Formation of Imidazolidines by Reaction of Aziridines and Oxalyl Chloride

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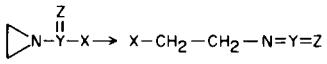
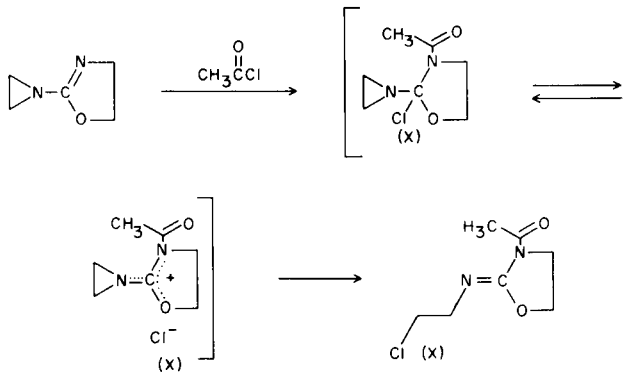
Recently we described a general class of aziridine rearrangements which involves a 1,4-migration of X accompanied by the formation of an -N=Y=Z group as shown below:



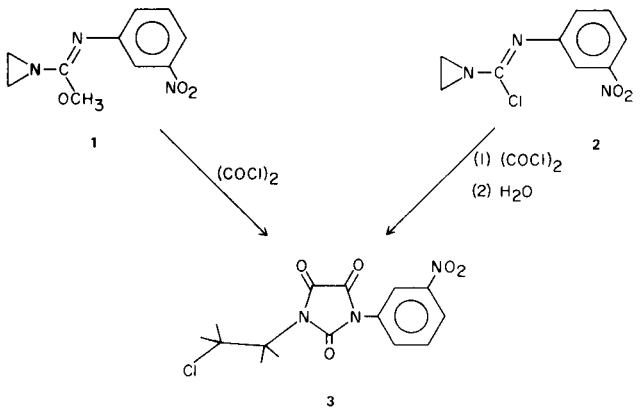
These rearrangements, which are skeletally analogous to the well known homoallylic rearrangements in the cyclopropane series (1), have been shown to be useful for the preparation of isocyanates (2,3), isothiocyanates (4), sulfinylamines (5), and carbodiimides (6). When X is a labile function (*e.g.* Cl^-) ionization to an aziridinyl-α-methinyl cation is a conceivable intermediate. When X is not particularly labile, aziridine ring opening may proceed prior to the departure of the X group. The mechanism for the isomerization of 1-(arylthiocarbonyl)aziridines is an example of this latter reaction pathway (3).

Another variation of this general rearrangement may be seen in the reaction of aziridinyl oxazolines with acid halides (7). In this case an intermediate is generated *in situ* wherein a labile X group is formed. This intermediate then rearranges with analogous skeletal changes. The reaction of 2-(1-aziridinyl)-2-oxazoline with acetyl chloride is an example of such a reaction:



Therefore, it appears that when a positive charge is generated on an atom adjacent to the aziridinyl nitrogen atom this type of skeletal rearrangement may be expected.

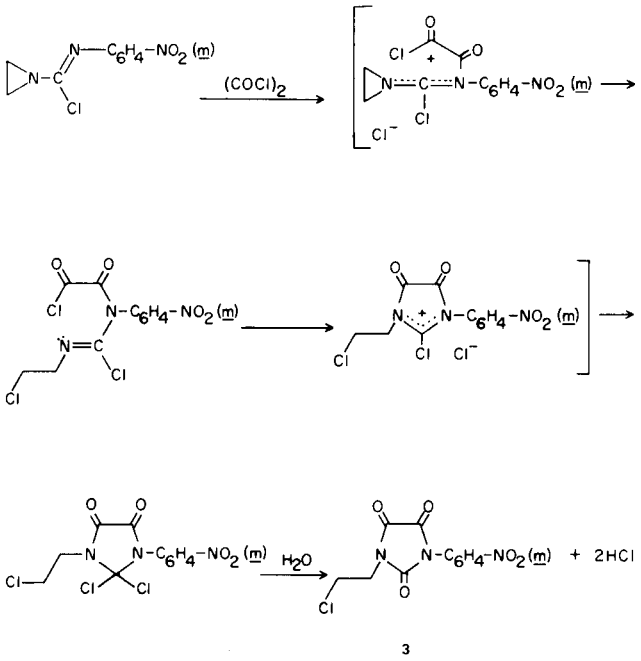
We wish to report another example of a reaction which supports this speculation. The reaction of methyl *N*-aryl-1-aziridinecarboximidates and oxalyl chloride yielded imidazolidine-2,4,5-triones. Imidazolidine-2,4,5-triones were also prepared by reacting *N*-aryl-1-aziridinecarboximidoyl chlorides with oxalyl chloride and hydrolysis of the product. These conversions are exemplified by the conversion of methyl *N*-(*m*-nitrophenyl)-1-aziridinecarboximidate (**1**) and *N*-(*m*-nitrophenyl)-1-aziridinecarboximidoyl chloride (**2**) to 1-(2-chloroethyl)-3-(*m*-nitrophenyl)-imidazolidine-2,4,5-trione (**3**):



