The Mass Spectra of 1,2,4-Oxadiazolines (1)

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Contribution from the Metcalf Chemical Laboratories, Brown University

The fragmentation patterns of seven oxadiazolines (compounds I-VII) were obtained from mass spectral data. Fragmentations *a* and *b* (Figure 1) are more important than *c*. Some of the novel cracking pathways are discussed.

The fragmentation pattern of 3,5-diphenyl-1,2,4-oxadiazole has been reported recently by Cotter (2) and other 1,2-oxaza ring systems have been studied by mass spectrometry (3). The 4,5-dihydro-1,2,4-oxadiazole (oxadiazoline) ring system offers initial fragmentation patterns that are not very probable in the oxadiazole ring (containing two double bonds rather than one). For that reason we studied the mass spectra of seven oxadiazolines (I-VII).

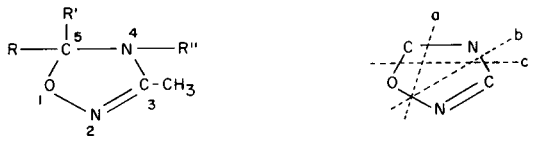


Figure 1.

I. R = C_6H_5, R' = H, R'' = C_6H_5.

II. R = C_6H_5, R' = D, R'' = C_6H_5.

III. R = m-O_2N-C_6H_4, R' = H, R'' = C_6H_5.

IV. R = p-Cl-C_6H_4, R' = H, R'' = C_6H_5.

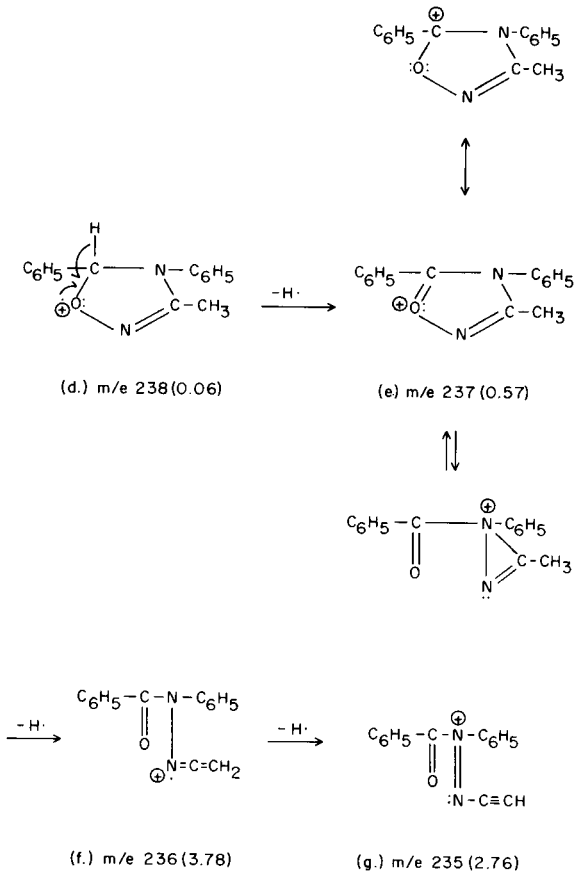
V. R = C_6H_5, R' = H, R'' = p-CH_3O-C_6H_4.

VI. R = p-O_2N-C_6H_4, R' = H, R'' = t-C_4H_9.

VII. R = m-O_2N-C_6H_4, R' = CH_3, R'' = C_6H_5.

In the oxadiazoline ring, there are five possible directions of cleavage but the strong double bond reduces the number to three most probable pathways, dotted lines, *a*, *b*, and *c* (Figure 1). The weak N-O bond (~ 53 K cal/mole) also makes cleavages *a* and *b* more probable than *c*. These working hypotheses were borne out by the experimental results, following a pattern more closely related to that of the five-membered thiazoline ring (4) than to that of the oxadiazoles (2).

