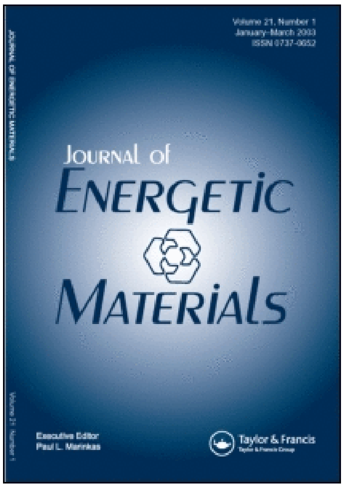

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MS/MS OF ENERGETIC COMPOUNDS. A COLLISIONAL INDUCED DISSOCIATION STUDY OF SOME POLYNITROBISHOMOCUBANES

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ABSTRACT

A collisional induced dissociation (CID) study was done on 3,5,5-trinitropentacyclodecane and 5,5-dinitropentacyclodecane-3-carboxylic acid using tandem high-resolution MS/MS. Fragmentation pathways were determined in the EI ionization mode. It was found that fragmentation of the C-N bonds - resulting in losses of the NO_2 groups - takes place before the fragmentation of the C-C bonds.

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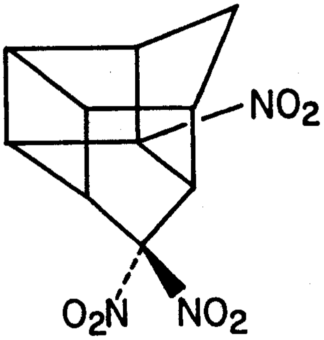
INTRODUCTION

There is considerable interest in the synthesis and chemistry of strained energetic compounds which could serve as explosives having improved performances. As part of the synthesis program at the U.S. Army Armament Research and Development Center on polynitro organic ring systems with potential high energy output and thermal stability, a polynitrobishomocubane has been recently synthesized.[1]

The objective of this study was to determine the mass spectral fragmentation pathways of this bishomocubane, 3,5,5-trinitropentacyclodecane (1) (TPCD) and of 5,5-dinitropentacyclodecane-3-carboxylic acid (2) (DPCD-Ac), an intermediate in the synthesis of TPCD.



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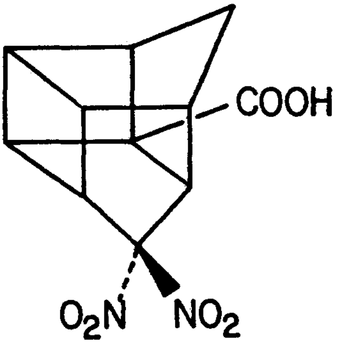

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A great deal of research has been done on the mass spectrometry of explosives[2] because of some interesting parallels between the early stages of decomposition by explosive shock and the fragmentation under electron impact (EI) in the mass spectrometer.[3,4] In EI mass spectrometry, the ions formed, containing excess energy, decompose into a series of fragments. The resulting mass spectrum indicates only the presence of the ions but does not give any information on their routes of formation. A powerful tool for the study and determination of fragmentation pathways of individual ions is Tandem Mass Spectrometry, or

MS/MS. This method can be used either in the unimolecular decomposition or the collisional induced dissociation (CID) mode.[5] Ions undergoing unimolecular decomposition in the field free region of the mass spectrometer have lower average internal energies than those decomposing in the ion source. Therefore, such metastable ions only represent the mass spectral reactions of lowest activation energy, such as rearrangements.[6] In CID, when using magnetic mass spectrometers, a beam of precursor ions having translational kinetic energies of several keV collides with an inert gas, which transforms some of the translational energy of the ions into internal excitation energy.[7] The products of these reactions arise from simple bond cleavages and therefore are useful for ion structure elucidation. It is assumed that the CID mass spectrum is related to the precursor ion structure in the same way as the EI mass spectrum is related to the molecular structure.[7] Hence the similarity between CID and EI spectra. A study of the MS/MS CID spectra of the molecular ion and daughter ions of a compound will provide information leading to the determination of the fragmentation pathways of the compound.

