Tetrahedron. Vol. 32, pp. 2289 to 2294. Pergamon Press 1976. Printed in Great Britain

MECHANISM OF THE EXCLUSIVE CYCLIC 1,3-REARRANGEMENT OF O-BENZOYL-N-(*p*-TOLUENESULFONYL)-N-ARYLHYDROXYLAMINES[1a]

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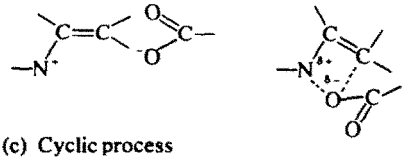
(*Received in Japan* 23 *February* 1976; *Received in UK for publication* 26 *April* 1976)

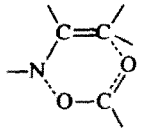
Abstract—O-(*p*-Substituted benzoyl)-N-(*p*-toluenesulfonyl)-N-arylhydroxylamines (1) were found to rearrange thermally giving *o*-acyloxy-*p*-toluenesulfonanilides (2) in quantitative yields. An intramolecular concerted cyclic process is considered to be in operation for the rearrangement on the basis of ^{18}O tracer and kinetic experiments. The effects of both substituents and solvents on the rate of this novel 1,3-acyloxy migration were also examined. While the effect of solvent was small, the electronic effect of substituents on both N and O atoms plays a significant role in determining the mechanism of the rearrangement, especially the mode of cleavage of the N–O bond at the transition state of the 1,3-acyloxy migration.

The reactions of aromatic and heteroaromatic amine N-oxides with various acylating agents have been quite useful in studying the mechanism of 1,3-acyloxy migrations accompanying the N–O bond cleavage since these 1,3-rearrangements have been found to proceed via various mechanistic routes depending on the structure of the substrate, the acylating agent and the polarity of solvent.[1b,1c] These reactions which involve concurrent N–O bond cleavage and O–C bond formation have been divided into three classes, i.e. (a) scrambling process,[2] (b) sliding process[3] and (c) cyclic process. These three processes involve the transition states as schematically shown below respectively.

(a) Scrambling process (b) Sliding process

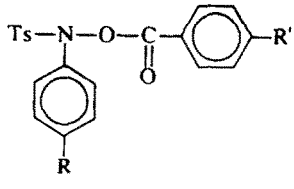


(c) Cyclic process



Many examples of 1,3-rearrangements which proceed through path (a) and path (b) have been found on the basis of ^{18}O tracer experiments. The cyclic mechanism was once deemed most appropriate to account for many 1,3-acyloxy migrations in heterolytic rearrangements.[4] Detailed studies with the use of ^{18}O tracer technique on these rearrangements, however, ruled out such a mechanism[2a,5] except for the Cope-like rearrangement of 2-butenyl trifluoroacetate in gas phase.[6] Thus, no 1,3-acyloxy migration via path (c) has hitherto been observed in liquid phase reactions.

This paper deals first with the results obtained in the ^{18}O tracer and kinetic experiments on the thermal rearrangement of O-(*p*-substituted benzoyl)-N-(*p*-toluenesulfonyl)-N-arylhydroxylamines (1) and their implications on the mechanism, together with a discussion on the effects of migrating and functional groups attached directly to the N atom on the mode of the 1,3-acyloxy migration. Then, the results obtained in the similar ^{18}O tracer experiment on the thermal rearrangement of O-benzoyl-N-benzoyl-N-phenylhydroxylamine will be discussed, together with the general mode of various 1,3-acyloxy migrations.



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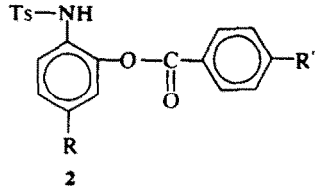
R = CH_3, H, Cl R′ = NO_2, Cl, H, CH_3, OCH_3



