4. R. Y. Ning, J. F. Blount, W. Y. Chen, and P. M. Madan, J. Org. Chem., 40, 2201 (1973).
5. V. Nelson, A. Serianz, and P. Kovacic, J. Org. Chem., 41, 1751 (1976).
6. B. T. Newbold, J. Org. Chem., 27, 3919 (1962).

A SYDNONEIMINE BASE

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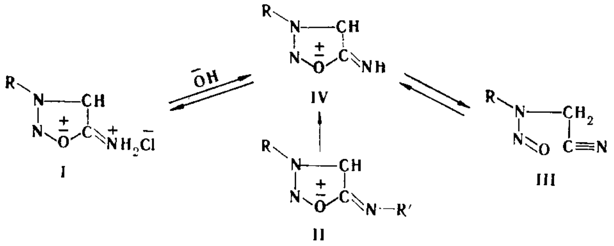
It was shown by means of the UV spectra that a sydnoneimine base is formed from 3-cyclohexylsydnoneimine hydrochloride by the action of an equivalent amount of sodium hydroxide in solutions of absolute alcohols. The sydnoneimine base is also formed in the case of solvolysis of N_6-trimethylsilyl-3-cyclohexylsydnoneimine 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.



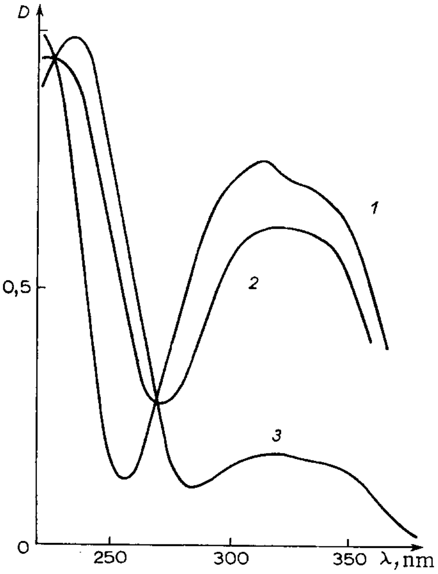


Fig. 1. UV spectra of N_6-trimethylsilyl-3-cyclohexylsydnoneimine in absolute methanol (Δt = 10 min).

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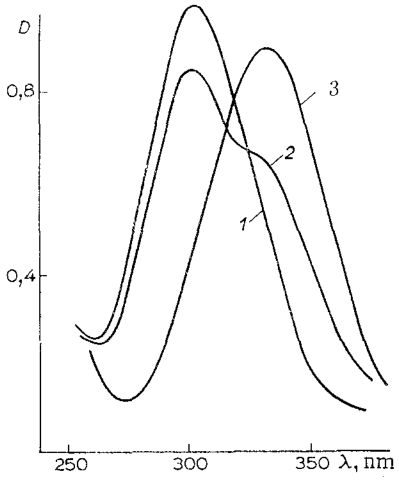

Fig. 2

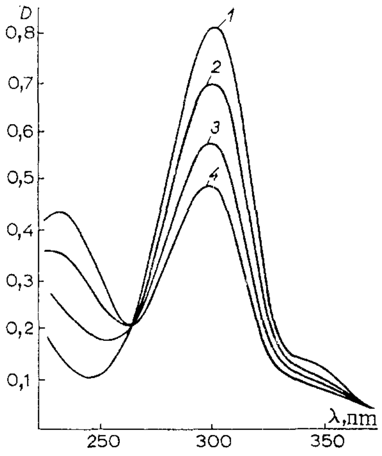

Fig. 3

Fig. 2. UV spectra in isopropyl alcohol: 1) 3-cyclohexylsydnoneimine hydrochloride; 2) the same with added KOH; 3) the same with phenyl isocyanate.

