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SYNTHESIS AND SPECTRAL CHARACTERISTICS OF VINYLTETRAZOLINONES

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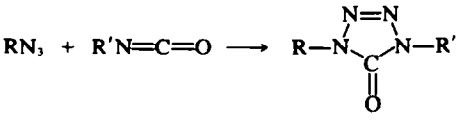
Abstract—Several methods have been worked out to synthesize 1 - vinyl - 4 - substituted - Δ^2 - tetrazolin - 5 - ones. NMR spectra showed typical AMX-patterns for the vinyl protons with chemical shifts and coupling constants almost independent of the nature of the other N-substituent. From the shielding increments, it was concluded that the tetrazolinone group exercises a strong inductive electron-withdrawing effect, but only a small resonance effect on the vinyl group. This paper also describes the first cycloreversions of azide adducts, induced by electron impact. Other significant fragmentation patterns of several mono- and disubstituted tetrazolinones are discussed.

We reported recently[1] that the reactions of alkyl azides with aryl isocyanates, acyl isocyanates, carboalkoxy isocyanates, and sulfonyl isocyanates, as well as the reactions of aryl azides with sulfonyl isocyanates, provide a convenient method for the synthesis of 1,4 - disubstituted - Δ^2 - tetrazolin - 5 - ones (**1**).



1

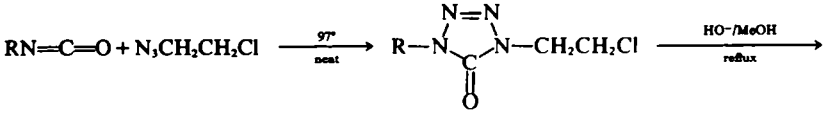
R = alkyl and R′ = aryl, acyl, sulfonyl
R = aryl and R′ = sulfonyl

We have now extended this investigation to the synthesis of vinyl substituted tetrazolinones which constitute a new and interesting class of vinyl monomers for polymerization.[2] This paper describes synthetic methods leading to vinyltetrazolinones avoiding use of the highly explosive vinyl azide.[3] The tetrazolinone shielding effects on the vinyl protons are then determined and the phenomenon of cycloreversion of 1,4 - disubstituted - Δ^2 - tetrazolin - 5 - ones upon electron impact is discussed.

1-Vinyl-4-alkyl (or aryl) - Δ^2 - tetrazolin - 5 - ones **3**. A good method of preparing aryl substituted vinyltetrazolinones **3** is the treatment of aryl isocyanates with a three-fold excess of β-chloroethyl azide, followed by dehydrochlorination of the adducts **2** with dilute base (Scheme 1). The results are summarized in Table 1.

The only disadvantage of this method is the long reaction time (5–6 weeks at 97°) needed to accomplish the first cycloaddition step. Indeed, alkyl azides have been shown[1] to react only slowly with aryl isocyanates and not at all with alkyl isocyanates or aryl isocyanates bearing electron-donating substituents In order to obtain vinyltetrazolinones with alkyl substituents or electron-rich aryl substituents at the 4-position, an indirect method can be used which profits from the activating effect of a sulfonyl group in isocyanate cycloadditions (Scheme 2). The reaction route to be followed is further analogous to that used for the synthesis of N-vinylcarbazole,[4] N-vinyltetrazoles[5] and N-vinyl-1,2,4-triazole.[6] The results are given in Table 2.

The overall yields shown in Table 2 for the synthesis of **2** from **4** are fairly good and the only side reaction observed is the formation of compounds of type **7**, resulting from the interaction of **4** with the alcohol used (Scheme 3). Note also from Table 2 that method 2 is inferior to method



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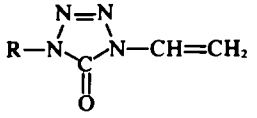