2

Ts = *p*-$CH_3C_6H_4SO_2$

RESULTS AND DISCUSSION

^{18}O Tracer experiment. During the study of the nucleophilic substitution on the trivalent N atom with acyloxy group as leaving group, we have found that 1 rearranges thermally to give the corresponding *o*-acyloxy-*p*-toluenesulfonanilides (2) in quantitative yields. The compound 1 was heated in DMSO or in other solvents at 110–120° until the completion of rearrangement. An ^{18}O tracer experiment was carried out with carbonyl-^{18}O labeled 1 (R′=H, R=CH_3, H, Cl) to clarify the mode of the 1,3-benzoyloxy migration. The isotopic analysis of the starting material was performed for both benzamide prepared from the starting ^{18}O labeled benzoyl chloride and benzhydrazide 3 formed by hydrazinolysis of the labeled 1 with ^{18}O. The product 2 was cleaved by treating it with hydrazine like in the case for the hydrazinolysis of

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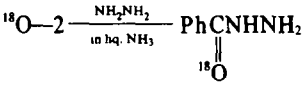
1 to give 3 which was

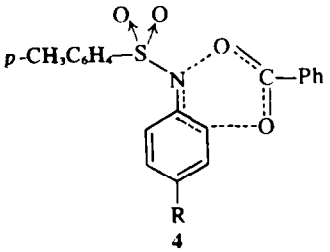


3

subjected to the ^{18}O analysis in order to determine the ^{18}O distribution in the product. These results are collected in Table 1.

Inspection of the result suggests that the isotopic labeling in the carbonyl oxygen of the starting material 1 was achieved without any oxygen scrambling. The same data also show that there was no oxygen exchange during the hydrazine cleavage of 2. Since there is no possibility of oxygen exchange both in the migration and the hydrazinolysis, comparison of the isotope contents of these hydrazides 3 obtained from 1 and 2 clearly indicates the isotope distribution in the carbonyl and phenolic oxygens of the product 2.

The amount of ^{18}O in the hydrazide 3, obtained from the rearranged product 2, was found to be nearly natural regardless of the nature of the solvents used. This observation suggests strongly the mechanism of the rearrangement to involve an intramolecular concerted cyclic migration as follows.



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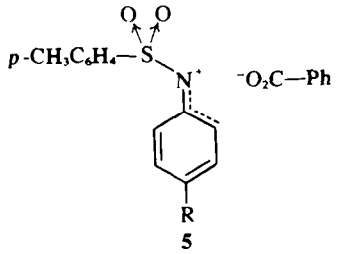
There have been a few cases of 1,3-acyloxy migrations in the reaction of N-oxides of pyridine bases with acylating agents in which uneven distribution of ^{18}O in the resulting esters were observed due mainly to the very fast recombination of the picolyl cation derivative and the acyloxy anion formed by the N–O bond cleavage of the anhydrobase intermediate.[7] However, in no case, such an exclusively cyclic process via 4 has been found.

A prominent factor to rationalize the rather exclusively cyclic mechanism is the strong electron-withdrawing nature of the sulfonyl group attached to the N atom and the poor leaving ability of the benzoyloxy group as migrating group to suppress the heterolytic cleavage of the N–O bond, thus inviting synchronous N–O bond cleavage and O–C bond formation in the cyclic transition state 4 which may resemble that of a typical sigmatropic rearrangement.[8] In this case, the stepwise mechanism involving the intermediate 5 would be unfavorable.



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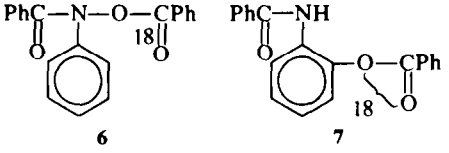
Meanwhile, introduction of an electron-releasing *p*-Me group which is known to stabilize the anilinium intermediate[9] resulted in a small but partial scrambling of ^{18}O in the resulting ester 2. The enhanced rate of the *p*-Me derivative also seems to support a partial contribution of the ion-pair mechanism via 5.

^{18}O *Tracer study on the rearrangement of* O - *benzoyl* - N - *benzoyl* - N - *phenylhydroxylamine.* We prepared O - benzoyl - carbonyl - ^{18}O - N - benzoyl - N - phenylhydroxylamine (6) in order to campare the effect of the CO function attached directly to the N atom on the ^{18}O distribution in the rearranged product 7 with that of the sulfonyl function. Although no ^{18}O tracer study on the mechanism of 1,3-rearrangement of 6 has been carried out, the hydroxylamine 6 has been known to rearrange to give the ester 7 in a good yield.[10] Indeed, we also observed the same result.



