

ELECTRON-IMPACT-INDUCED HYDROGEN MIGRATION IN ORGANIC MOLECULES—III :
DOUBLE HYDROGEN MIGRATION IN SUBSTITUTED TERT-BUTYLBENZOATES

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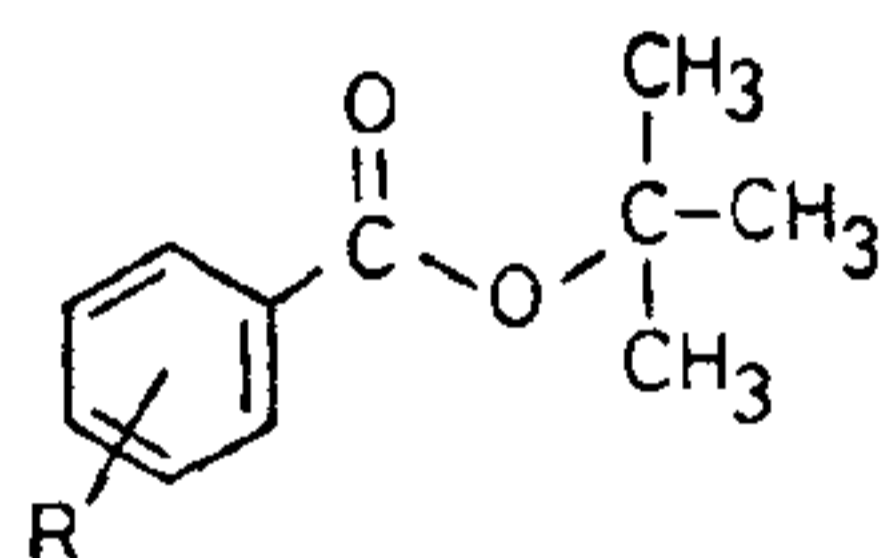
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ABSTRACT

The mass spectra of substituted tert-butylbenzoates contain fragments resembling the corresponding protonated acids, the formation of which involve a double hydrogen rearrangement in the molecular ion. The mechanism and the substituent effect of this process are discussed.

INTRODUCTION

THE fragmentation involving double hydrogen transfer is noticed in the mass spectra of aliphatic esters¹⁻⁷, higher alkyl benzoates^{8,9,10}, N-alkylmaleimides¹¹, substituted diaziridinones¹², substituted uracils¹³, methoxy carbonyl hydrazones¹⁴ and certain organophosphorus esters^{15,16}. Labelling studies have shown that the observed double hydrogen transfer is non-site specific in nature and the mechanism of this process is not clearly established in many of the cases. This paper presents a double hydrogen migration observed in the mass spectra of tert-butylbenzoates (I to IX) (Scheme I).



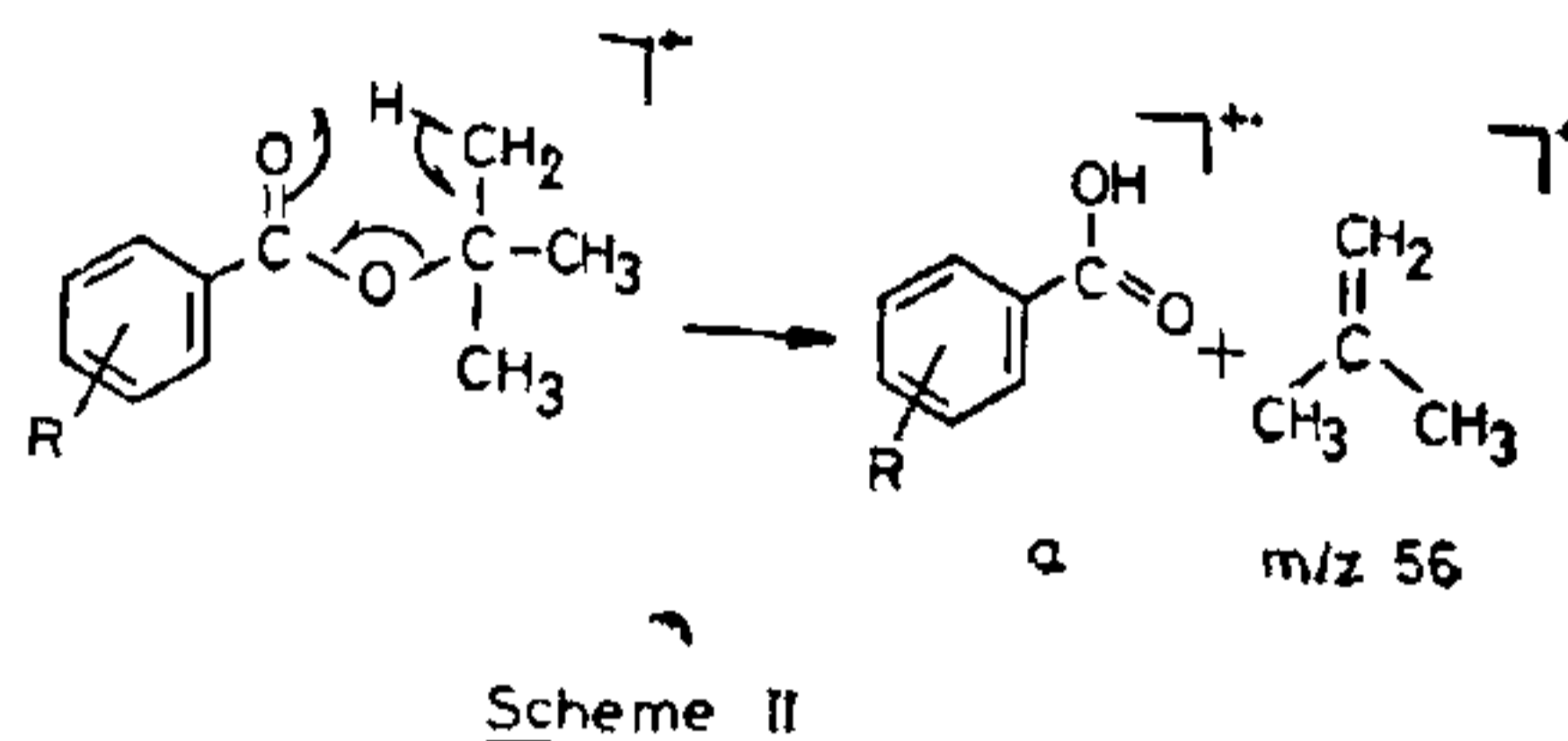
- I R = H
- II R = o-CH₃
- III R = m-CH₃
- IV R = p-CH₃
- V R = p-OH
- VI R = o-COOH
- VII R = o-NO₂
- VIII R = m-NO₂
- IX R = p-NO₂

