61 71.26	9.53 9.65	12.53 12.81	70.88	9.15	12.72	59
VIII	194—195 (2)	1.0450	1.5267	68.89	69.07	$C_{14}H_{22}N_2O$	71.75 72.04	9.70 9.60	11.86 12.06	71.75	9.46	11.95	53