SYDNONES AND SYDNONE IMINES

XXXVI. Influence of Substituents on the Kinetics and Mechanism of the Alkaline Ring-Opening of Sydnone Imines*

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For a number of sydnone imines with nonaryl substituents in position 3 the influence of structural factors on the kinetics of alkaline ring-opening has been studied and it has been found that the stability of the heterocycle falls with an increase in the electronegativity of the substituents. On passing from 3-aryl- to 3-nonaryl-substituted sydnone imines the mechanism of the reaction of alkaline ring-opening changes.

Table 1

Pseudomonomolecular Rate Constants for the Ring-Opening of the Sydnone Imines I

R	σ^* [11]	$k_\psi \cdot 10^{-5}$, sec^{-1}, pH 8.75	Reference to the synthesis of the sydnone imine
CH_3	0.00	64.4	5
C_2H_5	−0.10	62.2	5
i-C_3H_7	−0.19	24.0**	6
n-C_4H_9	−0.13	74.2	5
i-C_4H_9	−0.125	79.0	7
sec-C_8H_{17}		46.2	7
C_6H_{11}	−0.15	26.0	6
$C_6H_5CH_2$	+0.215	232.0**	8
$C_6H_5CH(CH_3)$	+0.11	87.9	9
$C_6H_5CH_2CH_2$	+0.08	104.5	9
$C_6H_5CH_2CH(CH_3)$	+0.02*	78.5	10
$HOCH_2CH_2$	+0.198	158.6	7
$C_6H_5CH(OH)CH(CH_3)$	+0.17*	104.0	7
$C_6H_5OCH_2CH_2$	+0.32*	123.0	7

*Calculated by the rules of additivity and of the damping of the induction effect [11].

**Value refined in comparison with that given previously [2].

Previously, in a study of the influence of substituents on the equilibrium constant of the alkaline ring-opening of the cations of 3-substituted sydnone imines I to N-substituted N-nitrosoaminoacetonitriles II it was shown [1] that in the case of nonaryl substituents the stability of the heterocycle rises with a decrease in the electronegativity and an increase in the volume of the substituents in accordance with Taft's equation:

$$\lg K = -6.63 + 2.44\sigma^* + 0.46\ E_s^c, \qquad (1)$$

and in the case of meta- or para-substituted phenyls as substituents only the induction effect [2, 3] was exerted:

$$\lg K = -7.71 + 2.44\sigma^*. \qquad (2)$$

In a cooperative comparison of the induction components in both groups of substituents with Taft's σ^* constants it was found that the points fell on two parallel straight lines, one for aryl and the other for nonaryl substituents [2, 3], which was explained by the existence in the case of the aryl substituents of conjugation of the phenyl and the sydnone imine rings. A study of the influence of substituents on the kinetics of the alkaline ring-opening of the sydnone imines has shown [2, 3] that the pseudomonomolecular constants for the rate of this process (k_ψ) for the 3-aryl derivatives obey the equation (for phenyls $\sigma^* = \sigma^0 + 0.600$):

$$\lg k_\psi = -2.97 + 1.00\sigma^* \text{ (at pH 8.75)}. \qquad (3)$$

In the present work we have used the polarographic method to study the kinetics of the alkaline ring-opening of fourteen sydnone imines with nonaryl substituents in position 3 of the ring.

In the course of the investigations it was found that the polarographic wave of the reduction in an alkaline medium of each of the hydrochlorides of the sydnone imines mentioned gradually decreases, and a second reduction wave corresponding to a nitrosoaminonitrile appears in the more negative region. Since a number of the sydnone imines I and the final nitrosoaminonitriles II were being polarographed for the first time, we have determined the half-wave potentials for their reduction ($E_{1/2}$, see Table 2). An analysis of the results obtained has shown that the rate of ring-opening in all cases is first-order with respect to the initial sydnone imine:

$$V = k_\psi \cdot C_I. \qquad (4)$$

The calculation of the rate constants was carried out by the graphical method, and the results are given in Table 1. It was found that the pseudomonomolecular rate constants k_ψ of the sydnone imines studied, with the exception of the compound with R = $C_6H_5OCH_2CH_2$, correlate well (r = 0.960, s = 0.08) with Taft's induction constants (Fig. 1).

Table 2

Half-Wave Potentials of the Sydnone Imines I and the N-Substituted N-Nitrosoaminoacetonitriles II.

R	$-E_{1/2}$, V, SCE	
	I	II
sec-C_8H_{17}	0.79	—
$C_6H_5CH(CH_3)$	0.80	1.22
$C_6H_5CH_2CH_2$	0.82	1.20
$C_6H_5CH_2CH(CH_3)$	0.84	—
$HOCH_2CH_2$	1.02	1.34
$C_6H_5CH(OH)CH(CH_3)$	0.84	1.28
$C_6H_5OCH_2CH_2$	0.74	1.12

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*For part XXXV, see [7].

$$\lg k_\psi = -3.19 + 1.86\sigma^*. \qquad (5)$$

Consequently, the influence of the substituents is predominantly an induction effect, the stability of the heterocyclic falling with an increase in their electronegativity. The fact that no steric influence was observed shows the absence of the "spreading" of the substituents at the stage of the formation of an active complex from the sydnone imine cation, i.e., shows the planar structure of this complex. Apparently, the structure is closer to the initial sydnone imine than to the final nitrosoaminonitrile.