6 7

Table 1. ^{18}O Analytical result of the thermal rearrangement of 1 at 110–120°

Compound	Substituent R	Solvent	^{18}O Excess atom %
$PhCONH_2$[a]	----	----	1.31
$PhCONHNH_2$[b]	H	----	1.31
$PhCONHNH_2$[c]	H	----	1.31
$PhCONHNH_2$[d]	H	DMSO	0.02
	Cl	DMSO	0.03
	CH_3	DMSO	0.07
	H	Benzene	0.03
	H	$ClCH_2CH_2Cl$	0.04
	H	CH_3CN	0.03

a Derived from PhCOCl, used for the preparation of 1.

b Obtained from the reaction of 1 with NH_2NH_2 in liq. NH_3.

c Obtained from the reaction between carbonyl-^{18}O labeled 2, which was prepared by the reaction of o-hydroxy-p-toluenesulfonanilide with $PhC^{18}OCl$, and NH_2NH_2 in liq. NH_3.

d Derived from 2 with given R which was obtained by thermal rearrangement of 1 in the given solvent.

The isotopic analyses of the starting material and the product were performed in a similar way as that for the hydroxylamine 1. The ^{18}O analytical data are summarized in Table 2. The data in Table 2 shows clearly that there is no oxygen exchange in the degradation steps during the preparation of ^{18}O analytical samples since the ^{18}O content of the starting material 6 is in good agreement with the sum of ^{18}O content in both carbonyl and phenolic oxygens in the resulting ester 7. The ^{18}O concentrations of both carbonyl and phenolic oxygens in the *o*-benzoyloxy group are 0.05 and 1.01 excess at.% of ^{18}O respectively, which indicate the rearrangement to proceed mostly through a concerted cyclic mechanism with a partial scrambling of ^{18}O during the reaction.

Comparison of the results in Tables 1 and 2 reveals that the N-benzoyl group in 6 increases the oxygen scrambling a little as compared to the N-*p*-toluenesulfonyl group in 1. The weaker inductive effect of the CO group of 6 than the sulfonyl group of 1 on the stabilization of the transition

Table 2. ^{18}O Analytical result of the rearrangement of **6** at 110–120°

Compound	Solvent	^{18}O Excess atom %
$PhCONHNH_2$ [a]	----	1.06
$PhCONHNH_2$ [b]	DMSO	0.05
 [c]	DMSO	1.91

a Obtained from the reaction of 6 with NH_2NH_2 in liq. NH_3;

b Derived from the reaction of 7 which was obtained by the thermal rearrangement of 6 in DMSO with NH_2NH_2 in liq. NH_3;

c Derived from the reaction between o-hydroxybenzanilide which was formed by the reaction of 7 with NH_2NH_2 along with benzhydrazide and KOH in refluxing CH_3OH.

state **4** is expected to increase the contribution of the transition state **5**. Therefore, the increasing oxygen scrambling may be ascribed to the increased contribution of the ionic transition state of the rearrangement of **6** as compared to the rearrangement of **1**.

Thus, the change of polar substituent attached to the N atom does change somewhat the mode of the 1,3-benzoyloxy migration.

Substituent and solvent effects on both the rate of rearrangement and the ^{18}O distribution. The nature of solvent is expected to effect on the mode of the bond-breaking, i.e. homolytic vs heterolytic cleavages and also on the migration mode, such as intramolecular or intermolecular rearrangement. The solvation, indeed, is suggested to play an important role in the acyloxy migration.[1c] Strong solvation would assist the rearrangement to proceed via ion-pair path.[6,11] However, it would be difficult to predict a clear direction of the solvent effect in the 1,3-rearrangement between tertiary amine N-oxides and acylating agents since solvent effects on the rate and the ^{18}O distribution are complicated owing to the multisteps nature of the reaction of these 1,3-rearrangements. However, it is interesting to study the solvent effect on this one-step 1,3-benzoyloxy migration of **1** in order to obtain further evidence for the exclusive cyclic 1,3-rearrangement.

