INTRAMOLECULAR THERMAL CYCLIZATION OF QUATERNARY AMMONIUM SALTS WITH THE PARTICIPATION OF THE AROMATIC RING OF AN ARYLMETHYL GROUP AS A DIENE FRAGMENT*

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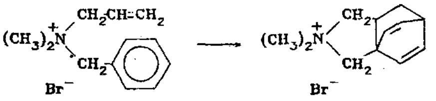
UDC 547.333.4'754:542.953:543.422

The intramolecular thermal cyclization of dimethylallylbenzylammonium bromide and dimethylallyl(α-methylnaphthyl)ammonium chloride led to the formation of 2,2-dimethyl-7,7a-dihydro-3a,6-vinyleneisoindolinium bromide and 2,2-dimethyl-7,7a-dihydro-3a,6-vinyleneisoindolinium bromide and 2,2-dimethyl-7,7a-dihydro-3a,6-vinylene-4,5-benzisoindolinium chloride, respectively, the alkaline cleavage of which leads to 3-methyl-4-dimethylaminomethylstyrene and 2-methyl-4-vinyl-1-dimethylaminomethylnaphthalene.

Quaternary ammonium salts that contain a 2,4-alkadienyl group in addition to a 2,3-unsaturated group undergo intramolecular thermal cyclization to give di- and tetrahydroisoindolinium salts [1-4]. Furyl and thienyl groups have been successfully used as diene fragments [5-7]; as expected, milder conditions than in intermolecular diene synthesis with the participation of furan [8] and thiophene derivatives [9] are required to accomplish the reaction.

Little study has been devoted to the diene synthesis with the participation of benzene. It has been indicated that severe conditions and active dienophiles are necessary. Milder conditions are required for intramolecular cyclization [12].

In fact, the intramolecular cyclization of dimethylallylbenzylammonium bromide (Ia) occurs at 140-145°C and after 200 h leads to the formation of 2,2-dimethyl-7,7a-dihydro-3a,6-vinyleneisoindolinium bromide (IIa):



Ia IIa

The IR spectrum of cyclization product IIa does not contain the absorption bands of the vinyl group (1640, 920, and 990 cm^{-1}) of starting salt Ia. The absence in the IR spectrum of IIa of the large number of narrow absorption bands that are characteristic for an aromatic ring (650-1000 and 1000-1250 cm^{-1}) also constitutes evidence for the participation of the benzene ring in intramolecular thermal cyclization. The bands at 1650 and 3020 cm^{-1} were interpreted as characteristic for the cyclohexadiene ring [13].

The UV spectroscopic data also constitute evidence for a cyclization reaction. The UV spectrum of IIa does not contain the absorption typical for an aromatic ring (263 nm) that appears in the spectrum of the starting salt in the form of resolved spectral bands.

The cyclization of salt Ib proceeds more rapidly. An intramolecular cyclization product, viz., 2,2-dimethyl-7,7a-dihydro-3a,6-vinylene-4,5-benzisoindolinium chloride (IIb), was obtained after heating at 140-145°C for 100 h:

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*Communication 177 from the series "Research on amines and ammonium compounds." See [15] for communication 176.

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 475-478, April, 1984. Original article submitted July 19, 1983; revision submitted September 14, 1983.

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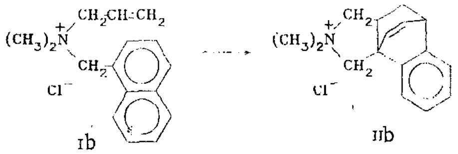
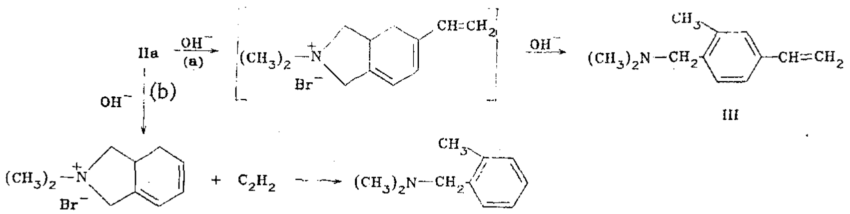


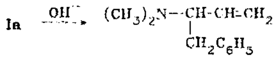
Ib IIb

In contrast to salt IIa, the structure of IIb is somewhat complicated due to the benzene ring that is retained after cyclization. This leads to superimposition of the principal frequencies at 1550-1650 and 3000-3100 cm^{-1}. Judgment in favor of participation of the terminal vinyl group in the cyclization was consequently made on the basis of the disappearance of the intense bands of deformation vibrations of the $CH=CH_2$ groups.

