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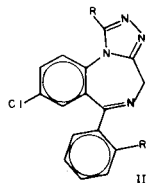
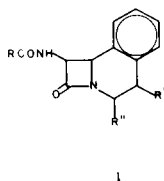
04510 México, D. F.

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A series of new 2-methylthio-7-(*p*-R-phenyl)-8-phenoxy-4,5-benzo-3-aza-2-nonem, IIIa, have been synthesized by regiospecific cycloaddition of phenoxyacetyl onto 2-methylthio-4-(*p*-R-phenyl)-3*H*-1,5-benzodiazepines IV. The structure was established by ir, ¹H-nmr and ms spectral data together with ¹³C-nmr spectral data of desulfurization products, VIa. Likewise, a study has been made of the fragmentation upon electron impact of IIIa and IV. All the spectra analyzed contain molecular ions and the principal fragmentation routes takes place either from the molecular ion or from *m/e* (*M*⁺ - 134) ion. This ion is the base peak for all the compounds analyzed.

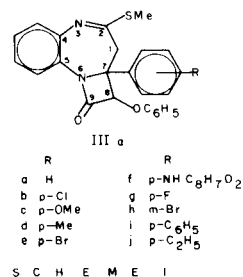
J. Heterocyclic Chem., **20**, 161 (1983).

The search for structural analogues of cephalosporin and penicillin with specific activity and therefore with therapeutical applications has continued in recent years (4). Recently, a series of benzo-fused analogues, I, of cephalosporin with antibacterial activity have been reported (5). On the other hand, compounds possessing a benzodiazepine moiety often exhibit an interesting spectrum of biological activities: for example, II has been shown to have useful anxiolytic and hypnotic activity (6).



It appeared of interest to us to combine the two functionalities and prepare compounds in which the β -lactam moiety is integrated into the benzodiazepine system and to investigate their pharmacological profile.

This paper reported the synthesis and mass spectrometry studies of ten new compounds of general structure IIIa (Scheme 1, *p*-R = H, Cl, Me, OMe, Br, NHC₈H₇O₂, F, Et, C₆H₅ and *m*-R = Br).



S C H E M E I

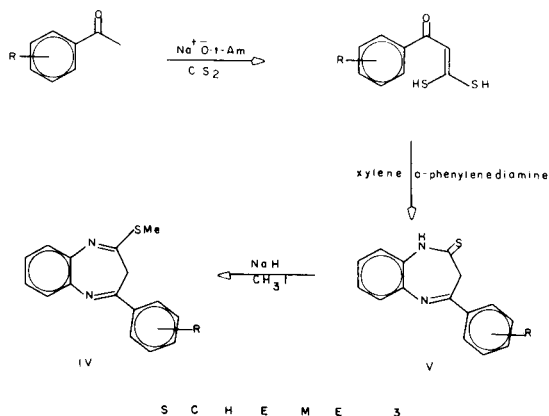
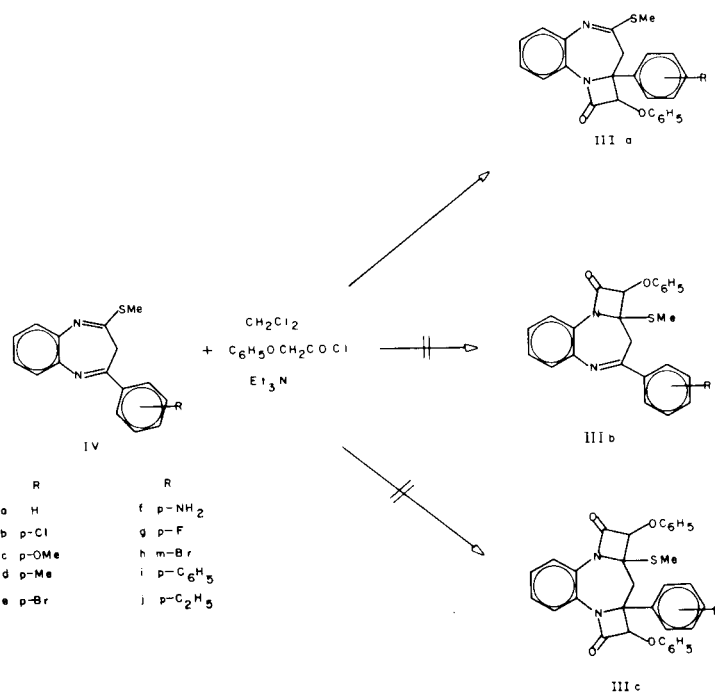
Our first goal was the methylthioimino ether IV. Treatment of a 1,5-benzodiazepine-2-thione V with sodium hydride and methyl iodide in refluxing xylene afforded IV. The thiolactam intermediates V were prepared similarly to literature methods as outlined in Scheme 2 (7).