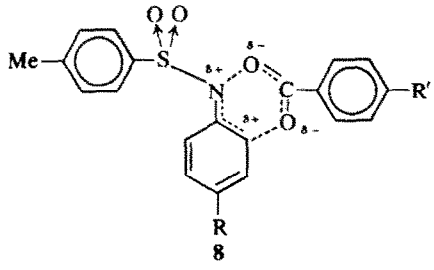
The reaction was carried out in several solvents and the kinetic measurements were performed by following the gradual decrease of IR absorption band which appear at around 1756–1774 cm^{-1}, a characteristic band of the CO group of **1**. The rates of rearrangement were correlated nicely with the usual first-order rate equation. The rate constants and the ^{18}O analytical results obtained are summarized in Tables 1, 3 and 4. Data in Table 3 reveal that the rate of rearrangement is not much affected by the change of solvent. Even the change in polarity of the solvent from chloroform to acetonitrile changes the rate not more than 1.4 fold. This seems to indicate that the cyclic transition state **4** of the rearrangement is not much polar. This observation is supported from the fact that ^{18}O distribution in the product did not vary with the polarity of solvents used; namely, ^{18}O content of the hydrazide **3** obtained from **2** stays almost natural, even though the solvent changes from benzene to DMSO as indicated in Table 1. Therefore, the reaction is believed to proceed via the 6-membered cyclic transition state **4** on the basis of both ^{18}O tracer and kinetic results.

On the contrary, a good linear Hammett correlation of the substituent (R′) constants with the rates of the rearrangement was observed except for such an electron-donating as OMe as indicated in Fig. 1. The large negative values of activation entropy shown in Table 4 indicate that the reaction involves the cyclic transition state as illustrated by **4**, in accordance with the ^{18}O tracer result. Thus, these values of activation entropy are quite in contrast with that ($\Delta S^{\neq} = +13.4$ e.u.) of the rearrangement of N-arenesulfonoxy-isocarbostyril in which the N–O bond cleavage is to be rate-determining step similar to the S_Ni solvolytic reaction.[12] Furthermore, Hammett ρ value (*ca.* +1.5) suggests the N–O bond cleavage to be rate-determining step, indicating that the rearrangement could not proceed through an ideal cyclic transition state. Since the activation entropy of this 1,3-acyloxy migration strongly requires the rigid structure of the transition state, one can assume the reaction to proceed via a cyclic transition state with an ionic character like **8**.

Table 3. Effect of solvent on the rate of rearrangement of **1** (R=R′=H) at 100.6°

Solvent	D [a]	$10^5 k_1$ (sec^{-1})	Rel. rate
$CHCl_3$	4.7	2.21±0.05	1.0
$ClCH_2CH_2Cl$	10.4	2.49±0.22	1.1
CH_3CN	37.5	2.97±0.17	1.3

a Dielectric constant.



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Effects of substituents R in the aniline ring of **1** on the rate of rearrangement are apparently complicated since the rates can be correlated by neither σ nor σ^+ values as seen from Table 4. Electron-releasing *p*-Me group (R=Me, R′=H), however, is expected to stabilize the transition state **8**. Consequently, the rate of reaction is expected to increase substantially. In fact, the reaction was accelerated 27 times by Me group. Furthermore, a partial scrambling of ^{18}O by this Me group would be attributable to the increased ionic character and the contribution of the heterolytic process via **5** would increase the scrambling of ^{18}O at the transition state.

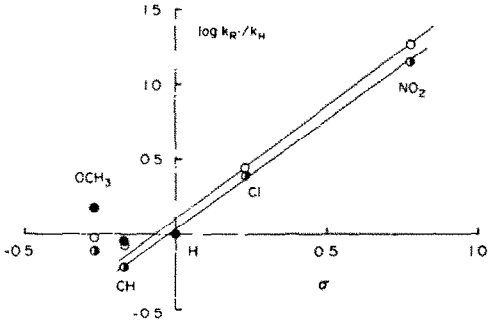


Fig. 1. Plot of the log $k_{R'}/k_H$ for the rearrangement of **1** with given R in $CHCl_3$ against Hammett σ values. ○, R=Cl (at 100.6°C); ◑, R=H (at 100.6°C); ●, R=CH_3 (at 60.1°C).

