Mechanism of the Thermal Rearrangement of *N*-Aroyl-*O*-(*NN*-dimethylthiocarbamoyl)-*N*-methylhydroxylamines

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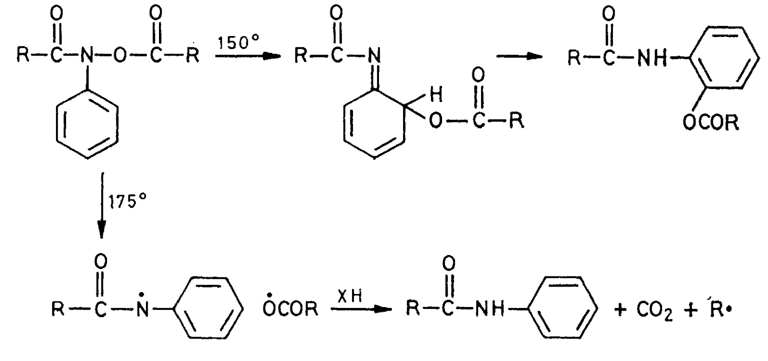
Mechanistic investigations on the thermolysis of *N*-aroyl-*O*-(*NN*-dimethylthiocarbamoyl)-*N*-methylhydroxylamines lead to the conclusion that the thiono–thiolo rearrangement proceeds, at least in part, by a radical cage process. This is accompanied by a reaction, due to escaped amidyl radicals, leading to the corresponding amide in a hydrogen abstraction process. The proposed mechanisms are supported by CIDNP effects, kinetic studies with diphenylpicrylhydrazyl, and measurement of the activation parameters of the observed unimolecular reaction.

THE acylation of hydroxamic acids has been studied in great detail owing to the importance of the Lossen rearrangement in organic synthesis.[1] The thermal decomposition of *ON*-diacylhydroxylamines, which normally occurs above 100°, is however not completely understood as a complex mixture of products is usually formed, including amine, carboxylic acid, carbon dioxide, and anhydride.[2] It is usually assumed that these products are derived from intermediate isocyanate.

Acyl derivatives of *N*-alkylated hydroxamic acids are considerably more stable, and their thermal decomposition has not been investigated in any detail. The *N*-phenyl analogues, however, rearrange at 150°, probably by an intramolecular mechanism,[3] by analogy with Claisen[4] and Polonovski[5] rearrangements. At higher temperatures, however, amide is formed (*ca.* 25% at 175°), presumably by homolysis of the N–O bond, as evidence of radical formation has been obtained.[2]



The decomposition of thioacylated hydroxamic acids

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[1] P. A. S. Smith ' Open Chain Nitrogen Compounds ', Benjamin, New York, 1966, vol. II, p. 81.

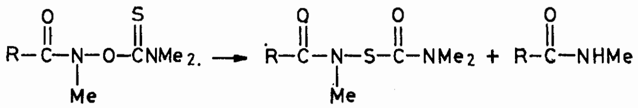
[2] C. Walling and A. Naglieri, *J. Amer. Chem. Soc.*, 1960, **82**, 1820.

[3] L. Horner and H. Steppan, *Annalen*, 1957, **606**, 24; P. G. Sammes, *J. Chem. Soc.*, 1965, 6608.

[4] L. Claisen, *Ber.*, 1912, **45**, 3157.

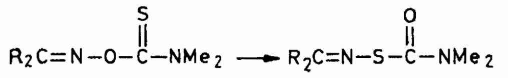
[5] V. Boekelheide and D. L. Harrington, *Chem. and Ind.*, 1955, 1423.

does not appear to have been investigated, but we have recently found thiocarbamoylated *N*-methylhydroxamic acids to rearrange readily in the 25—40° range[6] to give the thiolo isomer as the main product. As the temperature increases, the yield of amide increases to become the major product above 100°. The rate of rearrangement is insensitive to substitution at the carbonyl group and to change of solvent. By analogy with the similar rearrangement of thiocarbamoylated



$$\mathrm{R{-}\overset{\overset{\large O}{\|}}{C}{-}\underset{\underset{\large Me}{|}}{N}{-}O{-}\overset{\overset{\large S}{\|}}{C}NMe_2.} \longrightarrow \mathrm{R{-}\overset{\overset{\large O}{\|}}{C}{-}\underset{\underset{\large Me}{|}}{N}{-}S{-}\overset{\overset{\large O}{\|}}{C}{-}NMe_2} + \mathrm{R{-}\overset{\overset{\large O}{\|}}{C}{-}NHMe}$$

(I) (II) (III)



$$\mathrm{R_2C{=}N{-}O{-}\overset{\overset{\large S}{\|}}{C}{-}NMe_2} \longrightarrow \mathrm{R_2C{=}N{-}S{-}\overset{\overset{\large O}{\|}}{C}{-}NMe_2}$$

oximes,[7] we have suggested a radical cage mechanism for the rearrangements, although no free radicals are detected in the e.s.r. spectrometer. In order to investigate this suggestion further, a mechanistic investigation into this reaction has been made with the results here described.

