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EI-MS UNIDIRECTIONAL TRIPLE HYDROGEN REARRANGEMENT.
II. THE CASE OF LONG CHAIN BENZOATES

BIANCA MOLDOVAN [a)], IOAN OPREAN [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. Similarly with our previously reported EI-MS spectra of long chain phenylazobenzoates, unidirectional triple hydrogen rearrangement was also observed in the series of some diazobenzoates and analog long chain esters as well as in the series of some benzoate long chain esters containing electron withdrawing substituents in the aromatic moiety. The intensity of the triple hydrogen rearrangement ion is in good agreement with σ- Hammett values.

Keywords: EI-MS spectrometry, triple hydrogen rearrangement, σ- Hammett, benzoates

INTRODUCTION

In a previous work [1] we reported an unidirectional triple hydrogen rearrangement in the mass spectra of some long chain chlorophenylazobenzoates.

Unidirectional double hydrogen rearrangement reactions are characteristic features in the mass spectra of many esters [2], whereas unidirectional triple hydrogen migrations are extremely rare [3]. This phenomena was observed only in the particularly case of the *n*-alkyl esters of the trimellitic anhydride.[4].

The aim of the present work was to determine if the chlorine atom, the azo-group or the aromatic ring have an influence on the occurrence and the abundance of the triple hydrogen rearrangement ion. Therefore, we intended to synthesize a series of *n*-alkyl esters of phenyldiazobenzoates without the chlorine atom in the *p'*-position as well as series with modified diazo-group.

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.

The tetradecyl ester of N-(4-carboxybenzylidene) aniline **2** was prepared by the condensation of aniline with the tetradecyl ester of terephthalaldehydic acid by refluxing 4 hours in benzene and in the presence of catalytic amounts of toluene-*p*-sulfonic acid, in analogy with the alkyl N-benzylideneanthranylates [5].

The tetradecyl ester of 4-carboxyl-N-(benzylidene)aniline **3** was prepared by the condensation of benzaldehyde with the tetradecyl *p*-aminobenzoate in benzene 4 hours under reflux in the presence of catalytic amounts of toluene-*p*-sulfonic acid, in analogy with the alkyl N-benzylideneanthranylates [5].

The tetradecyl ester of 4-carboxystilbene **4** was prepared by the condensation of cinnamic acid with the diazonium salt of tetradecyl *p*-aminobenzoate in analogy with other alkyl esters of 4-carboxystilbene [6].

The tetradecyl *p*-aminobenzoate **5** was prepared by treatment of the sodium *p*-aminobenzoate with myristyl bromide (Sigma) in dimethylformamide at 130°C, in analogy with other long chain benzoates [7].

Substituted alkyl benzoates **6-11** were prepared from differents benzoyl chlorides, tetradecyl alcohol, pyridine and benzene. The initial mixture was refluxed for one hour [8]. The corresponding nitro- and cyanobenzoyl chlorides are commercially available products (Sigma). The terephthalaldehydic acid chloride was prepared by boiling the terephthalaldehydic acid with thionyl chloride [9].

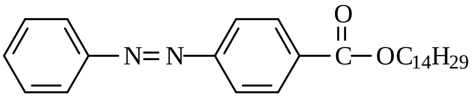
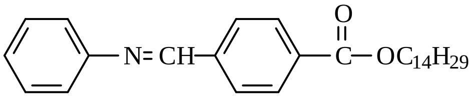
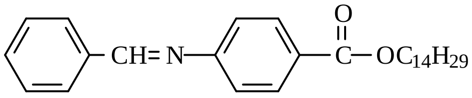
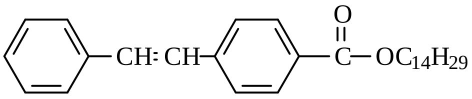
The tetradecyl *p*-nitrobenzenesulfonate **12** was prepared from commercial *p*-nitrobenzenesulfonyl chloride and myristyl alcohol in analogy with other long chain benzenesulfonates[10].

RESULTS AND DISSCUSION

The triple hydrogen rearrangement is not limited to the mass spectra of long chain esters of *p*-(4'-chlorophenylazo)benzoates previously described [1]. In Table 1 are presented some selected data from the mass spectra of different aromatic long chain esters. From the examples it is to conclude that the presence of the chlorine atom in the phenylazobenzoates is not necessary, but it is useful for fragments identification.

