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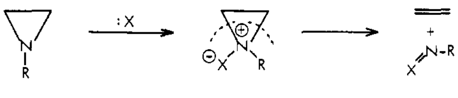
Fragmentation Reaction of Ylide. 6. A New Type of Fragmentation Reaction of Aziridinones

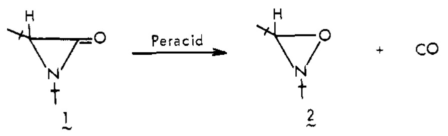
Sir:

Reaction of a number of sustituted aziridines with carbene causes fragmentation of both C–N bonds of the aziridine ring in a single step forming a olefin and imine derivatives.[1] Aziridine *N*-oxide which is considered to be an intermediate in the oxidation reaction of aziridine by peroxy acid also reacts in a manner resembling that of aziridinium ylide because of similar electronic circumstances.[2,3] Here, we report a new type of fragmentation reaction observed in the oxidation of α-lactams by peroxide in various solvent systems.



X : Oxygen or Carbene

1,3-Di-*tert*-butylaziridinone is one of the most stable α-lactams known; several days of refluxing is necessary to solvolyze it with methanol.[4] In acid-catalyzed methanolysis, 2-methoxy-3,3-dimethyl-*N*-*tert*-butylbutyramide has been reported as the sole reaction product.[4] In our experiment, however, 1,3-di-*tert*-butylaziridinone disappeared immediately upon addition of *m*-chloroperbenzoic acid in methanol at 0 °C with vigorous gas generation and was converted into 2,3-di-*tert*-butyloxaziridine in quantitative yield. The structure of the oxaziridine (**2**) was determined by comparison with an authentic sample which was prepared according to literature.[5]

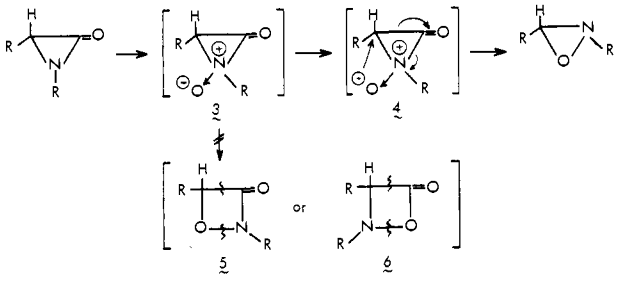


The generated gas, collected in a gas trap and analyzed by VPC, using a Porapak QP column (50–80 mesh) at room temperature, contained 90% carbon monoxide, 10% oxygen, and 0.5% carbon dioxide. The observed yield of carbon monoxide to the starting α-lactam was 80%. Although this value was not quantitative, the yield was not so high as expected, perhaps because of the difficulty in collecting the gas.

Methanol was a suitable solvent for a smooth reaction. However, aprotic solvents, for example, dichloromethane, benzene, ether and hexane, also gave a good yield of oxaziridine. *m*-Chloroperbenzoic acid and peracetic acid were used as oxidation reagents for the new fragmentation of α-lactams and we found that 1 mol equiv of peracid was enough to cause the reaction. Hydrogen peroxide in water was also tried and gave oxaziridine in good yield accompanied by formation of a small amount of unidentified byproduct which may have been due to hydrolysis of the starting material or a reaction intermediate.

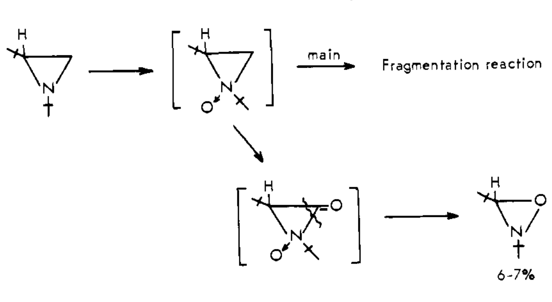
1-*tert*-Butyl-3-phenylaziridinone[6] also underwent the same reaction as 1,3-di-*tert*-butylaziridinone with peracid. Here, the α-lactam ring was very sensitive to the acid in *m*-chloroperbenzoic acid or peracetic acid and the yield of 2-*tert*-butyl-3-phenyloxaziridine was very low. However, addition of lithium carbonate to the reaction system to prevent the reaction of free carboxylic acid with lactam improved the yield of 2-*tert*-butyl-3-phenyloxaziridine to 60–70% in methanol solution.

