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A mechanism of fragmentation for five membered heterocyclic-substituted acids is proposed. The suggested four centered transition state for the CO<sub>2</sub> elimination is based on the resulting deuterium-labelled ions.

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In spite of the fact that benzoic acid derivatives characterize themselves by intense peaks at  $m/e$   $M^+ - 17$  and  $M^+ - 45$  by electron impact in mass spectrometry (2), other aromatic compounds such as pyrrole and furan carboxylic acid derivatives do not lose these fragments (3).

Although much literature is found regarding the fragmentation patterns of furan and pyrrole heterocyclic systems (3,4), little attention had been given to the mechanism of cleavage of their carboxylic acid derivatives. Since these carboxylic acids are thermally unstable, the decarboxylation process can be thought to take place mainly as simple decarboxylation and not as a result of electron impact inside the mass spectrometer (3,5). In a previously reported mechanism for furan (3) and pyridine (7) substituted carboxylic acids, an interaction between the heteroatom in the ring and the acid func-

tion was proposed prior to the elimination of CO<sub>2</sub>.

In the heterocyclic systems studied, Figure 1, we have found strong evidences to believe that the CO<sub>2</sub> elimination process occurs through a one step mechanism by electron impact.

In addition to the metastable ions observed, deuterium labelled fragments were observed as a result of the R-COOD cleavage and transposition of the deuterium atom from the molecular or intermediate ions after ionization. The labelled fragments were found deuterated at the same position where previously the carboxyl group was attached, Fig. 1, similarly as it was observed in fragments originating in the fragmentation of deuterated 2,3-diformylbenzo[*b*]furan, carbonates and carbamates (8,9). Thus a four centered transition state is proposed involving migration of the deuterium to the radical site formed as is shown in Fig. 2.

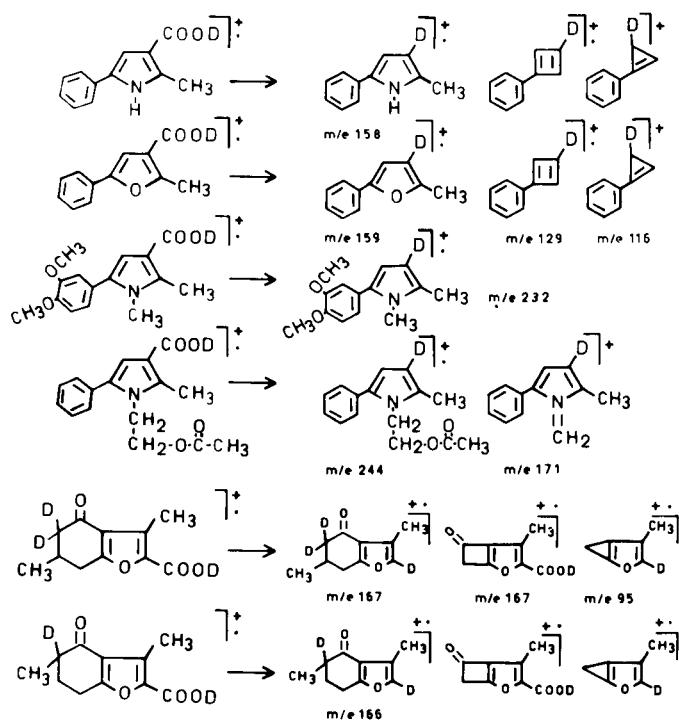


FIGURE 1

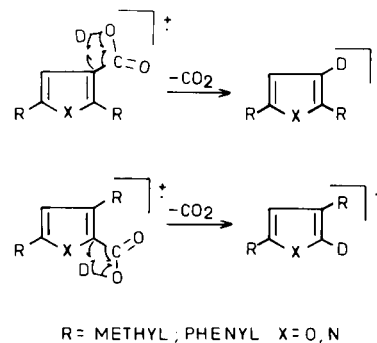


FIGURE 2

## EXPERIMENTAL

The 75 eV mass spectra of these compounds were determined on a Hitachi-Perkin-Elmer RMU-7 H double focusing mass spectrometer using the direct inlet system. The samples were recorded at ionization chamber temperature of ca. 215°. All compounds were synthesized following reported procedures (10,11). The H/D interchange was made in a sealed tube employing deuteriomethanol/deuterium oxide in a 1:1 relationship.

## REFERENCES AND NOTES

- (1) Contribution N° 506; from the Instituto de Química, U.N.A.M.
- (2) T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **33**, 386 (1961); S. Meyerson and J. L. Corbin, *J. Am. Chem. Soc.*, **87**, 3045 (1965).
- (3) R. I. Reed and W. K. Reid, *J. Chem. Soc.*, 5933 (1963); H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman and J. M. Wilson, *J. Chem. Soc.*, 1949 (1964).
- (4) A. H. Jackson, G. W. Kenner, H. Budzikiewicz, C. Djerassi and J. M. Wilson, *Tetrahedron*, **23**, 603 (1967); M. Salmón, O. Villarino, A. Jiménez and R. Zawadzki, *Rev. Latinoam. Quím.*, **4**, 59 (1973).
- (5) R. Marchelli, W. D. Jamieson, S. H. Safe, O. Hutzinger and R. A. Heacock, *Can. J. Chem.*, **49**, 1296 (1971).
- (6) R. J. Moser and E. V. Brown, *Org. Mass Spectrom.*, **4**, 555 (1970); E. V. Brown and R. J. Moser, *J. Heterocyclic Chem.*, **8**, 189 (1971).
- (7) A. Shafiee, *ibid.*, **12**, 177 (1975).
- (8) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden Day, 1967, Chapter 15.
- (9) H. Stetter and R. Lauterbach, *Chem. Ber.*, **93**, 603 (1960). E. Cortés and M. Salmón, *Org. Mass Spectrom.*, **6**, 85 (1972); M. Salmón and E. Cortés, *Rev. Latinoam. Quím.*, **3**, 66 (1972).
- (10) L. Lederer and C. Paal, *Ber.*, **18**, 2591 (1885).