The Thermal Decomposition of *N,O*-Diacyl-*N*-*t*-butylhydroxylamines

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Several *N,O*-diacyl-*N*-*t*-butylhydroxylamines and *O*-acyl-*N*-*t*-butylhydroxylamines were prepared, and their thermal decompositions were studied. The thermal decompositions of *N,O*-diacyl-*N*-*t*-butylhydroxylamines in tetralin gave substituted *N*-*t*-butylbenzamides, carboxylic acids, 1,1′-bitetralyl, and 1,2-dihydronaphthalene as the major products, together with small amounts of carbon dioxide, *t*-butylamine, and benzanilides. In the thermal decompositions of *O*-acyl-*N*-*t*-butylhydroxylamines, the products were *t*-butylamine, carboxylic acids, substituted *N*-*t*-butylbenzamides, 1,1′-bitetralyl, and 1,2-dihydronaphthalene.

It is well known that such chemical bonds as the O–O bonds in diacyl peroxides are cleaved on heating in both homolytic and heterolytic manners.[1] Although a number of workers have investigated the thermal decomposition of diacyl peroxides, few surveys of the thermal properties of the acylated hydroxylamines have appeared in the literature.[2] *N,O*-Dibenzoylhydroxylamine decomposes thermally, giving mainly phenyl isocyanate and benzoic acid (Lossen rearrangement), and the decomposition initiates the polymerization of methyl methacrylate.[2a] Horner and Steppan examined the thermal decomposition of *N,O*-diacyl-*N*-arylhydroxylamines at 180—190 °C and found *N,O*-diacyl-*o*-aminophenols as the main products, together with 20—30% of carbon dioxide. They suggested that at least 20—30% of the decomposition underwent the homolytic cleavage of the N–O bond. On the other hand, the thermal decomposition of *N,O*-diacyl-*N*-*t*-alkylhydroxylamines has not yet been studied. The alkyl group on the nitrogen atom would suppress such reactions as the Lossen rearrangement and the migration of the acyloxyl group; hence, a different type of thermolysis would result. In order to obtain further information about the thermal properties of the N–O bond in hydroxylamine derivatives, we have studied the thermal decompositions of *N*-*O*-diacyl-*N*-*t*-butylhydroxylamines and *O*-acyl-*N*-*t*-butylhydroxylamines, with tetralin as the solvent.

Results and Discussion

Preparation of N,O-*Diacyl*-N-t-*butylhydroxylamines.* The *N,O*-diacyl-*N*-*t*-butylhydroxylamines (**1**) and *O*-acyl-*N*-*t*-butylhydroxylamines (**2**) were prepared by the reactions of *N*-*t*-butylhydroxylamine and the corresponding acyl chlorides in the presence of pyridine. The reactions of *N*-*t*-butylhydroxylamine with an excess of acyl chlorides gave **1a**—**d**; the results are summarized in Table 1. On the other hand, the reaction of *N*-*t*-butylhydroxylamine with an equivalent of acyl chloride afforded **2** as the main product. The results are summarized in Table 2. Under reduced pressure, *O*-benzoyl-*N*-*t*-butylhydroxylamine (**2a**) and *O*-*p*-toluoyl-*N*-*t*-butylhydroxylamine (**2b**) could be isolated by distillation, although the distillation was accompanied by a slight decomposition. The other hydroxylamines

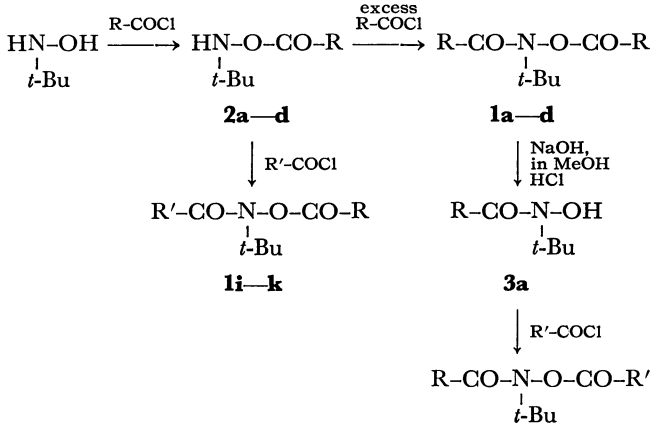
TABLE 1. YIELDS AND PHYSICAL PROPERTIES OF *N,O*-DIACYL-*N*-*t*-BUTYLHYDROXYLAMINES