The fragmentation pattern of 3-methyl-4,5-diphenyl-1,2,4-oxadiazoline started with the molecular ion (m/e 238) of low relative intensity followed by successive losses of hydrogen atoms to an ion m/e 235. The following structures and their relative abundances (in parenthesis) are suggested as initial stages in the fragmentation. A peak of 1.74% relative intensity at M-17 next indicated the loss of OH to give m/e 221. The deutero compound confirmed this observation giving M-18 ion at m/e 221. In compounds III, IV, and V, the loss of M-17 was observed in an abundance of 0.58, 1.89, and 17.58%, respectively (Table III). Compound V showed a relatively high M-17 peak.



(d.) m/e 238 (0.06)

(e) m/e 237 (0.57)

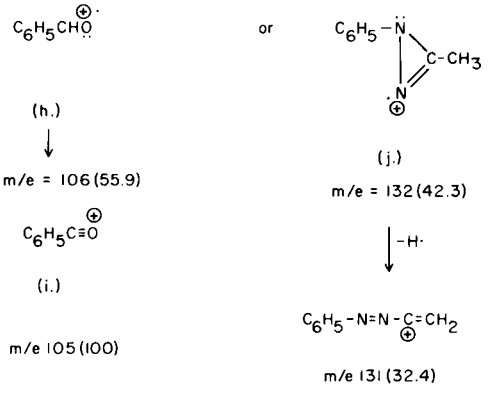
(f.) m/e 236 (3.78)

(g.) m/e 235 (2.76)

The fragments *d* to *g* represent the scission of the weak N-O bond in the heterocyclic ring and subsequent losses of hydrogen atoms. Other structural arrangements are

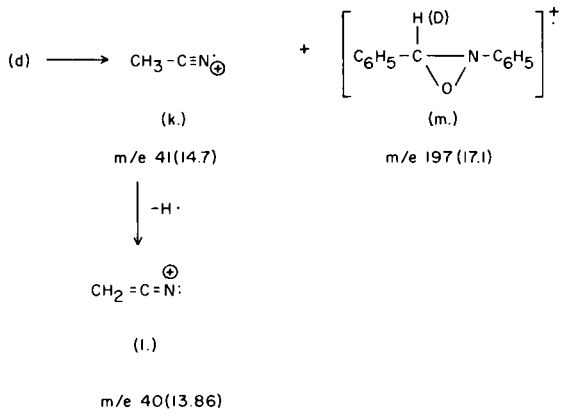
possible, however. In fragment (e) for example, the diazirine ring has an open chain analog as well as other resonance contributors.

The scission represented by dotted line *a* (above) may arise from (d) to give benzaldehyde and a diazirine m/e 132 (j). Alternatively the benzaldehyde may take the ion charge and lose a hydrogen atom to give m/e 105, the reference peak, (i).



The ^{13}C satellite peak at m/e 107 with relative intensity of 4.32% of the m/e 106 peak confirms that the structure contains seven carbons. The presence of benzaldehyde is further confirmed by the appearance of a metastable ion at m/e 56.5 arising from the transition $105^+ \rightarrow 77^+ + 28$ (Table IV) as observed by McCollum and Meyerson (5).

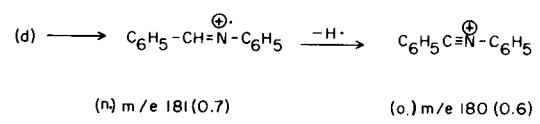
The second ring cleavage represented by line *b* eliminates fragments *k* and *m* from *d*.



When the deuterated compound II was fragmented, the expected m/e 197 ion was not entirely replaced by an m/e 198 ion although the relative intensity of m/e 198 was increased by 7.3% with respect to m/e 197. This suggests a second pathway of fragmentation in II (and I) in which D migrates from C_5 to N_2 followed by ring opening at the O-N bond and then migration of H (to O) from the CH_3 group. This gives rise to cleavage fragments $C_6H_5\text{-}\underset{\underset{OH}{|}}{C}\text{=}N\text{-}C_6H_5^{+\cdot} + CH_2\text{=}C\text{=}ND$, alternatives for *m* and *k* respectively. A high resolution mass spectrum (6) of compound II confirmed an m/e 197 ion (although the peak was small) of formula $C_{13}H_{11}NO$ (Calcd. mass: 197.08406; Found: 197.08416).