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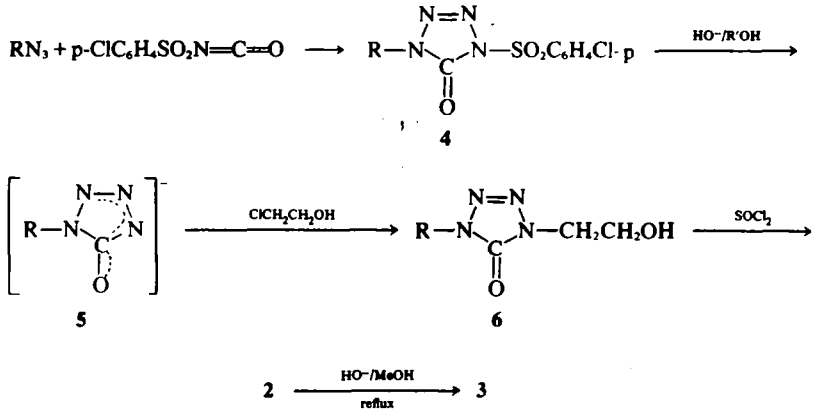
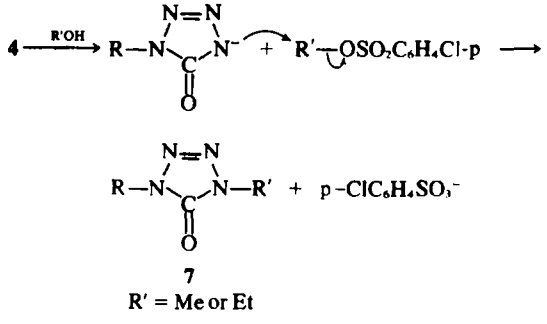
SCHEME 1.



SCHEME 2.

Table 1. Synthesis of 1 - Vinyl - 4 - aryl - Δ^2 - tetrazolin - 5 - ones **3** by Scheme 1

R	2 Time (weeks)	2 Yield (%)	2 M.p. (°C)	3 Yield (%)	3 M.p. (°C)
a C_6H_5	6	76	oil	40	35·5
b p-ClC_6H_4	5	71	65·0–65·5	46	82–83
c o,p-$Cl_2C_6H_3$	5 1/2	73	71	42	93·5–94·5



SCHEME 3.

1 for the synthesis of 1 - vinyl - 4 - phenyl - Δ^2 - tetrazolin - 5 - one **3a**.

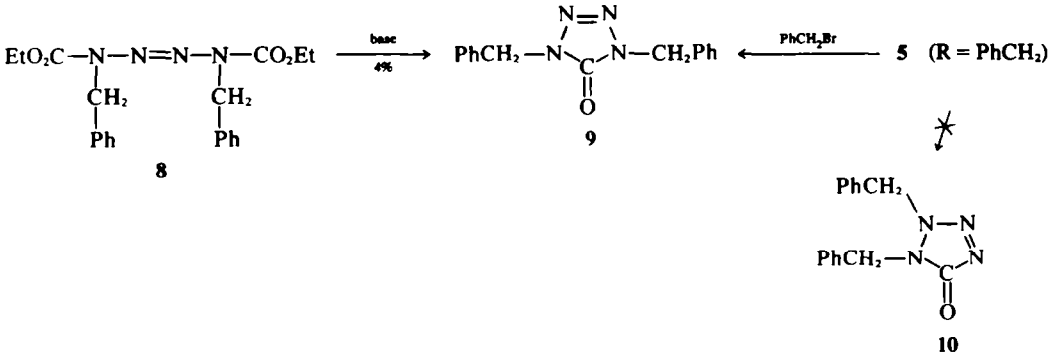
The regiochemistry of reaction **5**→**6** deserves clarification, especially in view of the known ambident properties of tetrazolinones towards diazomethane.[7] In all examples studied, the hydroxyethylation of **5** led to a single alkylated product to which the thermodynamically most stable 1,4-structure **6** was assigned. This assignment was verified by treating 1 - benzyltetrazolin - 5 - one anion (**5**, R = $PhCH_2$) with benzyl bromide in refluxing ethanol-water. The crystalline alkylated product obtained was identical in all respects with that reported by Wadsworth[8] from base induced cyclization of 1,4 - diethoxycarbonyl - 1,4 - dibenzyl - 2 - tetrazene **8**. In addition, our benzylated product exhibited in the nmr spectrum a four-proton singlet absorption at τ4·94, consistent with the symmetrical structure **9** but not with the unsymmetrical structure **10**. Prior to our work in this field, Raap and Howard[9] had reported that the reaction of tetrazolinone with ethyl bromoacetate in the presence of triethylamine furnished 1,4 - dicarbethoxymethyltetrazolin - 5 - one as the only product.

1 - *Vinyl* - 4*H* - Δ^2 - *tetrazolin* - 5 - *one* **13** *and* 1 - *Vinyl* - 4 - *sulfonyl* - Δ^2 - *tetrazolin* - 5 - *ones* **14**. The synthesis of these vinyl monomers is outlined in Scheme 4 and starts with a 1,3-dipolar cycloaddition of β-chloroethyl azide with sulfonyl isocyanates to give 1 - (β - chloroethyl) - 4 - sulfonyl - Δ^2 - tetrazolin - 5 - ones **11** in high yields (see Table 3). Compounds of type **11**, however, cannot be converted directly to **14** since the sulfonyl group is readily split off, even under solvolytic conditions. For instance, when **11** is refluxed in methanol or treated with 1 equiv of KOH in ethanol, compound **12** is obtained exclusively. The most obvious sequence to be followed for the preparation of **14** is dehydrochlorination of **12**

