The Thermal Decomposition of *N,O*-Diacyl-*N*-*t*-butylhydroxylamines. IV. A Novel Acyloxyl Migration in *N,O*-Diacyl-*N*-*t*-butylhydroxylamines

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Synopsis. Several *N,O*-diacyl-*N*-*t*-butylhydroxylamines were prepared, and their thermal decompositions were studied. *N*-Propionyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine gave *N*-*t*-butyl-2-benzoyloxypropanamide, together with the decomposition products, *N*-*t*-butylpropanamide and benzoic acid, upon thermal decomposition in tetralin. Similar benzyloxyl migrations were found in the thermal decomposition of *N*-butyryl, *N*-valeryl, and *N*-(3-phenylpropionyl) derivatives.

In the previous papers, we have reported that *N,O*-diaroyl-*N*-*t*-butylhydroxylamines gave amides and carboxylic acids upon the thermolysis in tetralin.[1] On the other hand, *N*-[2-(methylthio)benzoyl]-*O*-acyl-*N*-*t*-butylhydroxylamines gave rearranged products, *N*-*t*-butyl-2-(acyloxymethylthio)benzamides.[2] As a continuation of those studies, we have now studied the thermal decomposition of *N*-acyl-*O*-benzoyl-*N*-*t*-butylhydroxylamines (**1**) and found a novel benzoyloxyl migration reaction.

Results and Discussion

Several *N*-acyl-*O*-benzoyl-*N*-*t*-butylhydroxylamines (**1a**—**g**) were prepared by the reaction of *O*-benzoyl-*N*-*t*-butylhydroxylamine and the corresponding acyl chlorides in the presence of pyridine in benzene at 70 °C. However, the reaction of *O*-benzoyl-*N*-*t*-butylhydroxylamine with phenylacetyl chloride under the same conditions did not afford the corresponding *N*-phenylacetyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1h**), but *N*-*t*-butyl-2-chloro-2-phenylacetamide (**3**), as the major product. When the reaction was carried out in diethyl ether at room temperature, **1h** was detected as the product, together with **3**, but the attempted isolation of **1h** from the mixture was unsuccessful.

The thermal decomposition of **1** was carried out in tetralin at 210 °C in a degassed ampule. In the thermal decomposition of *N*-acetyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1a**), the products isolated were *N*-*t*-butylacetamide (**4a**), benzoic acid (**5**), acetic acid (**6a**), *N*-*t*-butylbenzamide (**7**), and carbon dioxide. 1,1′-Bitetralyl (**8**) and 1,2-dihydronaphthalene (**9**) were formed from the solvent. The yields of the products are summarized in Table 1. Similar results were also obtained in the thermal decomposition of *N*-isopropionyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1b**) and *N*-cyclohexylcarbonyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1c**).

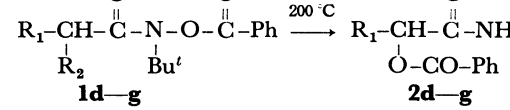
Table 1. Thermal decomposition of *N*-acyl-*O*-benzoyl-*N*-*t*-butylhydroxylamines in tetralin at 210 °C

Compd			Time	Products yields/mol%[a]							
	R_1	R_2	h	2	4[b]	5[c]	6[d]	7[e]	CO_2[f]	8[g]	9[g]
1a	H	H	24	0	48	61	[h]	30	9	30	43
1b	CH_3	CH_3	40	0	47	58	14[f]	13	7	42	15
1c	$-(CH_2)_5-$		40	0	57	73	18	18	3	44	16
1d	CH_3	H	24	27	47	60	[h]	10	4	31	22
1e	C_2H_5	H	25	24	60	67	18[f]	12	3	36	25
1f	C_3H_7	H	25	10	70	70	[h]	11	1	[h]	[h]
1g	$PhCH_2$	H	25	23	64	63	8	11	5	[h]	[h]

a) The yields were estimated by GLC. b) $RCONHBu^t$. c) $PhCO_2H$. The yields were estimated after methylation with diazomethane. d) RCO_2H. e) $PhCONHBu^t$. f) Estmated by titration. g) Based on 1. h) Not determined.

The results given in Table 1 show that two kinds of amides and acids, originating from the two acyl groups of the starting materials, were formed in each decomposition. The mode of decomposition is quite similar to that previously reported for the thermolysis of *N,O*-diaroyl-*N*-*t*-butylhydroxylamines.[1] The minor acid (**6**) and the amide (**7**) must be formed by means of an acyl-exchange reaction between the major acid (**4**) and the amide (**5**).[1]

On the other hand, *N*-propionyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1d**) gave the rearranged product, *N*-*t*-butyl-2-benzoyloxypropanemide (**2d**), together with the decomposition products: *N*-*t*-butylpropanamide (**4d**), **5**, propionic acid (**6d**), **7**, and a small amount of carbon dioxide. A similar benzoyloxyl migration from the nitrogen atom to the α-carbon atom of the *N*-acyl group was found in the thermal decompositions of *N*-butyryl- (**1e**), *N*-valeryl- (**1f**), and *N*-(3-phenylpropionyl)-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1g**), all of which have α-methylene in the *N*-acyl group. The products were identified by a comparison of their physical properties with those of authentic samples. The structures of the rearranged products (**2**) were established by means of elemental and spectral analyses. The IR spectra of **2** showed bands at 3300—3320 (N–H), 1720—1725, and 1660—1665 cm^{-1} (C=O). The yields of the products were estimated by means of GLC analysis.



