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Mass Spectra of Some Alkyloxazoles

The mass spectra of 50 alkyloxazoles have been measured and the major peaks tabulated. The compounds were synthesized by general methods and purified by gas chromatography. The major mass spectral fragmentations of the alkyloxazoles are β scission and β scission with hydrogen rearrangement.

The analysis of volatile flavor constituents of foods by GC–MS frequently results in large numbers of mass spectra which cannot be interpreted because of the lack of published spectra. The publication of mass spectra of families of food compounds, such as alkylpyrazines by Bondarovich et al. (1967), bicyclic pyrazines by Pittet et al. (1974), and alkylthiazoles by Buttery et al. (1973) and Vitzthum and Werkhoff (1974), has allowed other researchers to identify such compounds in various food products.

In order to interpret some unknown mass spectra, we synthesized and obtained mass spectra of a number of alkyloxazoles. As there are a limited number of published mass spectra of alkyloxazoles available (Bowie et al., 1968; Vitzhum and Werkhoff, 1974; Ho and Tuorto, 1981), we report their spectra here in the hope that they may be of use to other researchers. Alkyloxazoles have been found in several foods, including roasted coffee (Stoffelsma and Pypker, 1968; Vitzthum and Werkhoff, 1974), roasted cocoa (Vitzthum et al., 1975), roasted barley (Harding et al., 1978), baked potato (Coleman et al., 1981), roasted peanuts (Lee et al., 1981), and meat products (Chang and Peterson, 1977; Mussinan and Walradt, 1974).

EXPERIMENTAL SECTION

Materials. Aliphatic ketones, aliphatic aldehydes, bromine, amides, acids were obtained from Aldrich Chemical Co.

Synthesis of α-Bromo Ketones. These were synthesized by the method described by Catch et al. (1948), which involves essentially direct bromination of the appropriate ketone. With unsymmetrical ketones, two bromoketones are formed. In all cases, the mixture of the two bromides was taken through the oxazole synthesis and the two isomeric oxazoles were separated by GC.

Synthesis of α-Bromo Aldehydes. These were synthesized by the method of Bedoukian (1944), which involves conversion of the corresponding saturated aldehyde to its enol acetate followed by the addition of bromine and then conversion to the dimethyl acetal and hydrolysis to the α-bromo aldehyde.

Synthesis of Alkyloxazoles. These were all synthesized by the method of Theilig (1953). One equivalent of α-bromo ketone or α-bromo aldehyde was allowed to react with 2 equiv of amide. Yields were all generally quite satisfactory at about 50%. The distilled products were purified by GC. Gas chromatography was performed on a Beckman GC-55 gas chromatograph, fitted with a 12 ft. long × $^1/_8$ in. o.d. stainless steel column packed with 10% SP-1000 on 80–100-mesh Chromosorb W. The flow rate was 30 mL/min. The column temperature was programmed from 50 to 230 °C at a rate of 5 °C/min. The purified oxazoles were then subjected to GC–MS analysis.