Scheme I

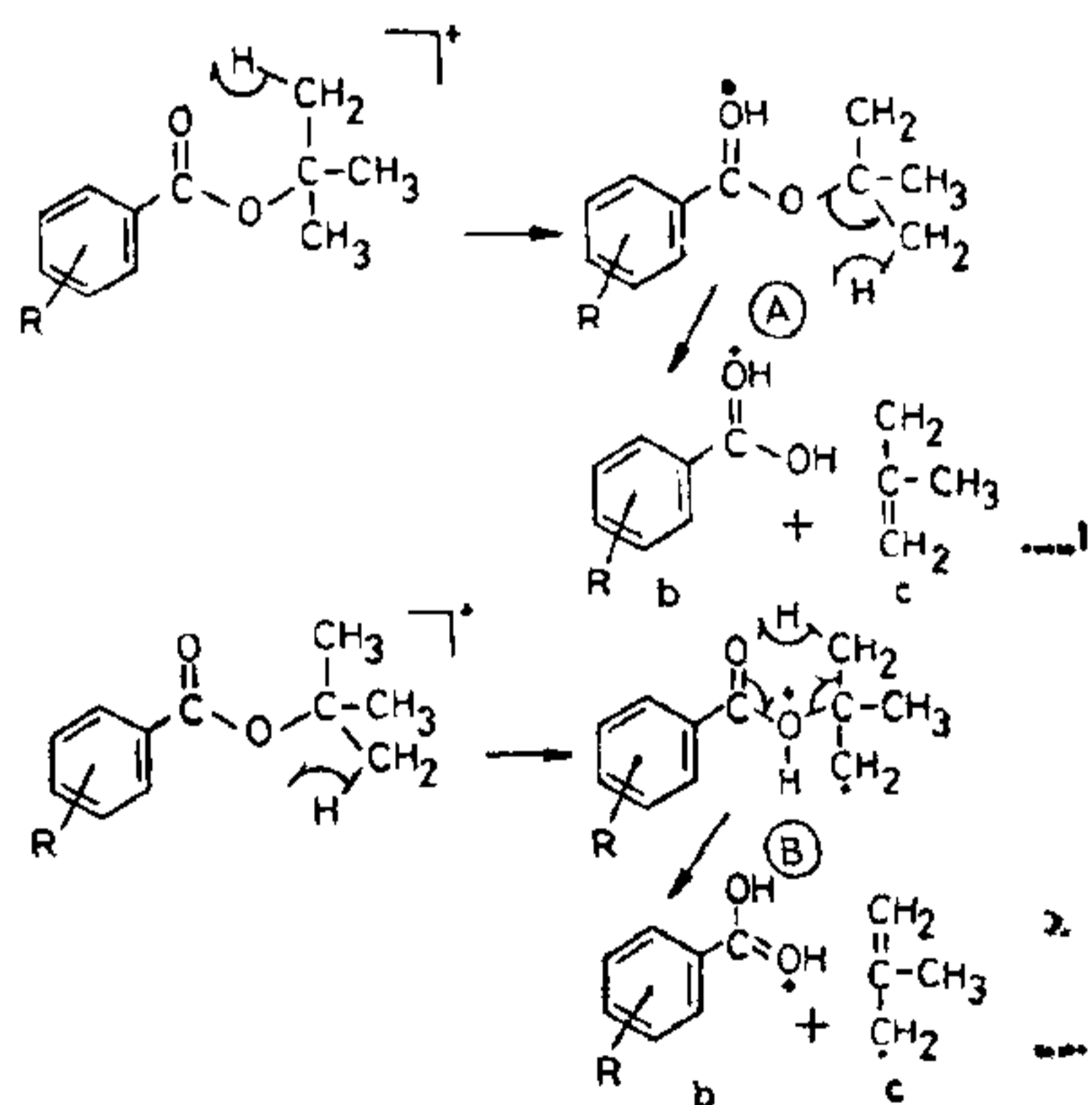
RESULTS AND DISCUSSION

The molecular ion is absent in the mass spectra of all the tert-butylbenzoates (Table I). The expected tert-butyl cation at *m/z* 57 happens to be either the base peak or an intense peak except in the case of compounds IV and V. The McLafferty rearrangement ion 'a' originating through a simple γ -hydrogen migration (Scheme II) is insignificant in all the mass spectra except in the case of III, but this mode of hydrogen transfer places the charge on the common fragment at *m/z* 56.

