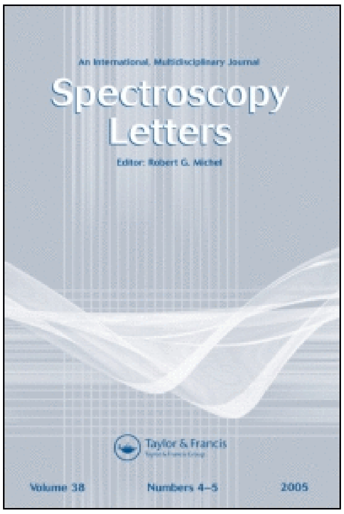
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Mass Spectra of Some 1,2,4-Triazoles

A. Aykut Ikizler[a]; Aysun Ikizler[a]; Yunus Erdoğan[a]; Mevlüt Serdar[a]
[a] Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey

To cite this Article Ikizler, A. Aykut , Ikizler, Aysun , Erdoğan, Yunus and Serdar, Mevlüt(1991) 'Mass Spectra of Some 1,2,4-Triazoles', Spectroscopy Letters, 24: 3, 423 — 436

To link to this Article: DOI: 10.1080/00387019108020667

URL: http://dx.doi.org/10.1080/00387019108020667

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 24(3), 423-436 (1991)

MASS SPECTRA OF SOME 1,2,4-TRIAZOLES

Key Words: Mass Spectrometry, 1,2,4-Triazoles,
McLafferty Rearrangements

A.Aykut İkizler, Aysun İkizler, Yunus Erdoğan and
Mevlüt Serdar
Department of Chemistry
Karadeniz Technical University, Trabzon, Turkey

ABSTRACT

The electron-impact induced fragmentation of some 4,5-dihydro-1,2,4-triazole derivatives was studied by conventional mass spectrometry. Some major fragment ions observed in the spectra were interpreted and fragmentation patterns involving McLafferty rearrangements were proposed.

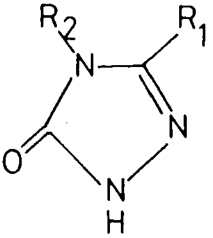
Correspondence Address:
Prof.Dr.Aykut İKİZLER
Karadeniz Teknik Üniversitesi
Kimya Bölümü 61080-Trabzon/TURKEY

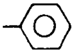
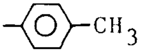
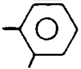
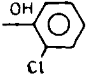
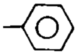
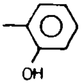
INTRODUCTION

A number of studies describing the fragmentation of 1,2,4-triazoles have been reported and characteristic fragmentation patterns given[1-5]. In general, the patterns comprise two predominant pathways involving the loss of RCN from the C-3 and C-5 positions of the ring and the formation of diazirine radical cations and subsequently nitrilium ions. Moreover,it has also been reported that various 4,5-dihydro-1,2,4-triazol-5-one derivatives show similar fragmentation pathways involving the elimination of RCN, HNCO or RNCO dominantly from the molecular ion[3,6-8]. Taking these facts into consideration, in this study, we have investigated the fragmentation patterns of eleven 4,5-dihydro-1,2,4-triazol-5-one derivatives (compounds I-XI) by using electron-impact technique. Since a complete survey of the mass spectra of 3-propyl- and 3-isopentyl-substituted-4,5-dihydro-1,2,4-triazol-5-ones has not been reported, their behaviour under electron-impact might be seem to be important. Indeed, McLafferty rearrangements and the fragmentation pathways differ from the general patterns were observed in the mass spectra of all the compounds studied. 3-propyl-, 3-propyl-4-amino-, 3-propyl-4-benzylidenamino-, 3-propyl-4-p-methylbenzylidenamino-, 3-propyl-4-o-hydroxybenzylidenamino-, 3-propyl-4-o-chlorobenzylidenamino- and 3-propyl-4-β-hydroxyethyl-4,5dihydro-1,2,4-triazol-5-ones (compounds I, II, III, IV, V, VI and VII, respectively) and 3-isopentyl-, 3-isopentyl-4-amino-, 3-isopentyl-4-benzylidenamino- and 3-isopentyl-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazol-5-ones (compounds VIII, IX, X and XI, respectively) were used in the study[9-11]. All the formulae of the compounds mentioned above are listed in Table 1.