Table I. Alkyloxazoles Synthesized

2,4-diethyloxazole
2-methyl-5-propyloxazole
2-propyl-4-methyloxazole
5-pentyloxazole
2-methyl-5-butyloxazole
2,4-dimethyl-5-propyloxazole
2-methyl-4-butyloxazole
2,4-diethyl-5-methyloxazole
2-propyl-4,5-dimethyloxazole
2-propyl-4-ethyloxazole
2-isopropyl-4,5-dimethyloxazole
2-isopropyl-4-ethyloxazole
2-butyl-4-methyloxazole
2-methyl-5-pentyloxazole
2-methyl-4-propyl-5-ethyloxazole
2-ethyl-5-butyloxazole
2-propyl-4-methyl-5-ethyloxazole
2-propyl-4-ethyl-5-methyloxazole
2,4-dipropyloxazole
2-isopropyl-4-ethyl-5-methyloxazole
2-butyl-4,5-dimethyloxazole
2-pentyl-4-methyloxazole
2-methyl-4-ethyl-5-butyloxazole
2-ethyl-5-pentyloxazole
2,5-diethyl-4-propyloxazole
2,5-dipropyl-4-methyloxazole
2-propyl-4-butyloxazole
2-butyl-4-methyl-5-ethyloxazole
2-butyl-4-ethyl-5-methyloxazole
2-butyl-4-propyloxazole
2-pentyl-4,5-dimethyloxazole
2-pentyl-4-ethyloxazole
2-hexyl-4-methyloxazole
2-ethyl-4-methyl-5-pentyloxazole
2,4-diethyl-5-butyloxazole
2-ethyl-4-pentyl-5-methyloxazole
2-propyl-4-methyl-5-butyloxazole
2-propyl-4-pentyloxazole
2-pentyl-4-methyl-5-ethyloxazole
2-pentyl-4-ethyl-5-methyloxazole
2-hexyl-4,5-dimethyloxazole
2-hexyl-4-ethyloxazole
2-heptyl-4-methyloxazole
2-pentyl-4-methyl-5-propyloxazole
2-pentyl-4-butyloxazole
2-hexyl-4-methyl-5-ethyloxazole
2-hexyl-4-ethyl-5-methyloxazole
2-hexyl-4-propyloxazole
2-heptyl-4-ethyloxazole
2-octyl-4-methyloxazole

Mass Spectra. Mass spectrometry was performed on a Du Pont 21-490 mass spectrometer with a jet separator interfaced to a Varian Moduline 2700 gas chromatograph fitted with an FID detector and a $^1/_8$ in. o.d. × 12 ft. stainless steel column packed with 10% OV-101 on 80–100-mesh Chromosorb W. The ionization voltage was 70 V.

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Table II. Approximate Relative Rates of β Scission and β Scission with Hydrogen Rearrangement in the Spectra of Oxazoles Containing the Pentyl Chain in the 5-Position

compound	$[M - C_4H_9]/[M]$	$[M - C_4H_8]/[M]$[b]	$[M - C_4H_9]/[M - C_4H_8]$
5-pentyloxazole	2.9	4.5	0.6
2-methyl-5-pentyloxazole	7.7	2.3	3.3
2-ethyl-5-pentyloxazole	6.3	1.3	4.8
2-ethyl-4-methyl-5-pentyloxazole	16.7	0.2	83.5
4-ethyl-5-pentyloxazole[a]	5.9	0.3	19.7

[a] Data taken from Ho and Tuorto (1981). [b] Contribution due to ^{13}C has been adjusted.

RESULTS AND DISCUSSION

Fifty new alkyloxazoles (Table I) were synthesized and their mass spectra were measured. A table which lists the mass spectra of the alkyloxazoles by using the method of presentation of Herz et al. (1971) is available as supplementary material (see paragraph at end of paper regarding supplementary material).

The mechanism of mass spectral fragmentation of some alkyloxazoles has been previously discussed by Bowie et al. (1968). There are two main types of fragmentation which are very characteristic of alkyloxazoles. They are (a) β scission and (b) β scission with hydrogen migration (McLafferty rearrangement). Alkyloxazoles with alkyl side chains (R) three carbons long or longer in the 2- or 4-positions show an intense ion at M − (R − 15).

Table II lists the ratio of $[M - C_4H_9]/[M]$ and $[M - C_4H_8]/[M]$ of five alkyloxazoles containing the pentyl chain in the 5-position. The ratio $[M - C_4H_9]/[M]$ and $[M - C_4H_8]/[M]$ will give the approximate relative rates of the β cleavage processed in these compounds (Bowie et al., 1968). From the data in Table II, it is evident that when there is a methyl or ethyl substituent in the 2- or 4-position, the McLafferty rearrangement is less favored and renders β scission the major fragmentation process. In the case of 5-pentyloxazole, McLafferty rearrangement is still the major process. When both 2- and 4-positions are substituted with methyl or ethyl groups, the rate of simple β scission is significantly enhanced.