Fragmentation pathways of several explosive compounds have been previously determined by MS/MS CID.[8-10]

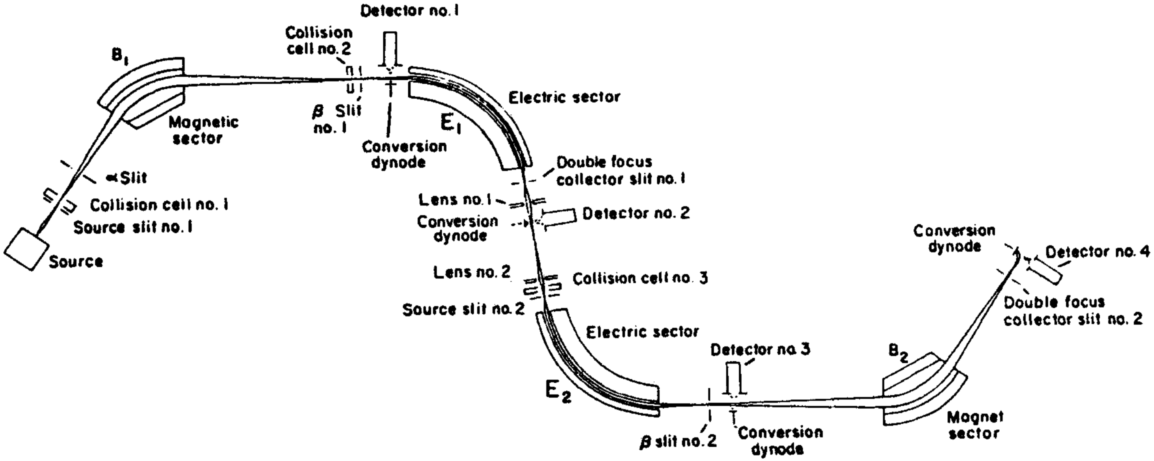
Thus we have studied the MS/MS CID spectra of TPCD and DPCD-Ac in order to determine the fragmentation processes of these compounds.

EXPERIMENTAL

The instrument used in this research was the VG ZAB 4F MS/MS at the NIEHS[11] (Figure 1) consisting of two high resolution mass spectrometers in tandem which include a magnetic Sector B_1, an electric sector E_1, a second electric Sector E_2 and a second magnetic sector B_2. Collisional induced dissociation was carried out in a collision cell located between the two electric sectors E_1 and E_2. Helium was used as collision gas. The pressure of the helium was adjusted so that the main beam intensity was reduced to half of its initial value. Mass spectra of both compounds were recorded in the EI mode at 70 eV; TPCD was also recorded in the CI mode with isobutane as reagent gas. CID spectra were recorded only from ions formed in the EI mode. The ion source was operated at a temperature of 200-250°C. The solid probe, through which the samples were introduced, was not heated separately.

The ultimate resolving power of MS-1 is 100,000, but since sensitivity was of primary concern it was operated at a resolution of 5000. The maximum resolution of MS-2 for daughter ions is 10,000. Although the two mass spectrometers are similar, the resolution in MS-2 is reduced because of the energy spread of the daughter ions. Again, due to sensitivity considerations, MS-2 was operated at a resolution of 1000.

FIGURE 1
VG ZAB 4F Tandem High Resolution Mass Spectrometer.



EI and CI mass spectra and CID spectra were obtained on a UV recorder and on a data system (VG 11-250 data system, based on a PDP 11/24 minicomputer).

Compounds were supplied by USAARDC, Dover, N.J.

RESULTS AND DISCUSSION

Figures 2 and 3 show the EI and CI-isobutane mass spectra of TPCD. The EI mass spectrum (Figure 2) has its base peak at m/z 128, formed by the $(M-2NO_2-HNO_2)^+$ ion. A highly abundant ion is observed at m/z 175 due to $(M-2NO_2)^+$. In addition a series of fragment ions are observed which are due to the fragmentation of the hydrocarbon and to losses of part of the NO_2 groups. The CI spectrum of TPCD (Figure 3) is characterized by a MH^+ base peak at m/z 268, and by successive losses of the NO_2 groups thus forming ions at m/z 222 $(MH-NO_2)^+$, m/z 176 $(MH-2NO_2)^+$ and m/z 130 $(MH-3NO_2)^+$.