Table 2. Synthesis of 1 - Vinyl - 4 - aryl (or alkyl) - Δ^2 - tetrazolin - 5 - ones **3** by Scheme 2

R	4 Temp (°C)	4 Time (days)	4 Yield (%)	4 M.p. (°C)	2 Yield[a] (%)	2 B.p. (°C)	3 Yield (%)	3 M.p. (°C)
a C_6H_5	77	30	39	177·5–178	46	146–147/0·9 mm	see Table 1	
d p-$CH_3C_6H_4$	87	6 1/2	35	195·5–196·5	55	146–162/0·9–1·0 mm	41	68–69
e $C_6H_5CH_2$	87	1	87	138	62	154 (1 mm)	45	48·5–49
f n-C_4H_9	77	4	90	80·5–81·5	59	115–117/1·7 mm	79	oil

[a]The yields of **2** are based on the overall conversion **4**→**5**→**6**→**2**.



under more forcing basic conditions, followed by reaction with a sulfonyl chloride (Scheme 4).

1 - (α - *styryl*) - 4 - *sulfonyl* - Δ^2 - *tetrazolin* - 5 - *ones* **16** *and* 1 - (α - *styryl*) - 4*H* - Δ^2 - *tetrazolin* - 5 - *one* **18**. Treatment of α - azido - β - iodostyrene with equimolar amounts of sulfonyl isocyanates yields 1 : 1 adducts **15** which can be dehydrohalogenated under mild conditions (1 equiv of NEt_3) without loss of the sulfonyl group (Scheme 5). This two-step synthesis affords 1 - (α - styryl) - 4 - sulfonyl - Δ^2 - tetrazolin - 5 - ones **16** in reasonable yields (see Table 4). To obtain 1 - (α - styryl) - 4H - Δ^2 - tetrazolin - 5 - one **18**, the 1 : 1 adducts **15** are solvolyzed in methanol to give **17**, followed by treatment with a base (Scheme 5).

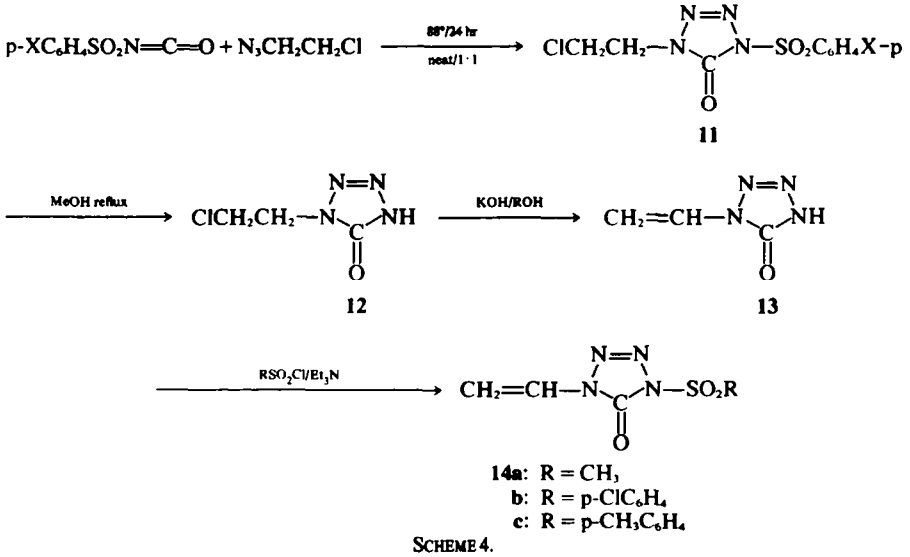
Analysis Nmr. The vinyltetrazolinones synthesized in this work show typical AMX-absorption patterns for the vinyl protons in the NMR spectra. The data, summarized in Table 5, indicate that the chemical shifts and coupling constants (J_{AM}, J_{AX} and J_{MX}) are almost unaffected by the nature of the substituents at the 4-position of the heterocyclic ring (τ_X only seems to be influenced slightly). If Z_{gem}, Z_{cis} and Z_{trans} are the respective shielding parame-

Table 3. Synthesis of 1 - (β - chloroethyl) - 4 - sulfonyl - Δ^2 - tetrazolin - 5 - ones **11**