As far as we can determine, the mass spectra of alkyloxazoles listed in the supplementary material had not previously been reported.

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Registry No. 2,4-Diethyloxazole, 84027-83-8; 2-methyl-5-propyloxazole, 80935-99-5; 2-propyl-4-methyloxazole, 24667-04-7; 5-pentyloxazole, 84027-84-9; 2-methyl-5-butyloxazole, 84027-85-0; 2,4-dimethyl-5-propyloxazole, 84027-86-1; 2-methyl-4-butyloxazole, 84027-87-2; 2,4-diethyl-5-methyloxazole, 84027-88-3; 2-propyl-4,5-dimethyloxazole, 53833-32-2; 2-propyl-4-ethyloxazole, 84027-89-4; 2-isopropyl-4,5-dimethyloxazole, 19519-45-0; 2-isopropyl-4-ethyloxazole, 84027-90-7; 2-butyl-4-methyloxazole, 24667-15-0; 2-methyl-5-pentyloxazole, 84027-91-8; 2-methyl-4-propyl-5-ethyloxazole, 84027-92-9; 2-ethyl-5-butyloxazole, 77311-04-7; 2-propyl-4-methyl-5-ethyloxazole, 84027-93-0; 2-propyl-4-ethyl-5-methyloxazole, 84027-94-1; 2,4-dipropyloxazole, 84027-95-2; 2-isopropyl-4-ethyl-5-methyloxazole, 84027-96-3; 2-butyl-4,5-dimethyloxazole, 84027-97-4; 2-pentyl-4-methyloxazole, 52713-58-3; 2-methyl-4-ethyl-5-butyloxazole, 84027-98-5; 2-ethyl-5-pentyloxazole, 84027-99-6; 2,5-diethyl-4-propyloxazole, 40953-17-1; 2,5-diethyl-4-methyloxazole, 84028-00-2; 2-propyl-4-butyloxazole, 84028-01-3; 2-butyl-4-methyl-5-ethyloxazole, 84028-02-4; 2-butyl-4-ethyl-5-methyloxazole, 84028-03-5; 2-butyl-4-propyloxazole, 84028-04-6; 2-pentyl-4,5-dimethyloxazole, 84028-05-7; 2-pentyl-4-ethyloxazole, 84028-06-8; 2-hexyl-4-methyloxazole, 84028-07-9; 2-ethyl-4-methyl-5-pentyloxazole, 84028-08-0; 2,4-diethyl-5-butyloxazole, 84028-09-1; 2-ethyl-4-pentyl-5-methyloxazole, 84028-10-4; 2-propyl-4-methyl-5-butyloxazole, 84028-11-5; 2-propyl-4-pentyloxazole, 84028-12-6; 2-pentyl-4-methyl-5-ethyloxazole, 84028-13-7; 2-pentyl-4-ethyl-5-methyloxazole, 84028-14-8; 2-hexyl-4,5-dimethyloxazole, 20662-87-7; 2-hexyl-4-ethyloxazole, 84028-15-9; 2-heptyl-4-methyloxazole, 84028-16-0; 2-pentyl-4-methyl-5-propyloxazole, 84028-17-1; 2-pentyl-4-butyloxazole, 84028-18-2; 2-hexyl-4-methyl-5-ethyloxazole, 84028-19-3; 2-hexyl-4-ethyl-5-methyloxazole, 84028-20-6; 2-hexyl-4-propyloxazole, 84028-21-7; 2-heptyl-4-ethyloxazole, 84028-22-8; 2-octyl-4-methyloxazole, 84028-23-9.

Supplementary Material Available: One table listing the mass spectra of 50 alkyloxazoles (10 pages). Ordering information is given on any current masthead page.

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