TABLE 1

3-Substituted -and 3,4-disubstituted-4,5-dihydro-1,2,4-triazol-5-ones



Compound no.	R_1	R_2
I	$CH_2CH_2CH_3$	H
II	$CH_2CH_2CH_3$	NH_2
III	$CH_2CH_2CH_3$	N=CH 
IV	$CH_2CH_2CH_3$	N=CH 
V	$CH_2CH_2CH_3$	N=CH 
VI	$CH_2CH_2CH_3$	N=CH 
VII	$CH_2CH_2CH_3$	CH_2CH_2OH
VIII	$CH_2CH_2CH(CH_3)_2$	H
IX	$CH_2CH_2CH(CH_3)_2$	NH_2
X	$CH_2CH_2CH(CH_3)_2$	N=CH 
XI	$CH_2CH_2CH(CH_3)_2$	N=CH 

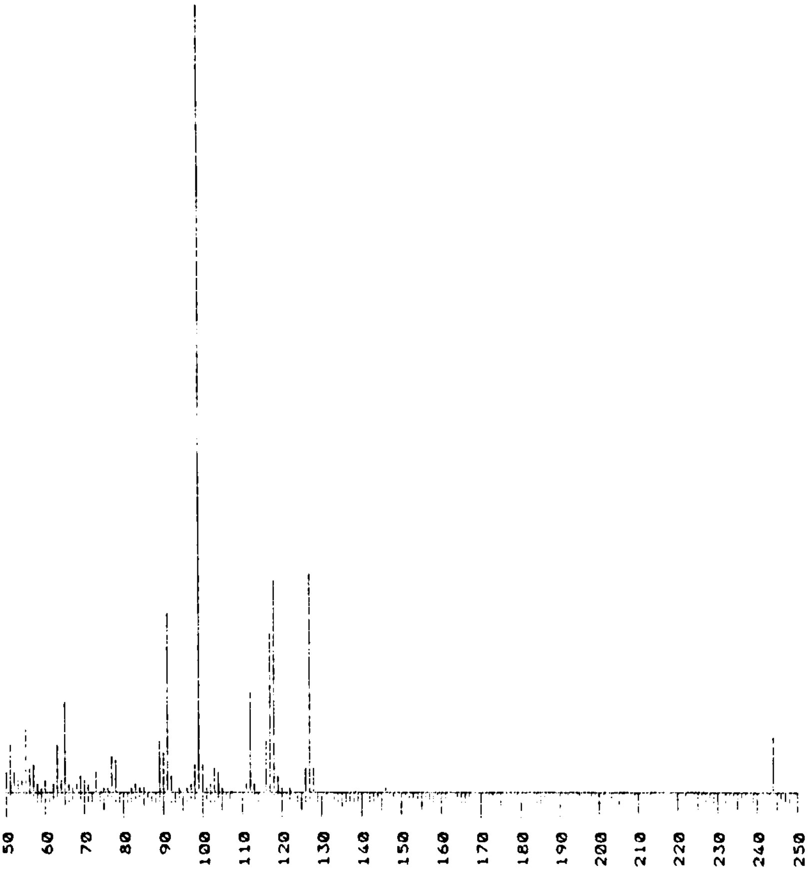


Fig.1 Mass Spectrum of Compound IV.

EXPERIMENTAL

The compounds studied were synthesized in analytical purity by using reported methods[9-11].

High resolution EI-MS were run on a Kratos MS-30 with a DS-55 data system, running in double beam mode at 70 eV with a 200^{o}C source temperature.

Two examples of the mass spectra studied are given below (Fig.1 and Fig.2)

Fig.2 Mass Spectrum of Compound VII.

RESULTS AND DISCUSSION

It was known that the general fragmentation patterns of 3-substituted- and 3,4-disubstituted- 4,5-dihydro-1,2,4-triazol-5-ones involve the loss of RCN, HNCO or R'NCO from the molecular ion[3,6-8]. Hence, it was likely that the behaviour of the compounds studied under electron-impact might be similar to the general routes.

