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MASS SPECTRAL FRAGMENTATION OF t-BUTYL GLYCIDIC ESTERS

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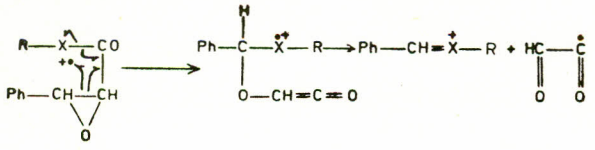
A number of t-butyl glycidic esters were prepared and they were subjected to mass spectral fragmentation analysis. The pattern of fragmentation supports the formation of tropylium ion as intermediates.

One of the more useful transformations of glycidic esters concerns their conversion to aldehydes and ketones. The most important method, which does not require any acid treatment, is the direct pyrolysis of t-butyl glycidic esters to isobutylene, carbon dioxide and the desired carbonyl compounds [1].

Knowing these results we wished to study the fragmentation pattern of t-butyl glycidic esters, presuming that these compounds would also undergo cleavage with electron impact. Although during the last fifteen years several mass spectral studies of epoxide containing groups have been undertaken (including an attempt to investigate the interaction of an epoxide ring with a closely situated carbonyl function as is found in glycidic esters) only a few aromatic representatives have been examined so far. On the basis of the mass spectra of a number of β-phenyl glycidic esters and amides it was postulated that the rearrangement of the molecular ion proceeds through the following skeletal rearrangement [2].

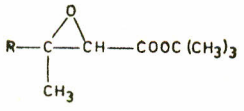


X = O, R = alkyl (in esters)

X = NH, R = H or alkyl (in amides)

RESULTS AND DISCUSSION

We prepared a number of t-butyl glycidic esters.



where R = $-C_6H_5$, $-C_6H_4NO_2$, $-C_6H_4Br$ and $-C_6H_4CH_3$ and subjected them to mass sepectrometric fragmentation analysis. The fragmentation pattern indicated cleavage of the epoxide ring with the formation of methyl tropylium ion. The normal course of fragmentation pattern is summarised in Scheme 1 and the relative abundance of these species are given in Table 1. No parent ion peak was observed due to the instability of the parent ion, a behaviour which is in conformity with the instability of such esters on pyrolysis.

Scheme 1

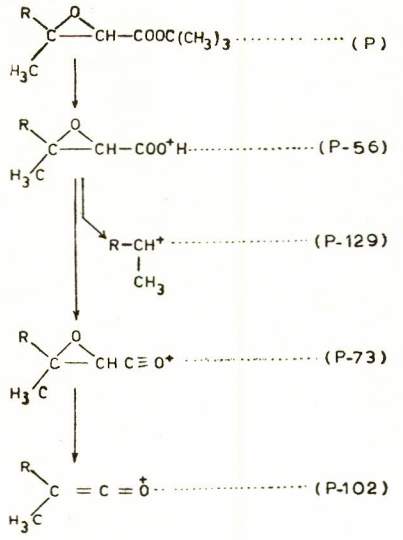


Table 1. Relative ion abundance of various fragments of t-butyl glycidic esters.

Compound where R=	$-C_6H_5$		$-C_6H_4NO_2$		$-C_6H_4Br$		$-C_6H_4CH_3$		
Parent ions	*m/e*	R.A.	*m/e*	R.A.	*m/e*	R.A	*m/e*	R.A.	Species formed
P	234	—	279	—	312	—	248	—	$C_{14}H_{18}O_3$
P—56	178	65	223	42	256	39	192	49	$XC_{10}H_{10}O_3+$
P—73	161	76	206	95	239	—	175	45	$XC_{10}H_9O_2+$
P—102	132	46	177	39	210	93	146	35	XC_9H_8O+
P—129	105	57	150	52	183	42	119	30	XC_8H_9+

X=NO_2, Br, CH_3, H.

EXPERIMENTAL

All t-buyl glycidic esters were prepared by condensation of the appropriate ketone with t-butyl α-chloro-

propionate following the reliable procedure of Johnson [3]. The IR spectra of all esters exhibited two bands in the carbonyl region [4-5].

Mass spectra were obtained using a CH-5 instrument at 70eV, and accelerating voltage of 8 kV, with the ionization chamber at 200°C. Pure samples were introduced with a direct insertion probe. The mass distribution of the molecular ion peak was calculated by binomial expansion method. The following isotope abundances were used in the calculation: ^{12}C, 98.89%; ^{79}Br, 50.54% ^{81}Br, 49.46%.

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