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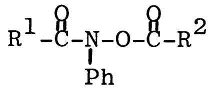
THE PHOTOLYSIS OF N,O-DIACYL-N-PHENYLHYDROXYLAMINES

Tadamitsu SAKURAI,* Shuichi YAMADA, and Hiroyasu INOUE
Department of Applied Chemistry, Faculty of Technology,
Kanagawa University, Kanagawa-ku, Yokohama 221

The photodecomposition of the title compounds yielded the rearrangement products derived from 1,3- and 1,5-aroyloxy migrations in addition to the fragmentation products typical of the aroyloxyl and amido free radicals. Crossover experiments indicate an intramolecular rearrangement, probably involving homolysis of the N-O bond. Sensitization and quenching studies demonstrate that the rearrangement and fragmentation proceed via the excited singlet state.

Thermal rearrangements of hydroxamic acid derivatives have been extensively studied from the mechanistic point of view and relatively well understood.1) Especially, a systematic study on the 1,3-aroyloxy migration of O-aroyl-N,N-(aroylaryl)hydroxylamines has revealed that the electronic effect on the heterolysis of the N-O bond plays a crucial role in determining the mechanism of 1,3-rearrangement.1f) However, there are only a few investigations concerning the photochemical rearrangements of hydroxamic acid derivatives.2) To gain further insight into the mechanism of acyloxy migration, we have prepared N,O-diacyl-N-phenylhydroxylamines (**1a**-**d**) and examined their photochemical behaviors based on the product distribution. We now wish to present the first observation of photochemical rearrangement of acyclic hydroxamic acid derivatives.



$$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{Ph}{\underset{|}{N}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2$$

1a-**d**

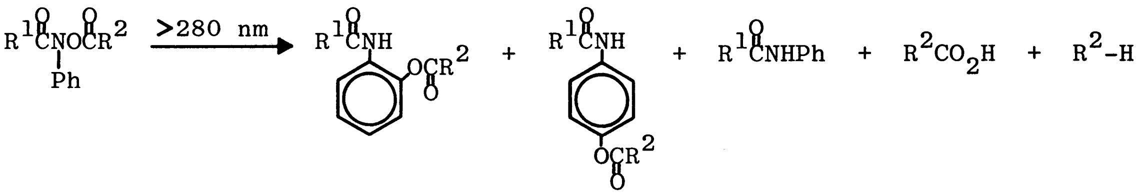
1a: R^1= 1-naphthyl (1-Np), R^2= p-tolyl (p-Tl)
1b: R^1= p-Tl, R^2= 1-Np
1c: R^1= R^2= 1-Np
1d: R^1= R^2= p-Tl

A solution of **1** in acetonitrile was irradiated by the Pyrex-filtered light from a 400-W high-pressure mercury lamp on a merry-go-round apparatus under a nitrogen atmosphere at room temperature. Each of reactions afforded the rearrangement products (**2** and **3**, 2-13%, HPLC yield3)) along with arylanilides (**4**, 10-28%), carboxylic acids (**5**, 30-70%), and aromatic hydrocarbons (**6**, 3-12%) as summarized in Table 1. These products were identified by comparing their HPLC behaviors at two different wavelengths (230 and 270 nm) with those of authentic samples. Irradiation of **1a** (0.0026 mol) in acetonitrile was continued under the same conditions until disappearance of **1a** was complete (monitored by TLC). Chromatography of the photolyzate allowed isolation of **2a** (4%, isolated yield), **3a** (8%), **4a** (20%), **5a** (10%), and **6a** (9%, GLC yield) except carbon dioxide (about 30%) which was

Table 1. Photolysis of 1a-d (0.0066 M) in CH_3CN at Room Temperature.

Compd.	Irradiation Time (min)	Conversion (%)	Yield (%) 2	3	4	5	6
1a	15	40	4	2	2	10	a)
	240	98	9	2	10	30	12
1b	15	43	~0	~0	3	11	a)
	240	97	1	1	28	65	3
1c	30	49	3	3	6	34	a)
	180	95	3	2	21	70	3
1d	30	33	5	3	3	14	a)
	240	76	10	3	15	53	12

a) Could not be detected.