Synthesis of the title compounds was accomplished by cycloaddition of phenoxyacetyl chloride onto methylthioimino ether IV. Cycloaddition was carried out in refluxing dichloromethane, in presence of excess triethylamine, in accordance with known methods (8a,b). With this general reaction, a total of three closely related compounds containing a β -lactam moiety are possible: IIIa, IIIb and IIIc (Scheme 3). Spectral data (ir, ¹H-nmr and ms; Table 1 and

Table 1

Relative Abundance of Principal Fragments of III
(Figures in parentheses indicate the nature of the ions)

Compound No.	R	<i>M</i> ⁺	<i>m/e</i>															
			<i>M</i> ⁺ - 134 (1)	<i>M</i> ⁺ - 93 (6)	<i>M</i> ⁺ - 94 (8)	<i>M</i> ⁺ - 167 (2)	259 + R (7)	250 + R (3)	218 + R (4)	193 + R (5)	102 + R	218 (4a)	191 (4b)	165 (4c)	77	65	63	51
IIIa	H	32.7	100	10.0	12.5	15.0	12.5	7.5	25.0	12.5	17.5	16.2	7.50	7.5	33.2	7.5	3.0	10.0
IIIb	<i>p</i> -Cl	22.5	100	7.50	6.0	10.0	8.0	10.0	7.50	12.5	10.0	17.5	7.50	9.0	38.4	10.0	5.0	10.0
IIIc	<i>p</i> -OMe	13.0	100	5.0	8.0	25.0	7.5	12.5	22.5	20.0	19.5	8.0	6.0	5.0	37.7	7.5	6.0	7.5
III d	<i>p</i> -Me	22.5	100	10.0	12.0	15.0	10.0	12.5	21.5	10.0	12.5	15.0	6.0	7.5	22.1	10.0	5.0	7.5
III e	<i>p</i> -Br	12.5	100	5.0	6.0	9.0	6.0	4.0	3.0	8.0	3.5	27.5	10.0	10.0	28.4	10.0	6.0	8.0
III f	<i>p</i> -NHC ₈ H ₇ O ₂	7.50	100	7.5	8.0	5.0	4.0	6.0	5.0	3.0	3.0	5.0	4.0	6.0	38.1	3.0	3.0	5.0
III g	<i>p</i> -F	17.3	100	3.0	3.0	10.0	7.5	3.0	10.5	10.0	5.0	—	3.0	—	7.5	—	—	—
III h	<i>m</i> -Br	17.0	100	5.0	10.0	7.5	6.0	5.0	5.0	7.5	3.5	20.0	10.0	6.5	20.0	5.0	6.0	7.5
III i	<i>p</i> -C ₆ H ₅	10.0	100	15.3	13.0	15.0	5.0	7.5	17.2	6.0	5.0	3.0	5.0	7.5	9.0	—	—	—
III j	<i>p</i> -C ₂ H ₅	12.0	100	11.0	11.0	12.0	7.5	6.0	10.0	5.0	4.5	10.0	3.0	—	3.0	—	—	—



3) rule out structure IIIc because they never show the presence of two β -lactams in the framework of products obtained. Thus, only two isomeric structures were possible: IIIa or IIIb.

However, with the spectral data of compounds obtained we could not differentiate any one of them.

Therefore, we took recourse to desulfurization of some of these compounds with Raney-nickel (Scheme 4). With this reaction we could obtain two isomeric products VIa or VIIb.

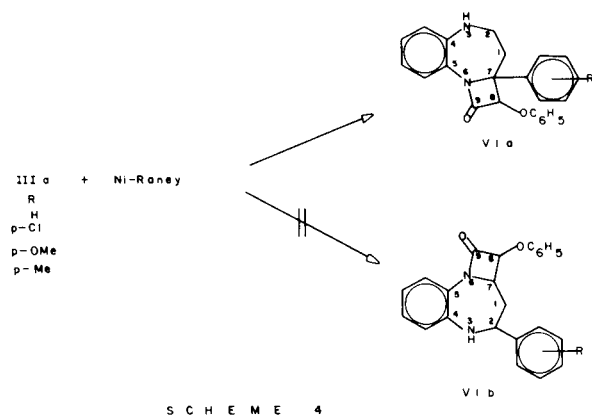
A further piece of information which the position of β -lactam in III has given us is the assignment of C-7 signal