Fig. 3. Kinetics of opening of the ring of 3-cyclohexylsydnoneimine hydrochloride at 27°C in a buffer at pH 9.18 (Δt = 2 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 [a R = C_6H_{11}, R' = $(CH_3)_3Si$] in an anhydrous medium. In the UV spectrum (Fig. 1) of imine IIa in methanol, as compared with its spectrum in ether (λ_{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 λ_{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 = C_6H_{11}) with an equivalent amount of sodium hydroxide in solutions of absolute methanol or isopropyl alcohol. In addition to the absorption band with λ_{max} 300 nm, in the spectra (Fig. 2) one clearly observes an absorption band with λ_{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 = C_6H_{11}, R' = C_6H_5HNCO) with λ_{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 ($\varepsilon \approx 8000$). The observed ≈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 λ_{max} 280 nm, base λ_{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 (λ_{max} 300 nm) and the final N-nitroso derivative (λ_{max} 235 nm), a band with λ_{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-

TABLE 1. Effect of Substituents in the 3 Position of the Ring on the Basicities of Sydnoneimines and on the Position of the Tautomeric Equilibrium IV $\rightleftarrows$ III*

R	pK_a	pK_T	% IV in equilibrium III $\rightleftharpoons$ IV	pK_p† [5] I $\rightleftharpoons$ III + H^+	$E_S{}^C$
CH_3	9,94	3,29	0,05	6,65	0,00
iso-C_3H_7	10,19	2,59	0,26	7,60	−1,08
n-C_4H_9	9,96	2,66	0,22	7,30	−0,70
iso-C_4H_9	10,04	2,30	0,50	7,74	−1,74
cyclo-C_6H_{11}	10,13	2,43	0,37	7,70	−1,40
$C_6H_5CH_2CH(CH_3)$	9,89	2,76	0,17	7,13	−1,20

*Standard error (average) ±0.04 logarithmic units.

†Calculated from the correlation equation $kP_{eq} = 6.63 - 2.44\sigma^* - 0.46E_S{}^C$ (r = 0.98).

TABLE 2. Effect of Substituents in the 3 Position of the Ring on its Basicities of Sydnoneimine Bases

R	pH	$k_{8{\cdot}75}$, $\min^{-1}$	pK_a	Corrections to pK_a	Av. pK_a value
CH_3	8,08	0,0102	9,71		9,94
	8,58		9,87		
	8,96		10,04		
	9,03		9,98		
	9,24		10,06		
	9,38		10,08	0,020	
	9,45		9,91	0,036	
	9,53		10,01	0,073	
iso-C_3H_7	8,58	0,0060	10,18		10,19
	8,82		10,09		
	9,03		10,19		
	9,45		10,25	0,024	
	9,53		10,27	0,035	
n-C_4H_9	8,58	0,0101	9,96		9,96
	8,82		9,93		
	9,03		10,06		
	9,45		9,99	0,064	
	9,53		10,05	0,100	
iso-C_4H_9	8,58	2,1472	9,99		10,04
	8,82		9,99		
	9,03		10,10	0,030	
	9,45		10,10	0,030	
	9,53		10,11	0,042	
cyclo-C_6H_{11}	8,28	0,0038	—		10,13
	8,58		9,96		
	8,82		9,95		
	8,96		10,30		
	9,03		10,13		
	9,24		10,09		
	9,38		10,10	0,020	
	9,45		10,27	0,025	
	9,53		10,17	0,025	
	9,56		10,30	0,025	
$C_6H_5CH_2CH(CH_3)$	8,28	0,0935	9,84		9,89
	8,58		9,96		
	8,82		9,78		
	9,03		9,91	0,020	
	9,45		9,91	0,020	
	9,53		9,98	0,025	

sible to calculate the pK_α values of the acids that are the conjugates of bases IV. The calculation was made from the formula

$$pK_a = pH + \lg\frac{[I]}{[IV]} = pH + \lg\frac{D_I}{D_{IV}}$$

(where D is the optical density) with allowance for the fact that $\varepsilon_I \simeq \varepsilon_{IV}$, and disregarding the absorption of salt I at 335 nm and the absorption of base IV at 300 nm. In calculations on the speed of the recorded spectra, we made a correction of −0.37 min. We found that the pK_α values of the bases (Table 1) do not change at various pH values. This constitutes rather strong evidence that we are actually observing a sydnoneimine base. It follows from the data in Table 1 that the sydnoneimines are strong bases ($pK_a \sim 10$) with strength close to those of aliphatic amines.

