CYCLIZATION OF 2-(1′-ALKYL-2′-ALKENYL)ANILINES IN POLYPHOSPHORIC ACID

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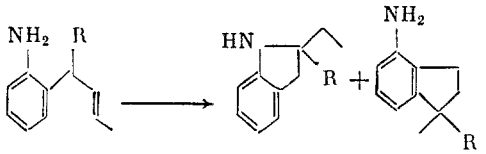
UDC 542.952.1:66.095.252.7:547.
551.2:546.185-325:547.665

The cyclization of 2-alkenylarylamines in polyphosphoric acid (PPA) with 1,2 and 1,3 shifts of the α-alkyl substituent of the alkenyl fragment leads to the formation of indoline and indane compounds. Cis- and trans-stereoisomers of 2-methyl-4-ethyl-1-aminoindane formed without displacement of the α-substituents as well as 2-methyl-2-propylindoline are obtained from 2-(1′-methyl-2′-pentenyl)-aniline.

The intramolecular cyclization of N- and 2-alkenylarylamines is a promising method for obtaining many nitrogen-containing heterocyclic compounds [1,2]. The use of polyphosphoric acid (PPA) as the cyclizing agent permits the synthesis of indole [3], indoline, and indane compounds [4] in high yield. We have shown that the cyclization of 2-(1′-methyl-2′-butenyl)-anilines involved 1,2 and 1,3 methyl shifts in the alkenyl substituent with subsequent formation of 2-methyl-2-ethylindolines and 4,4-dimethyl-1-aminoindanes [5].

In the present work, we studied the possibility of 1,2 or 1,3 alkyl shifts in 2-(1′-alkyl-2′-alkenyl)anilines during their reactions in PPA and the synthesis of sterically strained 2,2-dialkylindolines.

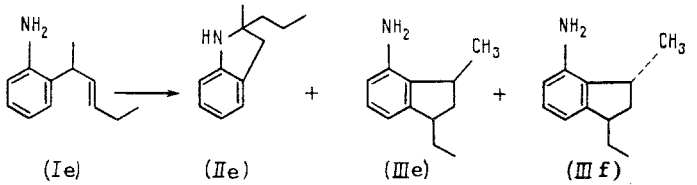
These experiments showed that 2-(1′-alkyl-2′-alkenyl)anilines (Ia) and (Ib) with methyl and isopropyl groups at $C^{1'}$ undergoes both 1,2 and 1,3 alkyl shifts with subsequent formation of 2,2-dialkylindolines (IIa) and (IIb) and 1-amino-4,4-dialkylindanes (IIIa) and (IIIb). Heating (Ic) in PPA gave only 1-amino-4-allyl-4-methylindane (IIIc) formed as a consequence of a 1,3 shift of the 1′-allyl group. The low yield of (IIIc) and the absence of indoline (IIc) is a result of considerable tar formation. The cyclization of (Id) in PPA is accompanied by a 1,2 shift of the 1′-ethyl group in the alkenyl substituent and leads to 2,2-diethylindoline (IId). The lack of (IIId), which would be formed as the result of a 1,3 shift of the 1′-ethyl group of the alkenyl substituent, is not readily explained.



(I) (II) (III)

(I)	(II), %	(III), %
(a) R=Me	75	15
(b) R=*i*-Pr	26	39
(c) R= allyl	–	17
(d) R=Et	36	–

The cyclization of 2-alkenylarylamine (Ie) gave a 1:1 mixture of the cis (IIIe) and trans stereoisomers (IIIf) of 1-amino-2-methyl-4-ethylindane in 95% total yield in addition to 2-methyl-2-propylindoline (IIe) obtained in 5% yield. We should note that (IIIe) and (IIIf) are formed without isomerization of the alkenyl fragment.



(Ie) (IIe) (IIIe) (IIIf)

The structures of these products were established by spectral methods. The IR spectra of the indolines show the disappearance of one band at 3300-3500 cm^{-1}, while this spectral region of

Institute of Chemistry, Bashkir Science Center, Urals Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2811-2814, December, 1990. Original article submitted October 2, 1989.

