

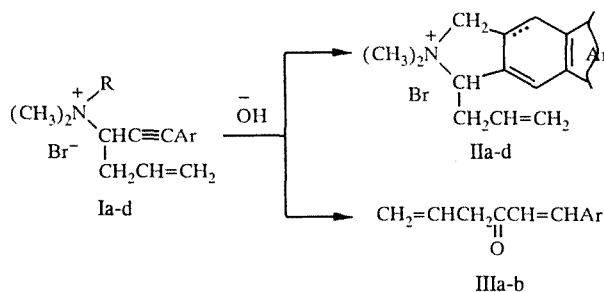
218.* INTRAMOLECULAR CYCLIZATION OF AN AMMONIUM SALT CONTAINING AN ALLYL SUBSTITUENT IN POSITION 1 OF THE DIENE FRAGMENT*

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It has been shown that, under basic catalytic conditions, dimethylpropargylallyl-(1-allyl-3-phenylpropargyl)- and -(1-allyl-3- α -naphthylpropargyl)ammonium salts undergo diene synthesis type intramolecular cyclization to form condensed analogs of isoindolenium and dihydroindolenium salts with an allyl substituent at position 1.

In the presence of catalytic amounts of base, dialkylpropargylallyl-(3-phenylpropargyl)- and -(3- α -naphthylpropargyl)-ammonium salts undergo ready intramolecular diene condensation to form condensed analogs of isoindolenium and dihydroisoindolenium salts [2-5].

Study of the effect of an allyl group on the behavior of dimethylpropargyl- (or allyl-) (1-allyl-3-phenylpropargyl)- (Ia, b) and -(1-allyl-3- α -naphthylpropargyl)ammonium salts (Ic, d) in aqueous base has shown that Ia, like 3-phenylpropargyl salts, cyclizes exothermically [2]. The cyclic product IIa, however, is formed in 60% yield.



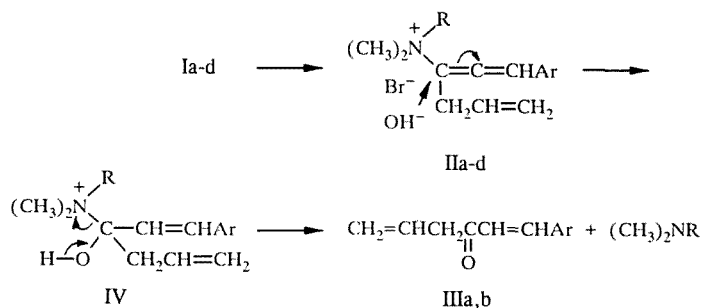
I, II a R = CH₂C≡CH, Ar = Ph; b R = CH₂CH=CH₂, Ar = Ph; c R = CH₂C≡CH, Ar = Nf; d R = -CH₂CH=CH₂, Ar = Nf; III a Ar = Ph, b Ar = Nf; II Yield : a (60%), b (66%), c (70%), d (72%)

Stepwise addition of base in the molar ratio salt:base 2.5:1 is necessary for cyclization of salt Ib. In contrast to other allyl salts with 3-arylpropargyl groups [3], cyclization of this salt occurs with a modest exotherm, the reaction temperature increasing slowly from 25 to 42°C. Cyclization of salt Ic, in contrast to 3- α -naphthylpropargyl analogs [4], needs moderate heating (40-42°C for 40 min).

As with other 3- α -naphthylpropargyl analogs [5], salt Id cyclizes upon heating at 90-92°C (1.5 h). It was found that cyclization of the salts I was accompanied by the side products III in 10-12% yields and tertiary amines, apparently formed via nucleophilic attack of a hydroxyl group at carbon one of the isomerized 1-allyl-3-arylpropargyl fragment and subsequent reaction of the intermediate salt.

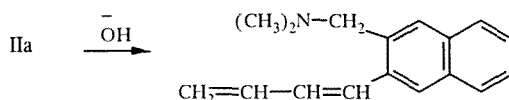
Communication 218 in the series "Investigations of amines and ammonium compounds." For Communication 217, see [1].

Institute of Organic Chemistry, Armenian Academy of Sciences, Yerevan 375094. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 213-216, February, 1994. Original article submitted October 12, 1993.



From this data, it is apparent that an allyl group in position 1 of a 3-phenyl- (or 3- α -naphthyl)propargyl fragment lowers the yield of cyclic product when compared with 3-arylpropargyl analogs [2-5].