Compd	Yield/%	Mp/°C	IR/cm^{-1} (KBr) C=O	Found (Calcd) (%)		
				C	H	N
1a	69	98.0—99.0 (lit, 98—99)[10]	1750, 1645	72.79 (72.70)	6.40 (6.44)	4.77 (4.71)
1b	62	114.5—115.5	1745, 1650	73.83 (73.82)	7.12 (7.12)	4.38 (4.30)
1c	55	90.0—91.0	1750, 1625	67.11 (67.21)	6.34 (6.49)	3.97 (3.92)
1d	65	112.5—113.5	1760, 1665	58.90 (59.03)	4.52 (4.68)	3.82 (3.82)
1e	82	95.0—96.0	1750, 1650	73.19 (73.29)	6.84 (6.80)	4.55 (4.50)
1f	52	73.0—74.0	1745, 1660	69.74 (69.70)	6.45 (6.47)	4.30 (4.28)
1g	67	90.0—91.0	1755, 1650	65.11 (65.16)	5.31 (5.47)	4.21 (4.20)
1h	91	63.0—64.0	1790, 1650	66.37 (66.36)	7.20 (7.28)	5.95 (5.95)
1i	79	115.0—116.0	1755, 1635	73.18 (73.29)	6.88 (6.30)	4.36 (4.50)
1j	71	101.5—102.5	1760, 1640	69.79 (69.70)	6.48 (6.47)	4.26 (4.28)
1k	73	130.5—131.5	1750, 1655	65.12 (65.16)	5.40 (5.47)	4.29 (4.22)

Table 2. Yields and physical properties of *O*-acyl-*N*-*t*-butylhydroxylamines

Compd	Yield/%	Mp (bp)/°C	IR/cm^{-1} (neat)		Found (Calcd) (%)		
			N–H	C=O	C	H	N
2a	78	(101—104/3 mmHg) (lit, 73/0.5 mmHg)[10]	3220	1720	68.47 (68.37)	8.06 (7.82)	7.25 (7.25)
2b	32	(109/3 mmHg)	3220	1715	69.85 (69.54)	8.56 (8.27)	6.77 (6.76)
2c	52	27.0—28.0	3220	1710	64.55 (64.55)	7.87 (7.68)	6.18 (6.27)
2d	70	23.0—24.0	3210	1720	58.16 (58.03)	6.11 (6.20)	6.06 (6.15)

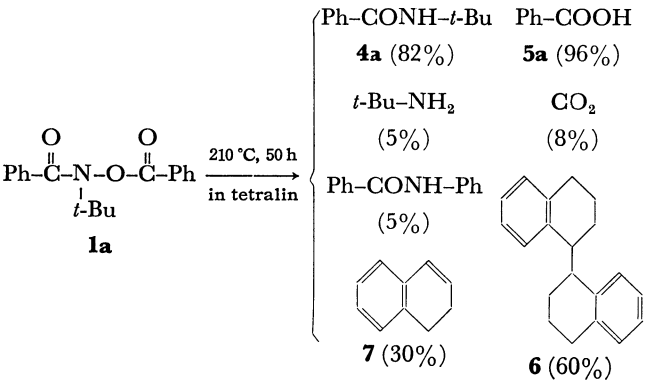
were isolated by recrystallization. The treatment of *N,O*-dibenzoyl-*N*-*t*-butylhydroxylamine (**1a**) with sodium hydroxide in methanol afforded *N*-benzoyl-*N*-*t*-butylhydroxylamine (**3a**) in a good yield. The *N,O*-diacyl-*N*-*t*-butylhydroxylamines (**1e—k**), bearing different acyl groups on the N and O aroms, were prepared by the acylation of **2a** and **3a**, as is shown in Scheme 1. The results are also given in Table 1.



1a, **2a**, and **3a** R=Ph
1b and **2b** R=*p*-CH_3–C_6H_4
1c and **2c** R=*p*-CH_3O–C_6H_4
1d and **2d** R=*p*-Cl–C_6H_4
1e and **1i** R=Ph, R′=*p*-CH_3–C_6H_4
1f and **1j** R=Ph, R′=*p*-CH_3O–C_6H_4
1g and **1k** R=Ph, R′=*p*-Cl–C_6H_4
1h R=Ph, R′=CH_3

Scheme 1.

