CONJUGATION OF AZIRIDINE AND BENZENE RINGS IN A NUMBER OF p-SUBSTITUTED N-PHENYLETHYLENEIMINES

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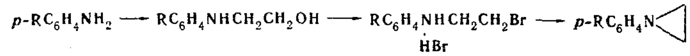
UDC 547.717:543.422.25.4.6

p-Methyl- and p-halo-substituted N-phenylethyleneimines were synthesized, and their structures were confirmed by their IR, UV, and PMR spectra. It was concluded that the introduction of the indicated substituents into the para position relative to the aziridine ring increases conjugation of the benzene and aziridine rings as compared with unsubstituted N-phenylethyleneimine.

Numerous literature data attest to the presence of a shift of the absorption band in the UV spectrum of N-phenylaziridine as compared with unsubstituted aziridine. It has been concluded that the two rings are conjugated. Research [1] has been devoted to the spectroscopic investigation of the conjugation of phenyl-substituted aziridines. X-ray diffraction studies [2] made in the case of N-(p-bromobenzoyl)ethyleneimine confirmed delocalization of the electron pair of the nitrogen atom and an increase in the p character of the C–N bond.

We set out to ascertain to what extent the presence of different para substituents in N-phenylethyleneimines affects the magnitude of the conjugation of the aromatic and ethyleneimine rings. For this, we investigated the IR, UV, and PMR spectra of p-methyl- and p-halo-substituted N-phenylethyleneimines. The p-substituted N-phenylethyleneimines were obtained by a general scheme [3, 4]:



I-V

I-V R = H, CH_3, Cl, F, Br

We were unable to obtain N-(p-nitrophenyl)ethyleneimine from N-(p-nitrophenyl)ethanolamine by means of this method. An attempt to synthesize N-(p-methoxyphenyl)ethyleneimine by cyclization of N-(p-methoxyphenyl)bromoethylamine was also unsuccessful, inasmuch as the reaction was accompanied by complete resinification of the starting compound.*

The maxima of the absorption bands of the UV spectra of II-V are shifted by up to 20 nm as compared with the spectra of I (Table 1). This is apparently explained by expansion of the molecular orbitals when the p-like electrons of the substituent (F, Cl, Br) are included in it or by hyperconjugation (CH_3). In addition, the intensities of the maxima of the absorption bands of III-V are 1.5-2.5 times greater than the corresponding value for I (Table 1).

Thus the introduction of substituents into the para position relative to the aziridine ring increases the capacity of the unshared pair of the nitrogen atom of the latter for conjugation with the π-electron sys-

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* In the course of the research reported in the present paper a communication regarding the synthesis of the indicated compounds from the tosylates of the appropriate amino alcohols by cyclization with sodium hydride appeared [5, 6].

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 70-72, January, 1975. Original article submitted April 2, 1973; revision submitted April 10, 1974.

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TABLE 1. UV and IR Spectra of p-Substituted 11-Phenylethyleneimines

Compound	R	λ_{max}, nm (lg ε)	IR spectrum, cm^{-1} (CCl$_4$)							
			$\nu_{CH_2}(s)$	$\nu_{CH_2}(as)$	ring pulsation	pendulum δCH_2	fan δCH_2	$\delta_{C\cdots C}$	out-of-plane δCH	in-plane δCH
I	H	236 (4,09)	3000	3070	1322	817	1165	1495	700—770	—
II	CH_3	250 (4,15)	3000	3070	1320	837	1177	1520	715	1110
III	Cl	256 (4,45)	3005	3077	1328	840	1175	1495	750	1100
IV	F	237 (4,25)	3005	3080	1325	850	1175	1508	715	1098
V	Br	245 (4,51)	3002	3075	1325	839	1167	1490	737	1073

TABLE 2. Intensities of the ν_{C-C} Ring Bands

Compound	$\Delta\nu^{a}{}_{1/2}$, cm^{-1}	ε, liter/mole · cm	A · 10^{-3} liter/mole · cm
I	10	249	10,8
II	35	143	23,0
III	15	463	17,8
IV	40	397	61,5
V	20	213	16,4

tem of the benzene ring, as a result of which the difference between the $\underbrace{\mathrm{NCH_2CH_2}}$ and $N(CH_3)_2$ groups decreases. Thus in this case one observes a pattern that is just the opposite of that presented in [1].

One should bear in mind that the reduction in the transition energy for II-V as compared with I is probably associated with a decrease in angle α between the aromatic carbon–nitrogen bond and the axis of the orbital of the unshared pair of the nitrogen atom (for I, α ~ 118°).

A decrease in angle α facilitates interaction of the electron pair of the nitrogen atom with the π system of the benzene ring, in this case increasing the coplanarity of the two rings. An electron diffraction study of I showed [7] that conjugation between the electron pair of nitrogen and the π system of the ring is realized if the projection of the orbital of the electrons on the axis perpendicular to the plane of the ring is maximal. It is possible that the intensification of the conjugation of the two rings in II-V can also be explained from this point of view.

The characteristic frequencies of the asymmetrical stretching vibrations of the methylene groups are higher by 10 cm^{-1} in the IR spectra of II-V, whereas the frequencies of the pendulum deformation vibrations of the methylene group are higher by ~20-30 cm^{-1} than the corresponding values for I.