This new fragmentation reaction of α-lactam probably proceeds by the formation of aziridinone *N*-oxide in the first step, although weak nucleophilicity is expected at the lone pair of nitrogen of the aziridinone ring.[7,8] After the formation of aziridinone *N*-oxide (**3**), two possibilities remain: (a) direct fragmentation of the *N*-oxide as shown in **4** or (b) decarbonylation of the four-membered intermediate **5** or **6** which is formed by ring expansion of the *N*-oxide.



Analogous four-membered compounds of **5** and **6** have already been described as a cycloaddition product between ketenes and nitroso derivatives. The **5** analogue is generally stable thermally under usual reaction conditions and reportedly undergoes a dissociation reaction to isocyanate and carbonyl compounds with strong heating. The four-membered analogue of intermediate **6** is usually unstable and decomposes to imine and carbon dioxide.[9] These characteristic properties of the four-membered-ring analogues **5** and **6** are very different from those found in our oxidation reaction of α-lactams. Therefore, **5** and **6** probably are not found in our reaction and aziridinone *N*-oxide may be converted in a single step to oxaziridine as shown in **4**.[10]

In the oxidation reaction of 1,2-di-*tert*-butylaziridine with *m*-chloroperbenzoic acid in methanol solution at 0 °C, we also observed a 6–7% yield of 2,3-di-*tert*-butyloxaziridine within the main reaction product, 2-methyl-2-nitrosopropane.[11] The reaction seemed to proceed via formation of aziridine *N*-oxide and aziridinone *N*-oxide as shown. We believe that this is the first example of oxidation of the carbon atom in an aziridine structure by organic peroxide.[12]



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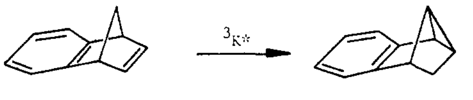
Chemical Titration of Thermally Generated Triplets[1]

Sir:

A unique feature of 1,2-dioxetanes is their selective production of triplet excited states on thermal decomposition.[2] The difficulty, however, has been the accurate and reliable quantitation of these chemienergized triplets. The very first attempts at chemically titrating triplets used cis,trans isomerization of stilbene or the dimerization of acenaphthene,[3] but unfortunately these titrimetric methods are not sufficiently spin specific and thus total excited-stated yields, i.e., singlets and triplets, are determined. In a now classical experiment, it was shown[4] that triplet acetone, chemienergized from tetramethyl-1,2-dioxetane (**1a**), selectively isomerizes fumaronitrile into maleonitrile. The drawbacks are that maleonitrile easily isomerizes thermally back to fumaronitrile during GLC analysis, resulting in large errors.[4,5]



(1)

2a **2b**

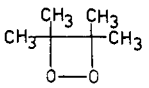
It is, therefore, not surprising that luminescence techniques, such as triplet-singlet energy transfer to 9,10-dibromoanthracene (DBA),[6] have been preferred over chemical titration methods for the quantitative determination of thermally generated triplets. Unfortunately, for low triplet excitation yields and for CIEEL-active substrates,[7] the DBA method can be unreliable.[8] Furthermore, a great deal of uncertainty still persists concerning the crucial triplet-singlet energy transfer efficiency, i.e., reported values range between 0.2 to 0.4,[9] leading to large errors in the DBA-measured triplet yields.

Clearly a convenient, reliable, and general chemical titrant is required for the quantitative determination of chemienergized triplet states. Ideally, the chemical titrant should (a) be spin specific, (b) have a high quantum efficiency of conversion to permit detection of low triplet yields, (c) form the photoproduct irreversibly so that photostationary corrections are unnecessary, (d) afford a volatile and thermally stable product to utilize GLC quantitation, and (e) be readily available. Fortunately, the triplet ketone-sensitized ($^3K^*$) di-π-methane rearrangement of benzonorbornadiene (**2a**) into the tricyclic product **2b** optimally[10] satisfies the above requisites (eq 1).

