

Mass Spectra of 1,2,4-Triazoles: A Novel Skeletal Rearrangement

R. Krishna Mohan Rao Kallury, Tumbalam G. Surendra Nath and
Vankipuram R. Srinivasan

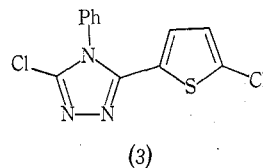
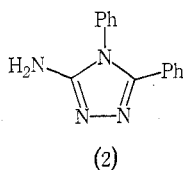
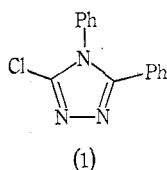
Department of Chemistry, Osmania University,
Hyderabad-7, India.

Abstract

The mass spectra of 3-chloro-4,5-diphenyl-4*H*-1,2,4-triazole (1), 3-amino-4,5-diphenyl-4*H*-1,2,4-triazole (2) and 3-chloro-5-(5'-chloro-2'-thienyl)-4-phenyl-4*H*-1,2,4-triazole (3) revealed a novel skeletal rearrangement involving the migration of the 3-substituent to the C5 carbon of the triazole ring followed by a concerted loss of nitrogen and benzonitrile.

Mass spectral studies on heterocycles brought to light several skeletal rearrangements. Of these, the most extensively investigated ones were the formation of the fluorenyl cation from a number of diaryl five-membered heterocycles¹ and the ring expansion of alkyl-substituted heterocycles.² Investigations on the mass spectra of 1,2,4-triazoles were only of recent origin.³⁻⁸ The methyl and phenyl derivatives of 1,2,4-triazoline-3-thiones were found to be the most complex in their mass spectral behaviour, the other derivatives of this parent triazole system being relatively simpler.

During the course of our investigations on 1,2,4-triazoles, we had occasion to examine the mass spectra of three triazoles (1)-(3). All three revealed a novel skeletal rearrangement, as evidenced from the following discussion.



The molecular ion peaks were found to be the base peaks in the case of (2) and (3), whereas with (1), the parent ion was the second most abundant in the spectrum (the

¹ Simons, B. K., Kallury, R. K. M. R., and Bowie, J. H., *Org. Mass Spectrom.*, 1969, **2**, 739, and references therein.

² Spiteller, G., in 'Physical Methods in Heterocyclic Chemistry' (Ed. A. R. Katritzky) Vol. 3, pp. 223-96 (Academic Press: New York 1971).

³ Briggs, P. R., Parker, W. L., and Shannon, T. W., *Chem. Commun.*, 1968, 727.

⁴ Jennings, A. L., and Boggs, J. E., *J. Org. Chem.*, 1964, **29**, 2065.

⁵ Becker, H. G. O., Beyer, D., and Tempe, J. H., *J. Prakt. Chem.*, 1970, **312**, 869.

⁶ Kametani, T., Hirata, S., Shibuya, S., and Shio, M., *Org. Mass Spectrom.*, 1971, **5**, 117.

⁷ Blackman, A. J., and Bowie, J. H., *Aust. J. Chem.*, 1972, **25**, 335.

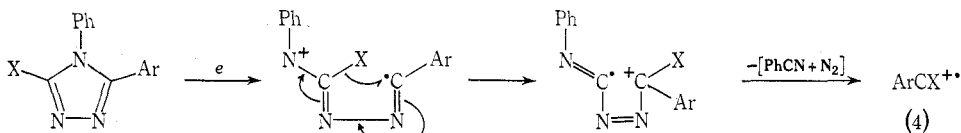
⁸ Potts, K. T., Armbruster, R., and Houghton, E., *J. Heterocycl. Chem.*, 1971, **8**, 773.

mass spectra of the three triazoles are given in Table 1). This is in keeping with the high stability of the parent 1,2,4-triazole to electron impact (see³). All the three triazoles exhibited considerable $M-1$ peaks, the abundances of which were high

Table 1. Mass spectral data for triazoles (1)–(3)