The following pathways are possible in the alkaline cleavage of salt IIa:



Neither acetylene nor N,N-dimethyl-2-methylbenzylamine was detected in the reaction products, and this excludes scheme (b). In connection with the presence of uncyclized salt Ia as an impurity in the reaction mixture, dimethyl(α-benzyl)allylamine was detected in the products of alkaline cleavage; this was a consequence of Stevens rearrangement of salt Ia [14]:

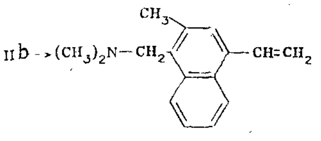


$$\text{Ia} \xrightarrow{OH^-} (CH_3)_2N-\underset{\displaystyle CH_2C_6H_5}{\underset{|}{CH}}-CH=CH_2$$

IV

It was established by means of gas—liquid chromatography (GLC) that the amine fraction consists of 90% amine III and 10% amine IV.

Aqueous alkaline cleavage of salt IIb leads exclusively to 2-methyl-4-vinyl-1-dimethylaminomethylnaphthalene (V):



V

The complex spectral structure that is characteristic for the benzene ring was regenerated in the IR spectra of the products of alkaline cleavage of salts IIa, b. Characteristic absorption bands at 1610, 1570, and 1510 cm^{-1} provide evidence for substituents in the benzene ring of III in the 1, 2, and 4 positions. The regions of overtones and composite tones is characterized by absorption bands at 1770, 1800, and 1900 cm^{-1}. In addition, the out-of-plane deformation vibrations of aromatic C—H bonds are found at 827 and 870 cm^{-1}. The frequencies of the stretching vibration of the vinyl group (1630 cm^{-1}) and of the deformation (910 and 995 cm^{-1}) and stretching (3030 and 3090 cm^{-1}) vibrations of the C—H bonds characterize terminal vinyl groups in conjugation with a benzene ring. The absorption at 3015 and 3055 cm^{-1} was assigned to C—H vibrations of the benzene ring. The UV spectrum contains a characteristic $n-\pi^*$ transition at 254 nm.

Compound V also has similar spectral characteristics. The spectrum contains characteristic absorption bands of a naphthalene ring at 1600, 1515, and 1400 cm^{-1} and a number of bands at 700-900 cm^{-1}. The terminal vinyl group is characterized by absorption bands at 1630, 920, 970, 3020, and 3060-3075 cm^{-1} (superimposition with the C—H stretching vibrations in naphthalene is possible in the high-frequency region). Absorption maxima at 225, 273, 282, and 293 nm, which are associated with $n-\pi^*$ transitions that are characteristic for compounds with condensed benzene rings, are observed in the UV spectrum of V.

EXPERIMENTAL

The UV spectra were recorded with an SF-4A spectrophotometer. The IR spectra were obtained with a UR-20 spectrometer. Thin-layer chromatography (TLC) of the quaternary ammonium salts was carried out on Silufol UV-254 plates with butyl alcohol—ethanol—water—acetic acid [7:5:3:1 (A) and 10:7:3:2 (B)]. Gas-liquid chromatography (GLC) was carried out with a Tsvet-104 chromatograph (2-m-long column, Chromaton N-AW, d = 0.20-0.25 mm, 5% E-30 silicone, He flow rate 6 liters/h).

Quaternary Ammonium Salt Ia. Equimolar amounts of dimethylbenzylamine and allyl bromide were mixed in ether—acetonitrile to give salt Ia, with mp 88-89°C and R_f 0.57 (A), in 95% yield. IR spectrum: 710, 930, 960, 990, 3015, 3070, 3090, and 1645 cm^{-1}. UV spectrum, λ_{max}: 210, 252, 255, 262, and 268 nm. Found: Br 31.5; N 5.4%. $C_{12}H_{18}BrN$. Calculated: Br 31.3; N 5.5%.

Quaternary Ammonium Salt Ib. Equimolar amounts of dimethylallylamine and α-chloromethylnaphthalene were mixed in ether—acetonitrile to give salt Ib, with mp 157-158°C and R_f 0.51 (B), in 90% yield. IR spectrum: 730, 760, 790, 920, 955, 990, 1520, 1580, 1600, 1645, 3015, 3025, 3050, and 3100 cm^{-1}. UV spectrum, λ_{max}: 225, 285, and 278 nm. Found: Cl 13.8; N 5.0%. $C_{16}H_{20}ClN$. Calculated: Cl 13.5; N 5.4%.