Table 2
Relative Abundance of Principal Fragments of IV
(Figures in parentheses indicate the nature of the ions)

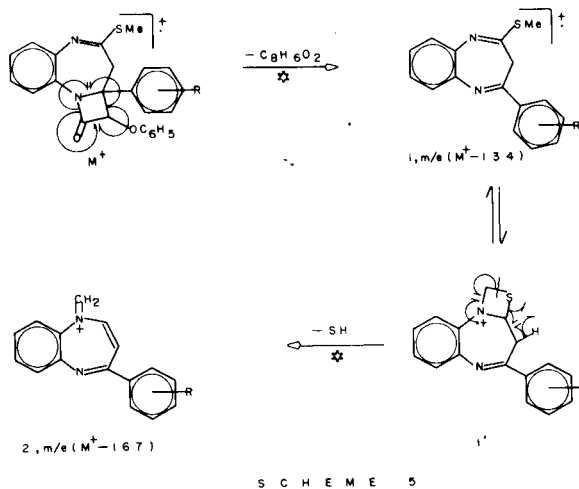
Compound	R	M ⁺ (1)	M ⁺ -1	m/e												
				250+R (3)	218+R (4)	M ⁺ -48 (2)	M ⁺ -33 (5)	193+R	102+R	218 (4a)	191 (4b)	165 (4c)	77	65	63	51
IVa	H	100	10.0	17.5	92.7	45.4	27.5	42.5	23.0	45.4	5.0	10.0	42.5	11.0	20.0	17.5
IVb	<i>p</i> -Cl	100	15.0	17.5	26.0	15.0	18.0	60.8	17.5	90.0	6.0	7.5	16.0	5.0	26.0	15.0
IVc	<i>p</i> -OMe	100	9.0	12.5	33.9	14.0	22.5	25.0	30.3	13.0	3.0	3.0	20.0	5.0	16.5	5.0
IVd	<i>p</i> -Me	100	10.0	16.5	48.5	30.7	25.3	29.4	24.8	15.0	3.5	8.6	39.3	7.5	24.3	16.5
IVe	<i>p</i> -Br	100	10.0	8.0	8.0	6.0	9.0	21.0	5.5	76.9	7.5	8.0	12.5	3.0	16.0	8.0
IVf	<i>p</i> -NH ₂	100	8.0	13.5	21.0	10.0	8.7	27.5	10.0	12.1	4.0	6.5	15.0	10.0	7.5	5.0
IVg	<i>p</i> -F	100	11.0	20.0	58.8	36.5	24.0	44.9	15.0	3.0	2.0	2.0	10.0	2.0	9.0	3.0
IVh	<i>m</i> -Br	100	10.0	10.0	9.0	10.0	10.0	21.0	3.8	84.1	8.0	7.5	13.0	3.0	10.0	8.0
IVi	<i>p</i> -C ₆ H ₅	100	13.0	17.5	53.9	25.0	21.0	17.5	15.0	10.0	3.0	20.0	13.0	2.0	6.0	4.0
IVj	<i>p</i> -C ₂ H ₅	100	12.0	17.5	26.0	23.0	17.5	12.0	7.5	36.1	2.0	2.0	2.0	—	—	—

