A SYDNONEIMINE BASE

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It was shown by means of the UV spectra that a sydnoneimine base is formed from 3-cyclohexylsydnoneimine hydrochloride by the action of an equivalent amount of sodium hydroxide in solutions of absolute alcohols. The sydnoneimine base is also formed in the case of solvolysis of N₆-trimethylsilyl-3-cyclohexylsydnoneimine in methanol. The sydnoneimine base in solutions exists in equilibrium with the chain isomer, viz., the nitrile. The fraction of the cyclic isomer increases as the electron-donor properties of the substituent in the 3 position become more pronounced.

Sydnoneimines — nitrogen analogs of sydnones — are known only in the form of salts I or N-exocyclic derivatives II [1]. Assumptions involving the hypothetical intermediate of these products, viz., sydnoneimine base IV, have been expressed in studies of alkaline ring closing [2] and the polarographic reduction of salts I [3], as well as in the formation of derivatives II from N-nitrosoaminoacetonitriles III in the presence of bases [4]; however, no confirmation whatsoever of its existence has yet been obtained.

![Diagram of sydnoneimines](image)

Fig. 1. UV spectra of N₆-trimethylsilyl-3-cyclohexylsydnoneimine in absolute methanol (Δt = 10 min).


In the present research we used a spectrophotometric method to attempt to confirm the actual existence of base IV and to study some of its properties. We initially proposed to isolate base IV by solvolysis by methanol of the specially prepared unstable $N_6$-trimethylsilyl-3-cyclohexylsydnoneimine II ($R = \text{C}_6\text{H}_{11}$, $R' = (\text{CH}_3)_3\text{Si}$) in an anhydrous medium. In the UV spectrum (Fig. 1) of imine IIa in methanol, as compared with its spectrum in ether ($\lambda_{\text{max}}$ 340 nm) one observes a significant broadening of the absorption band (plateau at 305-340 nm), the intensity of which increases relatively slowly with time. One also observes a simultaneous increase in the absorption band with $\lambda_{\text{max}}$ 235 nm, viz. ring-opening product IIa, i.e., $N$-nitrosomethylaminoacetonitrile IIIa. In all likelihood, the plateau observed in the spectrum can be assigned to the overall absorption of starting imine IIa and the resulting base IVa, the absorption maxima of which were found to be close. A similar pattern occurred in the case of 3-cyclohexyl- and 3-phenylisopropyl analogs of imine IIa. Although in these experiments we were unable to identify distinctly base IV, we did demonstrate the fundamental possibility of the detection of base IV during a period of time that is sufficient for recording with a spectrophotometer.

More unambiguous results were obtained in the treatment of 3-cyclohexylsydnoneimine hydrochloride (Ia, $R = \text{C}_6\text{H}_{11}$) with an equivalent amount of sodium hydroxide in solutions of absolute methanol or isopropyl alcohol. In addition to the absorption band with $\lambda_{\text{max}}$ 300 nm, in the spectra (Fig. 2) one clearly observes an absorption band with $\lambda_{\text{max}}$ 335 nm, which can be assigned to base IVa. To confirm the validity of this assignment, phenyl isocyanate was added to the solution in the cuvette, as a result of which we observed the virtually instantaneous formation of $N(6)$-phenylcarbamoyl derivative (II, $R = \text{C}_6\text{H}_{11}$, $R' = \text{C}_6\text{H}_5\text{HNCO}$) with $\lambda_{\text{max}}$ 345 nm. The intensities of the absorption bands of salt Ia and base IVa decreased with time.

From the spectra recorded immediately after the addition of a solution of potassium hydroxide we were able to calculate the molar extinction coefficient of the base ($\varepsilon = 8000$). The observed $\pm 35$-nm shift of the absorption band of the base to the visible region as compared with the cation is similar to the shift that occurs in the neutralization of salts of $N_6$-acylsydnoneimines II (cation $\lambda_{\text{max}}$ 280 nm, base $\lambda_{\text{max}}$ 320 nm) [4].

Taking into account the fact that the alkaline opening of the sydnoneimine cation Ia at low pH values takes place rather slowly [5], we, with the use of aqueous buffer solutions with pH 8.2-9.60, again observed in the UV spectra, in addition to bands of the starting cation ($\lambda_{\text{max}}$ 300 nm) and the final $N$-nitroso derivative ($\lambda_{\text{max}}$ 235 nm), a band with $\lambda_{\text{max}}$ 335 nm, which belongs to base IIa (Fig. 3).

Just as for other sydnoneimines, for salt Ia one observes that, along with a decrease in the intensities of I and IV with time, their ratio remains unchanged. This makes it pos-