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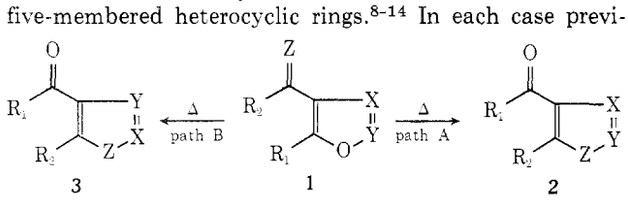
Thermal Valence Rearrangement of 4-Acylisoxazoles to 4-Acyloxazoles

Summary: A number of 3-phenyl-4-acyl-5-alkylisoxazoles have been found to undergo thermal rearrangement to 2-phenyl-4-acyl-5-alkyloxazoles; the formation of the rearranged oxazole requires bonding between the 3 carbon of the isoxazole ring with the oxygen atom of the acyl group; a mechanism involving the intermediacy of a 2*H*-azirine is suggested.

Sir: The photoisomerization of many different five-membered heterocyclic ring compounds has been shown to proceed by a path in which two of the ring atoms interchange their position under the influence of uv light.[1] The demonstration of a ring-contraction–ring-expansion process in these reactions was first documented by Ullman and Singh for the photorearrangement of 3,5-diarylisoxazoles to 2,5-diaryloxazoles.[2] An analogous pathway nicely rationalizes the major products produced in the photoisomerization of other five-membered heterocyclic rings.[3-7] There are also a number of reports in the literature which describe the thermally induced valence isomerizations of five-membered heterocyclic rings.[8-14] In each case previ-

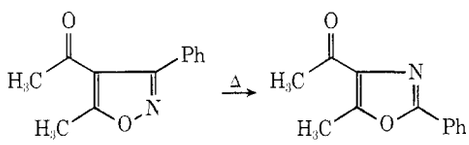


3 1 2

X = N, C; Z = N, O; Y = N, C

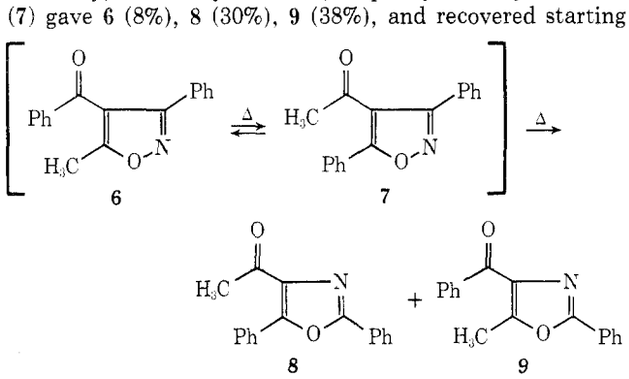
ously studied, the product obtained can only be rationalized by a sequence involving homolytic cleavage of the O–Y bond to produce a reactive acyclic intermediate which subsequently recloses to produce the rearranged heteroaromatic compound (*i.e.*, **1** → **2** *via* path A). In this communication we wish to describe the thermally induced rearrangement of several 4-acylisoxazoles which follow a ring-contraction–ring-expansion sequence (path B).

It is well known that, when two heteroatoms of higher electronegativity than carbon (*e.g.*, nitrogen, oxygen) are linked together through a single bond, the bond dissociation energy of such a linkage is considerably lower than that of a C–C single bond.[15,16] Taking this into consideration, we decided to examine the thermal behavior of 3-phenyl-4-acetyl-5-methylisoxazole (**4**).[17] Thermolysis of isoxazole **4** at 230° under a nitrogen atmosphere for 2 hr afforded 2-phenyl-4-acetyl-5-methyloxazole (**5**), mp 78–79°, in quantitative yield [nmr ($CDCl_3$) τ 7.50 (s, 3 H), 7.42 (s, 3 H)]. The structure of the rearranged product was unambiguously established by an independent synthesis.[18]



4 5

When 3-phenyl-4-benzoyl-5-methylisoxazole[17] (**6**) was subjected to similar thermolysis conditions, a mixture of three new compounds was produced. Analysis of the crude reaction mixture by nmr showed that it contained 3,5-diphenyl-4-acetylisoxazole (**7**, 8%), 2,5-diphenyl-4-acetyloxazole (**8**, 29%), and 2-phenyl-4-benzoyl-5-methyloxazole (**9**, 39%), as well as unreacted starting material (24%). Similarly, thermolysis of 3,5-diphenyl-4-acetylisoxazole (**7**) gave **6** (8%), **8** (30%), **9** (38%), and recovered starting



