

obtained. The similar iodination of UV (the alkaline treatment was also omitted) gave V as the sole product.

At present, a possible mechanism for the formation of the O⁶,2'-cyclostructure would be as summarized in Chart 1. The C₄-amino group in I thus may play an important role in the intramolecular iodination reaction, which in turn would be followed by the cyclic ether formation to yield IV.

The signs of the Cotton effect in II and III were both negative (Fig. 3). According to Ulbricht, *et al.*, who recorded a rule for predicting the sign of the Cotton effect with reference to the configuration of pyrimidine nucleosides,⁵⁾ the signs of the Cotton effect in II and III should be positive. Our results, therefore, present a discrepancy with their rule and more detailed studies should throw light on this problem.

Further attempts to synthesize O⁶,3'-6-hydroxycyclouridine from 1-β-D-xylofuranosylcytosine are now in progress.

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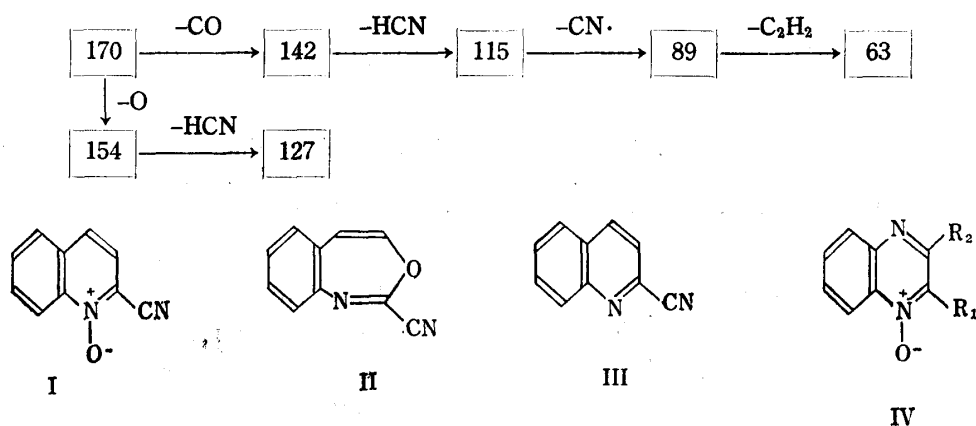
A Novel Skeletal Rearrangement of Aromatic N-Oxides upon Electron Impact

The formation of unstable oxaziridines in photochemical reactions of aromatic N-oxides has been postulated in order to account for the various photo-products such as oxazepines and pyridones.¹⁻⁷⁾ The first step of these transformations is most conveniently depicted in terms of the $n-\pi^*$ excited state of the N-oxides. The related reactions would be expected under the electron impact induced ionization as well, because the

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ionization presumably involves the removal of an electron from the non-bonding orbital of the oxygen atom and the resulting species would be very similar to the $n-\pi^*$ excited state of the N-oxides. Therefore, one might expect the transient formation of oxaziridine ions during the mass spectral fragmentation reaction. In this communication, the mass spectra of some aromatic N-oxides are re-examined in an attempt to provide evidence for this possibility.

As a pertinent example, the spectra of 2-cyanoquinoline 1-oxide (I) and related compounds are shown in Fig. 1. The following fragmentation sequences of I are substantiated by the appearance of appropriate meta-stable ion peaks. The elemental compositions of each fragment ion were confirmed by accurate mass measurement.



A striking feature in the spectrum of I is the appearance of an M-CO ion of a moderate intensity (m/e 142). This requires prior formation of a C-O bond in a molecular ion and virtually indicates the isomerization of N-oxide ion (a) to the oxaziridine species (b). This oxaziridine ion (b) would then rearrange to the corresponding oxazepine ion (c) before the fragmentation takes place.

The intermediacy of the oxazepine ion (c) was established by the comparison of the spectrum of 3,1-benzoxazepine-2-carbonitrile*¹ (II), which was derived photochemically from I.⁷⁾ As is shown in Fig. 1, the significant peaks of II are almost identical with those observed in I.