Thermal Decomposition of N,O-*Diacyl*-N-t-*butylhydroxylamines.* *N,O*-Diacyl-*N*-*t*-butylhydroxylamines (**1**) were quite stable in comparison with *N,O*-dibenzoylhydroxylamine[2a] or *N,O*-diacyl-*N*-arylhydroxylamines,[2b] and no detectable decomposition was observed below 180 °C. Therefore, the thermal decompositions of **1** were carried out in tetralin as the solvent above 205 °C. In the thermal decompositions of **1a—d**, bearing the same acyl groups on the N and O atoms, the corresponding substituted *N*-*t*-butylbenzamides (**4**) and carboxylic acids (**5**) were formed as the products in good yields. These products were isolated by extraction from the reaction mixture with an alkaline solution and by means of column chromatography, and then identified by comparing their properties with those of authentic samples. The yields of the products were estimated by means of GLC; the results are summarized in Table 3. A detailed product analysis was performed for the thermal decomposition of **1a**; *N*-*t*-butylbenzamide (**4a**) and benzoic acid (**5a**) were found along with minor amounts of *t*-butylamine as the salt of benzoic acid, benzanilide, and carbon dioxide. 1,1′-Bitetralyl (**6**) and 1,2-dihydronaphthalene (**7**) were also obtained as the products derived from tetralin. On the gas chromatogram of the reaction mixture, the stereoisomers of **6** showed two distinct peaks of approximately equal intensities, as had been reported by Williams.[3]



Scheme 2.

In each of the thermal decompositions of **1e—k**, bearing different acyl groups on the N and O atoms, two kinds of amides (**4**) and acids (**5**), originating from the two different acyl groups, were formed. These results are also given in Table 3. For example, on heating in tetralin at 210 °C for 26 h, **1e** was completely decomposed, giving *N*-*t*-butylbenzamide (**4a**) (82%) and *p*-toluic acid (**5b**) (82%) as the major products plus small amounts of *N*-*t*-butyl-*p*-toluamide (**4b**) (13%), benzoic acid (**5a**) (9%), and carbon dioxide (4%).

Oae and Sakurai studied the reaction of *N*-aroyl-*O*-3,5-dinitrobenzoyl-*N*-phenylhydroxylamines with sodium cyanide in dipolar aprotic solvents at room temperature.[4] The products were aroylanilides and a small amount of carbon dioxide. They suggested that the reaction proceeds *via* the decarboxylation of a Meisenheimer-type complex formed as an intermediate, as in the displacement reaction of polynitro aromatics. Although the formation of the anilides is quite comparable to the present results of thermal decompositions, the mechanisms of those two reactions must be quite

Table 3. Thermal decomposition of *N,O*-diacyl-*N*-*t*-butylhydroxylamines in tetralin (0.1 M) at 210 °C

Compd	Time/h	Yields/mol%										
		4[a]				5[b]				CO_2[c]	6[d]	7[d]
1a	50	**4a**	82			**5a**	96			8	60	30
1b	40	**4b**	92			**5b**	86			6	49	42
1c	40	**4c**	94			**5c**	99			3	38	43
1d	40	**4d**	97			**5d**	89			3	42	42
1e	26	**4a**	82	**4b**	13	**5b**	82	**5a**	9	4	33	52
1e	9[e]	**4a**	93	**4b**	3	**5b**	84	**5a**	1	f)	f)	f)
1f	26	**4a**	80	**4c**	16	**5c**	76	**5a**	16	5	36	41
1g	40	**4a**	70	**4d**	19	**5d**	76	**5a**	15	2	58	23
1h	36	**4a**	71	**4e**	18	**5e**	67[e]	**5a**	25	9	64	19
1i	40	**4b**	71	**4a**	21	**5a**	72	**5b**	22	f)	58	39
1j	24	**4c**	75	**4a**	21	**5a**	79	**5c**	20	f)	56	27
1k	36	**4d**	78	**4a**	21	**5a**	76	**5d**	21	f)	56	37

a) R–CONH-*t*-Bu **4a**; R=Ph, **4b**; R=*p*-CH_3–C_6H_4, **4c**; R=*p*-CH_3O–C_6H_4, **4d**; R=*p*-Cl–C_6H_4, **4e**; R=CH_3. b) Acids were estimated after methylation with diazomethane. R–CO_2H **5a**; R=Ph, **5b**; R=*p*-CH_3–C_6H_4, **5c**; R=*p*-CH_3O–C_6H_4, **5d**; R=*p*-Cl–C_6H_4, **5e**; R=CH_3. c) Estimated by titration. d) Based on **1**. e) In the presence of 10 mol% of *t*-butylammonium benzoate at 205 °C. f) Not determined.