1d—g **2d—g**

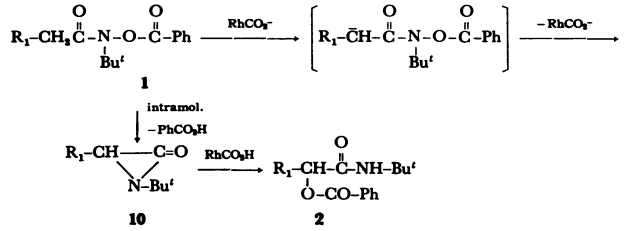
1d, 2d; $R_1 = CH_3$, $R_2 = H$ **1e, 2e**; $R_1 = C_2H_5$, $R_2 = H$
1f, 2f; $R_1 = C_3H_7$, $R_2 = H$ **1g, 2g**; $R_1 = PhCH_2$, $R_2 = H$

When the thermal decomposition of **1e** was carried out in the presence of an equimolar amount of *p*-toluic acid, both the benzoate (**2e**) and the toluate (**2i**) were formed. These results suggest that the rearrangement is an intermolecular reaction.

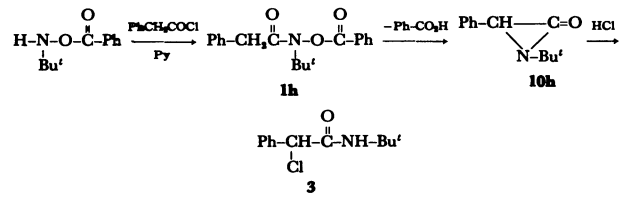
Baumgarten[3] reported that *N*-*t*-butylphenylacetamide gave *N*-*t*-butyl-2-*t*-butoxy-2-phenylacetamide on treatment with potassium *t*-butoxide and *t*-butyl hypochlorite. The formation of 1-*t*-butyl-3-phenylaziridinone (**10h**) *via* *N*-*t*-butyl-*N*-chlorophenylacetamide as an intermediate was suggested.

Although, a strong base was not used in the present thermolysis of **1**, α-lactam (**10**) may also contribute to the benzoyloxyl migration reaction as an intermediate. In previous papers,[1,2] we have proposed that nucleophilic displacement at the nitrogen atom was involved in the thermal decomposition of *N,O*-diacyl-*N*-*t*-

butylhydroxylamines. By analogy, the following scheme can be presented for the reaction involving the initial abstraction of the α-proton by the carboxylate ion; the resulting anion would cyclize to give **10**. Another possibility is the intramolecular elimination of benzoic acid from **1**, by either a 5- or 7-membered transition state, directly giving **10**. The α-lactam would react with carboxylic acid to give the rearranged product (**2**).



The unexpected results of the reaction of *O*-benzoyl-*N*-*t*-butylhydroxylamine with phenylacetyl chloride, which gave **3** instead of **1h** in benzene, may also proceed by a similar process involving the reaction of the α-lactam with hydrogen chloride.[4]



The absence of the rearranged products in the thermal decompositions of **1a**—**c** may be due to the instability of the intermediate (**10**). 1-*t*-Butylaziridinone (**10a**) is an unknown compound, and 1-*t*-butyl-3,3-dimethylaziridinone (**10b**)[5] and 1-*t*-butyl-3,3-pentamethyleneaziridinone (**10c**)[6] are known to decompose under milder conditions (above 75 °C). Thus, **2a**—**c** if formed, would decompose under the conditions employed for the thermolysis of **1**.

Experimental

All the melting points and boiling points are uncorrected. The IR spectra were recorded on a Shimadzu IR-430 infrared spectrometer. The NMR spectra were recorded on a Varian EM-360 spectrometer, using TMS as the internal standard.

Preparation of N-*Acyl*-O-*benzoyl*-N-*t*-*butylhydroxylamine* (*1*). A typical procedure was as follows: A mixture of propionyl chloride (9.3 g, 100 mmol), *O*-benzoyl-*N*-*t*-butylhydroxylamine (19.3 g, 100 mmol),[1] and pyridine (7.9 g, 100 mmol) in benzene (100 cm³) was stirred at 70 °C for 6 h. The reaction mixture was washed with dil HCl, aq $NaHCO_3$, and water, and then dried over Na_2SO_4. The benzene was removed *in vacuo* to give crude *N*-propionyl-*O*-benzoyl-*N*-*t*-butylhydroxylamine (**1d**) (24.7 g), which was recrystallzed from petroleum ether (17.9 g, 72%): mp 56.5—57.5 °C. Found: C, 67.60; H, 7.83; N, 5.60%. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62%. By the same procedure, **1a**—**c** and **1e**—**g** were prepared by the reactions of *O*-benzoyl-*N*-*t*-butylhydroxylamine with the corresponding acyl chlorides. The results were as follows: **1a**; 86%, bp 125 °C/3 mmHg.†† Found: C, 66.49; H, 7.49; N, 5.98%. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95%. **1b**: 87%, mp 79—80 °C. Found: C, 68.44; H, 8.25; N, 5.22%. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32%. **1c**: 92%, mp 118.5—119.5 °C. Found: C, 71.26; H, 8.49; N, 4.42%. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62%. **1e**: 68%, bp 136 °C/4 mmHg. Found: C, 68.13; H, 8.19; N, 5.21%. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32%. **1f**: 67%, mp 41—42 °C. Found: C, 69.32; H, 8.37; N, 4.90%. Calcd for $C_{16}H_{23}NO_3$: C, 69.28; H, 8.36; N, 5.05%. **1g**: 71%, mp 76—77 °C. Found: C, 74.00; H, 7.22; N, 4.13%. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30%.