The subsequent loss of CO and HCN from c to give intense peaks at m/e 142 and 115 is explicable by assuming that the fragmentation reactions are similar to those observed in benzofuran⁸⁾ and oxazoles.⁹⁾ Therefore, it may be concluded that 2-cyanoquinoline

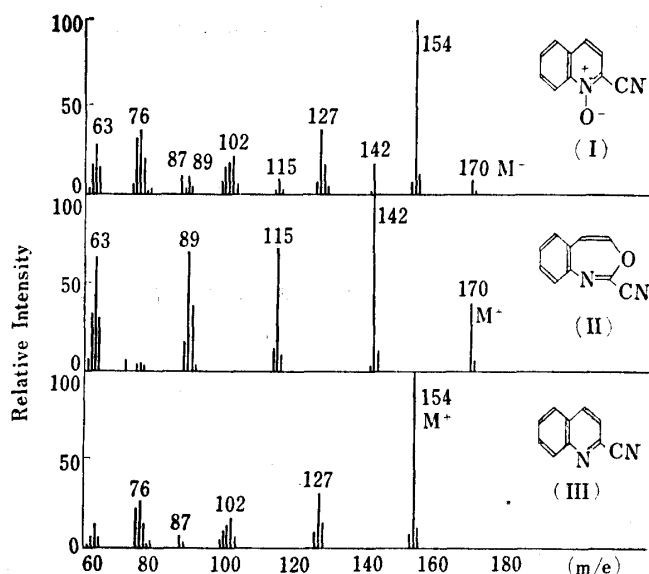


Fig. 1. Mass Spectra of 2-Cyanoquinoline 1-Oxide and Related Compounds

*¹ Recent experiments^{6,7)} demonstrate that the photo-products assigned to have the 1aH-oxazirino[2,3-a]-quinoline structure in the previous works²⁾ have the 4,5-benz-1,3-oxazepine structure.

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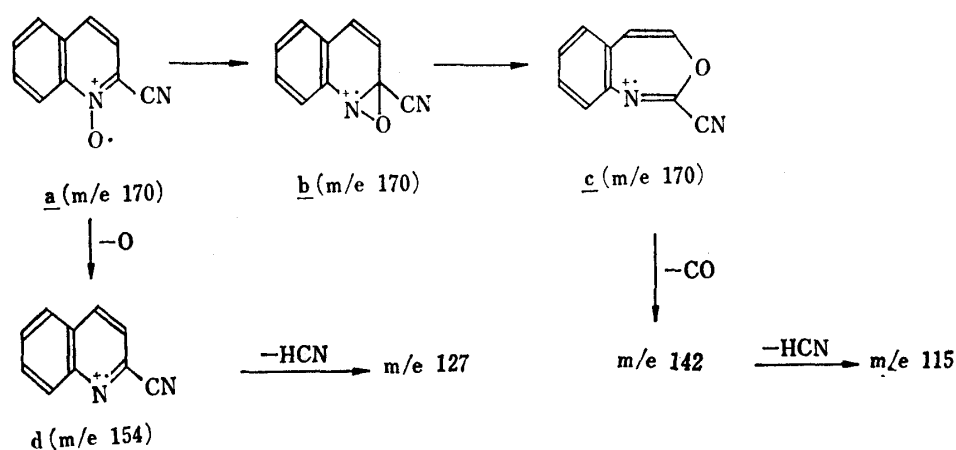


Chart 2.

1-oxide (I) undergoes essentially the same skeletal rearrangement upon electron impact as in photochemical reactions.

On the other hand, the loss of oxygen from the molecular ion (a) to afford the quinoline ion (d) is characteristic for most aromatic N-oxides.¹⁰⁾ Thus, quinoline-2-carbonitrile (III) itself showed the same intense peaks at m/e 154 and 127.

In the case of substituted quinoxaline 1-oxides (IV), the corresponding M-CO peaks were also observed. While the relative intensities of the peak seemed to be almost independent of the substituents in the 3 position (see Table I), our preliminary experiments have shown that the mode of the above fragmentation reaction in quinoxaline—as well as quinoline N-oxides is distinctly affected by the type of substituents in the 2 position. We are currently investigating these structural effects and further extending the work to other aromatic N-oxides.

TABLE I. Intensities of M-CO Peaks of Quinoxaline 1-Oxides (IV)

Substituent		Relative Intensity of M-CO Peak (%)	Base Peak
R ₁	R ₂		
H	H	15	M
H	Et	14	M
H	iso-Pr	15	M-15
CN	H	14	M
Ph	Et	14	M-17
Ph	iso-Pr	16	M-16
Ph	CN	14	M-16
Ph	OMe	15	M-16
Ph	CONH ₂	12	M-16

The mass spectra were determined with a Hitachi RMU-6E double-focussing mass spectrometer with an all-glass heated inlet system.

The measurement of high-resolution mass spectrum of II was kindly performed by Dr. T. Aoyama of Japan Electron Optics Laboratory Co., Ltd. by using a JMS-O1S double-focussing mass spectrometer.

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