SYNTHESIS OF DIALKYL 4-METHYLNAPHTH[f]ISOINDOLINIUM SALTS*

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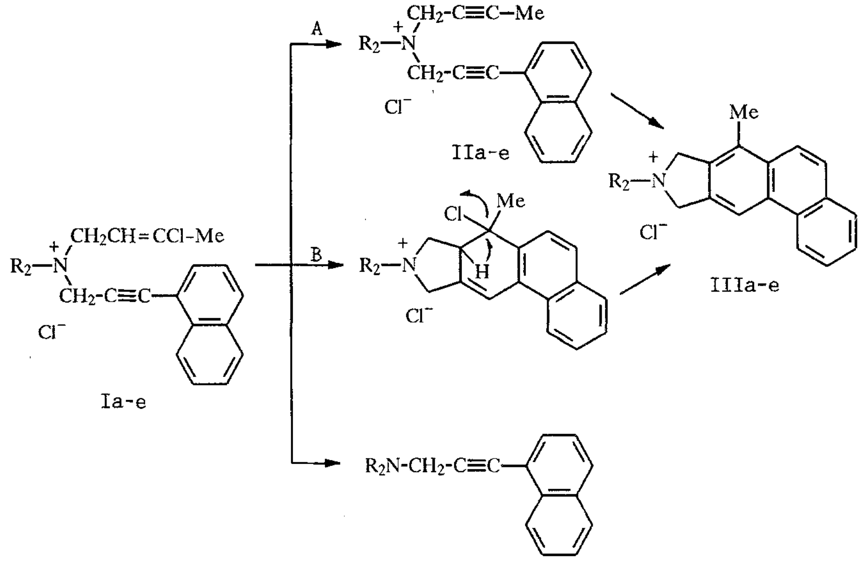
Dialkyl(3-chloro-2-butenyl)(3-α-naphthylpropargyl)ammonium chlorides undergo dehydrochlorination-cyclization in basic medium to give condensed isoindolinium salts.

We have previously shown [2] that quaternary ammonium salts containing both allyl and 3-α-naphthylpropargyl groups can undergo base catalyzed cyclization upon heating.

In order to obtain novel phenanthrene-type nitrogen heterocycles we have studied the reaction of dialkyl(3-chloro-2-butenyl)(2-α-naphthylpropargyl)ammonium chloride salts (Ia-e) with aqueous alkali. Based on these salt structures it is apparent that formation of final cyclization products IIIa-e can occur by two routes A and B which differ in the order of the dehydrochlorination and cyclization stages. According to route A, the starting salt dehydrochlorinates and the intermediate salt is cyclized. For route B the cyclization precedes the dehydrochlorination.



Ia-IIIa R_2=Me_2; Ib–IIIb R_2=Et_2; Ic–IIIc R_2=$(CH_2)_4$ Id-IIId R_2=$(CH_2)_5$; Ie-IIIe R_2= =$(CH_2)_2O(CH_2)_2$

Because the order of these steps could not be determined from the final material, we studied the reaction of salts Ia, b, d with 1.5 moles of aqueous alkali at room temperature. In all cases, the reaction mixture underwent almost complete formation of 1 g-atom of ionic chlorine from 1 mole of starting salt.

With salts Ia, b, d, titration of the reaction mixture at fixed intermediate reaction times measured the percent of ionic halogens formed (Table 2). From this table it is apparent that the cyclic reaction products are obtained in low yields. The dehydrochlorination products IIa, b, d were also obtained. These results show that dehydrochlorination of salts Ia, b, d precedes cyclization. Evidently the intermediate salts IIa, b, d, do not fully cyclize under these conditions. A separate experiment has shown that salt IId quantitatively forms salt IIId upon heating for 15-20 min at about 90°C in the presence of catalytic amounts of base. Thus propargyl salts with 3-arylpropargyl groups undergo base-catalyzed cyclization at room temperature with self-heating. Cyclization of the allyl analogs requires heating for 2-3 h, also pointing in favor of route A [3-5].

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TABLE 1. Parameters for the Starting (Ia-e) and Cyclized (IIIa-e) Salts