Reaction of O-*Benzoyl*-N-*t*-*butylhydroxylamine with Phenylacetyl Chloride.* A mixture of phenylacetyl chloride (15.4 g, 100 mmol), *O*-benzoyl-*N*-*t*-butylhydroxylamine (19.3 g, 100 mmol), and pyridine (7.9 g, 100 mmol) in benzene (300 cm³) was stirred at 70 °C for 3 h. The reaction mixture was washed with dil HCl, aq $NaHCO_3$, and water, and then dried over Na_2SO_4. The benzene was removed *in vacuo* and the residue was recrystallized from petroleum ether–dichloromethane to give *N*-*t*-butyl-2-chloro-2-phenylacetamide (**3**) (37%); mp 125.5—126.5 °C. NMR (CCl_4): δ 1.38 (9H, s), 5.14 (1H, s), 6.38 (1H, broad), 7.35 (5H, s). IR (KBr); 3300, 1550 (N–H), and 1655 cm⁻¹ (C=O). Found: C, 64.04; H, 7.38; N, 6.12%. Calcd for $C_{12}H_{16}ClNO$: C, 63.85; H, 7.15; N, 6.21%.

Thermal Decomposition of N-*Acyl*-O-*benzoyl*-N-*t*-*butylhydroxylamine* (*1*). A solution of **1** (2 mmol) in tetralin (20 cm³) was sealed in a degassed tube and heated at 210 °C in a constant-temperature bath. The product analyses and isolation were the same as those reported previously.[1] The properties of the rearranged products (**2**) were as follows: **2d**; mp 160—161 °C. IR (KBr); 3300 (N–H), 1720, 1660 cm⁻¹ (C=O). NMR (CCl_4): δ 1.35 (9H, s), 1.54 (3H, d, J=7 Hz), 5.28 (1H, q, J=7 Hz), 6.0 (1H, broad), 7.2—8.2 (5H, m). Found: C, 67.42; H, 7.91; N, 5.84%. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62%. **2e**; mp 124—125 °C. IR (KBr): 3300 (N–H), 1725, 1665 cm⁻¹ (C=O). NMR (CCl_4): δ 0.98 (3H, t, J=7 Hz), 1.34 (9H, s), 1.98 (2H, m), 5.14 (1H, t, J=7 Hz), 5.8 (1H, broad), 7.2—8.2 (5H, m). Found: C, 68.50; H, 8.34; N, 5.06%. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32%. **2f**; mp 98—99 °C. IR (KBr): 3300 (N–H), 1720, 1660 cm⁻¹ (C=O). NMR (CCl_4): δ 0.97 (3H, t, J=7 Hz), 1.33 (9H, s), 1.4—2.3 (4H, m), 5.18 (1H, t, J=6 Hz), 5.8 (1H, broad), 7.2—8.2 (5H, m). Found: C, 69.23; H, 8.51; N, 4.92%. Calcd for $C_{16}H_{23}NO_3$: C, 69.28; H, 8.36; N, 5.05%. **2g**; mp 153—154 °C. IR (KBr): 3320 (N–H), 1720, 1665 cm⁻¹ (C=O). NMR (CCl_4): δ 1.23 (9H, s), 3.25 (2H, d, J=6 Hz), 5.38 (1H, t, J=6 Hz), 5.6 (1H, broad), 7.20 (5H, s), 7.2—8.1 (5H, m). Found: C, 73.66; H, 7.21; N, 4.13%. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.13; N, 4.30%. **2i**; mp 123—124 °C. IR (KBr): 3300 (N–H), 1720, 1660 cm⁻¹ (C=O). NMR (CCl_4): δ 0.95 (3H, t, J=7 Hz), 1.32 (9H, s), 1.88 (2H, m), 2.24 (3H, s), 5.10 (1H, t, J=6 Hz), 5.8 (1H, broad), 7.21 (2H, d, J=10 Hz), 7.90 (2H, d, J=10 Hz). Found: C, 69.19; H, 8.58; N, 4.95%. Calcd for $C_{16}H_{23}NO_3$: C, 69.28; H, 8.36; N, 5.05%.

†† Throughout this paper 1 mmHg≈133.322 Pa.

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