Table 3
Analytical and Spectral Data of III

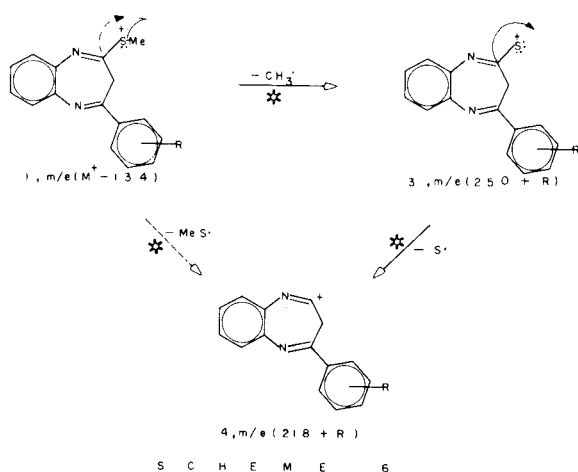
Compound No.	Mp °C	Yield %	Molecular Formula	Analysis %			Spectral Data
				C	H	N	
IIIa	165	58	C ₂₄ H ₂₀ N ₂ O ₂ S	71.97 (71.90)	5.03 (5.00)	6.99 (7.01)	nmr (deuteriochloroform) δ 8.4-6.8 (m, 14H), 5.28 (s, 1H), 3.85 (d, 1H, J = 14 Hz), 3.1 (d, 1H, J = 14 Hz), 2.21 (s, 3H)
IIIb	205	60	C ₂₄ H ₁₉ ClN ₂ O ₂ S	66.27 (66.17)	4.40 (4.35)	6.44 (6.41)	nmr (deuteriochloroform) δ 8.4-6.8 (m, 13H), 5.28 (s, 1H), 3.80 (d, 1H, J = 14 Hz), 3.15 (d, 1H, J = 14 Hz), 2.23 (s, 3H)
IIIc	127	50	C ₂₅ H ₂₂ N ₂ O ₃ S	69.74 (69.68)	5.15 (5.18)	6.50 (6.52)	nmr (deuteriochloroform) δ 8.5-6.8 (m, 13H), 5.35 (s, 1H), 3.95 (d, 1H, J = 14 Hz), 3.8 (s, 3H), 3.21 (d, 1H, J = 14 Hz), 2.38 (s, 3H)
III d	192	62	C ₂₅ H ₂₂ N ₂ O ₂ S	72.43 (72.36)	5.34 (5.30)	6.75 (6.85)	nmr (deuteriochloroform) δ 8.25-6.75 (m, 13H), 5.17 (s, 1H), 3.75 (d, 1H, J = 14 Hz), 3.1 (d, 1H, J = 14 Hz), 2.2 (s, 3H), 2.18 (s, 3H)
IIIe	190	70	C ₂₄ H ₁₉ BrN ₂ O ₂ S	60.13 (60.04)	3.99 (4.01)	5.84 (5.90)	nmr (deuteriochloroform) δ 8.4-6.8 (m, 13H), 5.28 (s, 1H), 3.8 (d, 1H, J = 14 Hz), 3.15 (d, 1H, J = 14 Hz), 2.25 (s, 3H)
III f	130	40	C ₃₂ H ₂₇ N ₃ O ₄ S	69.92 (70.01)	4.95 (5.01)	7.64 (7.60)	nmr (deuteriochloroform) δ 8.4-6.8 (m, 19H), 5.32 (s, 1H), 4.6 (s, 2H), 3.9 (d, 1H, J = 14 Hz), 3.2 (d, 1H, J = 14 Hz), 2.35 (s, 3H)
III g	148	51	C ₂₄ H ₁₉ FN ₂ O ₂ S	68.88 (68.70)	4.57 (4.60)	6.69 (6.71)	nmr (deuteriochloroform) δ 8.4-6.6 (m, 19H), 5.28 (s, 1H), 3.8 (d, 1H, J = 14 Hz), 3.1 (d, 1H, J = 14 Hz), 2.25 (s, 3H)
III h	141	65	C ₂₄ H ₁₉ BrN ₂ O ₂ S	60.13 (60.10)	3.99 (4.10)	5.84 (5.80)	nmr (deuteriochloroform) δ 8.4-6.8 (m, 13H), 5.26 (s, 1H), 3.8 (d, 1H, J = 14 Hz), 3.1 (d, 1H, J = 14 Hz), 2.3 (s, 3H)
III i	150	70	C ₃₀ H ₂₄ N ₂ O ₂ S	75.60 (75.51)	5.07 (5.00)	5.87 (5.92)	nmr (deuteriochloroform) δ 8.4-6.75 (m, 18H), 5.26 (s, 1H), 3.85 (d, 1H, J = 14 Hz), 3.15 (d, 1H, J = 14 Hz), 2.25 (s, 3H)
III j	147	68	C ₂₆ H ₂₄ N ₂ O ₂ S	72.87 (72.74)	5.64 (5.60)	6.53 (6.62)	nmr (deuteriochloroform) δ 8.4-6.7 (m, 13H), 5.25 (s, 1H), 3.8 (d, 1H, J = 14 Hz), 3.1 (d, 1H, J = 14 Hz), (q, 2H), 2.25 (s, 3H), 1.15 (t, 3H)



in the ¹³C-nmr spectrum of VI a (Table 5). The off-resonance decoupled spectrum of VI a showed a triplet for C-1 (40.99 ppm), a triplet for C-2 (41.56 ppm) and a singlet for C-7 (70.29 ppm), whereas the compound VI b would show a triplet for C-1, a doublet for C-2 and a doublet for C-7. This clearly indicates that the molecular skeleton, as indicated by structure III a, is correct and that it is not the other regioisomer III b. Thus, the cycloaddition of phenoxyacetyl chloride to methylimino ether IV is regio-specific.