The ion corresponding to m/e 197 in I was observed in the other compounds except VI and VII (Table III).

The third possible fragmentation represents the reversal of the synthetic route to oxadiazolines. Retro Diels-Alder reactions under the conditions of the mass spectrometer have been discussed (7) for the six-membered rings containing a double bond and one or more hetero atoms. Recently Klayman (4) has reported a similar reversal in the five-membered thiazoline ring. A Diels-Alder type of reversal in wet reactions involving 1,3-dipolar addition has not been reported. In the case at hand only a 0.7% relative abundance was observed for m/e=181 and 0.6% for m/e=180.



The deutero compound confirmed this picture without any doubt. The peak at m/e 181 (n) moved one unit higher with a relative abundance of 3.8% whereas the m/e 180 peak (o) remained in an abundance of 3.5%.

The other product in the pathway (d → n → o) would be acetonitrile oxide (or an oxazirane), but a charged specie at m/e 57 could not be detected at all in the labelled and unlabelled compounds.

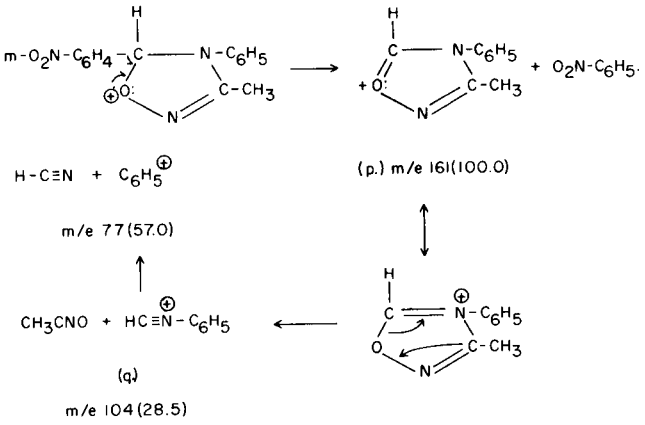
There are four peaks representing the ions m/e 90 to 93 in relative abundances of 3.00, 2.04, 4.1 and 20.4% in the unlabelled oxadiazoline and 5.27(90), 4.44(91), 5.00(92), and 6.52%(93) in the deutero compound II. The last three peaks are $C_6H_5\text{-}\ddot{N}^+$ (91), $C_6H_5\overset{+}{\ddot{N}}H$(92), and $C_6H_5\overset{+\cdot}{\ddot{N}}H_2$ (93). If the m/e 91 peak was due to tropylium ion, then the m/e 91 ion should disappear in the deutero compound but it did not. Presumably the peaks at m/e 92 and 93 originate from migration of H from the methyl group in fragment (j). Otherwise in II, the ion corresponding to m/e 92 should shift one unit higher (not observed). The m/e 93 ion might be $C_6H_5\overset{+\cdot}{\ddot{N}}D$ but $C_6H_5\overset{+\cdot}{\ddot{N}}H_2$ must be dominant because migration of D at C_5 to N_4 is unreasonable.

The expected fragmentations from the aromatic ring that have been observed by others (8a) also occurred in the

present work.

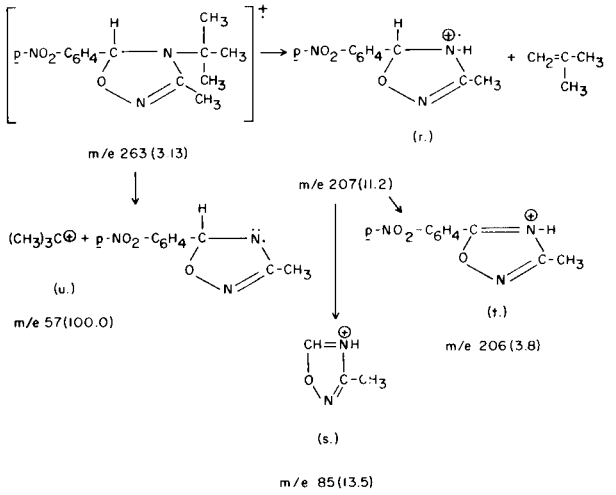
In 3-methyl-4-phenyl-5-*m*-nitrophenyl-1,2,4-oxadiazoline, the molecular ion was found in 46.37% abundance. The occurrence of the ions at m/e 226 in 24.6% and at m/e 225 in 13% abundance (corresponding to fragments (n) and (o) in I) indicated that the reversal of the synthetic route (fragmentation pattern *c*) is more significant in this derivative than in 3-methyl-4,5-diphenyl-1,2,4-oxadiazoline.