But the data obtained from the spectra showed that the fragmentation routes of the compounds I-XI were quite different from the general patterns. Only in some spectra, the loss of RCN or HNCO from the molecular ions were observed as peaks of weak intensities.

Taking the spectral data into consideration , the fragmentation routes of the compounds I-XI can mainly be schemed as shown below. (Schemes 1-3)

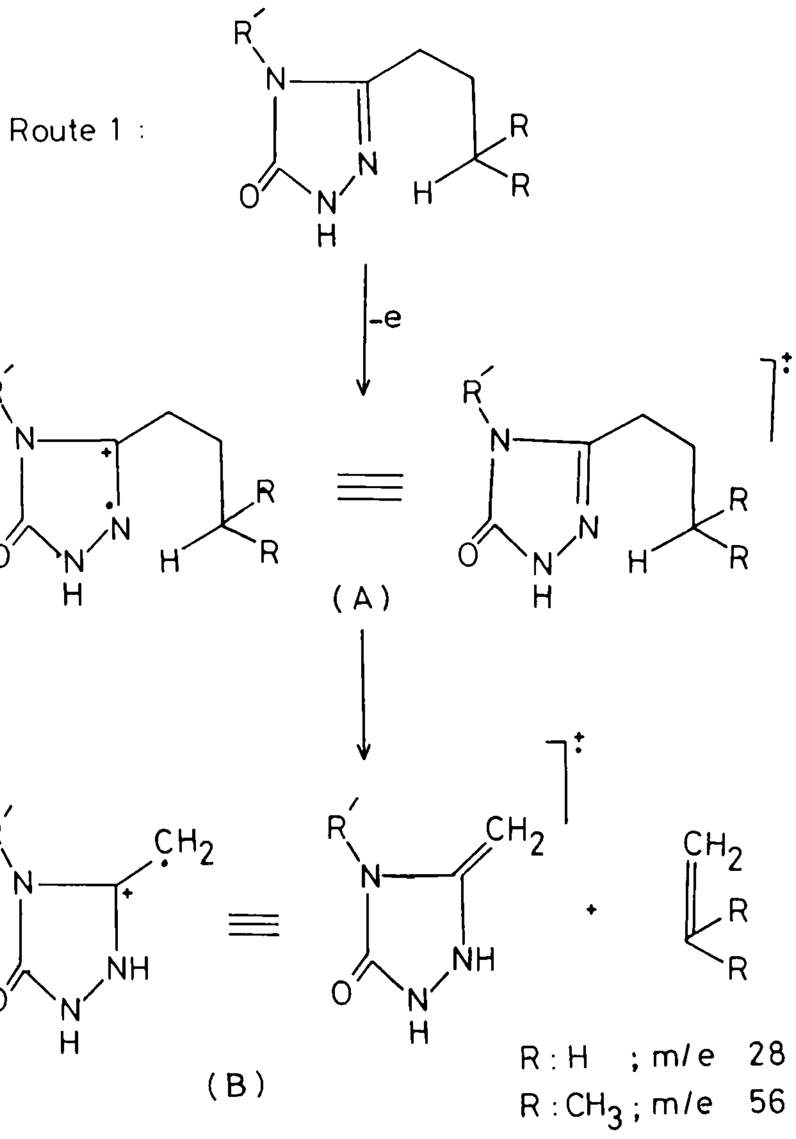
There is no doubt that Route (1) and Route (2) involve McLafferty rearrangements occurring with the elimination of C_2H_4 or $H_2C{=}C(CH_3)_2$.

According to spectral data, only compounds I, II, VIII and IX were subjected to McLafferty rearrangements via from the molecular ions under electron-impact. But, the initial loss of benzylidenamino or substituted-benzylidenamino group from N-4 position and the formation of (A) type ions must be considered for other six compounds (compounds III, IV, V, VI, X and XI). So, the further fragmentation of (A) type ions might occur in compliance with the routes schemed below