Table 4. Rate of the rearrangement of 1 in $CHCl_3$ and activation parameters

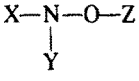
Substituents R	R'	Temp. (°C)	$10^5 k_1$[a] (sec^{-1})	Rel. rate	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
H	NO_2	100.6±0.1	31.2 ±0.94	14	26	-7
		109.0	65.5 ±2.9			
		116.5	133 ±7.4			
H	Cl	100.6	5.64±0.20			
H	H	100.6	2.21±0.05	1.0	21	-25
		109.0	4.66±0.10			
		116.5	7.17±0.26			
H	CH_3	100.6	1.34±0.08			
H	OCH_3	100.6	1.74±0.15	0.8	25	-14
		109.0	3.87±0.19			
		116.5	7.11±0.69			
Cl	NO_2	100.6	77.9 ±3.2			
Cl	Cl	100.6	11.4 ±0.35			
Cl	H	100.6	4.14±0.12	1.9	20	-25
		109.0	7.33±0.35			
		116.5	13.1 ±0.90			
Cl	CH_3	100.6	3.51±0.22			
Cl	OCH_3	100.6	3.90±0.20			
CH_3	H	50.0±0.05	2.03±0.22			
		55.1	3.11±0.23			
		60.1	4.30±0.45		15	-33
		100.6	58.9[b]	27		
CH_3	CH_3	60.1	3.77±0.50			
CH_3	OCH_3	60.1	6.44±0.53			
PhC(=O)-N(Ph)-OC(=O)-C$_6$H$_4$-NO_2		100.6±0.1	1.38±0.05	0.6	26	-12
		109.0	3.08±0.20			
		116.5	5.91±0.35			

a Error limits are standard deviation;

b Extrapolated value.

General discussion on the mode of 1,3-*acyloxy migration*

Next, we have turned our attention to the effect of substituents X, Y and Z on the mode of the 1,3-acyloxy migration of the hydroxylamine **9** and the results obtained are tabulated in Table 5 along with those reported by others.



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Inspection of the data in Table 5 reveals that the replacement of sulfonyl or benzoyl groups by phenyl group for the substituent X alters the mechanistic route from the cyclic path to the scrambling path when substituents Y and Z are phenyl and benzoyl groups respectively (lines 3, 4 and 6). As the leaving ability of the migrating group, i.e. OZ increases, the oxygen scrambling increases even though the substituent X suppresses the heterolytic cleavage of the N–O bond, since the 1, 3-acyloxy migration of **9** bearing dichloroacetoxy or arenesulfonoxy groups proceed via the scrambling path, while the introduction of benzoyloxy group with poor leaving ability for OZ resulted in an exclusive cyclic process during the rearrangement (lines 2, 4 and 5).

Table 5. Survey of 1,3-acyloxy migration of the hydroxylamine **9**, X—N(Y)—O—Z

	X	Y	Z	Mechanism	Ref.
1,	CH_3CO	Ph	Cl_2CHCO	Scrambling	2d
2,	PhCO	Ph	CF_3CO	Scrambling	2d
3,	Ph	Ph	PhCO	Scrambling	2b
4,	PhCO	Ph	PhCO	Cyclic with partial scrambling	This work
5,	PhCO	Ph	Ts*	Scrambling	2a
6,	Ts*	Ph	PhCO	Cyclic	This work
7,	Ts*	CH_3-C$_6$H$_4$-	PhCO	Cyclic with partial scrambling	This work

* Ts=p-$CH_3C_6H_4SO_2$

Furthermore, a partial scrambling of ^{18}O was observed when Me group was introduced to the para-position of the phenyl ring as substituent Y (lines 6 and 7). Comparison of lines 1 and 2 indicates that the mode of 1,3-acyloxy migration is not affected by the change from benzoyl to acetyl groups for the substituent X of **9** when a good leaving group such as trifluoroacetoxy or dichloroacetoxy is the OZ group.