(1)	<i>m/e</i>	257	256	255(M^+)	254	220	190	180	179	178	166	165	164	152
	<i>I</i> (%)	27	33	82	60	5	5	5	5	8	5	5	8	5
	<i>m/e</i>	126	124	118	117	116	104	103	91	90	89	78	77	76
	<i>I</i> (%)	18	58	10	100	10	5	10	21	12	29	8	76	16
	<i>m/e</i>	63	51	50	45	39								
(2)	<i>m/e</i>	237	236(M^+)	235	194	193	180	179	178	166	165	164	134	133
	<i>I</i> (%)	18	100	70	5	5	23	2	2	5	4	4	2	14
	<i>m/e</i>	132	119	118	117	116	115	105	104	103	92	91	90	89
	<i>I</i> (%)	2	26	7	2	2	2	16	18	9	5	63	20	7
	<i>m/e</i>	75	74	64	63	62	50	39						
(3)	<i>m/e</i>	299	297	295(M^+)	294	262	260	168	166	164	154	152	140	138
	<i>I</i> (%)	11	66	100	16	17	43	5	33	45	3	9	11	33
	<i>m/e</i>	132	130	118	117	92	91	78	77	69	65	64	63	51
	<i>I</i> (%)	15	40	6	32	4	23	7	68	30	64	27	10	40
	<i>m/e</i>													

with (1) and (2). It was not possible, in the absence of deuterium labelling, to pinpoint the hydrogen lost in this process. Since the labelling of the 4-phenyl group in these triazoles by synthetic procedures is a tedious process, it was not attempted.



Scheme 1

The most interesting feature in the mass spectra of these triazoles, however, is the skeletal rearrangement involving the migration of the 3-substituent (chlorine or amino group) to the carbon atom at the 5-position of the triazole system. This migration is followed by the concerted loss of nitrogen and benzonitrile to afford the radical ion (4) (see Scheme 1). The process is substantiated, in each case, by an

Table 2. Composition and relative abundances of ions (4)

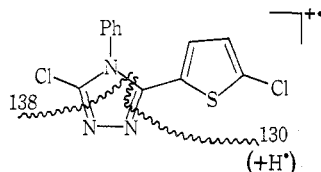
	Triazole (1)	Triazole (2)	Triazole (3)
Composition of ions (4)	C_7H_5Cl	C_7H_7N	$C_5H_2SCl_2$
<i>I</i> (%) at 70 eV	58	16	45
<i>I</i> (%) at 15 eV	15	8	11

appropriate metastable peak. The compositions of the ions were confirmed by exact mass measurements as well as by the isotopic abundance values and are given in Table 2. The process was also found to be a low-energy one, as evidenced by the relative abundances of (4) at 15 eV indicated in Table 2.

A possible general mechanism for this rearrangement is shown in Scheme 1.

Apart from this rearrangement, all the triazoles exhibited the basic cleavage of the triazole ring, viz., loss of RCN, where R is the 5-substituent on the triazole. This fragmentation was found to be preceded by the loss of chlorine in the case of (1) and (3). The aminotriazole (2) behaved in a different manner in that the amino group was lost only subsequent to the loss of benzonitrile. It was therefore concluded that, like other heterocycles, halotriazoles lose the halogen prior to ring cleavage.

Two fragmentations of (3), not observed for (1) and (2), are shown in Scheme 2.



Scheme 2

Experimental

The triazoles (1) and (2) were prepared by procedures earlier reported from these laboratories.⁹

Triazole (3) was obtained in 80% yield by the reaction of 4-phenyl-5-(2'-thienyl)-4*H*-1,2,4-triazol-3-ol¹⁰ with phosphorus oxychloride-phosphorus pentachloride mixture (1 : 1.3 molar ratio) for 6 h in a sealed tube at 150–160°C. Recrystallization from ethanol afforded the desired *product*, m.p. 146–147°C (Found: C, 48.3; H, 2.4; N, 14.2. C₁₂H₇Cl₂N₃S requires C, 48.6; H, 2.4; N, 14.2%).

The mass spectra of all the compounds were recorded on a Hitachi Perkin-Elmer RMU 6D mass spectrometer operating at 70 eV. Samples were introduced through the all-glass heated inlet system at 150°C. Exact mass measurements were performed on a CEC 21-110B mass spectrometer at a resolution of 10000 (10% valley definition) with heptacosafuorotributylamine to provide reference masses.

Acknowledgments

The authors are grateful to Professor N. V. Subba Rao, Head of the Department of Chemistry, Osmania University, for his interest in this work. One of us, T.G.S., acknowledges the C.S.I.R., India, with gratitude for the award of a Senior Research Fellowship.

Manuscript received 28 October 1974

⁹ Naqui, S., and Srinivasan, V. R., *J. Sci. Ind. Res., Sect. B*, 1962, **21**, 195.

¹⁰ Husain, S., Surendra Nath, T. G., and Srinivasan, V. R., *Indian J. Chem.*, 1971, **9**, 642.