The most interesting ion in the fragmentation of this nitro derivative was found at m/e 161 in 100% intensity. The oxadiazole is certainly more stable than the oxadiazoline itself. The charged specie of oxadiazole (p) must lose the acetonitrile oxide molecule giving m/e 104, as shown:



The assignment of the ion $C_6H_5\text{-}\overset{+}{N}\equiv CH$ at m/e 104 (q) is strongly supported by the occurrence of the metastable peak at m/e 56.8 for the transition $104^+ \rightarrow 77^+ + 27$ (Table IV). This interpretation was reinforced by observation of an m/e 118 (4.8%) peak from fragmentation of VII, $CH_3\text{-}C\equiv\overset{+}{N}\text{-}C_6H_5$ being the possible ion corresponding to (q) in III (8b). In III, the m/e 104 ion could originate from m/e 226 (*m*-nitrobenzalaniline) but from (p), the necessary accompanying fragment (CH_3CNO, mass 57) was not observed.

In 3-methyl-4-*tert* butyl-5-*p*-nitrophenyl-1,2,4-oxadiazoline, cleavage at the *tert*-butyl group leaves an $(M-56)^+$ ion at m/e 207 (r) (and isobutylene) which has the ring still intact. A peak at m/e 85 (13.5%) (s), which involves loss of the *p*-nitrophenyl group from $(M-56)^+$ ion also represents a prominent difference in behavior from the other oxadiazolines (except III). The α-cleavage with β-hydrogen



rearrangement is the most probable pathway. The work of Gohlke and McLafferty (9) unequivocally support our findings. Besides the $(M-56)^+$ ion (r), there is a peak at m/e 206 (t). The most intense peak in this spectrum was found at m/e 57 which has arisen from *tert*-butyl carbonium ion (u). Contribution of m/e 57 due to an ion of acetonitrile oxide can be rejected on the grounds that in all the other oxadiazolines, m/e 57 could not be detected. Compound VI also showed the loss of M-16, M-30 and M-46 giving ions at 247, 233 and 217 m/e units in low abundances of 0.24, 0.48 and 0.09%. The m/e 217 ion further lost C_2H_2 resulting in an ion at m/e 191. These phenomena are common for aromatic nitro compounds (10).

The metastable transitions strongly support the suggested pathway for fragmentation of compound VI (Table IV).

3-Methyl-4-*p*-methoxyphenyl-5-phenyl-1,2,4-oxadiazoline (compound V) gave an ion at m/e 57 in 15.75% intensity. Since none of the other compounds gave an ion representing the mass of the elements of acetonitrile oxide, it cannot be stated with certainty that this peak came from fragmentation pattern *c*. Compound V contained a trace of impurity (IR band at 1725 cm^{-1}) which was not removed by extensive purification but the intensity of the m/e 57 peak suggests that it did not arise from the impurity.