The general rationale for the electron impact induced mass spectral fragmentation of the compounds III a to III j is shown in Schemes 5-11. The relative abundances of relevant ions obtained as primary fragmentation products discussed in this paper are reported in Table 1. The transitions were substantiated by an appropriate metastable



peak and are indicated by an asterisk in the figures. Analysis of fragmentation patterns was aided by reference to the mass spectral data published for model compounds.

The molecular ions, $[M]^+$, were clearly observed in the electron impact mass spectra of all ten derivatives. The major fragmentation of the molecular ion proceeds along three pathways:

- (A) from $[M]^+$ to $m/e (M^+ - 167)$, $(193 + R)$ and $m/e 165$.
- (b) from $[M]^+$ to $m/e (M^+ - 93)$ and $m/e (259 + R)$.
- (C) from $[M]^+$ to $m/e (M^+ - 93)$ and $(M^+ - 94)$.

Pathway A.

In this pathway, loss of a phenoxyketene unit from the β -lactam moiety of 4,5-benzo-3-aza-2-nonem derivatives leads to the $m/e (M^+ - 134)$ ion which is depicted as a 2-methylthio-4-(*p*-R-phenyl)-1,5-benzodiazepine radical ion, **1**, (Scheme 5). The driving force for this process is undoubtedly the production of the stable fragment **1**. This ion is the base peak for all compounds analyzed and their abundant formation is rationalized as arising from two β -cleavages, one of those from the 6-ring nitrogen atom of 4,5-benzo-3-aza-2-nonem framework and another from the

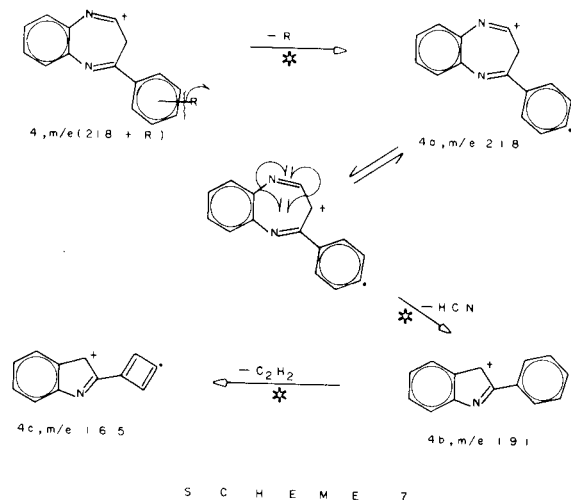
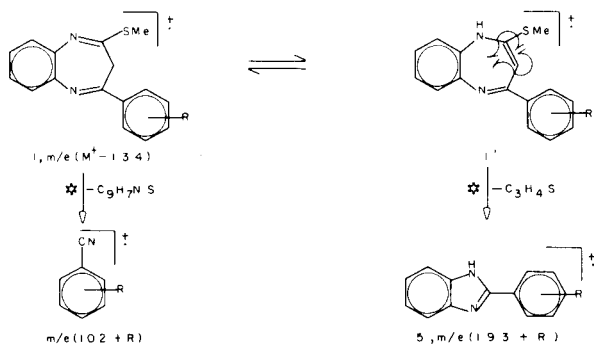