0568-5230/90/3912-2551$12.50

TABLE 1. Characteristics of (IIb), (IId), (IIe), (IIIb), (IIIc), (IIIe), and (IIIf)

Compound	Bp, °C n_D^{20}; R_f	IR (ν, cm^{-1})	PMR (δ, ppm)
(IIb)	R_f 0,49 n_D^{20} 1,5968	1380 (gem-CH_3) 3370 (NH)	0,97 t (CH_3), 1,03 d (CH_3), 1,29 m (CH_2, CH), 2,76 s (CH_2), 3,26 s (NH), 6,46–7,09 m (Ar)
(IId)	77° (2 mm)	3380 (NH)	0.84 t (CH_3), 1,54 q (CH_2), 2,79 s (CH_2), 3,48 s (NH), 6,45–7,03 m (Ar)
(IIe)	R_f 0,48 n_D^{20} 1,5893	3380 (NH)	0.91 t (CH_3), 1.20 s (CH_3), 1,23–1,66 m (CH_2–CH_2), 2,77 s (CH_2), 3,42 s (NH), 6,40–7,03 m (Ar)
(IIIb)	R_f 0,18 n_D^{20} 1,5716	1380 d (gem-CH_3) 3380–3460 (NH_2)	0,98 d (CH_3), 1,11 s (CH_3), 1,20–1,38 m (CH, CH_2), 2,80 m (CH_2), 3,60 s (NH_2), 6,45–7,00 m (Ar)
(IIIc)	R_f 0,18 n_D^{20} 1,5742	3370–3460 (NH_2)	1,26 s (CH_3), 1,34–2,74 m (CH_2/CH_2, CH_2), 3,46 s (NH_2), 5,05–6,00 m (CH=CH_2), 6,63–7,10 m
(IIIe,f)	119° (2 mm) n_D^{20} = 1,5704	3380–3450 (NH_2)	1,19 d (CH_3), 1,19 t (CH_3), 1,25 t (CH_3), 1,42–2,09 m, (CH_2, CH_2), 2,71–2,76 m (CH, CH), 3,46 s (NH_2), 6,42–7,01 m (Ar)

the aminoindanes is unchanged relative to the spectra of the starting compounds. The ^{13}C NMR spectra of 2,2-dialkylindolines show a singlet for C^2 at 63.58-66.32 ppm. The methylene group of the indoline ring appears in the PMR spectrum as a two-proton singlet at 2.76-2.79 ppm. The ^{13}C NMR spectrum of (IIIb) has a singlet at δ34.07 ppm, corresponding to the C^4 quaternary carbon atom. The methyl group at this carbon atom in the PMR spectra of (IIIb) and (IIIc) is seen as a three-proton singlet (Table 1).

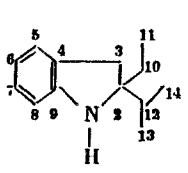
The IR signal of the NH_2 group of the mixture of stereoisomers (IIIe) and (IIIf) is seen at 3380 and 3450 cm^{-1}. The PMR spectrum of these stereoisomers contains a doublet for the methyl group at C^2 and two triplets for the methyl groups of the ethyl residue at 1.19 and 1.25 ppm. The ^{13}C NMR spectrum consists of two sets of signals, corresponding to the two stereoisomers in the indane fragment of the molecule. The identification of the cis and trans isomers was accomplished on the basis of the chemical shifts of C^3 in the ring and C^{11} of the ethyl substituents (Table 2). Trans isomer (IIIf) is characterized by diamagnetic shifts of these signals relative to cis isomer (IIIe) [6]. The molecular ion M^+ is seen in the mass spectrum with m/z 175 (40%).

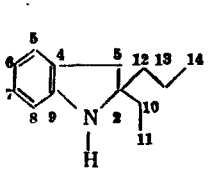
EXPERIMENTAL

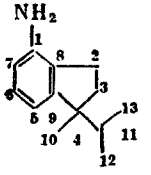
The purity of the starting reagents and products was checked by gas-liquid chromatography using a 3000 × 3-mm metal column packed with 5% SE-30 on Chromaton N-AW-DMCS and an LKhM-8MD chromatograph with a katharometer. The helium gas flow rate was 40 ml/min. The analysis was carried out with temperature programming from 130 to 200°C at a rate of 4 deg/min. The purity was also checked by thin-layer chromatography on Silufol. The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 100 MHz. The ^{13}C NMR spectra were taken in $CDCl_3$ on a Bruker WH-90 spectrometer with TMS as the internal standard. The mass spectrum was obtained on an MKh-13 mass spectrometer at 70 eV. The column chromatography was carried out on Lachema L 40/100 silica gel using 12:1 hexane-ether as the eluent.