different, since no efficient nucleophile is present and since a nonpolar solvent was used in the present reaction. Moreover, in the present case, the *O*-acetyl derivative (**1h**) can not form such a complex. It is also unlikely that the *O*-benzoyl, *O*-*p*-toluoyl, and *O*-*p*-methoxybenzoyl derivatives, without bearing such an electron-withdrawing substituent as a nitro group, would form a complex in tetralin. In addition, the product, **6**, derived from tetralin could not be explained in terms of such ionic mechanisms. The precursors of **6** are obviously the tetralyl radicals formed by the abstraction of a hydrogen atom from tetralin. Dihydronaphthalene (**7**) would also be formed from the tetralyl radicals by disproportionation. Thus, the formation of these products suggests a homolytic decomposition of **1**, giving the acylaminyl radical and the acyloxyl radical. However, the amount of carbon dioxide formed by the thermal decomposition is too small to be accounted for by the decarboxylation of the acyloxyl radical formed by the homolysis of the N–O bond of **1**.

In order to compare the yields of carbon dioxide, the thermal decomposition of benzoyl peroxide was carried out under the same conditions as in the thermolysis of **1a**. When benzoyl peroxide was heated in tetralin (0.05 M, 1 M=1 mol dm^{-3}) at 210 °C for 2 h, benzoic acid and carbon dioxide were formed in 37 and 60% yields respectively, based on benzoyl peroxide. These results indicate a facile decomposition of the benzoyloxyl radical at that temperature to give carbon dioxide rather than the abstraction of a hydrogen atom from the solvent to give benzoic acid. Moreover, no detectable amount of benzene was formed in the thermal decomposition of **1a**. It is also highly unlikely that the acetoxyl radical efficiently abstracts a hydrogen atom from tetralin to give acetic acid at this temperature, because the acetoxyl radical has been known to be unstable and more easily decarboxylates than the benzoyloxyl radical.[5] On the contraly, acetic acid was formed in a high yield by the decomposition of *N*-benzoyl-*O*-acetyl-*N*-*t*-butylhydroxylamine (**1h**). These results rule out the mechanism involving homolytic fission of the N–O bond of **1**, giving the acylaminyl radical and the acyloxyl radical, as the main process of the reaction.

A probable mechanism for the thermal decomposition of **1** which is in accordance with the present results is shown in Scheme 3. The thermal decomposition of **1** would be initiated by the attack of a nucleophile, which may consist of some trace impurities or the products formed by the thermal decomposition of the hydroxylamine itself. This is suggested on the basis of the facts that a certain induction period was observed in the thermal decomposition of **1e** at 205 °C, as is shown in Fig. 1. The addition of a small amount of *t*-butylammonium benzoate to the reaction solution obviously depressed the induction period and accelerated the rate