RESULTS AND DISCUSSION

CIDNP Studies—Radical pathways can, in suitable systems, be inferred from n.m.r. studies carried out under CIDNP conditions. The reaction has to be essentially complete within a few seconds and hence in the present case, temperatures considerably greater than those employed in following the rearrangement kinetically were employed.

Solutions of (I; R = Ph) in deuteriochloroform were placed in the preheated (120°) probe of a 14092 G n.m.r. spectrometer. Pronounced CIDNP effects were observed in the spectra of both the rearranged product and the amide. The methyl resonance of (II; R = Ph) at δ 3.30 appears in absorption, enhanced by a factor of 15 (v_{exp} 15), reaching a maximum 1—1.5 min after insertion of the sample into the pre-heated n.m.r. probe, and decaying rapidly over 5 min (Figure 1). Similar results were obtained for the other *N*-aroyl-*O*-(*NN*-dimethylthiocarbamoyl)-*N*-methylhydroxylamines (Table 1).

TABLE 1

Spin polarised n.m.r. resonances of the rearranged product (II), and amide (III) observed in the thermolyses of *N*-aroyl-*O*-(*NN*-dimethylthiocarbamoyl)-*N*-methylhydroxylamines in deuteriochloroform at 120°

R	NMe resonance (A) in (II)	V_{exp}	NMe resonance (E) in (III)		V_{exp}
Ph	3.36	5	2.97	3.03	−4
C_6H_4Me-*p*	3.30	15	2.92	3.00	−9
C_6H_4MeO-*p*	3.35	19	2.91	2.98	−2
$C_6H_4NO_2$-*p*	3.35	16	3.00	3.07	−2

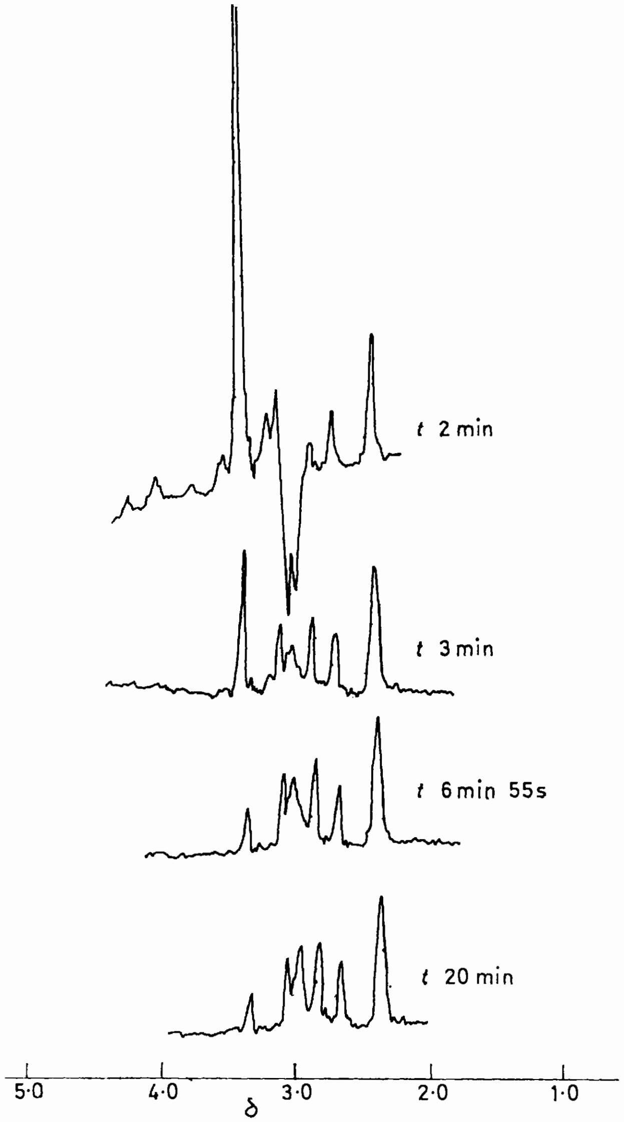


FIGURE 1 CIDNP Effects in the products of the thermolysis of *O*-(*NN*-dimethylthiocarbamoyl)-*N*-methyl-*N*-(*p*-toluoyl)-hydroxylamine in deuteriochloroform at 120°