Figure 4 shows the EI mass spectrum of DPCD-Ac. The base peak at m/z 128 is due to consecutive losses of $2NO_2$ and $COOH_2$ from the molecular ion (which is not observed). A major ion is observed at m/z 174 due to $(M-2NO_2)^+$. The highest mass ion observed - at m/z 249 - is probably due to $(M-OH)^+$. No CI spectrum could be obtained with this compound.

Two representative CID spectra are shown in Figures 5 and 6. The CID spectrum of the $(M-2NO_2)^+$ ion at m/z 174 of DPCD-Ac in Figure 5 and the CID spectrum of the $(M-2NO_2-OH)^+$ ion at m/z 158

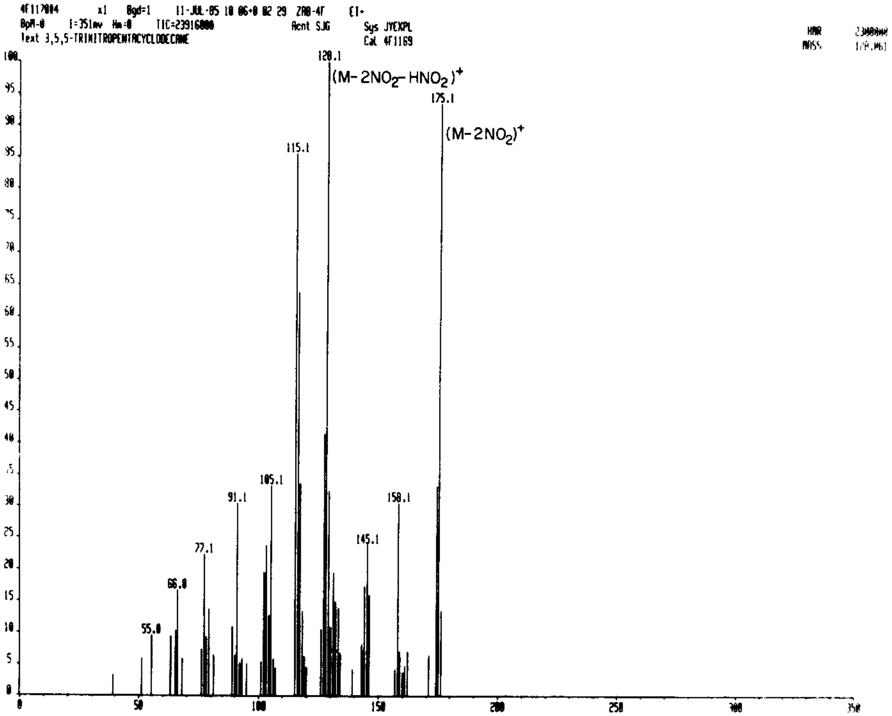


FIGURE 2
EI mass spectrum of 3,5,5-trinitropentacyclodecane.

