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EI-MS UNIDIRECTIONAL TRIPLE HYDROGEN REARRANGEMENT
I. THE CASE OF LONG CHAIN PHENYLAZOBENZOATES

IOAN OPREAN [a)], **BIANCA MOLDOVAN** [a)], **RADU OPREAN** [b)]

[a] *Faculty of Chemistry and Chemical Engineering, Organic Chemistry Department, "Babeş-Bolyai" University, 400028 Cluj-Napoca, Romania*
[b] *Faculty of Pharmacy, "Iuliu Haţieganu" University of Medicine and Pharmacy, Cluj-Napoca, Romania*

ABSTRACT. The aim of our study was to determine the various hydrogen rearrangements in the mass spectra of some long chain esters. We demonstrated that in the EI-MS spectra of long chain phenylazobenzoates appears a triple hydrogen rearrangement ion because of the migration of the hydrogen from the hydrocarbonated part to the phenyl rest of the molecule if the chain has more than 8 carbon atoms. The abundance of this ion proceeds to the extent of 0,5% to 70% of the basis peak of the mass spectrum and it exhibits an increase with the increase of the chain length.

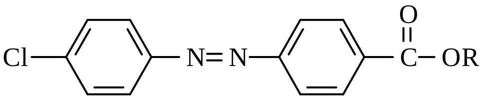
Keywords: mass spectrometry, hydrogen rearrangement, phenylazobenzoates

INTRODUCTION

Unidirectional double hydrogen rearrangement reactions are characteristic features in the mass spectra of many esters [1], whereas unidirectional triple hydrogen migrations are extremely rare [2]. This phenomenon was observed only in the particular case of alkyl esters of trimellitic anhydride.[3]

We have found that unidirectional hydrogen rearrangement reactions take place in the long chain esters of *p*-(4'-chlorophenylazo)benzoic acid **1** (CABE) with a greater probability that in the cases previously mentioned.

p-Phenylazobenzoates have been synthesized as useful derivatives of normal alcohols [4].



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The main aim of the present work is to report the EI mass spectra of more than 20 *n*-alkyl esters of *p*-(4'-chlorophenylazo) benzoic acid (CABE), devoting our attention to the factors that influence the appearance and the abundance of the triple hydrogen rearrangement ions.

EXPERIMENTAL

The saturated alcohols used were commercially available and obtained from Analabs (Germany) as a fatty alcohol kit, and odd carbon alcohols were purchased from Sigma Chemical Co. and used without further purification.

Mass spectra were recorded on a GC-MS system, at 70 eV, model Hewlett-Packard 5890 II/5972.

For the synthesis of *p*-(4'-chlorophenylazo)benzoates **1** we had to adapt the method of Hecker [5] to microscale. A mixture of 2,8 mg *p*-(4'-chlorophenylazo) benzoyl chloride (0,01 mM), the appropriate alcohol (0,015 mM), 10 µL pyridine and 1 mL benzene was left standing for 24 h by room temperature. The benzene solution was successively extracted twice with 0,1 N H_2SO_4, saturated $NaHCO_3$ solution and water, dried over sodium sulfate and filtered. The benzene solution was chromatographically separated on silicagel using benzene as eluent and the solvent was removed.

RESULTS AND DISCUSSION

Figures 1 and 2 show the EI mass spectra (70 eV) of *n*-butyl (C_4-CABE) and *n*-tetradecyl *p*-(4'-chlorophenylazo)benzoate (C_{14}-CABE), respectively.

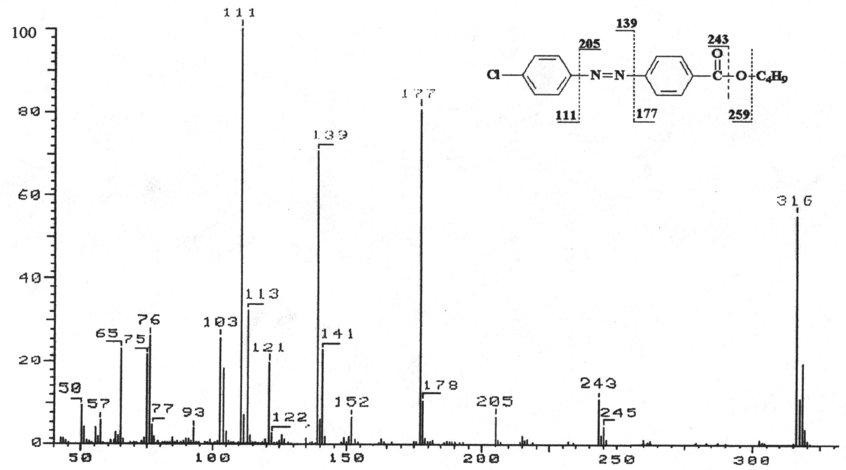


Fig. 1. *Mass spectrum of n-butyl-p-(4'-chlorophenylazo)benzoate* ***1d*** *(C_4-CABE)*