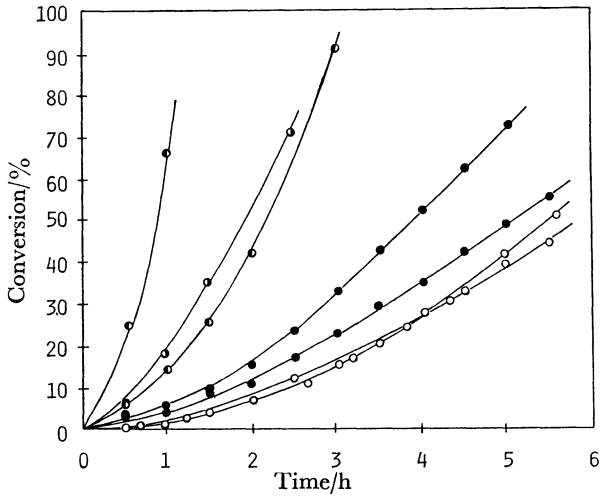
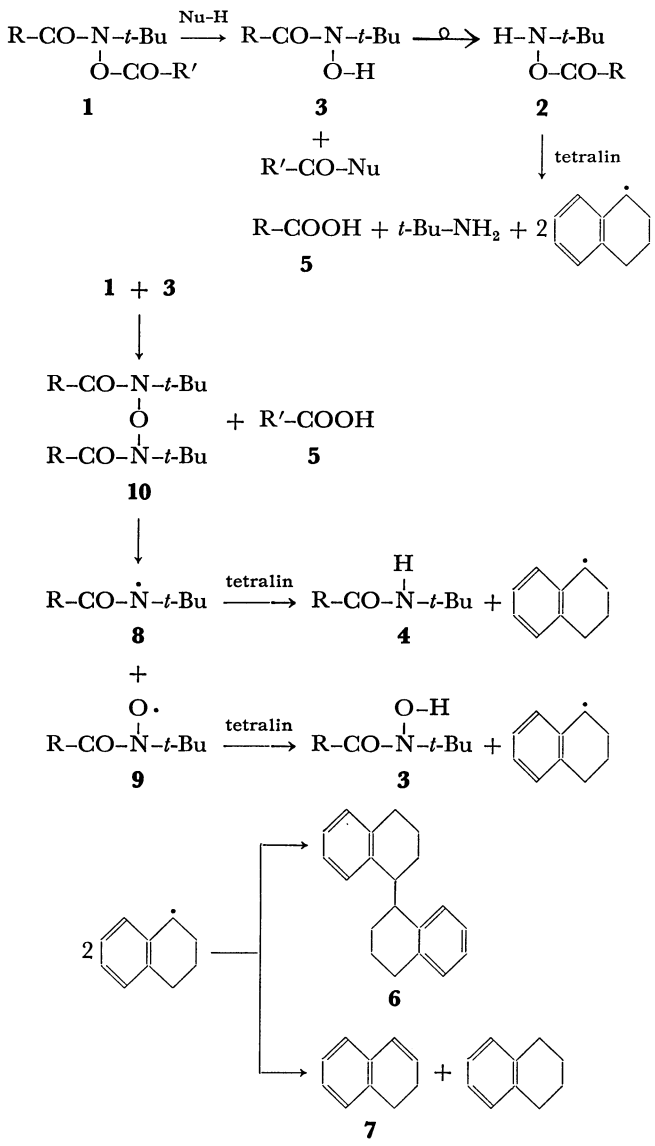


Fig. 1. Thermal decomposition of *N*-benzoyl-*O*-*p*-toluoyl-*N*-*t*-butylhydroxylamine in tetralin (0.1 M) at 205.0±0.2 °C.
○: No additive, ●: in the presence of an equilolar amount of benzoic acid, ◐: in the presence of 10 mol% of *t*-butylammonium benzoate, ◑: in the presence of 10 mol% of *N*-benzoyl-*N*-*t*-butylhydroxylamine (**3a**).

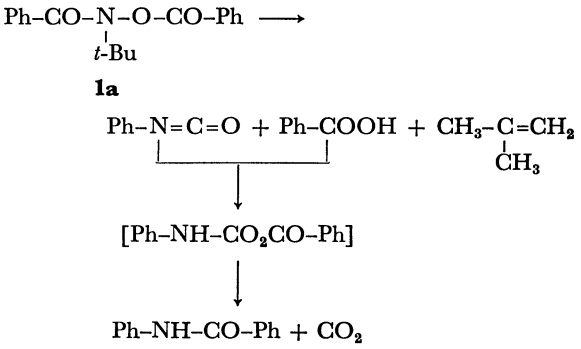


Scheme 3.

of the decomposition. The reactions of some *N,O*-diacylhydroxylamines with amines,[6] sodium methoxide, sodium azide, thiophenols, and sodium cyanide[4] have been studied. In those reactions, the nucleophiles attack the carboxylic carbonyl carbon atom of the reactant. By analogy, the nucleophile would attack the carboxylic carbonyl carbon atom of **1e** in the present reaction, giving *N*-benzoyl-*N*-*t*-butylhydroxylamine (**3a**) in the initiation reaction.

Although *t*-butylammonium benzoate accelerated the rate of the decomposition, the mechanism of the thermal decomposition of **1** requires the formation of radical species, because the hydrocarbons, **6** and **7**, are formed from the solvent. This can be explained by a mechanism in which the initial reaction gives *N*-acyl-*N*-*t*-butylhydroxylamine (**3**), which then reacts with **1** to give the acylaminyl radical (**8**), the acylaminoxyl radical (**9**), and carboxylic acid (**5**). These radicals and acid may be formed by the nucleophilic attack of **3** upon the N atom of **1**, thus forming **5** and the intermediate (**10**). This process was confirmed by the observation that the thermolysis of **1e** was apparently accelerated by the addition of a small amount of **3** as is shown in Fig. 1. The intermediate (**10**) probably collapses rapidly into the radicals (**8** and **9**) under the conditions used. The radicals (**8** and **9**) would then abstract hydrogen atoms from the solvent to form amide (**4**) and to regenerate **3** respectively. A similar substitution reaction on the nitrogen atom has been established in the reaction of *O*-acetyl-*N*-benzoyl-*N*-(*p*-methoxyphenyl)hydroxylamine with phenols, pyrrole, and indoles.[7]

