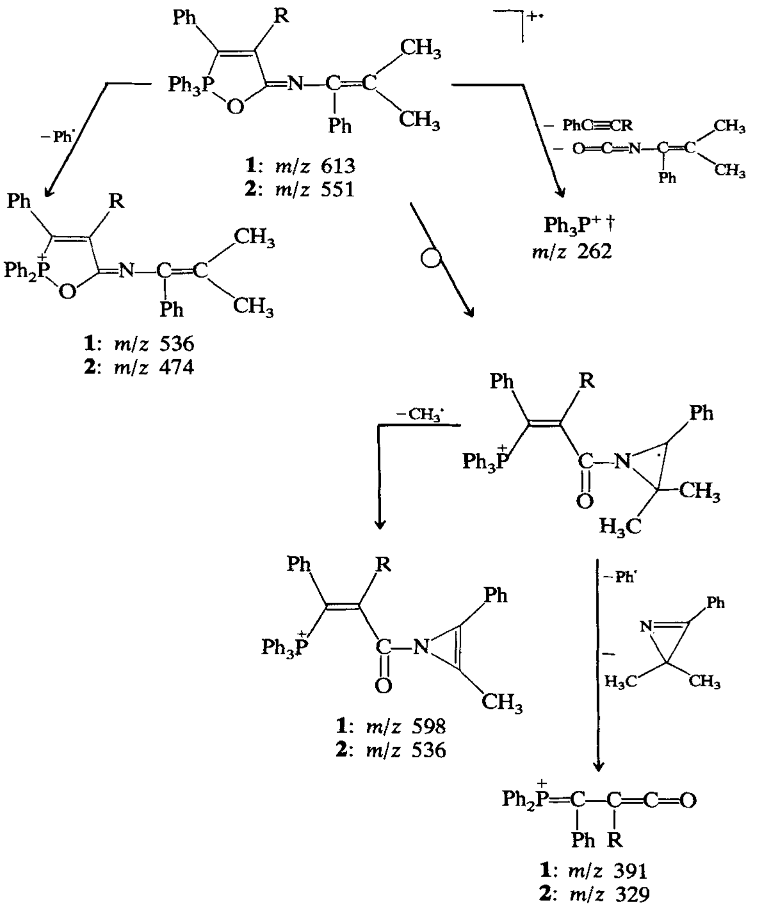
Table 1. Summary of MIKES of the molecular ion $[M]^{+\cdot}$(m/z 613)

m/z	Fragment ion rel. abund. in 70 eV EI spectrum	Neutral fragment lost
598	(26)	$CH_3^{\cdot}$
536	(13)	$Ph^{\cdot}$
508	(0.1)	
482	(0.3)	$(CH_3)_2C_2Ph^{\cdot}$
468	(3)	$(CH_3)_2C_2NPh$
440	(2)	$(CH_3)_2C_2(Ph)NCO$
391	(5)	$Ph^{\cdot} + (CH_3)_2C_2NPh$
335	(1)	Ph_3PO
262	(100)	$Ph_2C_2 + (CH_3)_2C_2(Ph)NCO$

m/z 262, we also observe peaks at $0.829E_1$, $0.786E_1$, $0.763E_1$, $0.718E_1$, $0.638E_1$ and $0.546E_1$ for the formation of product ions at m/z 508, 482, 468, 440, 391 and 335. The high intensities of the metastable transitions for the loss of methyl and the loss of phenyl + $(CH_3)_2C_2NPh$ at $0.638E_1$ suggest rearrangement processes. We, therefore, propose the fragmentation pathway shown in Scheme 1, the structures indicated are speculative and are meant to aid the visualization of the process. Solid arrows indicate transitions confirmed by MIKES for compound **1**.



Scheme 1

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Reference

1. A. Kascheres, A. C. Joussef and H. C. Duarte, *Tetrahedron Lett.* 1837 (1983).

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† The 70 eV mass spectrum of triphenylphosphine shows fragments at m/z 185, 183, 108 and 107.