An analysis of the effect of the substituents in the 3 position on the basicities of sydnoneimines IV showed that the latter increases as the electron-donor properties of the substituents increase and that the pK_a values correlate satisfactorily with the Taft induction constants (r = 0.976).

$$pK_a = 9.92 - 1.30\sigma^{+}\,. \qquad (1)$$

By means of the previously determined equilibrium constants for the conversiom of cation I to the corresponding nitrosonitrile III ($K_{eq} = C_{III}C_{H^+}/C_I$ [5] and the established K_a values, which can be expressed in the form $K_a = C_{IV}C_{H^+}/C_I$, we found that it was possible to determine the constants for the conversion of base IV to nitrile III, i.e., the constants of the ring-chain tautomeric equilibrium

$$K_T = \frac{C_{IV}}{C_{III}} = \frac{K_a}{K_{eq}};\ pK_T = pK_a - pK_{eq}\,. \qquad (2)$$

The pK_T values presented in Table 1 for a number of sydnoneimines make it possible to conclude that in the case of achieving the III $\rightleftarrows$ IV equilibrium the fraction of the cyclic form, viz., the base, amounts to only 0.05-0.5%.

By combining the previously found correlation equation [5] $pK_{eq} = 6.63 - 2.44\sigma^* - 0.46E_S{}^C$ with Eqs. (1) and (2) one can obtain the correlation equation $pK_T = 3.28 + 1.25\sigma^* + 0.46E_S{}^C$, which links the effect of the substituent in the 3 position on the position of the tautomeric equilibrium. It is apparent that the fraction of the cyclic tautomer in the equilibrium mixture increases as the electron-donor properties and size of the substituent increase.

Thus one may regard it as an established fact that the sydnoneimine base, previously assumed to be a hypothetical substance, does indeed exist, which fact makes more convincing the conclusion regarding the mechanisms of the reactions involved in the formation of sydnoneimines and expands our knowledge in the area of mesoionic compounds.

EXPERIMENTAL

$N_{(6)}$-Trimethylsilyl-3-cyclohexylsydnoneimine (IIa). A 5-ml sample of diethylaminotrimethylsilane was added to 4.06 g (0.02 mole) of 3-methylsydnoneimine hydrochloride in 10 ml of dry ether, after which the mixture was maintained at room temperature for 30 min. It was then evaporated *in vacuo* at 40°C to give a white crystalline precipitate that decomposed rapidly in air (λ_{max} 340 nm in ether).

Basicity Constants of the Sydnoneimine Bases. A 1-ml sample of an aqueous solution of the sydnoneimine hydrochloride was mixed with 19 ml of a buffer solution with a known pH value. The test solution was placed in a thermostated cuvette, and the optical densities at λ_{max} 300 and 335 nm were determined. The starting concentration of the sydnoneimine salt in the cuvette was $1 \cdot 10^{-4}$ mole/liter. The UV spectra were recorded immediately after mixing and at definite time intervals.

The buffer solutions were prepared by the addition of a 0.2 molar solution of potassium hydroxide to a mixture of boric, phosphoric, and acetic acids (c = 0.08 mole/liter). Potassium chloride (0.2 mole/liter) was added to the buffer solutions to maintain a constant ionic strength. The pH values of the solutions were determined with an LPM-60 M pH meter using glass and silver chloride electrodes at 20°C. The corrections to the pK_a values associated with the difference in the times involved in the recording of the maxima of cation I (λ 300 nm) and base IV (λ 335 nm) were calculated from the formula

$$pK_a^{\mathrm{true}} = pK_a{}^{\mathrm{exp}} - 0{,}16k_{8{,}75} \cdot 10^{2(\mathrm{pH}-8{,}75)},$$

where $k_{8.75}$ are the rate constants for alkaline opening of sydnoneimines I at pH 8.75 and 20°C and were calculated from the formula $k = (D_1^I - D_2^I)/(t_2 - t_1)$ (D is the optical density and t is the time). The error in the determination of the constants was 2%, whereas the error for the pK_a values did not exceed 0.04 of a logarithmic unit.