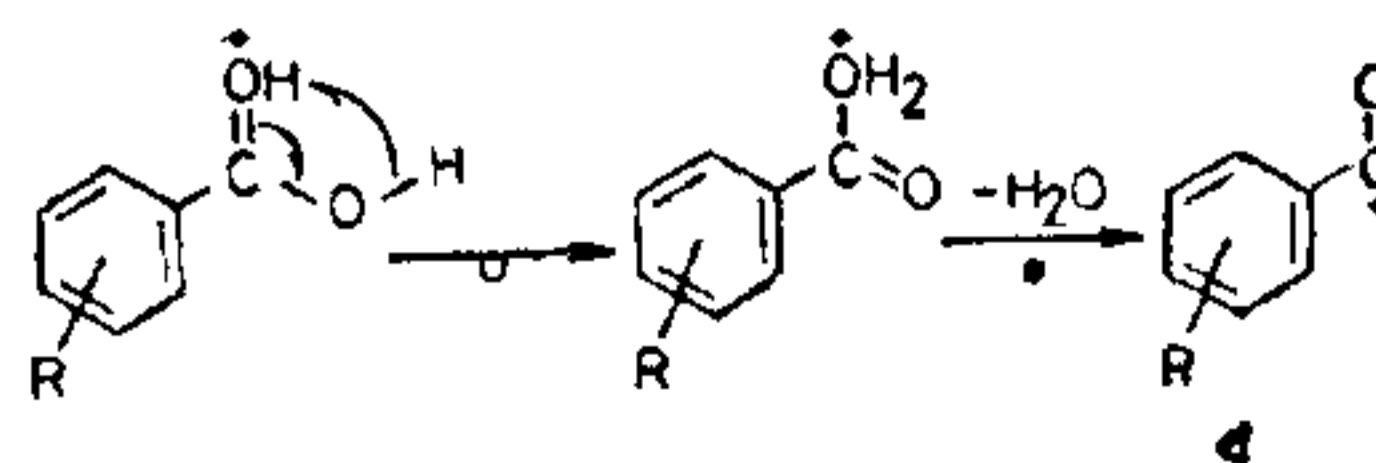
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The anticipated double hydrogen migration is observed (Table I) in almost all the compounds on electron-impact. The formation of a stable ion *b* resembling the corresponding protonated acid and a stable allylic radical *c* may be the driving force for the double hydrogen transfer. Two possible mechanisms can be envisaged for the double hydrogen migration process which are shown in Scheme III.