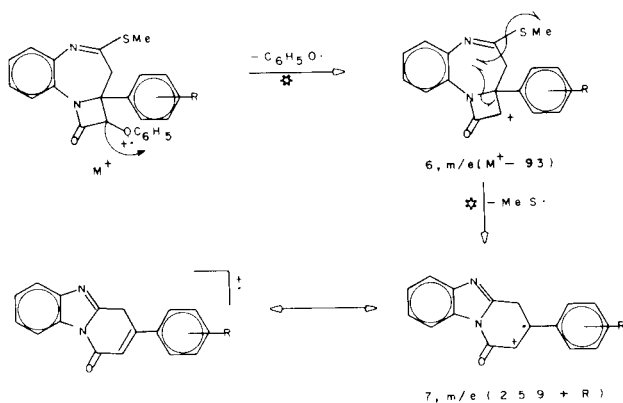
Table 4

Spectral Data of IV

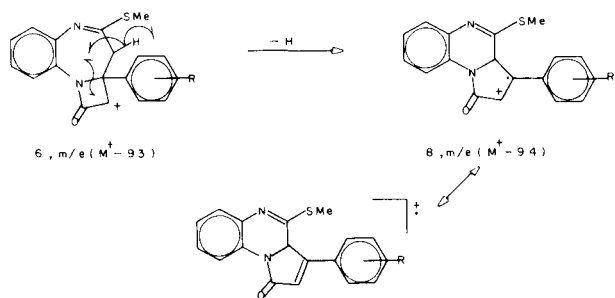
Compound No.	Yield %	Molecular Formula	Spectral Data
IVa (1) oil	80	C ₁₆ H ₁₄ N ₂ S	ir (neat): 1600, 1590, 1570, 755, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 8.0 (m, 2H), 7.5-7.1 (m, 7H), 3.3 (s, 2H), 2.4 (s, 3H); ms: M ⁺ at m/e 266
IVb (1) oil	75	C ₁₆ H ₁₃ ClN ₂ S	ir (neat): 1600, 1590, 1570, 840, 760, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9 (d, 2H), 7.3 (d, 2H), 7.5-7.05 (m, 4H), 3.25 (s, 2H), 2.4 (s, 3H); ms: M ⁺ at m/e 300
IVc (1) oil	85	C ₁₇ H ₁₆ N ₂ OS	ir (neat): 1600, 1590, 1570, 1250, 840, 760, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.95 (d, 2H), 6.8 (d, 2H), 7.5-7.05 (m, 4H), 3.75 (s, 3H), 3.25 (s, 2H), 2.38 (s, 3H); ms: M ⁺ at m/e 296
IVd (1) oil	79	C ₁₇ H ₁₆ N ₂ S	ir (neat): 1600, 1590, 1570, 840, 760, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.0-7.9 (m, 8H), 3.2 (s, 2H), 2.35 (s, 6H); ms: M ⁺ at m/e 280
IVe oil	83	C ₁₆ H ₁₃ BrN ₂ S	ir (neat): 1600, 1590, 1570, 840, 760, 680 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9 (d, 2H), 7.5 (d, 2H), 7.5-7.1 (m, 4H), 3.28 (s, 2H), 2.34 (s, 3H); ms: M ⁺ at m/e 344
IVf oil	84	C ₁₆ H ₁₃ N ₃ S	ir (neat): 3440, 3340, 1600, 1590, 840, 750, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.85 (d, 2H), 6.6 (d, 2H), 7.4-7.05 (m, 4H), 5.8 (b, 2H), 3.28 (s, 2H), 2.4 (s, 3H); ms: M ⁺ at m/e 281.
IVg (1) oil	76	C ₁₆ H ₁₃ FN ₂ S	ir (neat): 1600, 1590, 840, 760, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 8.1-6.9 (m, 8H), 3.25 (s, 2H), 2.4 (s, 3H); ms: M ⁺ at m/e 284
IVh oil	88	C ₁₆ H ₁₃ BrN ₂ S	ir (neat): 1600, 1590, 760, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 8.2 (t, 1H), 7.9 (d, 1H), 7.5-7.1 (m, 6H), 3.3 (s, 2H), 2.43 (s, 3H); ms: M ⁺ at m/e 344
IVi oil	78	C ₂₂ H ₁₈ N ₂ S	ir (neat): 1600, 1590, 850, 760, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 8.15 (d, 2H), 7.65 (d, 2H), 7.6-7.1 (m, 9H), 3.3 (s, 2H), 2.35 (s, 3H); ms: M ⁺ at m/e 342
IVj oil	81	C ₁₈ H ₁₈ N ₂ S	ir (neat): 1600, 1590, 840, 755, 675 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9 (d, 2H), 7.18 (d, 2H), 7.5-7.05 (m, 4H), 3.25 (s, 2H), 2.6 (q, 2H), 2.35 (s, 3H), 1.2 (t, 3H); ms: M ⁺ at m/e 294



S C H E M E 5



S C H E M E 6



S C H E M E 7

Table 5

Partial Carbon-13 Chemical Shifts of VIa in Deuteriochloroform (1)

R	C-1	C-2	C-7	C-8	C-9 (2)
H	40.99 (t)	41.56 (t)	70.29 (s)	87.97 (d)	163.53 (s)
Cl	40.88 (t)	41.60 (t)	70.50 (s)	88.8 (d)	163.76 (s)
OMe	40.93 (t)	41.47 (t)	70.35 (s)	88.06 (d)	163.87 (s)
Me	41.12 (t)	41.63 (t)	70.64 (s)	88.24 (d)	163.94 (s)

(a) Figures in parentheses indicate the signal multiplicity obtained from SFORD, s = singlet, d = doublet, t = triplet; chemical shifts are expressed in ppm relative to tetramethylsilane. (2) Numbering of carbons are shown in the structure.

oxygen of the 8-phenyl substituent, and α -cleavage to the carbonyl group. A similar fragmentation has been reported for monocyclic β -lactams (9).