Oxadiazolines have been synthesized recently by the 1,3-dipolar addition of benzonitrile oxide to a Schiff base (11). I to VII were prepared by adding the elements of acetonitrile oxide to the appropriate Schiff base. Mukaiyama and Hoshino (12) generated acetonitrile oxide *in situ* by reacting nitroethane and phenylisocyanate in the presence of a catalytic amount of triethylamine. They obtained fairly good yields of isoxazolines by dipolar addition of the acetonitrile oxide to olefins but only a 10%

TABLE I

Infrared and NMR Spectra of Schiff Bases

Compound				Ar-CR=NR^1 (Ar')				
				I.R.	NMR			
Ar	R	R^1 (Ar')	m.p., °C	ν, C=N	CH τ	Ar τ		R(Ar') τ
C_6H_5	H	C_6H_5	52 (a)	1632	1.65s	1.9	–	3.07
C_6H_5	D	C_6H_5	53-54	1625 (b)	–	1.9	–	3.07
m-$C_6H_4NO_2$	H	C_6H_5	66 (c)	1620	1.6s	1.34-2.05		2.27-3.05
p-C_6H_4Cl	H	C_6H_5	66-67 (d)	1632	1.67s	1.8	–	3.1
C_6H_5	H	p-$C_6H_4OCH_3$	72 (e)	1625	1.6s	1.84	–	3.34(f)
p-$C_6H_4NO_2$	H	t-C_4H_9	74-75.5 (g)	1650	1.7s	1.57-2.25 (h)		8.67s
m-$C_6H_4NO_2$	CH_3	C_6H_5	95-97	1625	–	1.16	–	3.34(i)

(a) Ref. 15. (b) ν C-D, 2165 cm^{-1}. (c) C. Schwalbe, *Chem. Zentr.*, 74, 1, 231 (1903). (d) A. Hantzsch and O. Schwab, *Ber.*, 34, 832 (1901). (e) P. Scheitz, *ibid.*, 31, 2706 (1898). (f) OCH_3 at τ 6.27 (s). (g) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, 85, 2843 (1963), m.p. reported, 72-75°. (h) AB pattern (J=9 cps). The first band of AB system overlapped with the CH=N peak and formed a single band. (i) Spectra taken in deuteriochloroform, CH_3 at τ 7.7 (s).

yield of an oxadiazoline from a Schiff base, benzalaniline. Mukaiyama and Hoshino used a ratio of 1:1 for the unsaturated compound and nitroethane with 1.8 moles of phenylisocyanate. This is not ideal for oxadiazoline formation. We have found that 80-100% yields of oxadiazoline can be obtained by using the following molar ratios and modifying the experimental conditions: Schiff base, 1: phenylisocyanate, 2.6: nitroethane, 1.3. Much less acetonitrile oxide is lost as the dimer, dimethylfuroxane, by this procedure (13).

Schiff bases and oxadiazolines are easily distinguished by the position of the methine proton in the nmr spectra of the two structures: near that of an aldehydic hydrogen in the Schiff base (τ, 1.7) and upfield (τ, 3.65 ± 0.2) in the oxadiazoline. In fact, the yield of oxadiazoline can be estimated within 5% in the crude reaction mixture by the integration of the area under these two nmr spectral peaks.

EXPERIMENTAL (14)

Infrared spectra were taken using a Perkin-Elmer Model 337-spectrophotometer in a nujol mull unless otherwise stated. The nmr spectra were determined in carbon tetrachloride solution with a Varian Model HA-60 or A-60A spectrometer and the peak positions are reported in τ values relative to TMS as internal standard. In nmr data, the symbols are b, broad; m, multiplet; s, singlet and t, triplet. The mass spectra were obtained using a Hitachi-Perkin-Elmer RMU-6D mass spectrometer operated at electron energies of 70 ev with sample heater temperature 150°, reservoir temperature 190°, and ion source temperature 200°. The samples were heated in the liquid sampler.

All the compounds except 3-methyl-4-phenyl-5-*m*-nitrophenyl-1,2,4-oxadiazoline, III, were sublimed twice before taking the spectra. The latter compound did not sublime but was recrystallized several times and dried thoroughly in vacuum. Compounds III and VII were introduced into the solid sampler, maintained at 140° while the chamber temperature remained at 220°.

General Procedure.

The Schiff bases derived from aldehydes were prepared by well known procedures (15) and that from *m*-nitroacetophenone and aniline by the method of Reddelien (16). Their nmr spectral peaks are given in Table I along with other properties. A procedure for preparing 3-methyl-4,5-diphenyl-1,2,4-oxadiazoline is given below and other oxadiazolines were prepared in a similar manner. Benzaldehyde-d_1 was obtained by the method of Wiberg (17).