The intensities of the characteristic bands of the C⋯C skeletal vibrations of the benzene ring are sharply increased for II-V as a consequence of conjugation between the benzene and aziridine rings. In order to obtain a quantitative evaluation of this effect, we measured the molar integral intensities by the method in [8]:

$$A = k\cdot\Delta\nu_{1/2}{}^{a}\cdot\frac{1}{c\cdot l}\ln\left(\frac{T_0}{T}\right)_{max}.$$

In conformity with the integral intensities (Table 2), para substituents in the benzene ring are arranged in the following order with respect to their capacity for intensification of conjugation: $F > CH_3 > Cl > Br$.

In the future we hope to obtain data on the role of the inductive effect and the effect of para substituents in N-phenylethyleneimines.

EXPERIMENTAL

The melting points of the compounds obtained in this research were determined with the microheater stage of the Boethius system. The UV spectra of 10^{-4} M solutions in acetonitrile at layer thicknesses of 0.5 and 1.0 cm were obtained with a Specord spectrophotometer. The IR spectra of $5 \cdot 10^{-2}$ M solutions in CCl_4 and (for pure liquids) (ring C⋯C band) with the aid of NaCl and LiF cuvettes 4- and 6-mm long were obtained with a UR-20 spectrometer; the slit width was 4 cm^{-1}. The PMR spectra of 10% solutions of the compounds were obtained with a Perkin–Elmer R-12A spectrometer (60 MHz) with tetramethylsilane as the internal standard.

N-phenylethyleneimine (I) and N-(p-tolyl)ethyleneimine (II) were obtained by the method in [4], and N-(p-fluorophenyl)ethyleneimine was obtained by the method in [9].

N-(p-Chlorophenyl)ethanolamine. A mixture of 255 g (2 mole) of p-chloroaniline and 80.5 g (1 mole) of ethylene chlorohydrin was heated in an autoclave at 135° for 14 h, after which it was made alkaline with 10% NaOH solution and extracted with 300 ml of ether. The extracts were dried, the ether was removed by distillation, and the residue was vacuum distilled to give a product with mp 153-154° (3mm) in 44% yield. Found: C 56.0; H 6.1; N 7.9%. $C_8H_{10}ClNO$. Calculated: C 56.0; H 5.8; N 8.2%.

N-(p-Chlorophenyl)bromoethylamine Hydrobromide. A 126-g (0.74 mole) sample of N-phenylethanolamine was mixed (with cooling) with 300 ml (5.5 mole) of 48% HBr, after which the mixture was distilled with successive collection of 82, 31, 26, 13, 11, and 7 ml of distillate. The mixture was boiled for another 3 h, and 109 ml of HBr was removed by distillation. The residue began to crystallize when the mixture was cooled, and the solid was recrystallized from absolute ethanol to give a product with mp 148-149° in 71% yield. Found: C 31.1; H 3.4; N 4.7%. $C_8H_{10}Br_2ClN$. Calculated: C 30.4; H 3.2; N 4.4%.

N-(p-Chlorophenyl)ethyleneimine (III). A solution of 94.5 g (0.3 mole) of N-(p-chlorophenyl)bromoethylamine in 120 ml of water and 80 ml of 95% ethanol was added dropwise to a heated (50° solution) of 115 ml of 6 N NaOH and 300 ml of ethanol, after which the mixture was heated at 85° for 1 h. A total of 220 ml of ethanol was removed by distillation, and the residue was extracted with 300 ml of ether. The extracts were dried, the ether was removed by distillation, and the residue was dried with anhydrous sodium sulfate and distilled to give a product with bp 84-85° (8 mm) and n_D^{18} 1.5701 in 45% yield. Found: C 63.0; H 5.4; Cl 23.2; N 9.12%. C_8H_8ClN. Calculated: C 62.6; H 5.2; Cl 23.1; N 9.1%. PMR spectrum: ring CH_2 8.05 ppm (4H), C_6H_4 2.95 and 3.24 ppm (4H).

N-(p-Bromophenyl)ethanolamine. The yield of this compound with bp 160-161° (1.4 mm) and mp 71-73° was 42%. Found: C 63.8; H 7.9; N 8.4%. $C_9H_{13}NO_2$. Calculated: C 63.7; H 7.8; N 8.4%.

N-(p-Bromophenyl)bromoethylamine Hydrobromide. This compound was obtained as a viscous oil in 87% yield by a method similar to that used to prepare the p-chloro isomer. This crude product was used to obtain V.

N-(p-Bromophenyl)ethyleneimine (V). This compound, with bp 100° (7 mm) and n_D^{20} 1.5950, was obtained in 35% yield. Found: C 48.0; H 4.2; Br 39.6; N 7.3%. C_8H_8BrN. Calculated: C 48.5; H 4.1; Br 40.3; N 7.1%. PMR spectrum: ring CH_2 8.07 ppm (4H), C_6H_4 2.82 and 3.30 ppm (4H).

N-(p-Methoxyphenyl)ethanolamine. This compound, with bp 171-172° (5 mm) and n_D^{20} 1.5749, was obtained in 30% yield. Found: C 63.8; H 7.9; N 8.4%. $C_9H_{13}NO_2$. Calculated: C 63.7; H 7.8; N 8.4%.

N-(p-Methoxyphenyl)bromoethylamine Hydrobromide. This compound, with mp 165-166°, was obtained in 87.3% yield. Found: C 34.9; H 4.2; N 4.7%. $C_9H_{13}Br_2NO$. Calculated: C 34.8; H 4.2; N 4.5%.

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