LITERATURE CITED

1. V. G. Yashunskii and L. E. Kholodov, Usp. Khim., 49, 54 (1980).
2. V. G. Yashunskii and S. A. Zotova, Zh. Org. Khim., 3, 942 (1967).
3. V. G. Yashunskii, L. E. Kolodov, and E. V. Borisov, Khim. Geterotsikl. Soedin., 4, 702 (1968).

4. V. G. Yashunskii, V. V. Ogorodnikova, and L. E. Kholodov, Khim. Geterotsikl. Soedin., No. 9, 1244 (1980).
5. L. E. Kholodov and V. G. Yashunskii, Khim. Geterotsikl. Soedin., No. 3, 328 (1965).

HOMOGENEOUS H–D EXCHANGE OF HETEROCYCLES AND SOME HYDROCARBONS WITH D_2O IN THE PRESENCE OF Pt(II) COMPLEXES

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The homogeneous isotope exchange of O-, N-, and S-containing heterocyclic compounds and a number of hydrocarbons with D_2O in the presence of platinum(II) complexes, viz., potassium tetrachloroplatinite, platinum(II) monochlorodiethylenetriaminepentaacetate, chlorodiethylenediamineplatinum(II), dichloroethylenediamineplatinum(II), dichloroethylenediaminetetraacetatoplatinum(II) and, in the case of hydrocarbons, potassium tetrachloroplatinite, was investigated. The M factors were calculated for the H–D exchange of the hydrocarbons. It was shown that the H–D exchange of benzene has multiple character, whereas it has stepwise character in the case of cyclohexane.

The elucidation of the nature of the intermediate particles and the character of the substrate–catalyst interaction is a key problem in the investigation of the mechanisms of catalytic reactions. A study of H–D exchange reactions may be extremely effective for the solution of this problem [1-3]. Of particular interest is the study of the homogeneous H–D exchange of heterocycles that is catalyzed by complexes of group VIII metals, since many compounds that contain a heteroatom are catalyst poisons for heterogeneous metals or lead to reduction to the metal in the case of homogeneous catalysts. For these reasons, despite the fact that homogeneous-catalytic reactions of hydrocarbons, particularly H–D exchange reactions [2, 3], in the presence of complexes of group VIII metals have been studied in depth, there have been very few such studies devoted to heterocycles.

The homogeneous isotope exchange of heterocycles has been previously investigated [4] in the case of benzofurans in the presence of potassium tetrachloroplatinite.

In the present research we studied the homogeneous-catalytic H–D exchange of a number of heterocycles and hydrocarbons with D_2O in the presence of Pt(II) complexes, viz., potassium tetrachloroplatinite (complex I), dichloroethylenediamineplatinum(II) (complex II),

TABLE 1. Homogeneous-Catalytic Isotope Exchange of Hydrocarbons with D_2O at 120°C

No.	Substance	Time, t, h	Deuterium distribution, %							Σd_i, %	Catalyst
			d_0	d_1	d_2	d_3	d_4	d_5	d_6		
1	Benzene	6,9	18	14	16	17	16	12	7	82	I
2	Cyclohexane	8,0	72	26	2					28	I
3	Toluene	6,7	21	20	24	20	8	6	1	79	I
4	Naphthalene	7,0	6	18	31	30	13	2		94	I
5	Benzene	5,0	98	2						2	III
6	Cyclohexane	7,0	98	2						2	III
7	Toluene	7,0	100							0	III
8	Naphthalene	7,0	90	10						10	III
9	Tetralin	7,0	97	3						3	III
10	Benzene	6,9	97	3						3	—
11	Cyclohexane	7,3	97	3						3	—
12	Toluene	7,0	97	3						3	—

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