2,2-Dimethyl-7,7a-dihydro-3a,6-vinyleneisoindolinium Bromide (IIa) (State Registration No. 2243579). A solution of 6.3 g (0.024 mole) of salt Ia in 20 ml of dimethylformamide (DMF) was heated in a sealed ampul for 200 h, after which the DMF was removed, and the residue was dissolved in absolute ether and precipitated with ether to give 5.6 g (90%) of the salt. Repeated recrystallization gave individual salt IIa with mp 320°C (subl.) and R_f 0.67 (A). Found: Br 31.5; N 5.2%. $C_{12}H_{18}BrN$. Calculated: Br 31.3; N 5.5%.

2,2-Dimethyl-7,7a-dihydro-3a,6-vinylene-4,5-benzisoindolium Chloride (IIb). A solution of 5.0 g (0.019 mole) of salt Ib in 20 ml of DMF was heated at 140-145°C in a sealed ampul for 100 h to give 4.7 g (95%) of salt IIb with mp 215-216°C and R_f 0.55 (B). Found: Cl 14.0; N 5.8%. $C_{16}H_{20}ClN$. Calculated: Cl 13.5; N 5.4%.

3-Methyl-4-dimethylaminomethylstyrene (III). A 6.3-g (0.0246 mole) sample of salt IIa was heated in a twofold (molar) amount of a 20% aqueous solution of potassium hydroxide at 110-115°C in a flask fitted with a descending condenser and a wash bottle containing a standard solution of hydrochloric acid. The cleavage products were removed by steam distillation. The amine part was extracted with ether, and the extract was dried with magnesium sulfate and distilled to give 3.2 g (74%) of a fraction with bp 74-75°C (1 mm). Found by titration: M 169. $C_{12}H_{17}N$. Calculated: M 175. According to GLC, the fraction consisted of 3-methyl-4-dimethylaminomethylstyrene (90%) and a Stevens rearrangement product (10%), which were identified by comparison with genuine samples. Found: N 7.9%. $C_{12}H_{17}N$. Calculated: N 8.0%.

2-Methyl-4-vinyl-1-dimethylaminomethylnaphthalene (V). Cleavage of 4.7 g (0.018 mole) of salt IIb by the procedure used to cleave salt IIa gave 2.7 g (67%) of amine V with bp 134-136°C (1 mm). Found: N 6.1%. $C_{16}H_{19}N$. Calculated: N 6.2%.

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PORPHYRINS.

16.* THERMOLYSIS OF SCHIFF BASES OF MESO-FORMYLPORPHYRINS — A CONVENIENT METHOD FOR THE SYNTHESIS OF PORPHYRINS WITH A CYCLOPENTANE RING†

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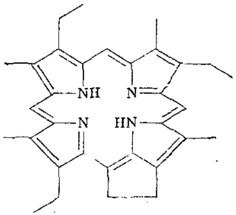
UDC 547.979.733'514.1:542.915:543.422'51

A new general reaction involving the thermal decomposition of Schiff bases of meso-formyloctaalkylporphyrins, which leads to porphyrins that contain a cyclopentane ring, was discovered. The optimum conditions in the synthesis of porphyrins with substituted and unsubstituted cyclopentane rings were worked out in the case of the thermolysis of Schiff bases of meso-formyletioporphyrin I, meso-formyletioporphyrin II, and octaethylporphyrin. The synthesized compounds were characterized by data from the electronic, PMR, and mass spectra.

Porphyrins with a cyclopentane ring of the so-called [M — 2] series or the deoxophylloerythroetioporphyrin (I) series are widely represented in the porphyrin fractions of sedimentary rocks, petroleum oils, and shales. The origin of such porphyrins has not been rigorously established, although their presence in geological formations serves as the principal argument for the biogenic formation of "geological" porphyrins.



I

Up until now, very little has been known regarding the chemical and spectral properties of porphyrins with a cyclopentane ring because of the lack of convenient methods for the synthesis of such compounds. These syntheses are usually multistep processes, and the final product is isolated in low yield [4-6]. It is also unknown whether porphyrins with alkyl substituents in the cyclopentane ring, the synthesis of which has become possible only owing to our observed thermal intramolecular cyclization of Schiff bases [7], to the description of which this paper is devoted, exist in nature.

In an investigation of the mass spectra of aminomethylporphyrins II ($R = H$ or CH_3, R^1 and $R^2 = H$ or alkyl) we established [8] that the primary fragmentation of the molecular ions for these compounds proceeds with detachment of amine NHR^1R^2; the possibility that fragment F_1 with an annelated cyclopentane ring is formed in this case was not excluded. In addition, an intense peak of an $[M - NR^1R^2 + H]^+$ fragment (F_2) was observed in the mass spectra.

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*See [1] for communication 15.
†See [2, 3] for preliminary communications.

Institute of Biophysics, Ministry of Public Health of the USSR, Moscow 123182. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 479-484, April, 1984. Original article submitted March 1, 1983.