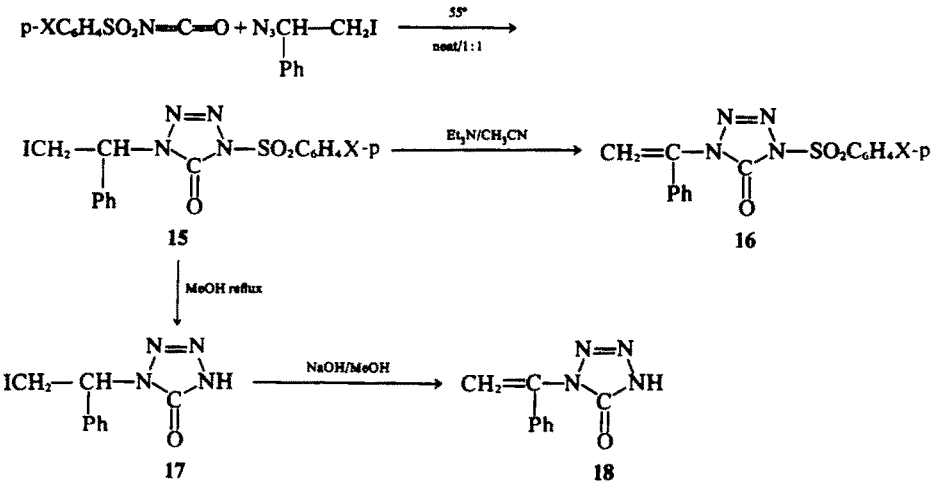
X	Yield (%)	M.p. (%)
a H	80–85	66·5–67·5
b Cl	80–85	117·5–119
c CH_3	89	103

Table 4. Synthesis of 1 - (α - styryl) - 4 - sulfonyl - Δ^2 - tetrazolin - 5 - ones (**16**) by Scheme 5

	15			**16**	
X	Time (weeks)	Yield (%)	M.p. (°C)	Yield (%)	M.p. (°C)
a H	4 1/2	74	109·5–110·5	73	99·5–100·5
b Cl	5	66	133·0–133·5	77	117·0–117·5
c CH_3	5 1/2	50	120·5–121·0	76	121·0–122·0



SCHEME 4.

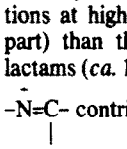


SCHEME 5.

ters of a tetrazolinone substituent in the gem-, cis- and trans-position to a proton, the following values are derived from Table 5 using τ4·73 as the resonance position for ethylene.[10,11]

$CDCl_3$/TMS	DMSO-d_6/HMDS
Z_{gem}: −1·70 ± 0·05	Z_{gem}: −1·70 ± 0·03
Z_{cis}: −0·65 ± 0·05	Z_{cis}: −0·43 ± 0·03
Z_{trans}: +0·15 ± 0·05	Z_{trans}: +0·17 ± 0·08

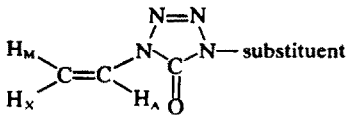
It is evident from these data that the tetrazolinone substituent exercises a strong inductive electron-withdrawing effect on the vinyl group, Z_{gem} lying between that of an SO_2-group (Z_{gem} = −1·55)[10] and an NO_2-group (Z_{gem} = −2·00).[12] It is also interesting to note that our Z_{gem}-value is smaller than that found for the normal N–CO substituent (Z_{gem} = −2·08).[10] This is in line with the observation that the vinyltetrazolinones exhibit ir C=O stretching vibrations at higher wave number (1720–1770 cm^{-1}, see exp. part) than the open-chain amides (1670–1630 cm^{-1}) or lactams (*ca.* 1700 cm^{-1}). For the latter, canonical structure



contributes more to the over-all resonance hybrid than in tetrazolinones.

The positive value of Z_{trans} indicates an increase in electron density at the β-carbon atom due to resonance.

Table 5. NMR Data of Vinyltetrazolinones (τ-values)



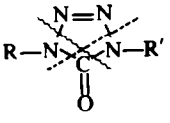
J_{AM} = 15·5–16·5 Hz
J_{AX} = 9·0–9·5 Hz
J_{MX} ≃ 1 Hz