From Fig.1 it is apparent that, in the case of the *n*-butyl *p*-(4'-chlorophenylazo) benzoate (C_4-CABE), the most abundant ions are generated by alternative C-N cleavage of phenylazo group [6] (m/z: 111, 139, 177, 205). Cleavage of the acyl-oxygen bond generates the m/z ion 243 (10%), while an oxygen-alkyl cleavage with concurrent transfer of one or two hydrogen atoms (m/z 260, respectively m/z 261) characteristic for *n*-butyl benzoate [1] has a minimal importance.(I<1%).

On the contrary, it was found from Fig.2 that, in the case of *n*-tetradecyl *p*-(4'-chlorophenylazo) benzoate (C_{14}-CABE) the peak of m/z ion 261 (28%) corresponding to the oxygen-alkyl cleavage with transfer of two hydrogens is accompanied by a more abundant peak at m/z 262 (53%) corresponding to a triple hydrogen transfer. Interesting was to remark that no C-C cleavage in the long chain of the ester was observed in contrast to the other esters [7]. Partial spectra of C_1-C_{18} alkyl *p*-(4'-chlorophenylazo)benzoates are shown in the Table 1.

From the Table 1 is to be observed that, compounds **1a**-**1d** (C_1-C_4 CABE) show very similar spectra with the *n*-butyl-*p*-(4'-chlorophenylazo)benzoate (C_4-CABE) from Fig.1. In the spectra of **1e-1g** (C_5-C_7 CABE) the peak m/z 260 (1H transfer)

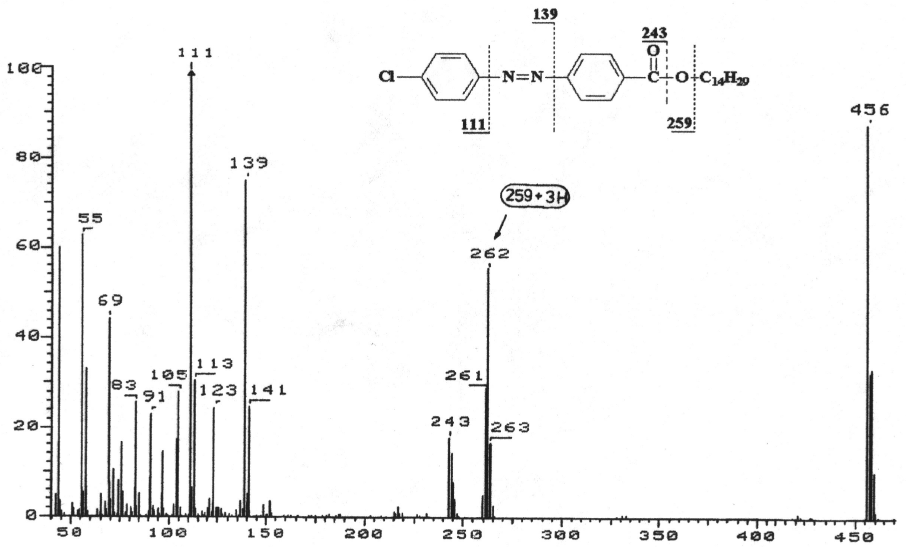


Fig. 2. *Mass spectrum of n-tetradecyl-p-(4'-chlorophenylazo)benzoate **1n** (C_{14}- CABE)*

Table 1

Partial EI-MS spectra of *n*-alkyl *p*-(4'-chlorphenylazo)benzoates **1** (R=alkyl) (C_1-C_{18} CABE)

Crt. No.	R	Relative intensity of ions (%)(base peak=100)	
		261* (2H)	262* (3H)
1a	CH_3	-	-
1b	C_2H_5	-	-
1c	C_3H_7	-	-
1d	C_4H_9	-	-
1e	C_5H_{11}	0,6	-
1f	C_6H_{13}	1,0	-
1g	C_7H_{15}	1,7	-
1h	C_8H_{17}	3,4	0,5
1i	C_9H_{19}	6,0	8,0
1j	$C_{10}H_{21}$	7,2	7,0
1k	$C_{11}H_{23}$	14,0	35,0
1l	$C_{12}H_{25}$	19,2	30,0
1m	$C_{13}H_{27}$	27,0	60,0
1n	$C_{14}H_{29}$	27,0	53,0
1o	$C_{15}H_{31}$	41,0	92,0
1p	$C_{16}H_{33}$	35,0	70,0
1q	$C_{17}H_{35}$	31,0	62,0
1r	$C_{18}H_{37}$	42,0	87,0