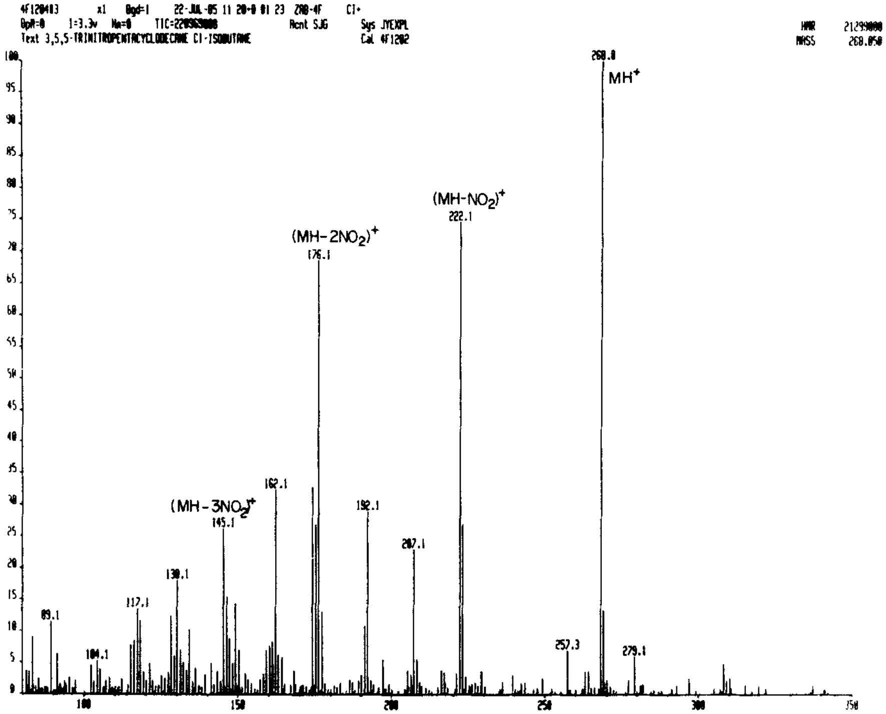


FIGURE 3
CI-isobutane mass spectrum of 3,5,5-trinitropentacyclodecane.

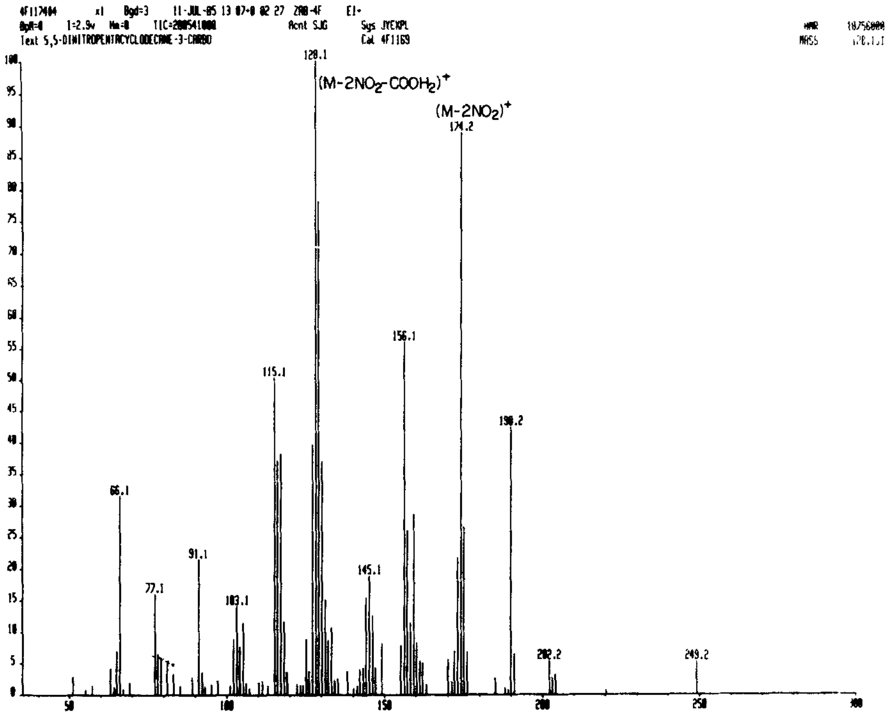


FIGURE 4

EI mass spectrum of 5,5-dinitropentacyclodecane-3-carboxylic acid.