Under severe conditions salt IIa undergoes fission to form 3-(1,3-butadienyl)-2-dimethylaminomethylnaphthalene in 55% yield. With these conditions ~30% of the amine polymerizes.



The IR spectra of the cyclic salts II show the absence of absorption bands for a disubstituted acetylene bond at 2220-2240 cm^{-1} seen in the starting salt I and a monosubstituted acetylene bond at 2110-2130 cm^{-1} seen in salts Ia, c. For salts II absorption bands at 720-780 cm^{-1} (ortho substitution) are seen, for salts IIa, b, a 1,2,4,5-substituted aromatic ring band at 870 and 880 cm^{-1} , and for IIc, d, a 1,2,3,4-substituted ring band at 810 cm^{-1} . The UV absorption maxima for the cyclic salts

TABLE 1. Parameters for Compounds Ia-d

Compound	Empirical formula	mp, °C (from ethanol)	IR Spectrum, cm^{-1}	UV Spectrum, λ_{max} , nm (log ϵ)
Ia	C ₁₇ H ₂₀ BrN	Hygroscopic	935, 970, 1570, 1590, 1640, 2130, 2240	225 (5,15), 242 (4,56)
Ib	C ₁₇ H ₂₂ BrN	Hygroscopic	920, 940, 960, 1640, 2230	228 (5,3), 243 (5,23), 290 (3,58)
Ic	C ₂₁ H ₂₂ BrN	150	720, 770, 800, 1500, 1640, 2110, 2230	210 (4,68), 222 (4,64), 230 (4,56), 290 (3,85), 302 (3,81), 312 (3,82)
Id	C ₂₁ H ₂₄ BrN	115	720, 740, 780, 800, 1500, 1590, 1640, 2230	228 (4,92), 290 (4,25), 302 (4,38), 312 (4,23)

TABLE 2. Parameters of Cyclic Compounds IIa-d

Compound	mp, °C (from water)	R _f	IR Spectrum, cm^{-1}	UV Spectrum, λ_{max} , nm (log ϵ)	Yield, %
IIa	219...220	0,53	720, 760, 870, 940, 970, 1540, 1605, 1640	228 (5,08), 270 (3,71), 280 (3,73), 305 (2,75)	60
IIb	222	0,58	730, 780, 930, 980, 1580, 1600, 1640	218 (4,43), 225 (4,36), 265 (4,11)	66
IIc	341...342	0,50	750, 810, 870, 940, 960, 995, 1500, 1600, 1640	215 (4,65), 225 (4,46), 255 (4,83), 300 (4,11), 320 (2,69), 335 (2,85), 355 (2,54)	75
II d	339	0,52	750, 770, 810, 910, 940, 980, 1510, 1540, 1610, 1640	235 (4,93), 320 (4,26), 335 (4,15)	71

IIa, b, when compared with starting salts Ia, b, show a long wavelength shift and have a lower log molar extinction coefficient (3.73; 4.11) due to the presence of the naphthalene ring [6, 7]. As might be expected, the α -band of salt IIc had the longest wavelength and the log molar extinction coefficient has a lower value (2.54-2.85) when compared with the starting salt Ic (3.81-3.85) [6, 7]. The nearly identical values of the log molar extinction coefficients for the α -band of salts Id and IId points to the presence of the naphthalene ring in both salts.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer using KBr tablets or vaseline oil and UV spectra in ethanol solvent on a Specord UV-vis spectrophotometer. Material purities were established by TLC on Silufol UV-254 plates using the system n-butanol-ethanol-acetic acid (8:2:3:1) or ether-hexane (1:3) and on alumina plates (Brockmann activity 2 grade) using benzene. Spots were visualized using iodine vapor.

N,N-Dimethyl-N-(1-allyl-3-phenylpropargyl)-, and N,N-dimethyl-N-(1-allyl-3- α -naphthylpropargyl)amines were obtained from the dimethylallyl(3-phenylpropargyl)- and dimethylallyl(3- α -naphthylpropargyl)ammonium bromides under Stevens rearrangement conditions [8].

The starting salts I were obtained by reaction of N,N-dimethyl-N-(1-allyl-3-phenylpropargyl)- and -(3- α -naphthylpropargyl)amine, 3-(1,3-butadienyl)-2-dimethylaminomethylnaphthalene, vinylbenzalacetone IIIa, and vinylnaphthalacetone IIIb agreed with those calculated.