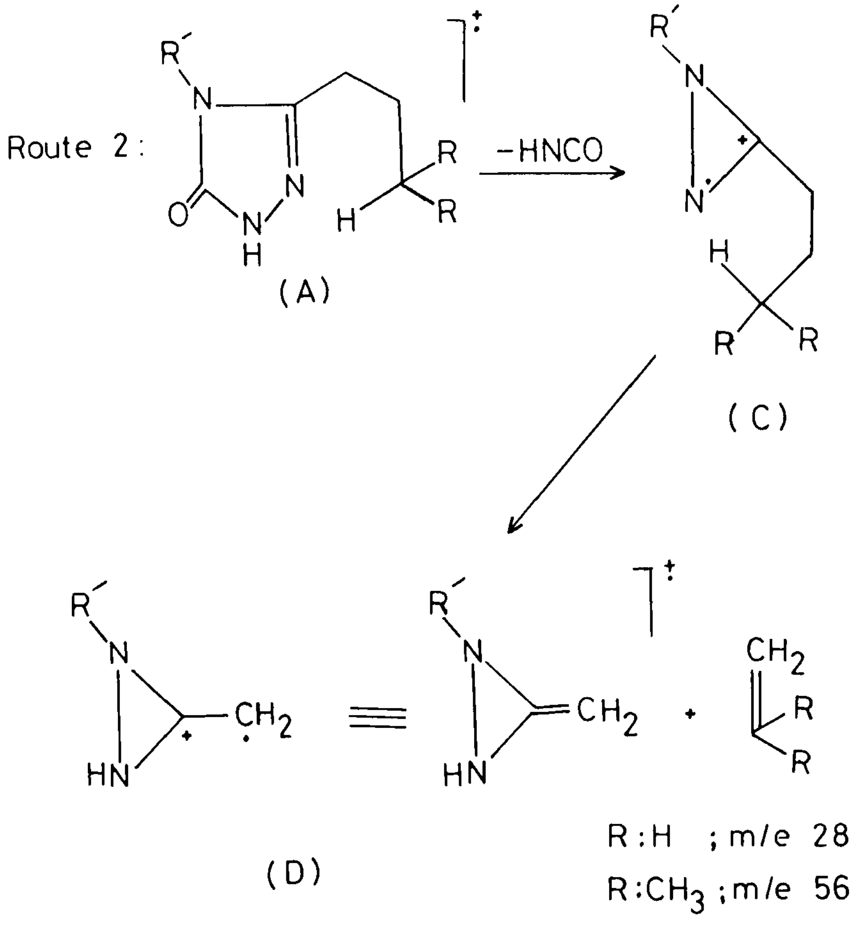
The ions confirmed with Routes 1,2 and 3 are shown in Table 2.

Apart from these and related ions, there were some other and usual fragments in the spectra studied. For example, the tropylium ion m/e 99 (100%) and the m/e 65 (12%) ion were observed in the spectrum of compound IV. In the spectra of I, II, III and VII, the m/e 69 and m/e 70 ions with weak intensity were probably butyronitrilium and protonated butyronitrilium ions, respectively. The m/e 229 (4%) ion seen in the spectrum of compound VI could be attributed to the loss of chlorine from the molecular ion.