Compound	Empirical formula	Mp, °C (from absolute ethanol)	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm	Compound	Empirical formula	Mp, °C (from absolute ethanol)	R_f*	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	
Ia	$C_{19}H_{21}Cl_2N$	***	765, 780, 1510, 1590, 1680, 2230	225, 288, 300, 312	IIa	$C_{19}H_{20}ClN$	291...292	0,34	730, 810, 870, 1600	215(4,04), 256(4,62), 275(4,07), 285(3,99), 295(4,10), 330(2,73), 350(2,64)	60
Ib	$C_{21}H_{25}Cl_2N$	108...109	755, 780, 1500, 1590, 1650, 2240, 3020	227, 290, 300, 312	IIb	$C_{21}H_{24}ClN$	279...280	0,37	730, 780, 830, 890, 1600	225(4,86), 258(5,09), 273(4,48), 290(4,38), 320(2,58), 325(2,43), 332(2,62), 345(2,34), 350(2,54)	72
Ic	$C_{21}H_{23}Cl_2N$	180	750, 780, 1500, 1590, 1660, 2240	227, 287, 300, 312	IIc	$C_{21}H_{22}ClN$	323	0,36	730, 780, 800, 880, 1510, 1600	215(4,85), 225(4,62), 250(4,99), 258(5,09), 280(4,54), 290(4,45), 300(4,54), 320(2,59), 325(2,51), 330(2,66), 340(2,45), 350(2,60)	70
Id	$C_{22}H_{25}Cl_2N$	168...169	750, 780, 1500, 1590, 1660, 2240	227, 288, 300, 312	IId	$C_{22}H_{24}ClN$	327	0,38	730, 770, 810, 870, 1510, 1600	215(4,87), 225(4,80), 252(4,83), 259(4,89), 285(4,46), 290(4,42), 303(4,46), 323(2,69), 337(2,72), 350(2,54), 353(2,64), 355(2,57)	67
Ie	$C_{21}H_{23}Cl_2NO$	143...144	740, 780, 1650, 1680, 2240	228, 290, 300, 310	IIe	$C_{21}H_{22}ClNO$	316...317	0,39	730, 770, 815, 870, 1515, 1600, 1610	256(4,63), 276(4,11), 285(4,03), 297(4,13), 315(2,70), 325(2,60), 330(2,72), 340(2,54), 350(2,64)	73

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*TLC on Silufol UV-254 plates in n-butanol—ethanol—water—acetic acid, 8:2:3:1.

**The quoted yields correspond to cyclization products obtained on heating salts Ia-e.

***Hygroscopic salt.

TABLE 2. Results of the Reaction of Salts Ia, b, d with 1.5 Gram Equivalents of Aqueous Alkali at Room Temperature

Compound	time, h	Amount of ionic halogen formed, %	Yield of hydrochlorination product,%	Yield of salt III, %
Ia	24	75		
	48	90	31	21
Ib	65	95	57	22
Id	3,5	38		
	24	70		
	96	92	41	32

Dialkyl-4-methylnaphth[f]isoindolinium salts IIIa-e are formed in high yields by direct heating (about 90°C) of salts Ia-e with 1.5 mole of aqueous base for 1-1.5 h.

Under conditions of base catalysis, both at room temperature and upon heating, salts Ia-e give salts III and also dialkyl-3-α-naphthylpropargylamines in 8-10% yields. The picrates of the latter do not depress the melting points of known samples [2].

In the IR spectra of the intermediate salts IIa, b, d the bands characteristic of disubstituted $C{=}C$ bonds at 1650-1680 cm^{-1} are absent and the intensity of the bands for a disubstituted $C{\equiv}C$ bond is intensified compared with the starting salts Ia, b, d.

The IR spectra of the cyclic salts IIIa-e have no bands for disubstituted double or triple bonds at 1650-1680 or 2230-2240 cm^{-1} as found in Ia-e but shows characteristic absorptions for ortho-, 1,2,3,4-, and a pentasubstituted benzene ring at 730-780, 800-830, and 870-890 cm^{-1}, respectively.

As expected, the UV spectra of IIIa-e show a least intense α-band with a marked increase in vibrational structure having typical molar extinction coefficients (log = 2.34-2.73) [6, 7].

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer for KBr tablets or vaseline mull. UV spectra were obtained in ethanol solvent on a Specord UV-vis instrument. TLC was carried out on Silufol UV-254 plates in the system n-butanol—ethanol—water—acetic acid (8:2:3:1) and visualized with iodine vapor.

The starting salts Ia-e were obtained in quantitative yields by treating dialkyl-3-α-naphthylpropargylamines with 1,3-dichloro-2-butene in acetonitrile. Parameters for the starting and cyclic salts are given in Table 1.

Elemental analytical data for I and III (Cl and N) agreed with those calculated.

General Method for Dehydrochlorination—Cyclization of Dialkyl-3-chloro-2-butenyl(3-α-naphthylpropargyl)ammonium Chlorides Ia, b, d. A. To a homogeneous solution of starting salt (7-9 mmoles) in water (4-6 ml) there was added KOH solution (2N, 5.3-6.7 ml) (molar ratio of salt to base 1:1.5). The mixture was left at room temperature. After the specified reaction time, the percent of ionic halogen was determined by titration (Table 2).

B. To a solution of salt I (5-7 mmoles) in water (2.5-3 ml) there was added KOH solution (2N, 3.8-5.3 ml) (molar ratio of salt to base 1:1.5) and the product was heated at about 90°C for 1.5 h and extracted with ether (2 × 20 ml). The cyclization products were separated by filtration. They did not suppress the melting points of salts IIIa-e, obtained from salts Ia-e at room temperature. The ether extract was treated with hydrochloric acid. Basification of the acid layer gave the dialkylaminomethylnaphthalenes in 8-10% yield. Their picrates did not suppress the melting points of known samples [2]. Traces of vinylacetylene were found as the nonamino product. Titration of the mother liquor showed the formation of 0.75-0.98 g-atoms of ionic halogen per mole of salt taken.

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