The mechanism shown in Scheme 3 does not involve the formation of carbon dioxide. In detailed product studies of the thermal decomposition of **1a**, benzanilide was found (5%). This suggests that a part of the **1a** undergoes Lossen rearrangement to form benzoic acid, phenyl isocyanate, and 2-methylpropene. The isocyanate would rapidly react with benzoic acid, giving benzanilide and carbon dioxide as follows:[8]



Under the same conditions, slow acyl-exchange reactions between the amides and acids were observed. That is, after the heating of **4a** with an equivalent of **5b** at 210 °C for 30 h, **4b** and **5a** were formed, both in 7% yields. On the other hand, the reaction of **4b** with **5a** under the same conditions gave **4a** and **5b** in 8 and 8% yields respectively. These results suggest that a route to give the minor amides (for instance, **4b** and **4c** from **1e** and **1f** respectively) and acids (for instance, **5a** and **5b** from **1e** and **1i** respectively) would be the subsequent acyl-exchange reaction between the major amide and the acid formed by the decompositions of **1e—k**.

In order to examine the prosess giving *t*-butylamine, which was found as a minor product in the thermal decomposition of **1a**, *N*-benzoyl-*N*-*t*-butylhydroxylamine (**3a**) was heated in tetralin. On heating **3a** in tetralin at 150 °C, a rearranged product (**2a**) was isolated and characterized. The further heating of the reaction mixture at 210 °C for 2 h gave *t*-butylammonium benzoate (50%). These results suggest that *t*-butylamine was derived from **3a** *via* **2a** during the thermal decomposition of **1a**. The same results also suggest an alternative route for the formation of minor amides (**4**) and minor acids (**5**) in the decomposition of **1e—k**, bearing different acyl groups on the N and O atoms. In the initiation reaction of the decomposition of **1**, the attack of *t*-butylamine upon the carboxylic carbonyl carbon atom of **1** gives the minor amide and **3**, which then subsequently decomposes to afford a minor acid and *t*-butylamine. The amounts of the minor amide and the minor acid, which appeared to be somewhat higher

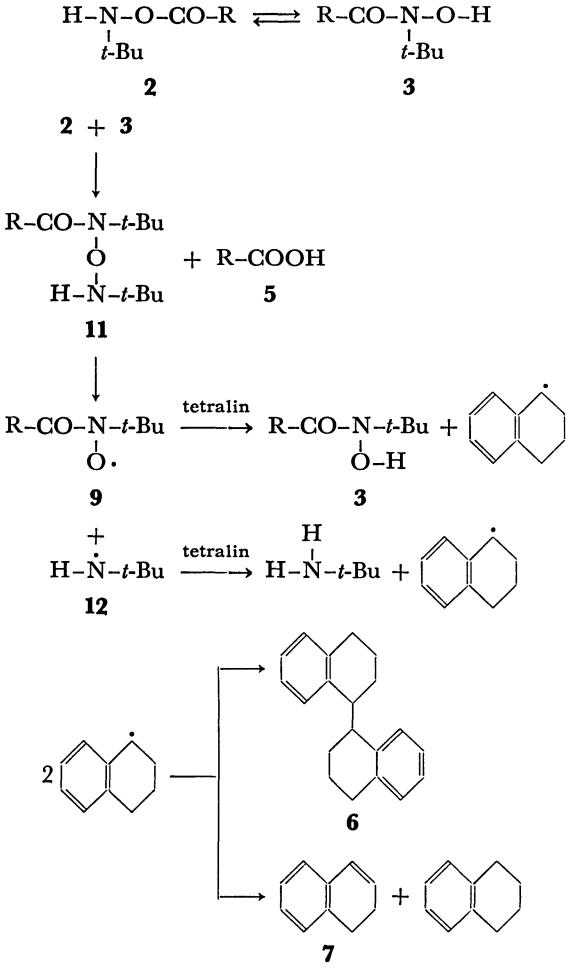
Table 4. Thermal decomposition of *O*-acyl-*N*-*t*-butylhydroxylamines in tetralin (0.1 M) at 210 °C