These are net polarisations, so the application of Kaptein's rules[8] $\Gamma_{ne} \doteq \mu\, \varepsilon\, \Delta g\, A_i$ enables the signs of the polarisations to be predicted from a knowledge of the signs of the parameters μ, ε, Δg, A_i. For the rearrangement of (I) we may assume that the radicals formed are generated from homolysis of the N–O bond, hence μ is negative. From e.s.r. studies the *g* value of the *N*-methylamidyl radical[9] is *ca.* 2.005, the value for *NN*-dimethylthiocarbamate radical[10] being *ca.* 2.05. The hyperfine coupling constant $A^{H}_{CH_3}$ of the *N*-methyl

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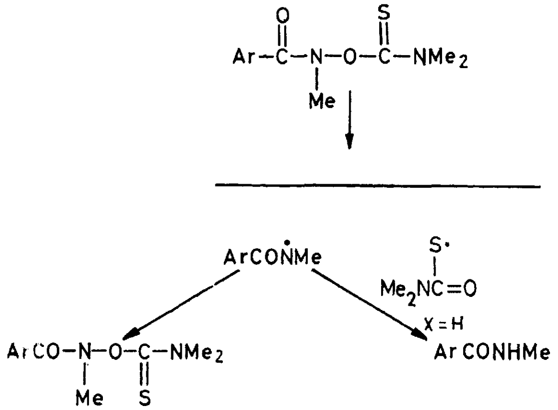
[6] W. B. Ankers, R. F. Hudson, and A. J. Lawson, *J.C.S. Perkin II*, 1974, 1826.

[7] R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J.C.S. Perkin II*, 1974, 869.

[8] R. Kaptein, *Chem. Comm.*, 1971, 732; *Adv. Free Radical Chem.*, 1975, **5**, 319.

[9] W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, 1972, **94**, 6853.

protons of (II) is positive,[10] and the *N*-methyl resonance of the product exhibits enhanced absorption, hence Γ_{ne} is positive. Consequently ε is positive, *i.e.* the formation of (II) occurs from the collapse of a radical pair within a solvent cage.



In addition to the thermal rearrangement, decomposition by a fragmentation pathway to the corresponding *N*-methylbenzamide occurs. Quantitative conversion to (II) and (III) is observed, the ratio increasing with increasing temperature. Thus fragmentation is the major pathway at 110—120°, the temperature necessary for the satisfactory observation of CIDNP effects. The resonances at δ 2.92 and 3.00 of (III; R = *p*-Me·C_6H_4) appear in emission as a doublet (Figure 1) and correspond to authentic *N*-methyl-*p*-toluamide resonances. The emission was large after 1.5 min decaying over several minutes to give the normal absorption signal, eventually observed as a singlet at δ 2.97. The results indicate that the amidyl radical formed in the homolysis abstracts hydrogen, rather than a deuterium atom, from the solvent. The eventual collapse of the doublet to a singlet is due to exchange with deuteriochloroform to give *N*-deuterio-*N*-methyl-*p*-toluamide.

Similar CIDNP results were obtained for the other *N*-aroyl-*O*-(*NN*-dimethylthiocarbamoyl)-*N*-methylhydroxylamines (Table 1).

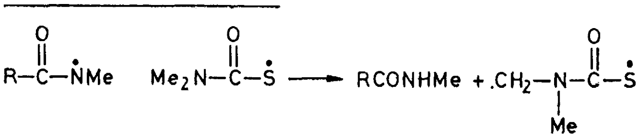
Analysis of these net polarisations by using Kaptein's rules gives a negative value for ε, *i.e.* the amide is produced by an amidyl radical which has escaped from the solvent cage. This is consistent with a radical cage mechanism for the thiono-thiolo rearrangement, as an increase in temperature results in the escape of radicals from the cage leading to secondary reactions.

The Reaction of Escaped Radicals.—N.m.r. analysis shows that quantitative conversion to rearranged product and amide occurs over the 25—120° range, the proportions of products changing from *ca.* 5 to 75% amide. The fate of the thiocarbamoyl group corresponding to the amide is difficult to ascertain. I.r. analysis of the reaction mixture shows that carbonyl sulphide is a minor product (*ca.* 5%) and this can be distilled together with deuteriochloroform from the mixture. This product arises from the fragmentation of the thiocarbamoyl radical, and similar decompositions have been observed in the thermolysis of other thiocarbonyl compounds, *e.g.* reaction (1).

$$PhCH{=}N{-}OC(S)Ph \longrightarrow PhCH{=}\dot{N} + PhCO\dot{S} \longrightarrow Ph{-}Ph + COS \quad (1)$$

Examination of the n.m.r. spectra taken under CIDNP conditions shows the initial formation of amide which eventually appears as the deuteriated compound. This surprising result shows that hydrogen is abstracted by the amidyl radical and not deuterium from the solvent. The origin of the hydrogen is not known with certainty but the hydrogen atoms of the dimethylamino-groups are the most likely source since a stabilised radical would be formed. The only additional product found is an intractable gum so far unidentified and thought to be an oligomer of the type $[-CH_2-N(Me)-C(O)S-]_n$, but further investigations are required on the structure of this substance.