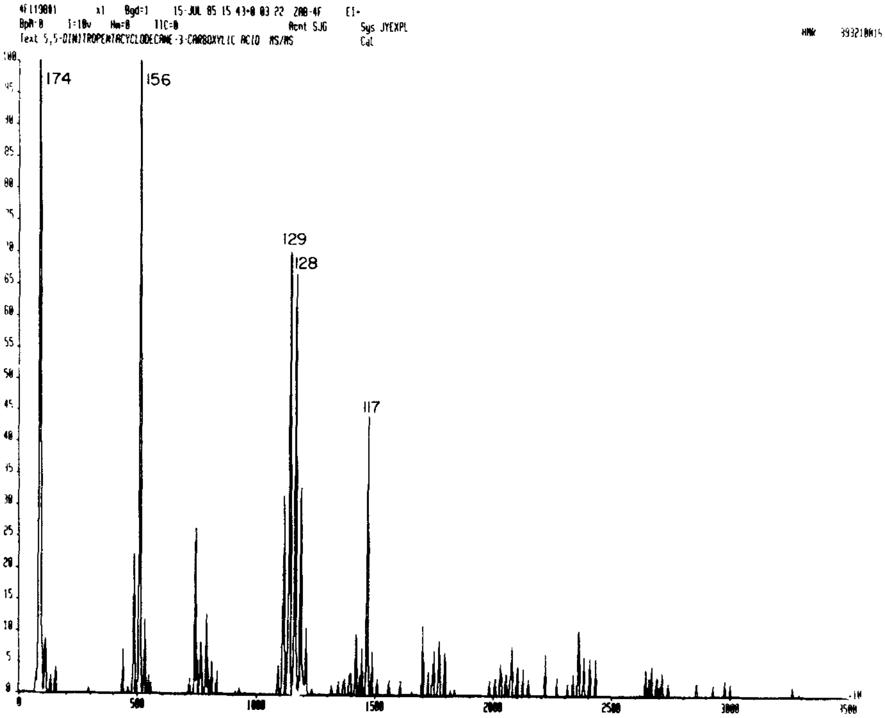


FIGURE 5
CID spectrum of m/z 174 ion of 5,5-dinitropentacyclodecane-3-carboxylic acid.

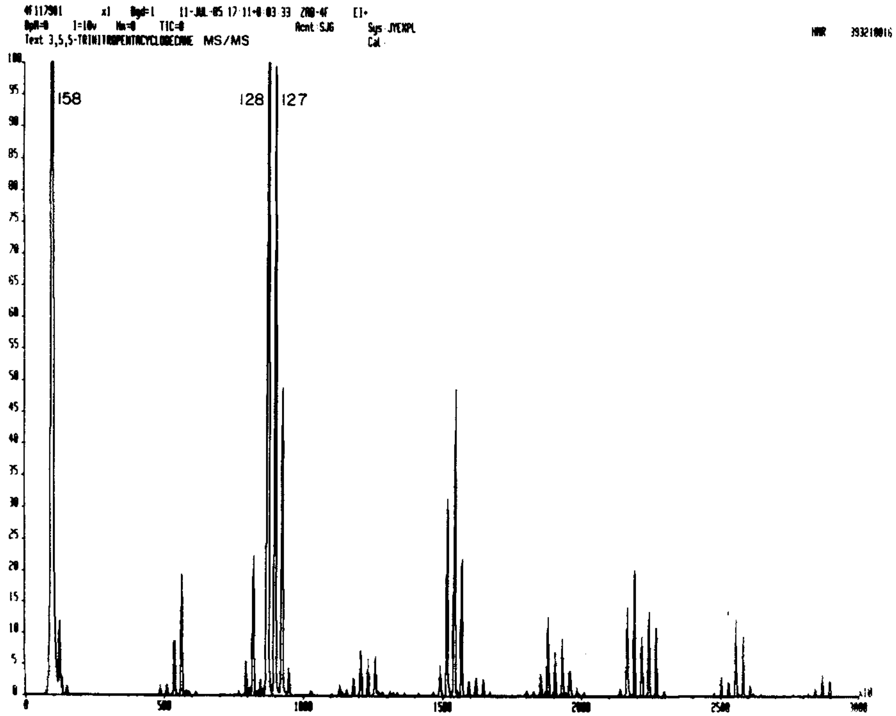


FIGURE 6
CID spectrum of m/z 158 ion of 3,5,5-trinitropentacyclodecane.

of TPCD in Figure 6. Figures 7 and 8 show the fragmentation pathway maps of the 2 compounds resulting from the CID spectra obtained. Only daughter ions having a relative abundance of at least 15% (relative to the most abundant daughter ion) were included. All parent and daughter ion intensities were established experimentally. Group losses were indicated only on daughter ions having relative abundances of 50% and more.