* corrected for naturally occurring heavy isotopic contributions

becomes more intensive and appears a new peak at m/z 261 (2H transfer). The peak m/z 262 corresponding to a triple hydrogen transfer (3H) proceeds in the compounds **1h-1r** to the extent of 0,5-70% of the base peak of spectrum. The abundance of this ion exhibits an increase with the increase of chain's length. The same chain length dependence shows the abundance of the ions m/z 261 (2H transfer) and m/z 244 (m/z 262-H_2O).

From the Fig. 3 we can observe that this dependence is more accentuated in the case of triple hydrogen transfer ions (m/z 262).

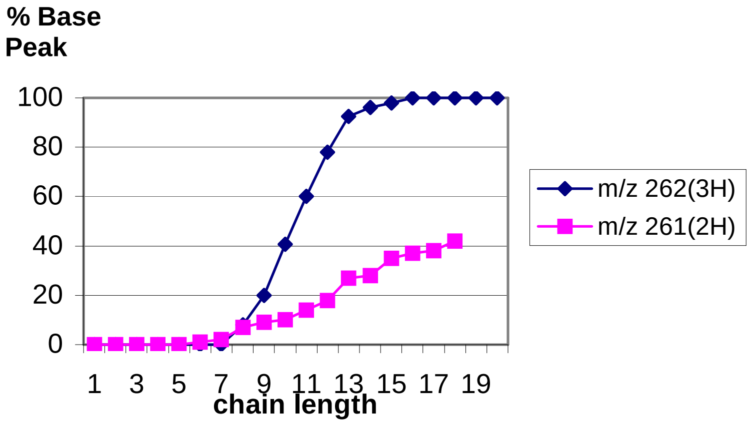
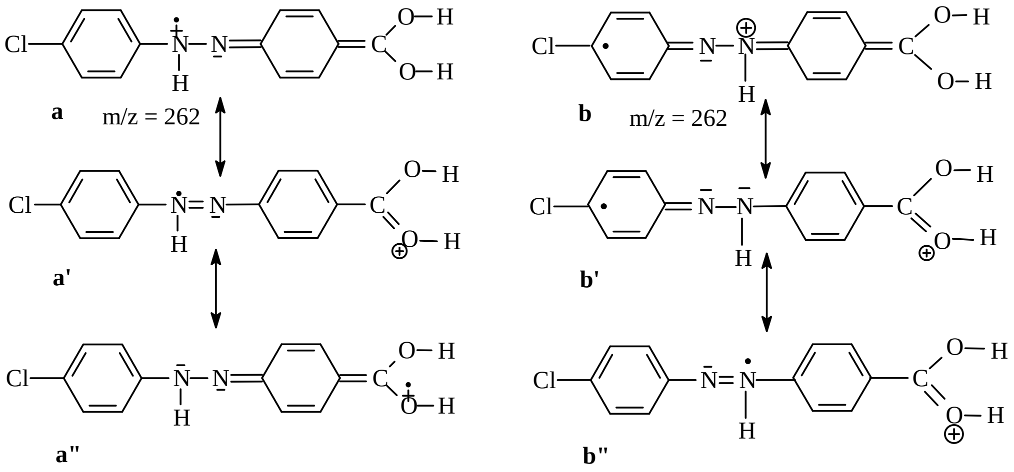


Fig. 3. *Effect of chain length on relative intensities of rearranged ions in C_1-C_{18} CABE*

The genesis of the ion m/z 262 (3H) is possible to explain through a long-range intramolecular interaction between alkyl chain and nitrogen atoms of the azo group accompanied by the expected transfer of two hydrogens typical for carboxylic acid esters, in a similar manner with hydrogen migration in long chain esters of trimellitic anhydride [3] . The multiple resonance formula of this ions (a, a', a" or b, b' ,b") explain, probably, its great abundance.



CONCLUSIONS

In the EI-MS spectra of long chain phenylazobenzoates appears a triple hydrogen rearrangement ion because of the migration of the hydrogen from the hydrocarbonated part to the phenyl rest of the molecule if the chain has more than 8 carbon atoms.

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