The amidyl radical abstracts hydrogen very rapidly under the experimental conditions employed. This could occur in the primary cage to give a diradical which then escapes to give one of the products. The escaped



$$R{-}\overset{O}{\overset{\|}{C}}{-}\dot{N}Me \quad Me_2N{-}\overset{O}{\overset{\|}{C}}{-}\dot{S} \longrightarrow RCONHMe + \cdot CH_2{-}\underset{Me}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\dot{S}$$

diradical could then be trapped by two molecules of scavenger, in accord with the observations.

However this in-cage disproportionation is not supported by the CIDNP effect, if the widely accepted diffusion model [8] is adopted. For this reason we assume that the escaped amidyl radical is captured by a solute molecule, probably the reactant. We have some evidence for this type of process in similar rearrangements, which may in certain cases lead to rapid chain reactions.

Although the CIDNP studies provide clear evidence that part at least of the amide is produced in a radical process, no free radicals are observed in the e.s.r. spectrometer. This shows that the escaped amidyl radicals are highly reactive as evidenced by the complete absence of the dimer. The presence of free radicals can be detected readily by reaction with diphenylpicrylhydrazyl (DPPH) and similar radical traps.[11] This enables a kinetic analysis of the out-of-cage process to be made as described below, to give results which can be compared with analyses of the reaction products.

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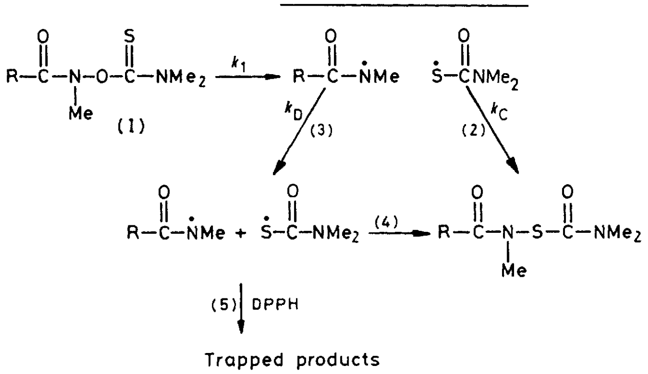
[10] C. Brown, R. F. Hudson, and A. J. Lawson, *J. Amer. Chem. Soc.*, 1973, **95**, 6500.

[11] A. R. Forrester, J. M. Hay, and R. H. Thomson, ' Organic Chemistry of Stable Free Radicals ', Academic Press, New York, 1968, pp. 137—179.

Assuming the Scheme, neglecting (4), and applying the steady state approximation gives equation (2).



SCHEME

Values of d[DPPH]/dt can be obtained from the slopes of the tangents to the curve obtained from a plot of

$$-\mathrm{d[DPPH]/d}t = 2k_{\mathrm{D}}k_1[(\mathrm{I})]_t/(k_{\mathrm{C}} + k_{\mathrm{D}}) \qquad (2)$$

[DPPH] against time. Appropriate values of $[(\mathrm{I})]_t$ can be obtained from the initial concentration of (I), *i.e.* $[(\mathrm{I})]_0$ and the known rate constant, k_1 (0.294×10^{-2} min^{-1} at 59.5°). The pertinent values of $-$d[DPPH]/dt and $[(\mathrm{I})]_t$ are given in Table 6 (see Experimental section) for the reaction carried out in benzene at 59°. The slope of the linear graph (Figure 2) of $-$d[DPPH]/dt against $[(\mathrm{I})]_t$ is 0.379×10^{-2} min^{-1}, and hence $k_{\mathrm{D}} = 1.81k_{\mathrm{C}}$.