1 2 3 4 5 6

characterized as barium carbonate. This result is consistent with that obtained by HPLC analysis. The structures of the rearrangement products were confirmed by comparing their physical properties with those of authentic samples, which were prepared from o- and p-aminophenols as the starting materials. Control experiments without the irradiation revealed that the starting hydroxylamines (1a-d) were recovered quantitatively. Furthermore, independent irradiations of the photoproducts clearly show that the rearrangement and fragmentation products undergo undesirable photodecompositions to different extent depending on the structure of the products (2a, 3a, and 3b, 30-40% decomposition during 2 h irradiation; 2b, 80%; 4, 5, and 6, 3-19%). The low yields of the rearrangement products, especially 2b, may be ascribed in part to this low photostability.

Since the photoreactions of 1a-d are formally analogous to the photo-Fries reactions,[4] it is reasonable to assume that the photolysis of these hydroxylamines involves the homolytic cleavage of the N-O bond in an excited state forming amido and aroyloxyl free radicals, which either recombine within the solvent cage to afford the rearrangement products or escape out of the cage to give the fragmentation products. The homolysis of the N-O bond is supported by the facts that all of the conceivable free radical products were identified, and that N,O-diacylhydroxylamines, whose structures are very similar to those of 1a-d, undergo the homolytic photolysis.[5]

To ascertain the intra- or intermolecularity of this interesting photorearrangement, an equimolar mixture of 1a and 1b in acetonitrile (0.0066 M) was irradiated for 2 h in the same manner as described above. Careful HPLC analysis of the photolyzate indicates the formation of negligible amounts of the crossover products (yields less than 0.03%). A similar finding was obtained also on the irradiation to a mixture of 1c and 1d. These findings indicate that the photorearrangements proceed by an exclusively intramolecular aroyloxy shift.

In order to examine the possible involvement of heterolysis of the N-O bond, **1a**-**d** were heated in dimethyl sulfoxide at 120-130°C for several hours. If the participation of an ionic mechanism would be responsible for the formation of **2** and **3**, the same rearrangement products should be obtained thermally, because the rearrangement of related hydroxamic acid derivatives is well known to proceed via the heterolytic scission of the N-O bond.1) As opposed to the expectation, the thermolyses of **1a**-**d** gave only o-(aroyloxy)arylanilides (**2a**, 13%; **2b**, 57%; **2c**, 39%; **2d**, 48%), accompanied by the recovered starting materials (**1a**, 51%; **1b**, 12%; **1c**, 51%; **1d**, 43%). Clearly, the products of the photolysis are quite different from those of the thermal decomposition, supporting that at least p-(aroyloxy)arylanilides (**3**) and the fragmentation products (**4**, **5**, and **6**) originate from the homolytic cleavage of the N-O bond. Although we cannot determine whether the 1,3-rearrangement proceeds through a free radical or an ionic mechanism without oxygen-18 labeling experiment, we prefer a radical pair mechanism at present to account for the formation of **2** and **3** as is analogized from the result that the N-O bond of diacylhydroxylamines readily undergoes homolytic cleavage in the excited states.5)

Preliminary sensitization and quenching studies6) on the photolysis of **1a** (0.0066 M, E_S= 377 kJ/mol, E_T= 247 kJ/mol)7) were performed with benzophenone (0.05 M, E_S= 310 kJ/mol, E_T= 289 kJ/mol)8) as a triplet sensitizer and 1,3-cyclohexadiene (0.1 M, E_S= 406 kJ/mol, E_T= 218 kJ/mol)8) as a triplet quencher to prove the excited states responsible for the formation of the rearrangement and fragmentation products.9) Although the fragmentation products (**4a**, **5a**, and **6a**) are formed by the sensitized photolysis in acetonitrile, no rearrangement is sensitized by benzophenone.10) Furthermore, neither rearrangement nor fragmentation reaction was quenched by 1,3-cyclohexadiene within the limits of experimental accuracy, suggesting that the rearrangement and fragmentation products come from the reaction in the excited singlet state. However, one cannot rule out the possibility11) that the triplet state is involved in this photolysis because the sensitized photoreaction gives the fragmentation products.