Scheme III



Scheme IV

TABLE I
Partial mass spectra of compounds I to IX

Compound									$\Sigma_{30}^{M^+}$ of <i>b</i>
R =		56	57	C ₆ H ₄ -R	<i>a</i>	<i>b</i>	<i>d</i>	M ⁺	
I.	H	35	69	34 (<i>m/z</i> 77)	9 (<i>m/z</i> 122)	100 (<i>m/z</i> 123)	95 (<i>m/z</i> 105)	1 (<i>m/z</i> 178)	25
II.	<i>o</i> -CH ₃	12	100	34 (<i>m/z</i> 91)	.. (<i>m/z</i> 136)	71 (<i>m/z</i> 137)	63 (<i>m/z</i> 119)	3 (<i>m/z</i> 192)	16
III.	<i>m</i> -CH ₃	30	93	86 (<i>m/z</i> 91)	87 (<i>m/z</i> 136)	59 (<i>m/z</i> 137)	100 (<i>m/z</i> 119)	3 (<i>m/z</i> 192)	8
IV.	<i>p</i> -CH ₃	100 (<i>m/z</i> 91)	.. (<i>m/z</i> 136)	69 (<i>m/z</i> 137)	74 (<i>m/z</i> 119)	.. (<i>m/z</i> 192)	18
V.	<i>p</i> -OH	24 (<i>m/z</i> 93)	.. (<i>m/z</i> 138)	85 (<i>m/z</i> 139)	100 (<i>m/z</i> 121)	.. (<i>m/z</i> 194)	34
VI.	<i>o</i> -COOH	35	100	.. (<i>m/z</i> 121)	.. (<i>m/z</i> 166)	18 (<i>m/z</i> 167)	70 (<i>m/z</i> 149)	.. (<i>m/z</i> 222)	4
VII.	<i>o</i> -NO ₂	42	100	.. (<i>m/z</i> 122)	.. (<i>m/z</i> 167)	11 (<i>m/z</i> 168)	50 (<i>m/z</i> 150)	1 (<i>m/z</i> 223)	2
VIII.	<i>m</i> -NO ₂	57	100	4 (<i>m/z</i> 122)	1 (<i>m/z</i> 167)	4 (<i>m/z</i> 168)	70 (<i>m/z</i> 150)	2 (<i>m/z</i> 223)	1
IX.	<i>p</i> -NO ₂	72	100	1 (<i>m/z</i> 122)	.. (<i>m/z</i> 167)	.. (<i>m/z</i> 168)	65 (<i>m/z</i> 150)	2 (<i>m/z</i> 223)	..

Marked substituent effect is noticed for the double hydrogen migration process. The intensity of this fragment *b* in terms of the total ion current is enhanced (Table I) by the electron releasing groups which stabilize the positive charge on the benzoyl carbon. On the contrary electron attracting groups deactivate the charge reducing the intensity of *b*.

EXPERIMENTAL

All the compounds discussed in this work are known in the literature and were prepared by the procedure already reported^{17,18}. The purity of the compounds was checked by TLC and the structures were confirmed by I.R. and N.M.R. spectral data.

All the mass spectra were run on a Varian MAT CH 7 Mass Spectrometer at an electron voltage of 70 eV and a trap current of 100 μ A. The temperature of the ion source was 150°C. A direct insertion probe at 20°C for compounds IV, VI and IX, 50°C for compounds VII and VIII and 120°C for compound V were used and the liquid inlet system (EMI) was used at a temperature of 150°C for compounds I, II and III.

- Kingston, D. G. I., Bursey, J. T. and Bursey, M. M., *Chem. Revs.*, 1974, 74, 228.
- McLafferty, F. W., *Interpretation of Mass Spectra*, Benjamin, W. A., Inc., 1967, p. 137.
- and Hamming, M. C., *Chem. and Ind. (London)*, 1958, p. 1366.

- Godbole, E. W. and Kebarle, P., *Trans. Faraday Soc.*, 1962, 58, 1897.
- Harrison, A. G. and Jones, E. G., *Can. J. Chem.*, 1965, 43, 960.
- Djerassi, C. and Fenselau, C., *J. Amer. Chem. Soc.*, 1965, 87, 5756.
- Benz, W. and Biemann, K., *Ibid.*, 1964, 86, 2375.
- Budzikiewicz, H., Djerassi, C. and Williams, D. H., *Mass Spectrometry of Organic Compounds*, Holden-Day Publ., Inc., San Francisco, 1967, p. 203.
- Bencit, F. M. and Harrison, A. G., *Org. Mass. Spectrom.*, 1976, 11, 1056.
- Tajima, S., Azami, T., Shizuka, H. and Tsuchiyz, T., *Ibid.*, 1979, 14, 499.
- Feast, W. J., Put, J., deSchryver, F. C. and Compennolle, F. C., *Ibid.*, 1970, 3, 507.
- Lengyel, I., Greene, F. D. and Pazos, J. F., *Ibid.*, 1970, 3, 623.
- Reiser R. W. *Ibid.*, 1969, 2 (5), 467.
- Maclead, J. K., Becher, D. and Djerassi, C., *J. Org. Chem.*, 1966, 31, 4050.
- Pritchard, J. G., *Org. Mass. Spectrom.*, 1970, 3, 163.
- Haake, P. and Ossip, P. S., *Tetrahedron*, 1968, 24, 565.
- Norris, J. F. and Rigby, G. W., *J. Amer. Chem. Soc.*, 1932, 54, 2099.
- Cwallina, G. E. and Gringawz, A., *J. Org. Chem.*, 1961, 26, 3344.