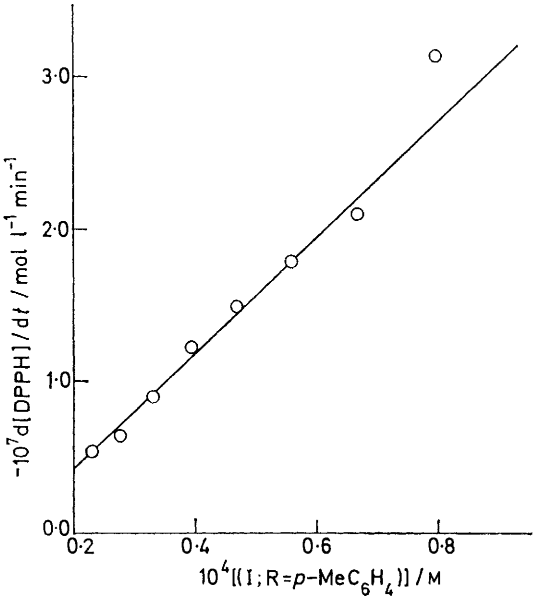


FIGURE 2 Relationship between $-$d[DPPH]/dt and concentration of *O*-(*NN*-dimethylthiocarbamoyl)-*N*-methyl-*N*-(*p*-toluoyl)hydroxylamine for the rearrangement in benzene at 59.2°

When (I) is heated in the presence of twice its own concentration of DPPH in benzene at 59.2°, 64.0% of the DPPH is decolourised. This gives a value of 1.78 for the ratio $k_{\mathrm{D}}/k_{\mathrm{C}}$, in close agreement with the kinetically determined value of 1.81.

According to the Scheme, the escaped amidyl radicals abstract hydrogen to give amide as the sole product, whereas the rearranged product (II) is formed in the radical cage. Thus product analysis should correspond to the $k_{\mathrm{D}}/k_{\mathrm{C}}$ ratios determined from the loss of DPPH. Integration of the NMe signals in the ^{1}H n.m.r. spectra of the two products formed in deuteriobenzene at 60° in 48 h showed a 59.1% conversion to *N*-methyl-*p*-toluamide and 40.9% conversion to (II) which gives a value of 1.44 for $k_{\mathrm{D}}/k_{\mathrm{C}}$. This is in approximate agreement with the former values. A higher concentration (*ca.* 10% w/v) of reactant is required in the n.m.r. analysis, which increases the possibility of out of cage recombination [reaction (4)], and this may be responsible for the lower value obtained in this experiment.

Activation Parameters.—The CIDNP effects discussed in a previous section show that part, at least, of the unimolecular rearrangement proceeds by a radical cage mechanism. In reactions of this kind which have been studied extensively, *e.g.* Stevens [12] and Meisenheimer [13] rearrangements, part of these reactions may be intramolecular with cyclic transition states. In some cases, where extensive retention of configuration of the migrating group is observed, the synchronous process is symmetry forbidden.[14] Similar considerations apply to 1,3 sigmatropic processes, where inversion and retention of the migrating group have been observed,[15] corresponding to symmetry allowed and forbidden rearrangements. It is unfortunate that in the reactions discussed here, stereochemical methods cannot be used, because of the rapid inversion at nitrogen and configurational instability of the N–S bond.[16] Other approaches have to be adopted to investigate the reaction mechanism further.

Our attempts to synthesise appropriate cyclic molecules, with configurations which preclude a cyclic mechanism for the rearrangement have so far proved unsuccessful. Moreover we believe that such molecules, if prepared, would not fragment for orbital symmetry reasons.

We have therefore measured the unimolecular rate constants for each compound at several temperatures and calculated the activation parameters. No significant deviations were observed in the log k against $1/T$ plots (*e.g.* Figure 3) over the temperature range where the

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[12] J. Meisenheimer, *Ber.* 1919, **52**, 1671; A. H. Wragg, T. S. Stevens, and D. M. Ostle, *J. Chem. Soc.*, 1958, 4057.

[13] T. S. Stevens and T. Thomson, *J. Chem. Soc.*, 1932, 69; U. Schollkopf and U. Ludwig, *Chem. Ber.*, 1968, **101**, 2224; U. Schollkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Letters*, 1969, 3415.

[14] R. B. Woodward and R. Hoffmann, *Angew. Chem., Internat. Edn.*, 1969, **8**, 781.

[15] J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, 1972, **94**, 8917; J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, 1972, **5**, 402; J. A. Berson, *ibid.*, p. 406.

[16] M. Raban, G. W. J. Kenney, and F. B. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 6677; C. Brown, B. T. Grayson, and R. F. Hudson, *Tetrahedron Letters*, 1970, 4925.

product composition changes considerably. This suggests, but does not necessarily prove, that both reactions proceed through a common intermediate in the rate-determining step (N–O homolysis). The data in Table 2 show that ΔS^* is in the range 0.3—8.6 *J* mol^{-1} K^{-1},