These observations suggest that the oxygen scrambling in the 1,3-acyloxy migration tends to increase by substituents X, Y and Z which promote the heterolytic cleavage of the N–O bond by stabilizing the cation or the anion formed by the heterolytic cleavage of the N–O bond. On the other hand, the 1,3-acyloxy migration involving a concerted cyclic transition state becomes predominant when the substituents X, Y and Z suppress the heterolytic cleavage of the N–O bond.

Thus, the mechanism of the 1,3-acyloxy migration of the hydroxylamine **9** can reasonably be interpreted in terms of the electronic effect of the substituents X, Y and Z on the heterolytic cleavage of the N–O bond.

EXPERIMENTAL

Materials and solvents. O - (*p* - Substituted benzoyl) - N - (*p* - toluenesulfonyl) - N - arylhydroxylamines (**1**) were prepared by benzoylation of N - (*p* - toluenesulfonyl)arylhydroxylamines, which were prepared from the reaction of arylhydroxylamines (2 mol) with *p*-toluenesulfonyl chloride (1 mol) in dry ether, with *p*-substituted benzoyl chlorides under usual Schotten–Baumann conditions and the physical properties of these hydroxylamines **1** are shown in Table 6. O - (*p* - Nitrobenzoyl) - N - benzoyl - N - phenylhydroxylamine, m.p. 127.5–128.5° (Found: C, 66.30; H, 3.78; N, 7.69. Calc. for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73%) and O - benzoyl - N - benzoyl - N - phenylhydroxylamine, m.p. 118.5–119.5° (lit. 118–119°)[10] were prepared by the reaction between N-benzoylphenylhydroxylamine and *p*-nitrobenzoyl chloride, and benzoyl chloride respectively under usual Schotten–Baumann condition. All the solvents were used after purification by the usual methods.

Product analysis. A typical run was as follows; 259 mg of O - benzoyl - N - (*p* - toluenesulfonyl) - N - phenylhydroxylamine was heated in 5 ml of DMSO at 110–120° for 6 hr and the soln was poured into 200 ml H_2O and extracted twice with 150 ml $CHCl_3$. The $CHCl_3$-soln was washed 3 times with H_2O and dried over anhyd Na_2SO_4. Removal of solvent from the extract afforded 256 mg of *o* - benzoyloxy - *p* - toluenesulfonanilide which was recrystallized from benzene-hexane to give white needles, m.p. 142–143° (Found: C, 65.32; H, 4.78; N, 3.53. Calc. for $C_{20}H_{17}NO_4S$: C, 65.38; H, 4.66; N, 3.81%). Structure of the rearranged product was confirmed by comparison of the physical properties (IR, m.p. 140–141°) of *o* - hydroxy - *p* - toluenesulfonanilide which was obtained upon alkaline hydrolysis of the rearranged product with that (IR, m.p. 139–140°, Found: C, 59.41; H, 5.02; N, 5.05. Calc. for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.32%) of the authentic sample which was prepared from the reaction of *o*-aminophenol (2 mol) with *p*-toluenesulfonyl chloride (1 mol) in dry ether. Physical properties of other rearranged products are summarized in Table 6.

^{18}O Tracer study. ^{18}O Labeled benzoyl chloride was prepared similarly according to the method reported in the previous paper.[5] Compounds **1** and **6** were synthesized with ^{18}O labeled benzoyl chloride in the same way as for the non-labeled hydroxylamines.

Preparation of ^{18}O analytical samples. A typical run was as follows. In a flask equipped with a stirrer, were placed 760 mg of the rearranged product, *o* - benzoyloxy - *p* - toluenesulfonanilide, 30 ml of liq. NH_3 and 240 mg of $NH_2NH_2 \cdot 2HCl$ under cooling in dry ice-MeOH bath and the whole mixture was mechanically stirred for 8 hr. After ammonia was distilled off, the residue was dissolved in 50 ml $CHCl_3$ and filtered off in order to remove NH_4Cl formed. Evaporation of $CHCl_3$ gave the mixture which afforded 340 mg of *o* - hydroxy - *p* - toluenesulfonanilide, m.p. 139–140°, and 150 mg of benzhydrazide, m.p. 112–114° using preparative TLC with 90% CH_2Cl_2–EtOH as developing solvent. Structures of these products were determined in comparison with those of the authentic samples. Benzhydrazide thus obtained was subjected to the ^{18}O analysis, while *o* - hydroxy - *p* - toluenesulfonanilide could not be subjected to the usual ^{18}O isotopic analysis because any attempt to cleave the N–S bond of the sulfonanilide was unsuccessful. Because of the failure to cleave the N–S bond, the presence of the two O atoms of the sulfonyl group lowers the accuracy of ^{18}O analysis.