In contrast to the general picture of the influence of substituents on the position of the equilibrium in the reaction studied (1), (2), in the case of the kinetics of ring-opening the straight lines in the plot of $\log k_\psi$ versus σ^* are not parallel—the magnitudes of ρ^* in Eqs. (3) and (5) are not equal. The change in the value of ρ^* is possibly connected with a change in the mechanism of the reaction on passing from 3-aryl- to 3-nonaryl-substituted sydnone imines. The investigation of the kinetics of the alkaline ring-opening of 3-isopropylsydnone imine carried out previously has shown that the rate of the reaction is first-order with respect to the sydnone imine and second-order with respect to hydroxyl ion [4]. In the case of the 3-aryl derivatives the order with respect to the sydnone imine is retained, and therefore, we have carried out an investigation of the dependece of the pseudomonomolecular rate constant of 3-phenyl-sydnone imine on the concentration of hydroxyl ions.

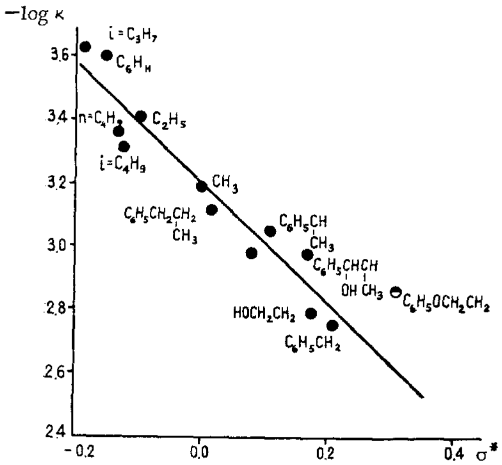
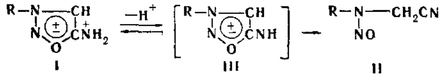


Fig. 1. Logarithms of the pseudomonomolecular rate constants of the ring-opening of sydnone imines with nonaryl substituents in position 3 of the ring as a function of Taft's induction constants σ^*.

It can clearly be seen from Fig. 2 that the tangent of the angle of slope of the straight line in the plot of $\log k_\psi$ versus pOH is 1.0 and therefore the pseudomonomolecular rate constant for the ring-opening of 3-phenylsydnone imine rises in proportion to the first degree of the OH^- concentration. Apparently, in this case as well, the first stage of the reaction is the splitting off of a proton from the sydnone imine cation with the formation of the unstable base III:



Then this base III, either through an active complex with water or spontaneously, but without the participation of the hydroxyl ion, as in the case of the 3-nonaryl-substituted compounds, undergoes ring-opening to give the nitrosoaminonitrile II. The ratio between the constants determined from experiment and the constants of the elementary processes can be determined from Eqs. (6) and (7):

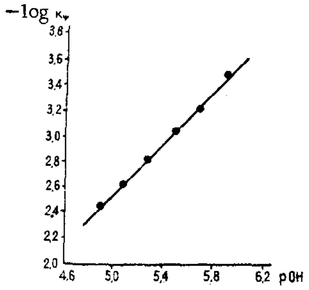


Fig. 2. Pseudomonomolecular rate constants for the ring-opening of 3-phenylsydnone imine as a function of pOH.

$$K_1' = \frac{C_{III} \cdot H^+}{C_I}, \qquad (6)$$

$$V = k_2 \cdot C_{III}, \qquad (7)$$

where K_1' is the apparent acid dissociation constant, and V is the rate of the reaction. After taking logarithms, from Eqs. (4), (6), and (7) we obtain:

$$\lg k_\psi = 13.68 + \lg k_2 \cdot K_1' - \mathrm{pOH} \qquad (8)$$

It is not difficult to see that the graph of Fig. 2 is described by Eqs. (8) and therefore the intercept cut off by the line on the axis of ordinates (4.6 logarithmic units) determines the value $13.68 + \lg K_1' k_2$, whence $k_2 \cdot K_1' = 1.15 \cdot 10^{-7}$ mole/l · min.

The observed difference in the mechanisms of the ring-opening of 3-aryl- and 3-nonaryl-substituted sydnone imines must apparently be explained by the conjugation of the phenyl and sydnone imine rings in the base III of the 3-arylsydnone imines.

EXPERIMENTAL

The determinations were carried out on a type LP-60 electronic polarograph (Czechoslovakia). The comparison electrode used was the saturated calomel electrode. The cell was thermostated at 25 ± 0.2° C. The cell was charged with 10 ml of the supporting electrolyte (Britton-Robinson buffer, pH 8.75 [1]), dissolved oxygen was driven out by the passage of nitrogen, and then 1 ml of an aqueous solution of a sydnone imine hydrochloride ($1 \cdot 10^{-3}$ M) was added, and polarographs of the reaction mixture were recorded after predetermined intervals of time.

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