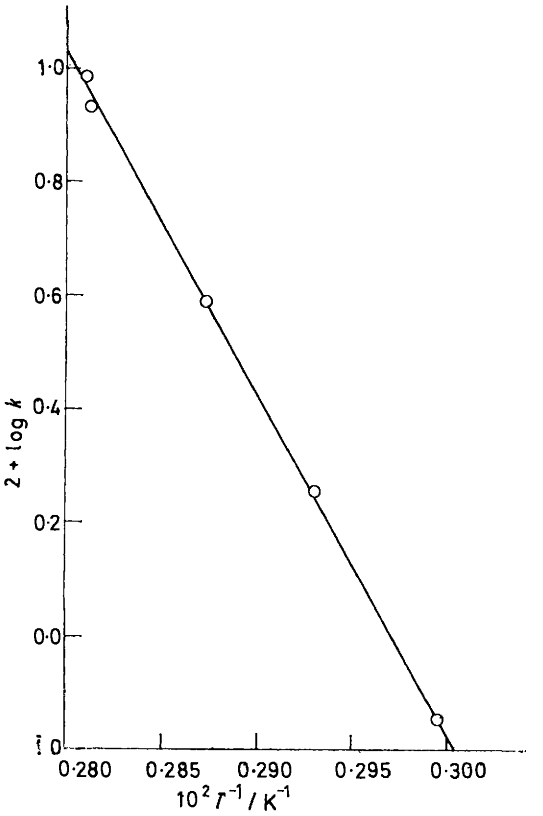

FIGURE 3 Arrhenius plot for the rearrangement of *O*-(*NN*-dimethylthiocarbamoyl)-*N*-methyl-*N*-(*p*-toluoyl)hydroxylamine in hexane

and these positive values support a mechanism involving a rate-determining homolysis rather than a cyclic transition state.

The activation entropy values increase with the activation enthalpy which is usual for reactions involving similar reactants (ΔH^* increases linearly with ΔS^*) The change in activation enthalpy is particularly interesting as a minimum is observed in the reaction of the unsubstituted compound. This indicates that both electron-attracting and -withdrawing substituents decrease the energy required to break the N–O bond, *i.e.* increase the stability of the amidyl radical formed.

TABLE 2

Activation parameters for the rearrangement of $RC_6H_4C(O)N(Me)OC(S)NMe_2$ in hexane

R	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} K^{-1}	R	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} K^{-1}
p-Me	114 ± 2.4	4.3 ± 1.9	H	121 ± 2.2	8.6 ± 1.6
p-MeO	113 ± 1.6	3.8 ± 1.1	*p*-NO_2	108 ± 3.8	0.3 ± 2.6

There is much controversy concerning the structure of amidyl radicals,[17] as both σ- and π-structures have been proposed. Moreover, SCF[18] and semi-empirical[19] (INDO) MO calculations lead to the conclusion that both σ- and π-radicals exist in several electronic states. These calculations support a π-structure with the electron localised on nitrogen. E.s.r. measurements[9] show the radical to be of the π-type, and recent n.m.r. measurements[20] (CIDNP) favour a delocalised π-structure. It should be noted that both INDO and SCF calculations with a minimal basis set are not reliable methods of estimating electronic energies of states separated by small energy differences. Reliance must be placed on experimental observation, which supports a π-delocalised structure (with a high electron density on nitrogen).

This discussion is relevant to the effect of substitution on the activation enthalpies. It is well known that many (carbon) π-radicals with aromatic substituents, are stabilised by both electron-attracting and -withdrawing substituents.[21] The decrease in activation energy with substitution in the aromatic ring (Table 2), follows the increase in stability of the corresponding amido radical in the π-state, which is also in agreement with a radical cage process for the rearrangement.

One further observation is worthy of note. The observed rate constant is almost insensitive to change in solvent, *e.g.* the rates in hexane and ethanol are almost identical. However, significant rate increases are observed in highly chlorinated solvents, and this may be due to the stabilisation of radical intermediates.[22]

TABLE 3

First-order rate constants for the rearrangement of $p\text{-}MeC_6H_4C(O)N(Me)OC(S)NMe_2$ in various solvents at 60.5°

Solvent	$10^2k/\text{min}^{-1}$	Solvent	$10^2k/\text{min}^{-1}$
Hexane	0.510 ± 0.007	Chloroform	1.41 ± 0.04
Ethanol	0.500 ± 0.01	[^{2}H]Chloroform	0.94 ± 0.02
Acetonitrile	0.292 ± 0.007	Carbon tetrachloride	1.90 ± 0.08
Benzene	0.294 ± 0.009		

EXPERIMENTAL

Preparation of Starting Materials.—These were prepared as described previously by the action of the corresponding *N*-methylbenzohydroxamic acid on *NN*-dimethylthiocarbamoyl chloride in dimethylformamide in the presence of triethylamine. The following *para*-substituted *N*-aroyl-*O*-(*NN*-dimethylthiocarbamoyl)-*N*-methylhydroxylamines were obtained: MeO, m.p. 87°; Me, m.p. 99—101°; NO_2, 132—134° (decomp.); and the unsubstituted compound,

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[17] E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, 1967, **89**, 4875.