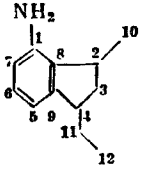
General Cyclization Procedure. The starting ortho-alkenylaniline was mixed with a portion of PPA (2:1 H_3PO_4–P_2O_5) equal to 10 times its weight and heated for 7 h at 140°C. The reaction mixture was cooled to room temperature and diluted with water and neutralized by the addition of saturated aq. NaOH with stirring. The product was extracted with benzene. The organic layer was separated and dried over K_2CO_3. The solvent was evaporated on a rotary evaporator. The residue was subjected to column chromatography or distilled in vacuum.

TABLE 2. ^{13}C NMR Spectra of (IIb), (IId), (IIe), (IIIb), (IIIe), and (IIIf)


(IIb)


(II, d, e)


(IIIb)


(III, e, f)

Compound	C¹	C²	C³	C⁴	C⁵	C⁶	C⁷	C⁸	C⁹	C¹⁰	C¹¹	C¹²	C¹³	C¹⁴
(IIb)		64,75 s	31,81 t	135,5 s	124,31 d	118,51 d	127,17 d	109,14 d	149,53 s	14,52 t	8,79 q	29,51 d	21,58 q	23,14 q
(IId)		66,32 s	39,70 t	128,17 s	124,66 d	117,72 d	127,13 d	108,49 d	150,49 s	31,51 t	8,41 q			
(IIe)		63.58 s	44,73 t	127,69 s	124,83 d	118,02 d	127,42 d	108,92 d	150,22 s	26,96 q		42,38 t	17,98 t	14,65 q
(IIIb)	145,82 s	26,66 t	33,59 t	34,07 s	117,25 d	126,22 d	112,52 d	125,87 d	143,64 s	19,03 q	28,13 d	32,08 q	32,29 q	
(IIIe)	143,73 s	33,16 d	29,65 t	27,91 d	119,93 d	126,17 d	112,74 d	126,78 s	142,04 s	24,36 q	27,22 t	19,33 q		
(IIIf)	143,64 s	32,29 d	25,23 t	27,52 d	117,85 d	126,17 d	112,74 d	126,05 s	142,39 s	22,37 q	24,36 t	19,07 q		

The physicochemical constants and spectral characteristics of these compounds are given in Tables 1 and 2.

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SYNTHESIS, ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR SPECTRA, AND CATHODIC BEHAVIOR OF N-CHLORO-1,2,4-TRIAZOLES

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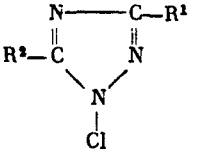
UDC 542.91:543.422.25:541.13:547.792.3

Syntheses are reported for N-chloro-1,2,4-triazoles and the NMR spectra of these compounds were studied. An investigation was also carried out on a platinum electrode in 0.1 N Bu_4ClO_4 in acetonitrile. The reduction proceeds with the transfer of two electrons and the formation of triazole and chloride ions. The half-wave potentials of the reduction of N-chlorotriazoles correlates well with the pK_a values of the corresponding NH-acids. The electrochemical reduction of N-chlorotriazoles is accompanied by the reaction of N-chlorotriazole with the chloride ion formed on the cathode, which leads to the NH form of 1,2,4-triazole through a series of chemical steps.

N-Chloro-1,2,4-triazoles are mild chlorinating and oxidizing agents [1,2] but there are no quantitative data on their oxidative capacity, for which reduction potentials may serve as an index. Furthermore, there is considerable interest in the cathodic reduction of these compounds as a possible pathway for the generation of N-centered triazole radicals. We studied the capacity of N-chloro-1,2,4-triazoles (Ia)-(If) to undergo electrochemical reduction.



(Ia—f)

$R^1 = Cl$, $R^2 = H$ (a); $R^1 = NO_2$, $R^2 = Me$ (b); $R^1 = NO_2$, $R^2 = H$ (c); $R^1 = R^2 = Cl$ (d); $R^1 = NO_2$, $R^2 = Br$ (e); $R^1 = NO_2$, $R^2 = Cl$ (f)

Chlorotriazoles (Ia) and (Id) were obtained according to Becker and Eisenschmidt [1] by the direct chlorination of the corresponding triazoles using gaseous chlorine in aqueous solution. Previously undescribed N-chloro-3-nitrotriazoles were synthesized by analogy. While the syntheses of (Ie) and (If) may be carried out smoothly in both neutral and alkaline media (the pK_a values of NH-acids of (Ie) and (If) are 3.05 and 3.00, respectively), (Ib)

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2814-2821, December, 1990. Original article submitted October 2, 1989.

0568-5230/90/3912-2554$12.50