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SYNTHESIS OF NEW CONDENSED ANALOGS OF ISOINDOLINIUM SALTS*

É. O. Chukhadzhyan, Él. O. Chukhadzhyan, K. G. Shakhatuni, and A. T. Babayan

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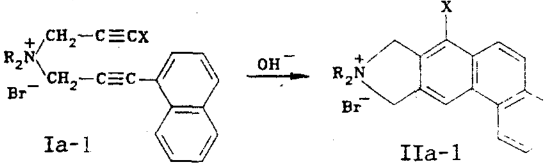
Quaternary ammonium salts that contain a 3-(α-naphthyl)propargyl group in addition to a group of the propargyl type undergo intramolecular cyclization of the diene-synthesis type under base-catalysis conditions to give condensed isoindolinium analogs.

Among the practically important nitrogen-containing heterocyclic compounds not much data relative to compounds of the isoindolinium series and their condensed analogs containing a phenanthrene ring are available.

It has been reported [2] that an accessible method for obtaining condensed dihydroisoindolinium salts was developed on the basis of the cyclization of ammonium salts containing a 3-(α-naphthyl)propargyl group in addition to a group of the allyl type.

In the present research, to synthesize potentially biologically active nitrogen-containing heterocycles with a phenanthrene ring we studied the cyclization of dialkylpropargyl[3-(α-naphthyl)propargyl]- (Ia-f) and dialkylbis[3-(α-naphthyl)propargyl]ammonium (Ig-l) salts.

It was established that salts Ia-l in the presence of an aqueous solution of 0.2 mole of alkali per mole of the salt, in contrast to the allyl analogs [2], undergo cyclization at room temperature rapidly with spontaneous heat evolution to give 2,2-dialkylnaphth[*f*]isoindolinium (IIa-e) and 2,2-dialkyl-4-(α-naphthyl)naphth[*f*]isoindolinium (IIg-l) bromides in almost quantitative yields (see Table 1).



Ia-l

IIa-l

I, IIa-f X=H, g-l X=α-naphthyl;a, R=CH_3, b,h R=C_2H_5, c,i R=C_3H_7; d,j R_2= =$(CH_2)_4$, e,k R_2=$(CH_2)_2O(CH_2)_2$

In [3], despite the data in [4], it was shown that dialkylbis(3-phenylpropargyl)ammonium salts undergo cyclization both in the presence and absence of a base when aqueous or aqueous alcohol solutions of them are heated. Salts Ig-l undergo almost quantitative cyclization under similar conditions.

The IR spectra of cyclic salts IIa-l do not contain the absorption bands of a disubstituted C≡C bond at 2230-2235 cm^{-1} that are characteristic for starting salts Ia-l and of a monosubstituted C≡C bond at 2120-2130 cm^{-1} that are characteristic for salts Ia-f; characteristic absorption bands of a 1,2,3,4-substituted aromatic ring at 810 cm^{-1}, of 1,2,4,5- and 1,2,3,4,5-substituted aromatic rings at 860-900 cm^{-1}, of a 1,2,3-substituted aromatic ring at 780-785 cm^{-1}, and of a 1,2-substituted aromatic ring at 730-770 cm^{-1} are observed.

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TABLE 1. Characteristics of the Starting (Ia-l) and Cyclic (IIa-l) Salts