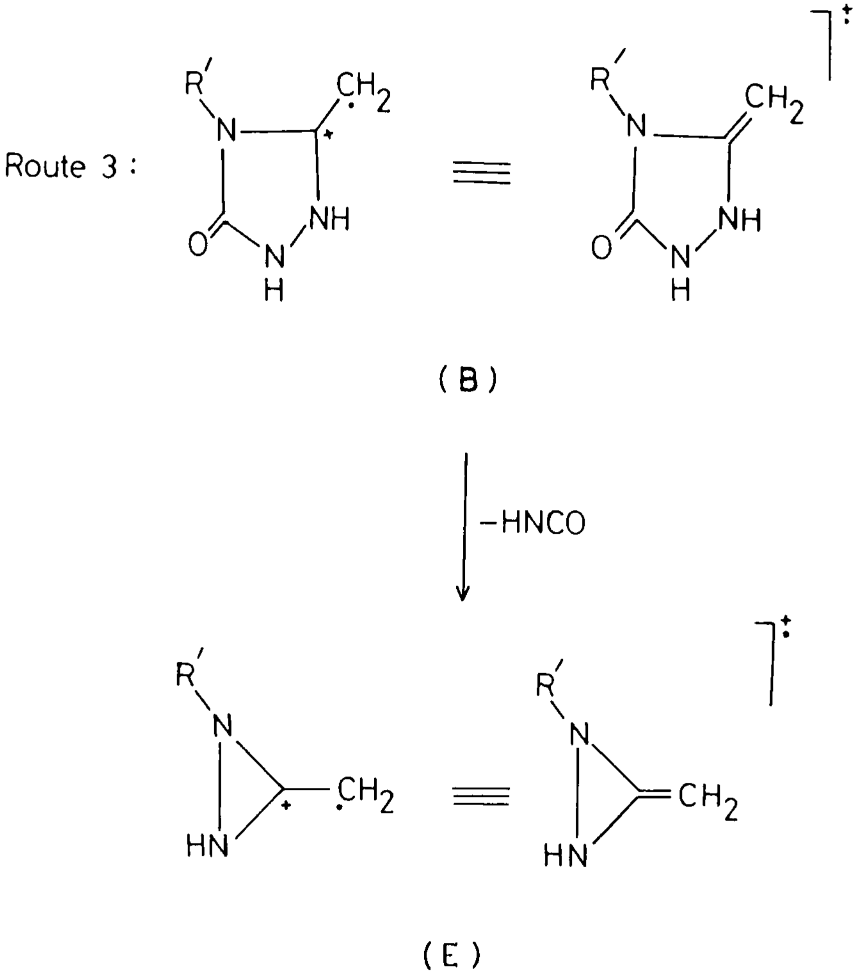
Furthermore, some common fragmentations observed in the spectra can be shown as in Table 3.



SCHEME 1


Route 2:
R´
N
N
N
H
O
H
R
R
(A)
]⁺·
-HNCO
R´
N
N
H
R
R
(C)
R´
N
HN
CH2
≡
R´
N
HN
=CH2
]⁺·
+
CH2
R
R
(D)
R:H ; m/e 28
R:CH3 ; m/e 56

SCHEME 2



SCHEME 3

TABLE 2

Compound no.	Route no.	R	R′	M^+ m/e(%)	ion A m/e(%)	ion B m/e(%)	ion C m/e(%)	ion D m/e(%)	ion E m/e(%)
1	1	H	H	127(52)	127(52)	99(100)	-	-	-
	2	H	H	-	127(52)	-	84(4)	56(30)	-
	3	H	H	-	-	99(100)	-	-	56(30)
2	1	H	NH_2	142(28)	142(28)	114(100)	-	-	-
3	1	H	H	230(35)	127(35)	99(100)	-	-	-
	2	H	H	-	127(35)	-	84(4)	56(15)	-
	3	H	H	-	-	99(100)	-	-	56(15)
4	1	H	H	244(7)	127(28)	99(100)	-	-	-
5	1	H	H	246(13)	127(19)	99(100)	-	-	-
6	1	H	H	264(4)	127(25)	99(100)	-	-	-
7	2	H	$HOCH_2CH_2$	171(22)	171(22)	-	128(100)	100(39)	-
8	1	CH_3	H	155(7)	155(7)	99(100)	-	-	-
	2	CH_3	H	-	155(7)	-	112(11)	56(5)	-
	3	CH_3	H	-	-	99(100)	-	-	56(5)

9	1	CH_3	NH_2	170(9)	170(9)	114(100)	-	-	-
10	1	CH_3	H	258(20)	155(5)	99(100)	-	-	-
	2	CH_3	H	-	155(5)	-	112(30)	56(9)	-
	3	CH_3	H	-	-	99(100)	-	-	56(9)
11	1	CH_3	H	274(10)	155(11)	99(100)	-	-	-
	2	CH_3	H	-	155(11)	-	112(14)	56(3)	-
	3	CH_3	H	-	-	99(100)	-	-	56(3)