[18] N. C. Baird and H. B. Kathpal, *J. Amer. Chem. Soc.*, 1976, **98**, 7532.

[19] T. Koenig, J. A. Hoobler, C. E. Klopfenstein, G. Hedden, F. Sunderman, and B. R. Russell, *J. Amer. Chem. Soc.*, 1974, **96**, 4573; T. Koenig and R. A. Wielesek, *Tetrahedron Letters*, 1975, 2007.

[20] C. Brown and A. J. Lawson, *Tetrahedron Letters*, 1975, 191.

[21] M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3353; R I. Walter, *ibid.*, 1966, **88**, 1930.

[22] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1966, **88**, 2322; C. D. Dijkgraaf and G. J. Hoijtink, *Tetrahedron Suppl.*, 1963, **2**, 199.

m.p. 55—56°. These were recrystallised from benzene–light petroleum ether (b.p. 40—60°) at 0°, and each was analysed for purity by t.l.c.

Solvents.—Hexane (Spectrograde), ethanol, carbon tetrachloride, and benzene were distilled before use. Acetonitrile was dried and purified by distillation twice from phosphorus pentaoxide and stored over calcium hydride. Chloroform (AnalaR grade) contained 2% ethanol. Ethanol-free chloroform was prepared by shaking the AnalaR sample with concentrated sulphuric acid several times, and washing thoroughly with water. It was then dried ($CaCl_2$) and fractionally distilled. The pure sample was stored in the dark.

TABLE 4

Temperature dependence of the first-order rate coefficients for the rearrangement of *p*-$RC_6H_4C(O)N(Me)OC(S)NMe_2$ in n-hexane

R = Me		R = MeO	
T/°C	10^2k/min^{-1}	T/°C	10^2k/min^{-1}
82.6	6.92 ± 0.12	82.6	9.64 ± 0.25
74.8	3.10 ± 0.05	74.8	3.87 ± 0.12
67.4	1.15 ± 0.04	68.0	1.78 ± 0.03
64.8	0.975 ± 0.008	60.6	0.707 ± 0.008
60.5	0.510 ± 0.007		
40.3	0.450 ± 0.006		
25.6	0.331 ± 0.007		
R = H		R = NO_2	
82.6	6.25 ± 0.009	82.6	7.15 ± 0.10
74.8	2.63 ± 0.05	74.8	2.64 ± 0.04
67.8	1.02 ± 0.02	68.5	1.31 ± 0.03
58.6	0.312 ± 0.006	60.4	0.580 ± 0.007

TABLE 5

Decolourisation of DPPH by *p*-$MeC_6H_4C(O)N(Me)OC(S)NMe_2$ in benzene at 59.2°. Initial concentrations 0.92×10^{-4}M

t/min	10^4[DPPH]/M	[DPPH] % loss	t/min	10^4[DPPH]/M	[DPPH] % loss
0	0.919	0	300	0.207	77.5
60	0.653	29.0	360	0.142	84.5
120	0.503	45.2	420	0.095	89.7
180	0.388	57.7	480	0.0595	93.7
240	0.289	68.6			

Kinetic Measurements.—(a) *U.v. method.* The rate of rearrangement was measured by continuously monitoring an appropriate u.v. absorption band using a Unicam SP 800 spectrometer fitted with a flat-bed Servoscribe recorder. Concentrations of the order of 10^{-4}M were used in several solvents, 3 ml of each solution being introduced into a 10 mm silica cell sealed with a Teflon stopper and placed in the temperature-controlled (±0.1°) brass block of the spectrometer. The progress of the reaction was followed by the decrease in intensity of a characteristic band of the reactant at the following wavelengths: 250 (hexane, ethanol, acetonitrile); 265 (chloroform); 270 (carbon tetrachloride); and 285 nm (benzene).

(b) *I.R. method.* The kinetics of the rearrangement in carbon tetrachloride, chloroform, and benzene were determined using 0.2M solutions, by i.r. analysis. In a particular experiment a 5% (w/v) solution of (I) (10 ml) in a stoppered flask was immersed in a thermostat at the appropriate temperature. At given times, samples (0.3 ml) were removed rapidly and diluted to 1 ml with the solvent. The i.r. absorption was measured at 1 288 (carbon tetrachloride), 1 286 (benzene), and 1 170 cm^{-1} (chloroform) using 0.5 mm sodium chloride cells. Calibration curves were constructed from the i.r. absorption of (I) taken at a series of concentrations, and the rate constants calculated from the concentration at a given time, using the Guggenheim method to determine the infinity value.