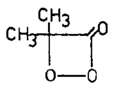
Table I. Thermally Derived Triplet Yields by Chemical Titration[a] with Benzonorbornadiene

dioxetane	[1], M	solvent	temp, °C	time, h	triplet yield, %[b]
1a	0.067	benzene	80	1	31 ± 1
1b	0.040	toluene	80[c,d]	1	1.1 ± 0.1
1c	0.10	benzene	145[e]	24	1.6 ± 0.1
1d	0.10	benzene	80	3	22 ± 1

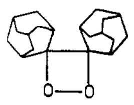
[a] For GLC conditions consult note 14. [b] Total triplet yields including direct and intersystem-crossing derived triplets. [c] Determined relative to dioxetane **1a** by duplicating exactly conditions of temperature, concentrations, time, etc., for **1b** that were used for **1a**; however, in view of the low thermal stability of **1b** vs. **1a**, clearly most of **1b** had already decomposed prior to reaching 80 °C. A control experiment for **1b** at 30 °C and 3 h gave the same results within experimental error as at 80 °C and 1 h. [d] Neither benzonorbornadiene (**2a**) nor its tricyclic isomer **2b** catalyze the decomposition of the α-peroxylactone **1b**, the most susceptible[15,16] member of the dioxetanes studied here. [e] Control experiments reveal that the photoisomerization quantum yield is independent of temperature, i.e., ~50%[10] over the temperature range employed in this work.



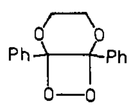
1a



1b



1c



1d

Presently, we demonstrate the general applicability and limitations of **2a** as chemical titrant of thermally generated triplet states derived from the 1,2-dioxetanes **1a–d.** With the help of tetramethyl-1,2-dioxetane (**1a**), which is more and more being used as relative standard for triplet yields,[11] we determine that the triplet acetone yield is 31 ± 1%, thus confirming that the DBA-determinated value of 30%[11] is reasonable. For the dimethyl α-peroxylactone (**1b**) we obtain a triplet acetone yield of 1.1 ± 0.1%, which establishes the lower limit of quantitative detectability of triplet excited states by this method.[12] The thermally quite stable diadamantylidene-1,2-dioxetane (**1c**) affords 1.6 ± 0.1% triplet adamantanone,[5] illustrating that the method can be used at temperatures up to ~150 °C. Finally, the dioxene-1,2-dioxetane **1d** gives 22 ± 1% triplet diester,[13] showing that this method is applicable to a variety of carbonyl triplet excited states. These results are detailed below.

Benzene solutions 0.067 M in dioxetane **1a** and variable molarity (0.285 to 0.713 M) in benzonorbornadiene (**2a**) were heated in a sealed tube at 80 °C until complete decomposition of **1a** (~60 min) and the ratio of **2b** to **2a** was determined by GLC[14] as a function of [**2a**]. A double inverse plot of the chemical yield of **2b** vs. [**2a**] afforded an intercept value of 6.5 ± 0.2 on triplicate analysis of three independent runs. Using the literature value of 0.50 for the photoisomerization yield of **2a** to **2b**, the triplet acetone yield from **1a** was found to be 31 ± 1% (Table I). This checks well with the 30% value determined by DBA fluorescence measurements[11] and matches the lower limit determined by fumaronitrile isomerization.[4] More significantly, our results suggest that a value of 0.20 for the triplet-singlet energy transfer efficiency for DBA[9] and the Hastings' calibration standard provide reliable triplet yield data, since these were used in the DBA fluorescence determinations.[11]

These encouraging results motivated us to determine the triplet acetone yield from α-peroxylactone **1b** because, at the time of commencing this study, no reliable values were known for α-peroxylactones.[12] Since **1b** can become involved in

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