

Rearrangement Ions in the Mass Spectra of some Trimethyl- and Dimethyl-silanes

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Summary Trimethylsilyl derivatives of phenols and aniline give peaks in their mass spectra for tropylium and substituted tropylium ions and have the $M - 15$ peaks as the base peak.

OUR initial communications¹ and subsequent paper² concerning the formation of the tropylium ion, in the mass spectra of cyclic phenylborolanes have aroused considerable

interest.³ However, the interest has centred around the applicability of the rearrangement to organoboranes and not to what to us appears as a general rearrangement in numerous main-group organometallic compounds. We have observed hydrocarbon rearrangements, to form tropylium ions, in the mass spectra of organo-derivatives of silicon, phosphorus,⁴ and arsenic⁵ and would predict that analogous rearrangements will be found in the mass spectra

Compound	TABLE		M^+	$(M - 15)^+$		Tropylium ions	
	Rel. intensity (%)	Rel. intensity (%)		Rel. intensity (%)	Rel. intensity (%)	Type	Rel. intensity (%)
$\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{C}_6\text{H}_5$	166	29	100	100	C_7H_7^+	10.0	
$\text{Me}_2\text{Si}(\text{O}\cdot\text{C}_6\text{H}_5)_2$	244	100	53	100	C_7H_7^+	18.7	
$\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Me}-p$	180	39	100	100	C_7H_7^+	27.0	
$\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}-p^a$	200	45.4	100	100	MeC_7H_6^+	5.0	
$\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2-p$	211	46	100	100	ClC_7H_6^+	3.0	
$\text{Me}_3\text{Si}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$	165	41	100	100	$\text{NO}_2\text{C}_7\text{H}_6^+$	4.2	
					C_7H_7^+	1.8	

* Abundance for ³⁵Cl-containing ions only.

of organo-derivatives of elements such as aluminium, germanium, and tin.

We report our findings on a series of organo-silanes. The Table lists the intensities of the molecular ions, $M-15$ ions and tropylium ions (confirmed by precise mass measurements) for the compounds studied, all spectra having been recorded at 70 eV.

Two points arise: (i) in the trimethylsilyl derivatives the

$M-15$ peak is the base peak in all of the compounds studied (this has recently been reported by Djerassi),⁶ and (ii) hydrocarbon rearrangements occur to give ions which can be assigned to the tropylium and monosubstituted ions.

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² R. H. Cragg, G. Lawson, and J. F. J. Todd, *J.C.S. Dalton*, in the press.

³ I. R. McKinley and H. Weigel, *Chem. Comm.*, 1970, 1022; R. J. Bose and M. D. Peters, *Canad. J. Chem.*, 1971, 49, 1766; P. B. Brindley and R. Davis, *Chem. Comm.*, 1971, 1165; C. Cone, M. J. S. Dewar, R. Golden, F. Maseles, and P. Rona, *ibid.*, p. 1522.

⁴ A. M. Adams, R. H. Cragg, and J. F. J. Todd, unpublished observations.

⁵ R. H. Anderson, R. H. Cragg, and J. F. J. Todd, unpublished observations.

⁶ G. G. Smith and C. Djerassi, *Org. Mass. Spectrometry*, 1971, 5, 487.