3-Methyl-4,5-diphenyl-1,2,4-oxadiazoline (I).

A solution of 14.6 g. (0.2 mole) of nitroethane and 10 drops of triethylamine in 20 ml. of benzene was stirred magnetically while a solution of 46.5 g. (0.4 mole) of phenylisocyanate and 27.2 g. (0.15 mole) of benzalaniline in 25 ml. of benzene was added dropwise over a period of an hour. The reaction mixture was kept near room temperature in a water bath during the addition and for another hour while the stirring was continued. The reaction mixture was then refluxed for an hour and subsequently cooled in ice to precipitate 41 g. (0.19 mole) of

TABLE II

Infrared and NMR Spectra of 1,2,4-Oxadiazolines

Compound	M.p., °C	Yield, %	ν (C=N) cm^{-1}	CH_3 (3)	R(Ar′) (4)	Ar (5)	CH (5)	ANALYSES C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
I	75-76	81	1620	8.05s	2.45	3.20	3.67s	75.60	75.58	5.92	5.88	11.76	11.64
II	77(a)	81	1625	8.07s	2.44	3.24	–	–	–	–	–	–	–
III	76-77(b)	58(c)	1620	8.04s	2.54-3.17	1.57-2.54	3.47s	63.56	63.39	4.62	4.50	14.84	14.80
IV	104-105(b,d)	80	1610	8.00s	2.4	3.37	3.5s	66.05	65.89	4.80	4.96	10.27	9.96
V	(e)	28(c)	1620(f)	8.22s	2.99-3.45	2.52-2.90	3.79s	71.64	71.37	5.98	6.07	10.45	10.40
VI	126-127(b,g)	100	1610(h)	7.83s	8.67	1.64-2.47(i)	3.54s	59.30	59.54	6.50	6.36	15.96	16.03
VII	146-147(j)	56.5	1610	8.14s(k)	1.70	3.30	–	64.63	64.87	5.08	5.14	14.14	14.03

(a) The compound contained at least 98.5% deuterium, confirmed by nmr. (b) Crystallized from 95% ethanol. (c) Yields are from the Mukaiyama and Hoshino procedure, ref. 12. (d) Sublimed at 85-88°/0.01 mm. (e) B. P. 85-90 (0.005 mm.); $ArOCH_3$, τ, 6.39 (s), I.R. in carbon tetrachloride. (f) Even the analytical sample had a strong band at 1725 cm^{-1}; ν CH of aromatic $-OCH_3$, 2850 cm^{-1}. (carbon tetrachloride); $-OCH_3$, τ, 6.39 (s). (g) Sublimed at 102-104/0.005 mm. (h) Overlapping the ν C=C of the aromatic ring; NO_2, 1525 and 1350 cm^{-1}; spectra taken in chloroform. (i) AB pattern (J = 9 cps); spectra taken in deuteriochloroform. (j) Crystallized from methanol, sublimes 118° (0.1 mm.). (k) Spectra taken in deuteriochloroform, one signal for two CH_3 groups.

TABLE III

Relative Abundances of Corresponding Fragments in the Mass Spectra of the Seven Oxadiazolines