The fragmentation of both compounds begins with the loss of two NO_2 groups. No molecular ion is observed in their EI mass spectra. In TPCD, the loss of two NO_2 groups is followed by the loss of the third NO_2 group. Only then will the fragmentation of the hydrocarbon structure occur.

Results indicate that fragmentation of the C-N bonds takes place before fragmentation of the C-C bonds, as expected. The fragmentation maps by themselves do not provide any information concerning the rate of decomposition of the investigated compounds.

It has been shown that there is a large deuterium kinetic isotope effect in the thermal decomposition of methyl deuterated TNT,[12,13] of deuterated RDX[14] and of deuterated HMX.[14,15] A comparison of the thermal decomposition rates of deuterated RDX and normal RDX by thermogravimetric analysis resulted[14] in a ratio of rate constants of $K_H/K_D=1.5$.

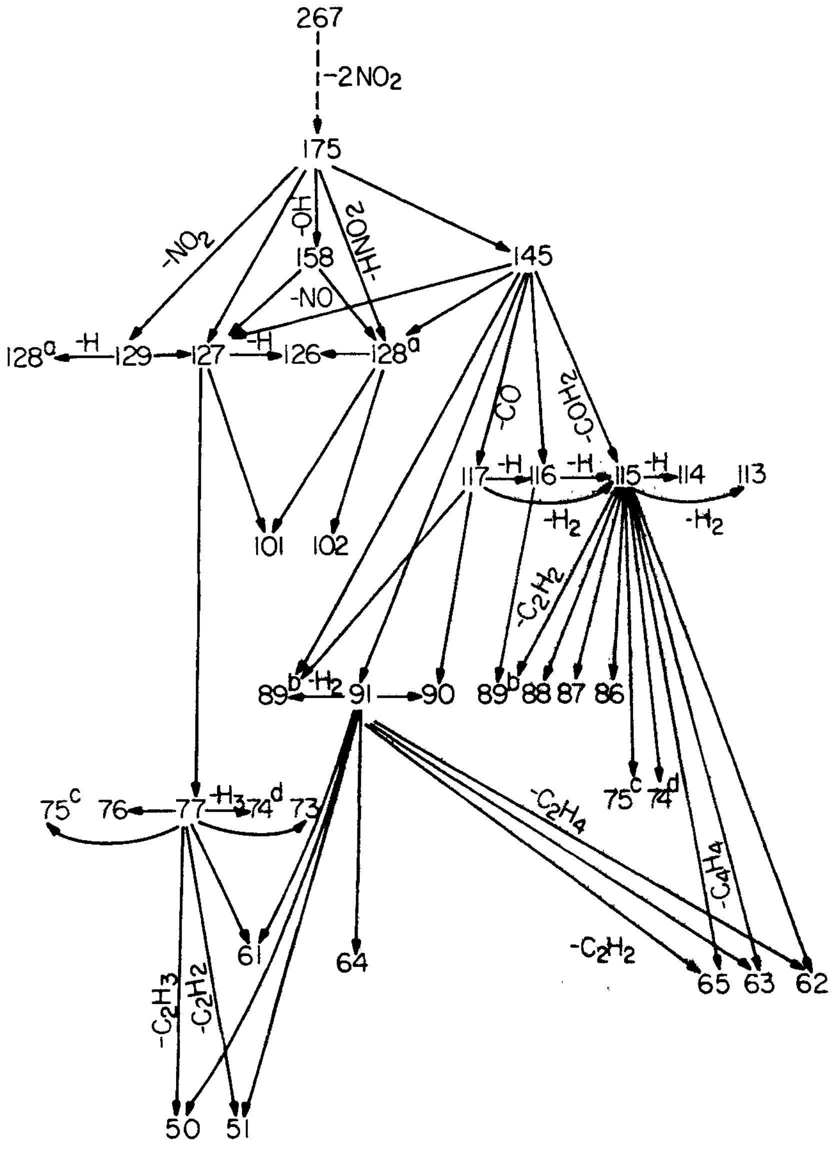


FIGURE 7
CID fragmentation pathway map of 3,5,5-trinitropentacyclodecane (molecular ion was not detected; dashed arrow denotes presumed pathway) a-a, b-b, c-c, d-d: similar letters denote identical ions - for simplicity of map drawing.