Compd	Time/h	Yield/mol%					
		t-$BuNH_2$[a]	**4**		**5**[b]	**6**[c]	**7**[c]
2a	4	65	**4a**	12	**5a** 81	47	35
2b	4	68	**4b**	13	**5b** 83	43	38
2c	4	76	**4c**	15	**5c** 82	47	25
2d	4	71	**4d**	15	**5d** 76	34	38

a) Isolated as the salt of the acid (**5**). b) Estimated after methylation with diazomethane. c) Based on **2**.

than would be expected from the slow acyl-exchange reaction alone, may be explained by these two processes, *i.e.*, the acyl-exchange reaction and the rearrangement reaction.

Thermal Decomposition of O-*Acyl*-N-t-*butylhydroxylamines.* In order to study the thermal properties of *O*-acyl-*N*-*t*-butylhydroxylamines (**2**), and also to prove the intermediacy of **2** during the thermal decomposition of **1**, several **2** were prepared and subjected to thermal decomposition. On heating at 210 °C for 4 h in tetralin, **2** decomposed completely, giving *t*-butylamine and carboxylic acid as a salt in high yields, together with a small amount of the amide (**4**). The products derived from tetralin, **6** and **7**, were also obtained in substantial yields. These results are summarized in Table 4. No



Scheme 4.

detectable amount of carbon dioxide was formed in the thermal decomposition of **2**. Thus, we can eliminate the possibility which involves the homolytic fission of the N–O bond of **2** to yield aminyl and acyloxyl radicals. The mechanism involving the nitrene intermediate is unlikely because *t*-butylnitrene does not afford *t*-butylamine in a good yield.[9] These results suggest that the decomposition of **2** involves the initial formation of *N*-acyl-*N*-*t*-butylhydroxylamine (**3**), which subsequently reacts with the starting material, resulting in the formation of an aminyl radical (**12**) and an acylaminoxyl radical (**9**), as is shown in Scheme 4. These radicals would abstract hydrogen atoms from tetralin to yield *t*-butylamine and to regenerate **3** respectively.

Experimental

All the melting points and the boiling points are uncorrected. The IR spectra were recorded on a Shimadzu IR-430 infrared spectrometer. The tetralin was washed succesively with concd H_2SO_4, aq NaOH, and water, dried over $CaCl_2$ and distilled under reduced pressure. The distillate was passed through a column of alumina and redistilled before use.

Preparation of N,O-*Diacy*-N-t-*butylhydroxylamines (1).* *(a)*: Benzoyl chloride (112.5 g, 0.800 mol) was added to a solution of *N*-*t*-butylhydroxylamine (30.0 g, 0.337 mol) and pyridine (63.3 g, 0.800 mol) in dry benzene (700 cm^3) at room temperature with stirring. The mixture was then heated at 60 °C for 15 h with stirring. The mixture was cooled, washed with aq NH_4OH, dil aq NaOH, dil HCl, and water, and dried over Na_2SO_4. The solvent was evaporated *in vacuo*, and the residue was recrystallized from CH_2Cl_2–petroleum ether, thus giving **1a** (69.3 g, 69%); mp 98.0—99.0 °C (lit, 98—99 °C).[10] By the reaction of *N*-*t*-butylhydroxylamine with the corresponding acyl chloride, **1b—d** were prepared similarly. The yields, physical properties, and elemental analyses are shown in Table 1.

(b): *p*-Toluoyl chloride (19.7 g, 0.127 mol), was added to a solution of **3a** (22.4 g, 0.116 mol) and pyridine (10.0 g, 0.127 mol) in dry benzene (200 cm^3), after which the whole mixture was stirred at 75 °C for 12 h. The reaction mixture was washed with aq NH_4OH, dil aq NaOH, dil HCl, and water, and dried over Na_2SO_4. The solvent was evaporated *in vacuo*, and the residue was recrystallized from CH_2Cl_2–petroleum ether, thus giving **1e** (29.5 g, 82%). By the same procedures, **1f**, **1g**, and **1h** were prepared by the reactions of **3a** with the corresponding acyl chlorides. The reactions of **2a** with the corresponding acyl chlorides gave **1i**, **1j**, and **1k**. The yields, physical properties, and elemental analyses are shown in Table 1.