Fragmentation of **1** ion then proceeds along five pathways. In one pathway, loss of an anhydrosulphide radical from 1,5-benzodiazepine radical ion, **1**, involving the 1-ring nitrogen atom and one hydrogen atom of 2-methylthio group, affords the ion **2** of $m/e (M^+ - 167)$ (Scheme 5). In another pathway, elimination of the 2-methyl substituent as a radical from **1** affords an ion at $m/e (250 + R)$, **3**. This ion then goes on to lose a sulphur atom radical giving **4** which is depicted as a 4-(*p*-R-phenyl)-1,5-benzodiazepine cation of $m/e (218 + R)$ (Scheme 6). The same fragments are also formed from **1** ion by loss of a methylsulphide unit.

In keeping with this structural assignment for the $m/e (218 + R)$ ion it fragments to a small extent by loss of the *p*-R-substituent to form an $m/e 218$ ion, **4a**. This ion then goes on to lose 27 amu (HCN) giving **4b** of $m/e 191$ which in turn loses an acetylene unit giving **4c** (Scheme 7).

In the third pathway (Scheme 8) loss of an ethynyl methyl thioether (72 amu) from **1'** yields **5** of $m/e (193 + R)$. The **1** ion also decomposed by loss of a C_9H_7NS unit to form the *p*-R-benzonitrile radical ion of $m/e (102 + R)$. Also, the latter ion and **5** have been observed in the electron impact mass spectra of different 1,5-benzodiazepine derivatives (10,11,12a,12b).

Pathway B.

Another interesting fragmentation pathway of 4,5-benzo-3-aza-2-nonem derivatives III is the elimination of the 8-phenoxy substituent from the molecular ion giving rise to a fragment at $m/e (M^+ - 93)$, **6**. Loss of a methylsulphide radical from **6** yields **7** of $m/e (259 + R)$ (Scheme 9).

Pathway C.

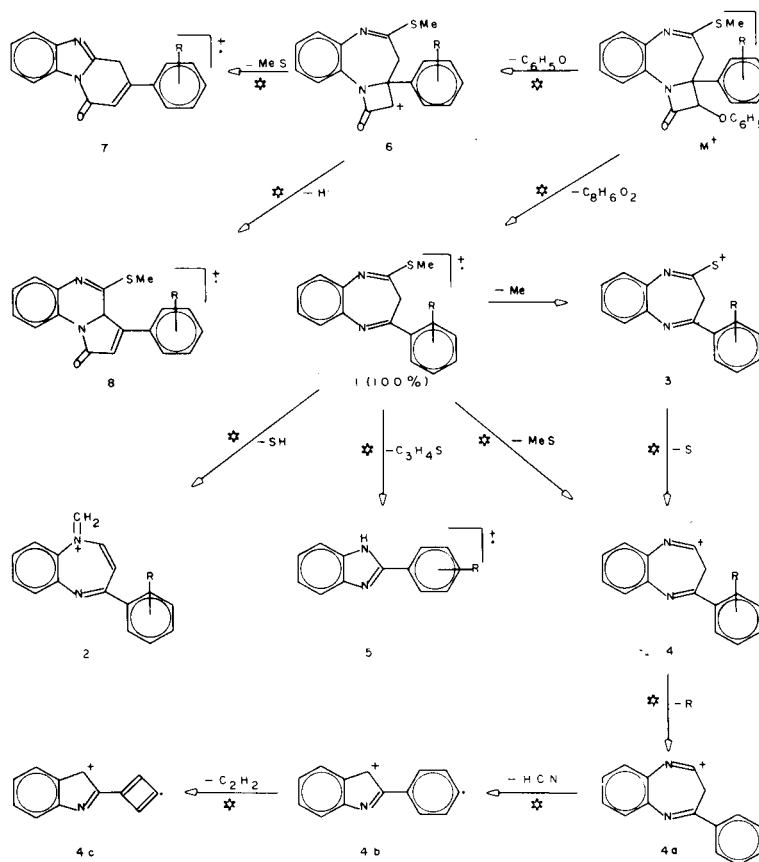
Loss of a 1-hydrogen atom from the **6** ion produces an $m/e (M^+ - 94)$ ion, **8** (Scheme 10).

The fragmentation patterns discussed above were corroborated by careful examination of the mass spectra of ten 2-methylthio-4-(*p*-R-phenyl)-3H-1,5-benzodiazepine derivatives IV. Most of the results given previously for III derivatives are similar for IV (Table 2). The molecular ion is the base peak for these compounds analyzed, and subsequently undergoes decomposition as the $m/e (M^+ - 134)$ ion, **1**, of III shown in Schemes 5-11 leading to the fragments **2**, **3**, **4**, **4a**, **4b**, **4c**, **5** and $m/e (102 + R)$.