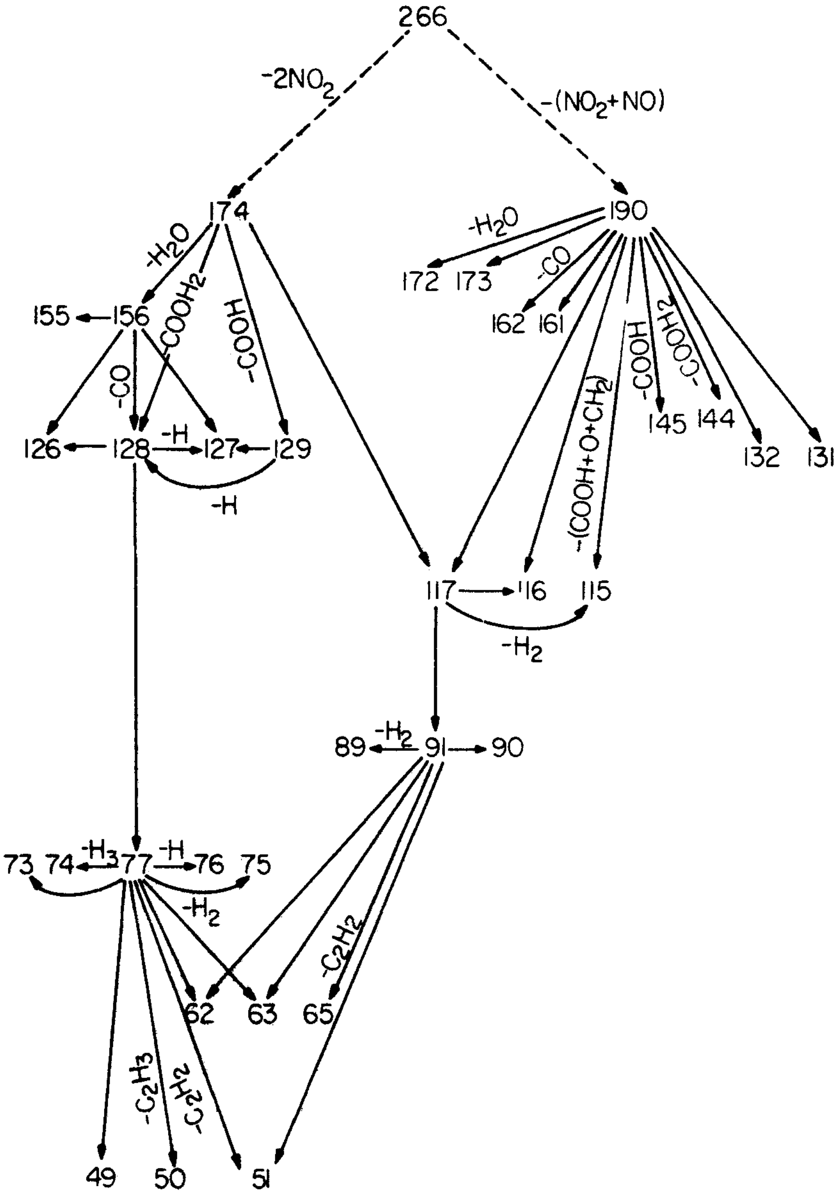


FIGURE 8
CID fragmentation pathway map of 5,5-dinitropentacyclodecane-3-carboxylic acid (molecular ion was not detected; dashed arrow denotes presumed pathway).

It would be therefore of interest to label with deuterium the investigated bishomocubanes and to obtain - by MS/MS CID - their fragmentation maps. A comparison of the fragmentation maps of the labeled and unlabeled compounds could give an indication of the relationship between the fragmentation processes and the rate of decomposition of these compounds.

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