The detailed accounts of these photolyses, including the mechanism of the photorearrangement, are now being investigated in this laboratory.

References

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3) The yields of the products depicted in Table 1 were determined by utilizing the linear calibration curves made for each product under the same conditions.

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5) C. Walling and A. N. Naglieri, J. Am. Chem. Soc., 82, 1820 (1960).

6) A 1-cm solution of copper sulfate pentahydrate (250 g per liter) was used as the filter for sensitization experiment. The band passed had a 90% transmittance (T) at 366 nm and a 9% T at 313 nm. The 313-nm line for quenching experiment was isolated with a 1-cm path of 0.002 M potassium chromate in a 1% aqueous solution of potassium carbonate. Molar absorption coefficients of 1a at 313 and 366 nm were estimated to be 1940 and 3 ($M^{-1}cm^{-1}$) in acetonitrile at room temperature, respectively.

7) The energy of the first excited singlet state (E_S) was calculated to be 377 kJ/mol from the absorption and the fluorescence of 1a in acetonitrile at room temperature. The 0-0 band of the phosphorescence appeared at 484 nm in acetonitrile at 77 K, corresponding to the first excited triplet state energy (E_T) of 247 kJ/mol.

8) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, Inc. New York (1973), pp. 3-7.

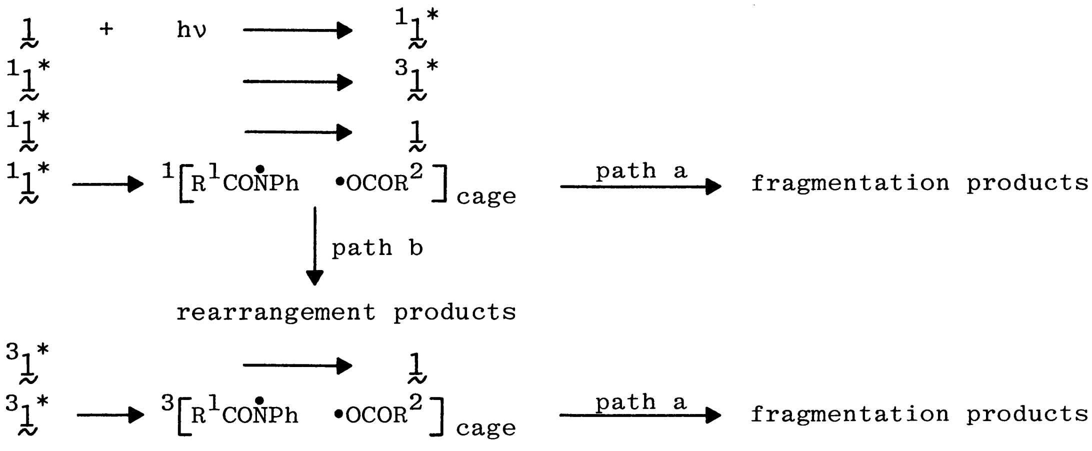
9) The phosphorescence of 1a in acetonitrile at 77 K was sensitized by benzophenone accompanying the quenching of sensitizer's phosphorescence, whereas 1,3-cyclohexadiene quenched the phosphorescence of 1a.

10) The result obtained by this sensitization experiment is shown below.

Sensitizer	Irradiation Time (min)	Conversion (%)	Yield (%) 2a	3a	4a	5a	6a[a)]
Benzophenone	15	96	<1	<1	3	34	10
None	15	10	1	1	1	7	b)

a) GLC yield. b) Could not be detected.

11) Taking this possibility into consideration, we present the following tentative scheme to interpret all of the results obtained. Since the rate of diffusion of the aroyloxyl and amido free radicals should be faster than the rate of the triplet-singlet intersystem crossing, the fact that no rearrangement products are formed by the triplet-sensitized photolysis may be explained in terms of the requirement that the triplet-singlet intersystem crossing must occur before the triplet radical pairs recombine within the cage.[12)]



path a, 'out-of-cage' reaction; path b, 'in-cage' reaction

12) T. Koenig and H. Fischer, "Free Radicals," ed by J. K. Kochi, Wiley-Interscience, New York, N. Y. (1973), Vol. I, pp. 179-180.

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