Table 1

The occurrence of hydrogen transfer ions in some diazobenzoates and analog long chain esters

Comp. No.	Structure	Rel. Int* %		
		[1H]	[2H]	[3H]
1		4	24	33
2		8	100	2
3		27	42	13
4		1	0,5	-

** corrected for naturally heavy occurring isotopic contributions*

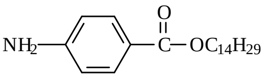
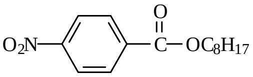
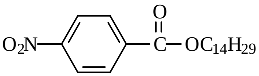
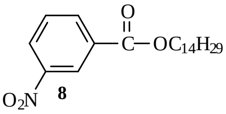
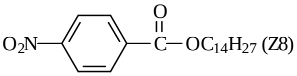
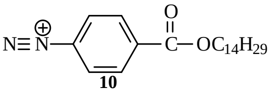
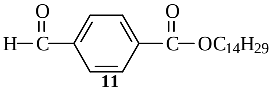
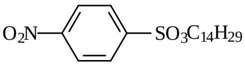
By alternative replacement of one nitrogen atom from the N=N group with CH group in the compound **1**, the abundance of the ion m/z 227 corresponding to the triple hydrogen migration decreases (compounds **2** and **3**). By replacement of both nitrogen atoms with CH=CH group the triple hydrogen migration disappears altogether (compound **4**).

This fact suggests that the substituent from the *para*-position of the benzoate ester may influence the appearance of the triple rearranged ion. To elucidate this supposition we studied the mass spectra of some benzoate long chain esters with different substituents on the aromatic ring. (Table 2)

The mass spectra of unsubstituted [1] *p*- and *m*-methoxy- as well as *p*-amino long chain long chain benzoates show no triple hydrogen rearrangement.

Table 2

The occurrence of hydrogen transfer ions in some substituted aromatic long chain esters

Structure	Rel. Int* %		
	[1H]	[2H]	[3H]
 **5**	100	8	-
 **6**	1	34	17
 **7**	1	37	81
 O$_2$N **8**	4	8	23
 **9**	1	29	76
 **10**	2	93	22
 **11**	2	100	57
 **12**	-	5	3

**corrected for naturally occurring heavy isotopic contributions*

The presence of a NO_2, CN, or CHO group in the *p*- or *m*- position in the long chain benzoates appears to be essential for the triple hydrogen transfer. This substituent effect on the triple hydrogen transfer is in good agreement with Hammet's σ_p values (Table 3).

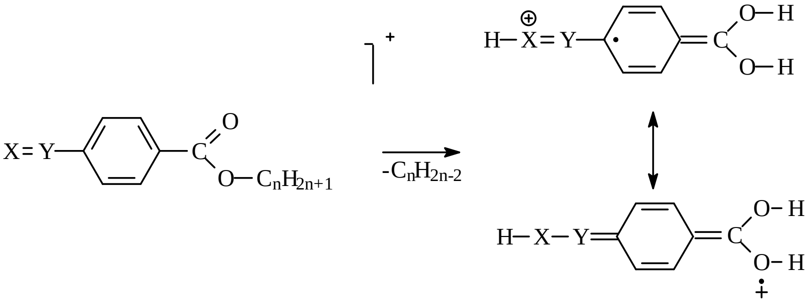
Table 3

The abundance *p*-X-$C_6H_4COOH_3$/ *p*-X-$C_6H_4COOH_2$ ratio and the σ_p values for several alkylbenzoates

X	[3H]/[2H]	σ_p
NH_2	0	-0,66
OCH_3	0	-0,27
H	0	0
CN	0,24	0,66
CHO	0,57	0,22
N=N-C_6H_5	1,37	0,64
NO_2	2,19	0,778

CONCLUSIONS

It may be concluded that electron withdrawing substituents in long chain benzoates favorise the building of triple hydrogen transfer ions. This phenomenon is present in the corresponding substituted long chain sulphonates too.



In view of their intrinsic interest as well as their significant mechanistic implications, we are continuing in our laboratory the examination of unidirectional triple hydrogen rearrangements in long chain compounds.

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