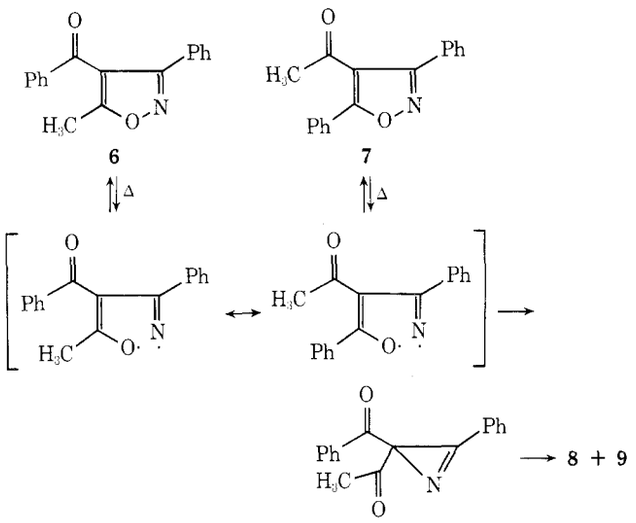
6 7 8 9

material (24%). Confirmation of the structure of isoxazole **7**, mp 93–94°, nmr ($CDCl_3$) τ 7.8 (s, 3 H), was obtained by comparison with an authentic sample prepared by treating 4-phenyl-3-butyn-2-one with benzonitrile oxide.[19] Structure **8** was established by comparison with an authentic sample.[18] Oxazole **9**,[19] mp 61–62°, nmr ($CDCl_3$) τ 7.32 (s, 3 H), was also independently synthesized by treating 5-methyl-2-phenyloxazole-4-carboxylic acid[18] with thionyl chloride in dimethylformamide to give the corresponding acid chloride, mp 131–133°, which in turn was treated with diphenylcadmium in benzene.

The thermal rearrangement of 4-carbonyl substituted oxazoles is a general reaction[8-12] which was first observed by Cornforth.[8] Consequently, it was of interest to determine whether oxazoles **8** and **9** were interconverted during the thermolysis conditions. Oxazole **8**, when subjected to thermolysis at 230° for 5 hr gave only a 5% yield of **9**. Similarly, **9** produced an insignificant (~4%) amount of **8** under identical reaction conditions. The lack of significant thermal interconversion of oxazoles **8** and **9** under the reaction conditions used rules out any regiospecific mechanism for the thermal rearrangement of **6** and/or **7**.

The formation of oxazole **8** from isoxazole **6** (or **9** from **7**) requires bonding, at some point in the reaction, between C-3 of the isoxazole ring and the oxygen of the benzoyl group. We believe that the experiments reported here require the intermediacy of a 2*H*-azirine (*i.e.*, **10**) to rationalize the transposition of the two ring atoms. The most reasonable pathway for the formation of **10** involves homo-

lytic cleavage of the relatively weak O–N bond of the isoxazole ring to form an acyclic intermediate which can either recyclize to generate rearranged isoxazole or close to



give a 3,3-diacyl-2-phenyl-2*H*-azirine (**10**) intermediate. The second step, **10** → **8** + **9**, most likely involves C–C bond rupture of the 2*H*-azirine ring followed by cyclization to the observed products.[20] Each step of the rearrangement is thermally induced, and the rates and products were not influenced by oxygen, radical inhibitors, or small amounts of acids and bases. It is interesting to note that 5-alkoxyisoxazoles have been reported to undergo a facile thermally induced skeletal rearrangement to alkyl 1-azirine-3-carboxylates.[21] This rearrangement provides good analogy for the first step of the proposed sequence. The literature also contains several references dealing with the thermal rearrangement of 4-isoxazolines.[22-26] Most of the rearrangements observed with these systems can also be attributed to a ring-contraction–ring-expansion sequence.

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Supplementary Material Available. Complete experimental data for this communication will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-1976.

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Sulfoxonium Salts as Reagents for the Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds

Summary: The generality of using sulfoxonium salts for oxidation of alcohols to carbonyl derivatives is illustrated.

Sir: We wish to report on a new method for the oxidation of alcohols to carbonyl derivatives which complements our previously described dimethyl sulfoxide–acetic anhydride procedure.[1] Since none of the previous methods based on dimethyl sulfoxide[2-4] give satisfactory results with all classes of compounds, our finding that reagents such as *p*-toluenesulfonyl chloride, *p*-toluenesulfonic anhydride, methanesulfonic anhydride, benzoyl chloride, and cyanuric chloride react with dimethyl sulfoxide (DMSO) at −20° to give sulfoxonium complexes useful in oxidizing alcohols to carbonyl derivatives opens up the possibility of choosing among these mild oxidative reagents to obtain good yields.

We have found that *p*-toluenesulfonyl chloride, *p*-toluenesulfonic anhydride, or methanesulfonic anhydride[5] with dimethyl sulfoxide in hexamethylphosphoramide (HMPA) at −20° oxidize secondary alcohols to ketones and primary alcohols to aldehydes in high yields. The overall mechanistic sequence is depicted in Scheme I for the oxidation of *p*-nitrobenzyl alcohol **2** to *p*-nitrobenzaldehyde **4**.

The following example demonstrates the simplicity and efficiency of the oxidative process and illustrates the typi-

Scheme I