2,2-Dimethyl-1-allylbenz[f]isoindolenium Bromide (IIa, C₁₇H₂₀BrN). A solution of KOH (2 ml, 2 N, 3.4 mmoles) was added to a homogeneous solution of salt Ia (20 mmoles) in water (~5 ml). The exothermic reaction raised the reaction temperature from 25 to 70°C. The mixture was extracted with ether (2 × 20 ml) and filtered to give salt IIa.

2,2-Dimethyl-1-allyl-3a,4-dihydrobenz[f]isoindolenium Bromide (IIb, C₁₇H₂₂BrN). A solution of KOH (2.3 ml, 2 N, 4 mmoles) was added to a homogeneous solution of starting salt Ib (23 mmoles) in water (6 ml). The reaction temperature increased from 25 to 42°C. After 1 h, a further aliquot of KOH (2.3 ml, 2 N) was added and the reaction mixture heated to 40-45°C for 30 min. Following extraction with ether (2 × 30 ml), filtration gave salt IIb.

The ether extracts, obtained from cyclization of salts Ia, b, were treated with hydrochloric acid. In both cases, chromatographically pure samples of vinylbenzalacetone IIIa were obtained from the ether layer in 11 and 12% yields, respectively. A 2,4-dinitrophenyl hydrazone could not be formed. Vacuum distillation caused decomposition. IR spectrum: 690, 760, 1510, 1580, 1600, 920, 980, 1640 (allyl group), 1660 cm⁻¹.

N,N-Dimethyl-N-(1-allyl-3- α -naphthylpropargyl)amine. Several drops of methanol were added to a vigorously stirred mixture of powdered dimethylallyl(3- α -naphthylpropargyl)ammonium bromide [5] (34 mmoles) and two mole equivalents of KOH. After standing at room temperature for ~1 h, the mixture was extracted with ether (3 × 30 ml). The ether extract was treated with hydrochloric acid. Basification of the acid solution and extraction with ether (3 × 30 ml) gave the amine. The ether extract was washed with water (2 × 10 ml) and dried with magnesium sulfate. After removal of ether, vacuum distillation gave the product (6.1 g, 76%) with bp 159-160°C (4 mm Hg) and n_D²⁰ = 1.6020. IR spectrum: 780, 1500, 1580, 1640, 2230 cm⁻¹. Picrate: mp 144-145°C.

2,2-Dimethyl-1-allylnaphth[f]isoindolenium Bromide (IIc, C₂₁H₂₂BrN). KOH solution (0.3 ml, 2.5 N, 5.4 mmoles) was added to a homogeneous solution of starting salt (3.2 mmoles) in water (3 ml). The mixture was heated for 40 min at 45-50°C and extracted with ether (2 × 15 ml). Filtration of the aqueous solution gave salt IIc.

The ether extract was treated with hydrochloric acid. Vinylnaphthalacetone IIIb was separated chromatographically pure from the ether layer in 9% yield, not forming a 2,4-dinitrophenylhydrazone. IR spectrum: 730, 930, 980, 1640 (allyl group), 1570, 1610, 1665 cm⁻¹.

Dimethylpropargylamine (7%) was characterized as the picrate, mp 148°C. It did not depress the melting point of an authentic sample [9].

2,2-Dimethyl-1-allyl-3a,4-dihydronaphth[f]isoindolenium Bromide (IId, C₂₁H₂₄BrN). Obtained similarly from salt Id (4.5 mmoles) in water (4 ml) and KOH solution (0.4 ml, 2.5 N). The mixture was heated for 1.5 h at 90-92°C. Dimethylallylamine, yield 8%, mp 100°C (picrate). It was identified by comparison with a known sample whose melting point was not depressed [10].

3-(1,3-Butadienyl)-2-dimethylaminomethylnaphthalene (C₁₇H₂₀N). A 3 molar amount of KOH solution (25%) was added to a solution of salt IIa (4 mmoles) in water (2 ml). The fission was carried out at 120-125°C with steam distillation of

the product. Heating was continued for 30-40 min and the distillate and reaction residue were extracted with ether (3 × 15 ml). The ether extract was treated with hydrochloric acid. Basification of the acid layer and extraction with ether (3 × 20 ml) gave the amine. The ether extract was washed with water (2 × 5 ml) and dried with magnesium sulfate. After distillation of the ether, vacuum distillation of the residue gave 0.5 g (50%) of chromatographically pure product with bp 152°C (2 mm Hg). IR spectrum: 760, 860, 915, 1600 cm⁻¹. UV spectrum: λ_{max} 265, 300 nm. Polymer of the product was also separated (0.3 g, 30%) with mp 121-122°C (picrate).

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