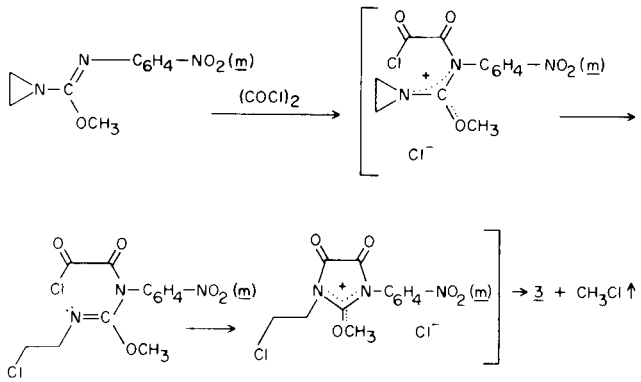
The conversions of both **1** and **2** to the imidazolidine-2,4,5-trione (**3**) are facile and high yield processes.

A mechanistic rational for these reactions is consistent with the fore-mentioned heteroatomic homoallylic type rearrangement. The reaction of **2** and oxalyl chloride was viewed as an acylation of the imidoyl nitrogen atom and formation of a cation adjacent to the aziridinyl nitrogen atom (8). Subsequent steps leading to product formation are rupture of the aziridine ring, ring closure, and attack

by chloride ion. The product, 1-(2-chloroethyl)-3-(*m*-nitrophenyl)-2,2-dichloroimidazolidine-4,5-dione, was smoothly converted to **3** with water (6). This mechanistic pathway is shown below:



The reaction of **1** with oxalyl chloride is very analogous to the reaction of aziridinyl oxazolines with oxalyl chloride (7). The difference being fragmentation and loss of methyl chloride whereas the chlorine is retained in the case of the oxazolines. A possible mechanism for the conversion of **1** to **3** is shown below:



EXPERIMENTAL

Methyl *N*-(*m*-Nitrophenyl)-1-aziridinecarboximidate (**1**).

A sample of *N*-(*m*-nitrophenyl)-3-aziridinecarboximidoyl chloride (6) (2.0 g., 8.9 mmoles) was dissolved in benzene (50 ml.) and sodium methoxide (0.61 g., 11 mmoles, Olin Mathieson Chemical Co.) was added over a period of ten minutes. The reaction solution was allowed to stand at room temperature for two days. The salt formed during the reaction was collected by filtration and the benzene filtrate was concentrated under a reduced pressure to yield 1.8 g. (92%) of a pale yellow, crystalline material. The product was recrystallized from ether and identified as methyl *N*-(*m*-nitrophenyl)-1-aziridinecarboximidate (**1**), m.p. 82-83°; ir spectrum (flurolube mull), 1640 cm^{-1} (-C=N-); nmr spectrum (acetonitrile-d_3), 7.18-7.96 δ (4H, m, aromatic protons), 3.81 δ (3H, s, -O-CH_3), 2.0 δ (4H, s, aziridinyl protons).

Anal. Calcd. for $C_{10}H_{11}N_3O_3$: C, 54.4; H, 5.02; N, 19.0. Found: C, 54.1; H, 5.06; N, 18.8.

1-(2-Chloroethyl)-3-(*m*-nitrophenyl)imidazolidine-2,4,5-trione (**3**).

A sample of **1** (0.5 g., 2.26 mmoles) in dichloromethane (5 ml.) was added dropwise to a solution of oxalyl chloride (0.43 g., 3.39 mmoles, Eastman Organic Chemicals) in dichloromethane (15 ml.) over a period of 10 minutes. The reaction solution was refluxed for an hour, and then the dichloromethane was removed under a reduced pressure to yield an off-white, granular material (0.55 g., 82%) which was washed with water and recrystallized from dichloromethane-ether. The material was identified as 1-(2-chloroethyl)-3-(*m*-nitrophenyl)imidazolidine-2,4,5-trione (**3**), m.p. 117-119°; identical in all respects (mixture m.p., ir, nmr) with an authentic sample of **3** (6).

Conversion of **2** to **3** has been described previously (6).

REFERENCES

(1) P. DeMayo, "Molecular Rearrangements," Interscience Publishers, New York, N. Y., Vol. I, 1964, p. 259.

(2a) D. A. Tomalia, J. N. Paige, *J. Heterocyclic Chem.*, **4**, 178 (1967); (b) C. K. Johnson, *J. Org. Chem.*, **32**, 1508 (1967).

(3) D. A. Tomalia, D. P. Sheetz and G. E. Ham, *ibid.*, **35**, 47 (1970).

(4) D. A. Tomalia, *J. Heterocyclic Chem.*, **3**, 384 (1966).

(5) D. A. Tomalia, *Tetrahedron Letters*, **27**, 2559 (1967).

(6) D. A. Tomalia, T. J. Giacobbe, and W. A. Sprenger, in press.

(7) D. A. Tomalia, N. D. Ojha, and B. P. Thill, *J. Org. Chem.*, **34**, 1400 (1969).

(8) Evidence for preferred electrophilic attack at the nitrogen β to the aziridine ring rather than the aziridine nitrogen is presented in reference 7.