Mass Spectra of *N*′-Isopropylidenealkanohydrazides

Recently, we have proposed *N*′-isopropylidenealkanohydrazides, R—CO—NH—N=C$(CH_3)_2$, as an alternative to methyl esters for chromatographic analyses of fatty acids in *O*-acyl lipids.[1] These derivatives are prepared by stepwise treatment of acyl lipids or methyl esters with hydrazine and acetone.[1] Because they strongly absorb light at 229 nm, their elution during high performance liquid chromatography is easily monitored by UV absorption.[2] The lower volatility of these compounds has made it feasible to analyse accurately short-chain alkanoic acids as their isopropylidenehydrazide derivatives.[3] Upon acidic hydrolysis or methanolysis of the isopropylidenehydrazide derivatives, either the acid or its ester can be regenerated.[1]

In this communication, the mass spectrum of *N*′-isopropylidenehexadecanohydrazide (**1**) has been described in order to illustrate the general mass spectral properties of fatty acid isopropylidenehydrazides. It is hoped that such a study will be helpful in analysis of fatty acids in lipids by gas–liquid chromatography/mass spectrometry, using the hydrazinolysis–acetonization method.

The mass spectrum of **1** contains a discernible molecular ion at m/z 310 (Fig. 1) and a strong $[M-CH_3]^+$ ion. The base peak of the spectrum is m/z 72. The second strongest peak in the spectrum, m/z 114, is formed by a McLafferty rearrangement.[4] The spectrum also contains structurally important ions having the general formula $[-(CH_2)_n-CO-NH-N=C(CH_3)_2]^+$, at m/z 127, 141, 155 ... A comparison of the spectrum of **1** with that of methyl hexadecanoate indicates that isopropylidenehydrazides are more amenable to mass spectral analyses than are methyl esters.

For the preparation of **1**, 1 g of methyl palmitate was refluxed with 20 ml of 50% hydrazine hydrate in ethanol for 3 h. To the reaction mixture was added 50 ml of water

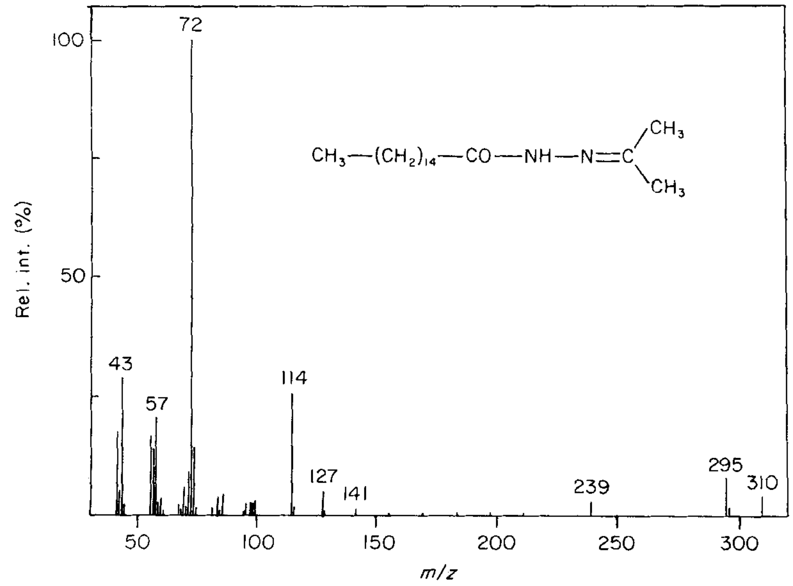

Figure 1. Mass spectrum of *N'*-isopropylidenehexadecanohydrazide (**1**).

and the resulting precipitate was filtered, washed with water and crystallized from 90% ethanol to yield pure palmitic acid hydrazide (m.p. 112–113°C). About 100 mg of the hydrazide was refluxed with 30 ml of acetone for 2 h. Acetone was removed under reduced pressure and the *N'*-isopropylidenehexadecanohydrazide was crystallized from acetone (m.p. 71–72°C). The mass spectrum was obtained by directly injecting the compound in a Varian-MAT CH7 mass spectrometer at 70 eV.

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References

1. V. P. Agrawal, *J. Lipid Res.* **24**, 216 (1983).
2. V. P. Agrawal and E. Schulte, *Anal. Biochem.* **131**, 356 (1983).
3. V. P. Agrawal, unpublished results.
4. H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco (1967).

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