In conclusion, the fragments **1**, **2**, **3**, **4**, **4a**, **4b**, **4c**, **5**, **6**, **7**, **8** and $m/e (102 + R)$ may be considered as characteristic peaks of pattern of fragmentation of 4,5-benzo-3-aza-2-nonem derivatives III (Scheme 11).

Table 6
Analytical and Spectral Data of VIa

R	Mp °C	Yield %	Molecular Formula	C	H	N	Spectral Data
H	165	75	C ₂₃ H ₂₀ N ₂ O ₂	77.50 (77.48)	5.65 (5.61)	7.85 (7.88)	ir (chloroform): 3350, 1750, 750 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9-6.6 (m, 14H), 5.25 (s, 1H), 4.0 (bs, 1H), 3.45-2.15 (m, 4H); M ⁺ at m/e 356
Cl	165	60	C ₂₃ H ₁₉ ClN ₂ O ₂	70.67 (70.64)	4.89 (4.90)	7.16 (7.14)	ir (chloroform): 3350, 1750, 750 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9-6.6 (m, 13H), 5.21 (s, 1H), 3.45-2.15 (m, 5H); M ⁺ at m/e 390
OMe	165	70	C ₂₄ H ₂₂ N ₂ O ₃	74.59 (74.51)	5.73 (5.72)	7.24 (7.21)	ir (chloroform): 3350, 1750, 750 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9-6.6 (m, 13H), 5.21 (s, 1H), 3.7 (s, 3H), 3.45-2.15 (m, 5H); M ⁺ at m/e 386
Me	185	72	C ₂₄ H ₂₂ N ₂ O ₂	77.81 (77.78)	5.98 (5.98)	7.56 (7.60)	ir (chloroform): 3350, 1750, 750 cm ⁻¹ ; nmr (deuteriochloroform): δ 7.9-6.55 (m, 13H), 5.2 (s, 1H), 3.4-2.15 (m, 5H), 2.21 (s, 3H); M ⁺ at m/e 370



EXPERIMENTAL

The compounds were synthesized following reported procedures (8a, 8b) with some modifications. The structures of compounds IIIa to IIIj were supported by ir and ¹H-nmr spectral data. The ir spectra for all compounds show a very strong band at 1760 cm⁻¹ in accordance with Manha's findings for similar moieties (13). The ¹H-nmr spectra (δ) of 1,5-benzodiazepine lactam III derivatives show a singlet between 2.18-2.38 which may be attributed to 2-SCH₃ protons and AB system for the methylene protons of position 1 between 3.1-3.21 and 3.75-3.9 (J_{AB}

= 14 Hz). We also observed a singlet between 5.17-5.35 which may be attributed to the H-8 proton together with the signal for aromatic protons between 6.6-8.5. In Table 3, chemical and physical data for the new compounds are recorded. All the compounds investigated gave satisfactory elemental analysis.

The IV compounds have been prepared from appropriate thiolactam intermediates V following reported procedures (7). Some have been reported (14): R = H, *p*-Cl, *p*-Me, *p*-OMe, *p*-F. The rest are described in Table 4.

The VIa compounds *p*-R = H, Cl, OMe, Me have been prepared from

the appropriate 4,5-benzo-3-aza-2-nonem, III, by Raney nickel desulfurization (8a). All the compounds gave satisfactory elemental analyses and in Tables 5 and 6, chemical and physical data for these new compounds are recorded.

The VIa compounds p -R = H, Cl, OMe, Me have been prepared from the appropriate 4,5-benzo-3-aza-2-nonem, III, by Raney nickel desulfurization (8a). All the compounds gave satisfactory elemental analyses and in Tables 5 and 6, chemical and physical data for these new compounds are recorded.

Melting points are uncorrected. The ir spectra were recorded on a Perkin-Elmer 283-B spectrophotometer, ^1H -nmr and ^{13}C -nmr spectra were recorded on a Varian FT-80A spectrometer operating at 80 MHz in deuteriochloroform solution containing tetramethylsilane as an internal standard with chemical shifts (δ) expressed in ppm downfield from TMS. Mass spectra were obtained with a Perkin-Elmer RMU-7H double focusing mass spectrometer and a Hewlett Packard 5985A quadropole mass spectrometer using the direct inlet system. The samples were recorded at an ionization chamber temperature of 190° and operating at 70 eV.

REFERENCES AND NOTES

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