COMPOUND	I		II		III		IV		V		VI		VII	
Fragment (see text)	m/e	Rel. Abund %	m/e	R.A. %	m/e	R.A. %	m/e	R.A. %	m/e	R.A. %	m/e	R.A. %	m/e	R.A. %
d			239	5.55										
(molecular ion)	238	0.06	238	1.66	283	46.37	272	2.31	268	9.60	263	3.13	297	2.32
e	237	0.57	237	3.33	282	21.60	271	2.84	267	2.68	–	–	M-15(t)	18.83
f	236	3.78	236	1.38	281	0.74	270	3.72	266	4.15	–	–	–	–
g	235	2.76	235	1.11	–	–	269	2.94	–	–	–	–	–	–
h(a)	106	55.9	107	41.38	151	21.04	140	38.86	106	54.56	151	3.17	165	19.07
i	105	100.00	105	100.00	150	39.10	139	100.00	105	100.00	150	6.18	150	100.00
j(a)	132	42.3	132	63.33	132	54.74	132	61.13	162	40.53	–	–	132	53.48
j-1	131	32.4	131	40.55	131	42.08	131	42.65	161	3.22	–	–	131	32.86
k(b)	41	14.7	41	16.94	41	11.73	41	20.31	41	29.52	41	36.58	–	–
k-1(l)	40	13.86	40	9.72	40	5.21	40	10.90	40	11.05	40	5.44	–	–
n(c)	181	0.7	182	3.61	226	24.58	215	1.07	211	5.37	(r)207	11.2	240	0.62
											(t)206	3.78	–	–
o	180	0.6	180	2.77	225	13.03	214	–	210	1.20	(t-1)205	0.65	225	0.77
p	–	–	162	8.61	161	100.00	–	–	191	4.36	(s) 85	13.5	175	5.19
q	–	–	–	–	104	28.50	–	–	134	6.93	(u) 57	100.00	104	27.90
m	197	17.10	197	20.27	242	9.05	231	14.38	227	14.33	–	–	–	–
M-17	221	1.74	–	–	266	0.58	255	1.89	251	17.58	–	–	–	–
M-18	–	–	221	0.83	–	–	–	–	–	–				

(a) (b) (c) Represent the fragmentation pattern of the oxadiazoline ring as shown by dotted lines in Figure 1. Besides the molecular ions, M+1 and M+2 were also observed. In compound IV, the isotopic abundance of ^{37}Cl was in appropriate proportion.

TABLE IV

Metastable Transitions of the Oxadiazolines

Compound	Transition	Metastable Ion	
I	(105) → (77) + 28	56.46	56.5
II	(105) → (77) + 28	56.46	56.5
III	(104) → (77) + 27	57.00	56.8
IV	(139) → (111) + 28	88.64	88.5
	–	–	50.7(a)
V	(105) → (77) + 28	56.46	56.5
VI	(56) → (41) + 15	30.00	29.50
	(207) → (85) + 22	34.90	35.00
	(93) → (65) + 28	45.43	44.50
	(263) → (207) + 55	162.9	163.00
	–	–	81.50(a)

(a) Small peak could not be accounted for.

diphenylurea. The diphenylurea was removed and washed on the filter with 15 ml. of benzene. The benzene washing and the brown filtrate were concentrated at ambient temperatures on a rotary evaporator to a dark brown oil. This crude product contained a small amount of dimethylfuroxane and starting material (detected by nmr).

The oil was transferred to a column of 300 g. of neutral alumina and eluted with 1.5 liters of hexane which removed some starting materials. Further elution with the same solvent removed a mixture of benzalaniline and oxadiazoline. Then elution with 900 ml. of benzene-hexane (1:4) and 900 ml. of benzene-hexane (1:1) yielded 29.0 g. (81%) of chromatographically pure 3-methyl-4,5-diphenyl-1,2,4-oxadiazoline. Some diphenylurea, dimethylfuroxane, and oxadiazoline remained on the column (3.6 g.) as was determined by subsequent elutions with benzene (2 g.) and 5% (then 10%) methanol in benzene (about 1.6 g.).

The detection of materials from the column was followed by thin layer chromatography on microslides using adsorbent Kieselgel G (Merck and Co.). A solvent of 2% methanol in benzene was used to move the materials and the spots were developed by exposing the plates to iodine vapor. The oxadiazoline had an R_f value of 0.35.

The analytical sample was obtained by recrystallization from ethanol after treatment with decolorizing charcoal to give colorless crystals, m.p. 75-76°. The sample sublimed without change at 57° (0.005 mm.). (Table II). A yield of 10% was reported by Mukaiyama and Hoshino (12) but they give no details on the work-up. We obtained a 50% yield with their ratios of reactants.

Acknowledgment.

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