Compound*	Empirical formula	mp, °C (from ethanol)	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Compound	mp, °C (from water)	R_f**	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log · ε)	Yield, %
Ia	$C_{18}H_{18}BrN$	141 ... 142	730, 775, 1500, 1590, 2130, 2230, 3030, 3060	225 (5,01), 282 (3,94), 300 (3,90), 312 (4,11)	IIa	273 ... 274	0,46	760, 810, 875, 1500, 1530, 1600, 3020, 3070	335 (2,83), 215 (4,69), 272 (4,36), 342 (2,52), 350 (2,85)	88
Ib	$C_{20}H_{22}BrN$	125 ... 126	735, 780, 1510, 1590, 2125, 2240, 3160	227 (4,98), 285 (3,89), 300 (4,00), 312 (4,03)	IIb	270 ... 271	0,51	760, 810, 870, 1510, 1520, 1580, 3060	215 (4,69), 255 (4,82), 298 (4,11), 335 (2,83), 350 (2,86)	96
Ic	$C_{22}H_{26}BrN$	Гигроск.	735, 780, 1500, 1580, 2130, 2230	228 (4,89), 290 (3,90), 305 (3,85), 315 (4,10)	IIc	240	0,53	730, 760, 810, 860, 1500, 1600	215 (4,83), 225 (4,78), 255 (4,90), 275 (4,52), 300 (4,18), 340 (2,83), 345 (2,54), 355 (2,85)	91
Id	$C_{23}H_{20}BrN$	161 ... 162	730, 780, 1540, 1590, 2120, 2240, 3150	225 (4,92), 288 (3,87), 318 (3,88), 320 (4,01)	IId	305	0,44	760, 810, 880, 1500, 1605	215 (4,86), 224 (4,85), 254 (4,84), 297 (4,38), 335 (2,71)	98
Ie	$C_{21}H_{22}BrN$	155	735, 790, 1540, 1590, 2120, 2330, 3150	225 (5,00), 285 (3,91), 300 (3,94), 312 (3,99)	IIe	301	0,56	760, 860, 1600, 3020, 3060	215 (4,62), 255 (4,79), 300 (3,98), 320 (2,45), 335 (2,53), 350 (2,43)	95
If	$C_{20}H_{20}BrNO$	162	730, 780, 1500, 1510 1590, 2120, 2240, 3150	225 (4,95), 292 (3,88), 305 (3,90), 315 (4,03)	IIf	313	0,48	730, 765, 810, 1600, 1610, 3020	215 (4,43), 255 (4,58), 280 (3,93), 348 (2,48)	96
Ig	$C_{28}H_{24}BrN$	70	750, 780, 1500, 1590, 2230, 3010, 3060, 3090	223 (5,11), 288 (5,48), 300 (5,51), 315 (5,38)	IIg	252	0,53	750, 785, 810, 870, 1500, 1590, 3015, 3060	220 (5,04), 260 (4,73), 275 (4,56), 283 (4,51), 300 (4,40), 340 (3,08), 355 (2,99)	88
Ih	$C_{30}H_{28}BrN$	111	745, 780, 1510, 1590, 2230, 3010, 3060	220 (5,03), 285 (5,40), 300 (5,61), 315 (5,35)	IIh	205	0,48	745, 780, 805, 875, 1510, 1590, 3010, 3065	222 (4,98), 260 (4,74), 285 (4,48), 300 (4,30), 330 (2,94), 350 (2,86)	94
Ii	$C_{32}H_{32}BrN$	176	735, 775, 1500, 1590, 2230, 3040, 3060	227 (5,13), 290 (5,50), 300 (5,59), 315 (5,32)	IIi	259	0,51	745, 780, 805, 875, 1500, 1590, 3010, 3065	220 (5,02), 260 (4,60), 283 (4,53), 300 (4,45), 335 (2,89), 350 (2,95)	95
Ij	$C_{26}H_{24}BrN$	68 ... 69	740, 760, 795, 1500, 1590, 2230, 3010, 3065	225 (5,58), 285 (4,53), 300 (4,63), 312 (4,48)	IIj	221 ... 222	0,52	750, 780, 800, 865, 1510, 1590, 3000, 3055	222 (5,09), 255 (4,85), 300 (2,83), 350 (2,76)	91
Ik	$C_{31}H_{25}BrN$	151 ... 152	750, 770, 1510, 1595, 2235, 3015, 3070	222 (5,51), 337 (4,54), 300 (4,66), 312 (4,54)	IIk	229	0,48	750, 805, 875, 1510, 1590, 3010, 3065	222 (4,06), 260 (4,89), 280 (4,59), 332 (2,87), 350 (2,81)	93
Il	$C_{30}H_{26}BrNO$	150	750, 780, 1500, 1590, 2230, 3015, 3060	225 (5,05), 290 (4,63), 300 (4,70), 310 (4,60)	IIl	266	0,55	750, 780, 800, 875, 1500, 1590, 3010, 3060	215 (4,69), 222 (4,58), 255 (4,82), 272 (4,36), 280 (4,30), 298 (4,11), 332 (2,78), 350 (2,85)	92

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*Compounds Ia-l and IIa-l are isomers.

**Thin-layer chromatography was carried out on Silufol UV-254 plates in an n-butanol—ethanol—water—acetic acid (8:2:3:1) system.

As expected, the UV spectra of the starting (Ia-l) and cyclic (IIa-l) salts contain three types of bands, viz., α, ρ, and β, which differ with respect to intensity and vibrational structure. For the phenanthrenes the α band is always the longest-wave band, and the relationship $\lambda_\alpha > \lambda_\rho > \lambda_\beta$ [5, 6] is retained for them; this is also observed for cyclic salts IIa-l. As expected, the intense absorption bands of the cyclic salts have lower values of the logarithms of the molar extinction coefficients (2.43-2.86) than those of the starting salts (3.99-4.11).

The introduction of substituents that have multiple bonds or unshared electron pairs into the molecules of the condensed aromatic compounds affects their absorption spectra [5]. In fact, the combination of a phenanthrene ring with a naphthalene ring in the case of salts IIg-l leads to an increase in the logarithms of the molar extinction coefficients (see Table 1).

EXPERIMENTAL

The IR spectra of KBr pellets or suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The UV spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. Thin-layer chromatography was carried out on Silufol UV-254 plates in an n-butanol—ethanol—water—acetic acid (8:2:3:1) system with development with iodine vapors.

Starting salts Ia-l were obtained in quantitative yields by the reaction of dialkyl-3-(α-naphthyl)propargylamines with propargyl bromide or 3-(α-naphthyl)propargyl bromide in absolute ether or absolute ether—acetonitrile. The physicochemical characteristics pertaining to the starting and cyclic salts are presented in Table 1.

The results of elementary analysis of salts I and II for N and Br were in agreement with the calculated values.

Isoindolinonium Salts II (General Method). A. A 0.3-0.8-ml sample, respectively, of 2 N KOH solution (the salt:base molar ratio was 5:1) was added to a solution of 3-8 mmole of starting salt Ia-l in 4-6 ml of water (if the salt was only slightly soluble, the solution was heated to 35-40°C, while 1.5-2 ml of ethanol was added until a homogeneous solution was obtained in the case of salts Ig-l). Rapid spontaneous warming up of the reaction mixture was observed 2-5 min after the addition of the aqueous alkali. The reaction mixture was then extracted with ether (1 × 15 ml). After 1-2 days, the cyclization product was isolated by filtration.

B. A solution of 0.8 mmole of dialkylbis[3-(α-naphthyl)propargyl]ammonium bromide Ig-l in 4 ml of water (if the starting salt did not dissolve on heating in water, 1-1.5 ml of ethanol was added) was heated at 90-92°C for 15 h (the solution of salt Ig was heated for 30 h). Compounds with characteristics that were identical to those of salts IIg-l obtained by method A were isolated by filtration or evaporation of the solvent to dryness.

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