Hydrolysis of o-hydroxybenzanilide. *o*-Hydroxybenzanilide, 570 mg, m.p. 168–169° which was obtained by hydrazinolysis of the rearranged product, *o*-benzoyloxybenzanilide, 1070 mg, m.p. 180–181° (lit. 179–180°)[10] in liq. NH_3 along with benzhydrazide, 210 mg, was hydrolyzed in 30 ml of 90% MeOH–H_2O containing 30% KOH under refluxing for 72 hr. After the mixture was neutralized with HCl, *o*-aminophenol was extracted 3 times with 30 ml of ether after removal of a solid mass, recrystallized from benzene–hexane to give crystals, m.p. 168–169°, 15% yield. *o*-Aminophenol and benzhydrazide thus obtained were subjected to the ^{18}O analysis.

Isotopic analysis. Analysis of ^{18}O content in the ^{18}O analytical samples was carried out as described previously.[5]

Rate measurement. A soln of 0.49–0.56 wt% the hydroxylamine

Table 6. Physical properties of the hydroxylamines **1** and the rearranged products **2**

Substituents R	Substituents R'	1 IR[a] (νCO), cm^{-1}	1 Anal.%, Found(Calc.)[b] C	H	N	2 IR[a] (νCO), cm^{-1}	2 M.p. (°C)[c]
H	NO_2	1774	58.31(58.25)	3.98(3.91)	6.63(6.79)	1742	189 -190
H	Cl	1765	60.59(59.77)	4.15(4.01)	3.29(3.48)	1731	152 -153
H	H	1762	65.28(65.38)	4.73(4.66)	3.72(3.81)	1735	142 -143
H	CH_3	1759	66.75(66.12)	5.05(5.02)	3.76(3.67)	1730	115 -116.5
H	OCH_3	1756	63.42(63.46)	4.86(4.82)	3.41(3.52)	1729	159 -160
Cl	NO_2	1774	54.41(53.76)	3.38(3.38)	6.24(6.27)	1743	178 -179
Cl	Cl	1765	55.84(55.05)	3.44(3.46)	3.14(3.21)	1737	161 -162
Cl	H	1764	59.84(59.77)	4.07(4.01)	3.35(3.48)	1740	132 -133
Cl	CH_3	1763	61.30(60.65)	4.36(4.36)	3.33(3.37)	1733	179 -181
Cl	OCH_3	1761	58.55(58.40)	3.69(4.20)	3.08(3.24)	1731	192 -194
CH_3	H	1761	66.34(66.12)	5.15(5.02)	3.51(3.67)	1727	130 -131
CH_3	CH_3	1759	66.57(66.81)	5.34(5.35)	3.46(3.54)	1727	154.5-155.5
CH_3	OCH_3	1760	64.57(64.21)	5.47(5.14)	3.42(3.40)	1725	153 -154

[a] All IR absorption spectra were taken in $CHCl_3$ with a model IR-G infrared spectrophotometer, Japan spectroscopic Co., Ltd.;

[b] Melting points of the hydroxylamines **1** could not be precisely determined because the thermal rearrangement occurred before melting in capillary;

[c] All melting points are uncorrected.

1 in a solvent was prepared and sealed into 5 ml amples, which were immersed in a constant temp. bath. At appropriate time intervals, the amples were taken out one by one and cooled in an ice-water bath to stop the reaction. The rate of rearrangement was then calculated by following the gradual decrease of the IR absorption band which appear at around 1756–1774 cm^{-1}, a characteristic band of the CO group of **1**. The reaction was found to follow a good first-order kinetic equation. The kinetic of the rearrangement of O - (*p* - nitrobenzoyl) - N - benzoyl - N - phenylhydroxylamine was carried out similarly.

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