TABLE 3

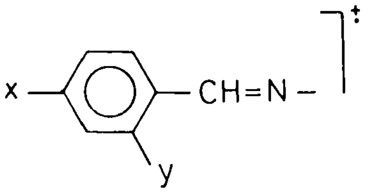
Compound no. →		I	II	III	IV	V	VI	VIII	IX	X	XI
Ion A-CH_3	m/e:	112	127	112	112	112	112	140	155	140	140
	Rel.Int:	39	13	53	13	15	18	3	4	12	4
Ion A-C_2H_5	m/e:	98	113	98	98	98	98	-	-	-	-
	Rel.Int:	30	6	13	3	5	5	-	-	-	-
Ion A-$(CH_3)_2CH$	m/e:	-	-	-	-	-	-	112	127	112	112
	Rel.Int:	-	-	-	-	-	-	11	5	30	14
Ion A+1	m/e:	128	143	128	128	128	128	-	-	-	-
	Rel.Int:	30	5	11	3	21	3	-	-	-	-
Ion B+1	m/e:	100	115	100	100	100	100	100	115	100	100
	Rel.Int:	9	6	15	4	6	5	5	6	11	8

TABLE 4

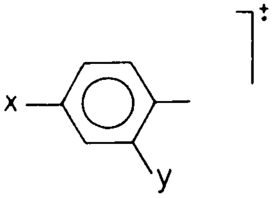
Ion C - CH_3 m/e:	113	Ion C + 1 m/e:	129
Rel.Int.:	16	Rel.Int.:	7
Ion C - C_2H_5 m/e:	99	Ion C - 1 m/e:	127
Rel.Int.:	47	Rel.Int.:	10
m/e 127-CH_3 m/e:	112	Ion C - 2 m/e:	126
Rel.Int.:	14	Rel.Int.:	13
m/e 126-CH_3 m/e:	111		
Rel.Int.:	32		

But, the peaks with strong intensity formed with expulsion of the same groups from ion C were observed in the spectrum of Compound VII (Table 4).

In addition, the ions of type F and G formed by benzylidenamino compounds under electron-impact are shown below (Table 5.)



(F)



(G)

TABLE 5

Compound no.	X	Y	ion F m/e (%)	ion F-1 m/e (%)	ion G m/e (%)
III	H	H	104(48)	103(25)	77(100)
IV	CH_3	H	118(27)	117(21)	-
V	H	OH	120(20)	119(25)	93(5)
VI	H	Cl	138(11)	137(5)	111(9)
X	H	H	104(28)	103(12)	77(53)
XI	H	OH	120(13)	119(14)	93(4)

TABLE 6

Compound no. →	V	XI
	m/e(%)	m/e(%)
Ion G - CHO	64(7)	64(4)
Ion G - CO	65(17)	65(11)
Ion F - CHO	91(12)	91(6)

Some peaks expected from phenolic compounds were also observed in the spectra of compounds V and XI (Table 6.)

Furthermore, in the spectra of compounds III and X, the m/e 51 peaks with strong intensity might be $C_4H_3^+$ cations formed by the loss of C_2H_2 from phenyl cations (m/e 77). Because of isotopic abundances, the m/e 140(3%) and m/e 113(4%) peaks in the spectrum of VI could be attributed to F and G type ions, respectively.

ACKNOWLEDGEMENT

The spectroscopic measurements were performed at City University, London. We thank Prof.S.A.Matlin and to the support of IOCD.

REFERENCES

1. A.L.Jennings, Jr. and J.E.Boggs, J.Org.Chem. 29, 2065 (1964).
2. P.R.Briggs, W.L.Parker and T.W.Shannon, Chem.Commun. 727 (1968).
3. H.G.O.Becker, D.Beyer and H.-J.Timpe, J.Prakt.Chem. 312 869 (1970).
4. K.T.Potts, R.Armbruster and E.Houghton, J.Heterocyl. Chem. 8, 773 (1971).
5. B.T.Heitke and C.G. McCarty, Can.J.Chem. 52, 2861(1974)
6. T.Kametani, S.Hirata, S.Shibuya and M.Shio, Org.Mass Spectrom. 5, 117 (1971).
7. A.A.İkizler and M.Toprak, Doğa Bilim Dergisi, A, 5, 15 (1981).
8. E.Ayça, A.A.İkizler and M.Serdar, Chim. Acta Turc. 11, 285 (1983).
9. R.Ün and A.İkizler, Chim.Acta Turc.3, 113 (1975).
10. A.A.İkizler and R.Ün, Chim. Acta Turc. 7, 269 (1979).
11. A.A.İkizler, A.İkizler and N.Yıldırım, unpublished study.

Date Received: 10/29/90
Date Accepted: 11/28/90