Preparation of O-*Acyl*-N-t-*butylhydroxylamines (2).* Benzoyl chloride (127 g, 0.90 mol) was added to a solution of *N*-*t*-butylhydroxylamine (80 g, 0.90 mol) and pyridine (78 g, 1.0 mol) in dry ether (500 cm^3), after which the mixture was refluxed with stirring for 15 h. The reaction mixture was then washed with aq NH_4OH, dil aq NaOH, dil HCl, and water, and dried over Na_2SO_4. The solvent was evaporated, and the residue was distilled under reduced pressure to give *O*-benzoyl-*N*-*t*-butylhydroxylamine (**2a**) (135 g, 78%); bp 101—104 °C/3 mmHg** (lit, 73 °C/0.5 mmHg).[10] The distillate was then further purified by chromatography on silica gel, with CH_2Cl_2 as the eluent. By the same procedure

** Through this paper 1 mmHg = 133.322 Pa.

as has been described above, **2b—d** were prepared. The yields, physical properties, and elemental analyses are shown in Table 2.

Preparation of N-*Benzoyl*-N-t-*butylhydroxylamine (3a).* A solution of NaOH (10.2 g, 0.255 mol) in water (40 cm³) was added to a stirred suspension of **1a** (43.7 g, 0.147 mol) in methanol (200 cm³). The mixture was then stirred at room temperature for 1.5 h. After the evaporation of the methanol under reduced pressure, water (200 cm³) and ether (50 cm³) were added to the residue. The separated water layer was acidified with HCl. The formed crystals were taken in ether, and the ethereal solution was washed with saturated $NaHCO_3$ and water, and dired over Na_2SO_4. The ether was then evaporated, and the residue was recrystallized from CH_2Cl_2–petroleum ether to give **3a** (23.4 g, 82%); mp 108—109 °C (lit, 109 °C).[10]

Thermal Decomposition of 1. A solution of **1** in tetralin (0.1 M, 20 cm³) was sealed in a degassed tube with break-off tips at both ends and then heated in a constant-temperature bath at 210 °C. The tube was opened in a vacuum system, and the carbon dioxide formed by the decomposition was introduced into an aq $Ba(OH)_2$ solution (0.1 M, 50 cm³) after having been passed through a cold trap by a nitrogen stream. The $Ba(OH)_2$ solution was filtered, and the filtrate (40 cm³) was titrated with HCl (0.1 M). An excess of an ethereal solution of diazomethane was added to the decomposition mixture, and the mixture was allowed to stand for 1 h. After the evaporation of the ether *in vacuo*, the reaction mixture was subjected to GLC analysis, with the addition of a known amount of biphenyl as an internal standard. The following three columns were used a 2-m column packed with Apiezon Grease L (30%) on Cerite 545 to analyze methyl benzoate; a 2-m column packed with Thermon 1000+H_3PO_4 (5+0.5%) on Chromosorb W to analyze the amides, bitetralyl, and methyl esters, and a 5-m column packed with polyethylene glycol 20 M (25%) on Shimalite 101 to analyze dihydronaphthalene. The results are summarized in Table 3.

Thermal Decomposition of 2. A solution of **2a** in tetralin (0.1 M, 20 cm³) sealed in a degassed ampule was heated in a constant-temperature bath at 210 °C for 4 h. After cooling, the precipitated *t*-butylammonium benzoate was collected by filtration, and washed with petroleum ether. The filtrate was subjected to GLC analysis after methylation with diazomethane.

Kinetic Procedure. A solution of **1e** (0.1 M, 25 cm³) in tetralin was placed in a reaction vessel fitted with a gas-inlet tube and a reflux condenser. It was heated in a constant-temperature bath (205.0±0.2 °C) after nitrogen had been bubbled into, for 30 min. Aliquots were withdrawn at scheduled intervals and quenched by chilling to 0 °C. The aliquot (100 mm³) and methanolic NaOH (0.25%, 10 cm³) were placed in a volumetric flask (25 cm³), and the mixture was heated in a water bath at 65 °C for 30 min. After a methanolic iron(III) chloride solution (10 cm³) had been added, the solution was diluted to the volume of the flask with methanol and the absorbance at 510 nm was measured. The iron(III) chloride solution was prepared by dissolving 5 g of $FeCl_3 \cdot 6H_2O$ in 1 dm³ of methanol containing HCl (0.0321 M) to prevent iron(III) hydroxide formation.[11]

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