Activation Parameters.—The first-order rate constants were measured at several temperatures for the reaction in hexane, selected because of its weakly solvating properties. Good linear Arrhenius plots were obtained for the four compounds studied, (*e.g.* Figure 3). Theoretical analysis of these data to give ΔH^* and ΔS^* values (Table 4) was made on an Elliott 4130 computer using a 'Dartmouth Basic Language' program.

Colorimetric Determination with DPPH.—The rate of decolouration of DPPH in the presence of (I) in benzene purged of dissolved air was followed colorimetrically. A benzene solution, equimolecular in (I) and DPPH (*ca.* 0.92×10^{-4}M) was prepared, and 3 ml pipetted into a 10 mm silica cell fitted with a Teflon stopper. The visible spectrum (300—700 nm) was immediately recorded (Unicam SP 800 spectrometer) and the change in absorption at 510 nm monitored as described above. The results of a typical run are given in Table 5.

From these values a curve of $[DPPH]_{t=0} - [DPPH]_t$ against time was constructed and tangents taken at appropriate points, to give values of $-d[DPPH]/dt$. These are then related to $[(I)]_t$ by calculating the latter from the first-order rate equation and the known first-order rate constant (0.294×10^{-2} min^{-1} at 59.2°), to give the data in Table 6.

TABLE 6

Variation of $-d[DPPH]/dt$ and [(I)] with time in benzene at 59.2°

t/min	$-10^7d[DPPH]/dt$/ M min^{-1}	10^4[(I)]/M	t/min	$-10^7d[DPPH]/dt$/ M min^{-1}	10^4[(I)]/M
0		0.951	300	1.213	0.394
60	3.132	0.797	360	0.896	0.330
120	2.096	0.668	420	0.642	0.277
180	1.789	0.560	480	0.528	0.232
240	1.490	0.469			

The graph of $-d[DPPH]/dt$ against [(I)] is linear (Figure 2) with a slope of 0.379×10^{-2} min^{-1}, from which the ratio of the diffusion rate and radical recombination rate can be calculated. At the end of the reaction, 2.5 ml of the solution was added to a three-fold excess of (I) and heated at 61.5° for ten half-lives. No further decolouration was observed indicating that all the DPPH had reacted.

In a further experiment the decolouration of a mixture of DPPH (0.763×10^{-4}M) and (I) (0.380×10^{-4}M) was determined. Under these conditions a 64.0% decrease in the DPPH concentration was recorded at the end of the reaction. Calibration experiments were made on successively diluted solutions of DPPH to show that Beer's law is accurately obeyed at 510 nm. In control experiments, the decolouration of DPPH in benzene and also in carbon tetrachloride solution was found to be very slow at 66°. *Ca.* 4% change in concentration was observed in 5 h.

Product Analysis by N.m.r. Measurements.—A 10% (w/v) solution of (I) in [$^2H_6$]benzene was sealed in an 8 mm n.m.r. tube containing tetramethylsilane as internal standard. The n.m.r. spectrum was recorded after 48 h at 60° using a Perkin-Elmer R10 spectrometer. Integration of the absorption due to the NMe protons of the rearranged product (II) at δ 3.30, and of the absorption due to the NMe protons at δ 2.92—3.00, of *N*-methyl-*p*-toluamide gave 40.9% conversion to (II) and 59.1% conversion to (III).

Product Analysis of the Thermolysis of (I; R = *p*-MeC_6H_4) *in Deuteriochloroform at* 120°.—Solutions of (I) in deuteriochloroform (10% w/v) were heated at 120° for 20 min, cooled, and analysed spectroscopically. The i.r. spectrum showed the presence of *N*-methyl-*p*-toluamide and (II) as the major products, with some carbonyl sulphide. The solvent was removed under vacuum, and the solid dissolved in AnalaR chloroform (2 ml). This solution was applied to three preparative t.l.c. plates and eluted with chloroform. The chromatogram contained two major bands which were removed, extracted with methanol and acetone, and filtered. The upper band yielded a yellow oil, identified as the rearranged product (II), by i.r. and n.m.r. spectra. The lower band gave long white prisms, m.p. 145°, identified as *N*-methyl-*p*-toluamide.

N.m.r. analysis of similar samples showed major peaks due to (II) and (III). Two small peaks at δ 3.02 and 2.60 were observed, their intensity increasing with temperature. These were due to a brown tar, which could not be purified satisfactorily by chromatography or crystallisation. A carbonyl band was observed in the i.r. spectrum at 1 705 cm^{-1}. These observations are consistent with a polymeric structure (see earlier).

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