Compound	Substituent	Solvent	H_A	H_M	H_X	Other absorptions
3a	C_6H_5	$CDCl_3$	3·02	4·08	4·89	1·92–2·70 (m, 5H)
3b	p-ClC_6H_4	$CDCl_3$	2·98	4·02	4·83	2·04 and 2·51 (two d, 4H, J = 9 Hz)
3c	o,p-$Cl_2C_6H_3$	$CDCl_3$	3·00	4·03	4·83	2·30–2·43 (m, 1H) and 2·47–2·63 (m, 2H)
3d	p-$CH_3C_6H_4$	$CDCl_3$	2·97	4·03	4·87	2·17 and 2·69 (two d, 4H, J = 9 Hz)
3e	$C_6H_5CH_2$	$CDCl_3$	3·08	4·13	4·94	2·63 (s, 5H) and 4·90 (s, 2H)
3f	n-C_4H_9	$CDCl_3$	3·07	4·13	4·93	6·03 (t, 2H, J = 7 Hz) and 7·80–9·30 (m, 7H)
13	H	DMSO-d_6	3·04	4·30	4·98[a]	
14a	CH_3SO_2	DMSO-d_6	3·01	4·27	4·82	6·36 (s, 3H)
14b	p-$ClC_6H_4SO_2$	DMSO-d_6	3·06	4·32	4·84	1·90 and 2·20 (two d, 4H, J = 9 Hz)
14c	p-$CH_3C_6H_4SO_2$	DMSO-d_6	3·05	4·32	4·85	2·01 and 2·47 (two d, 4H, J = 8·5 Hz); 7·54 (s, 3H)

[a] J_{MX} for compd **13** is less than 0·5 Hz.

This resonance contribution, however, is very small compared to N-vinylsubstituted amides for which $Z_{trans} = +0{\cdot}72$.[10] Finally, the negative value of Z_{cis} is explained by the anisotropic behavior of the tetrazolinone group located in cis-position (compare this value with $Z_{cis} = -0{\cdot}39$ for phenyl[11] and $Z_{cis} = -0{\cdot}7 \rightarrow -0{\cdot}9$ for a 2-triazolyl substituent[13]).

Analysis of Mass Spectra. Recently, two research groups[14] reported on the electron impact induced cycloreversion of 1,3-dipolar adducts. We have found that 1,4-disubstituted tetrazolin-5-ones **1** also cycloreverse in the mass spectrometer. The low-resolution mass spectrometric decomposition of **1** leads to fragment ions corresponding in elemental composition to $[R+42]^{\cdot+}$ or $[R'+42]^{\cdot+}$. Since both the azide and isocyanate functions possess 42 mass units, theoretically two bisections of the ring can be considered as shown below:



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High-resolution mass spectral measurements of some model compounds clear up the situation. The results, shown in Table 6, indicate that the two modes of decomposition are indeed observed. Although the ions $RNCO^{\cdot+}$ and /or $R'NCO^{\cdot+}$ are always present as strong peaks, the azide ions $RN_3^{\cdot+}$ and/or $R'N_3^{\cdot+}$ are less frequently seen in the spectra. The formation of isocyanate ions from **1** upon electron impact is revealed by the presence of metastable ion peaks. Furthermore, sulfonyl substituted tetrazolinones (e.g. **4a** and **11b**), which cycloreverse readily on thermolysis,[1] only show weak sulfonyl isocyanate ion peaks (< 2%). These observations substantiate the existence of a cycloelimination path induced by electron impact, although it does not exclude the possibility that thermal cycloelimination occurs to some (minor) extent. The differently substituted tetrazolinones will now be discussed in some more detail. In most cases studied, the molecular ion peaks are weak and in no case was a peak observed which corresponds to $[M-N_2]^{\cdot+}$

Fragmentation of aryl substituted tetrazolinones leads to base peaks of $ArNCO^{\cdot+}$ (including possibly $ArN_3^{\cdot+}$). These radical ions fragment by loss of 28 mass units to give nitrenium ions $ArN^{\cdot+}$.[15] Metastable peaks for both processes are observed in the spectra.

When an arylsulfonyl substituent is present on the tetrazolinone ring, the $ArSO_2NCO^{\cdot+}$ peak is of low intensity since formation of $ArSO_2^+$ from the molecular ion seems to occur more readily. This ion then further fragments to aryl ion with loss of SO_2.

The mass spectra of vinyltetrazolinones give rise to major peaks of $CH_2{=}CHNCO^{\cdot+}$ or $RNCO^{\cdot+}$ depending on the nature of the R substituent. The latter ion is important for 4-aryl substituted 1 - vinyltetrazolin - 5 - ones which then forms the base peak of the spectrum. The vinylisocyanate ion ($CH_2{=}CHNCO^{\cdot+}$) at *m/e* 69 is important for other cases and can fragment to a vinyl nitrenium ion ($CH_2{=}CHN^{\cdot+}$) or azirinium ion () of *m/e* 41, although this path is not supported by a metastable peak at *m/e* 24·4 ($= 41^2/69$). The data are listed in Table 7. Although we are discussing fragmentations in terms of isocyanate ions instead of azide ions or both, it should be realized that only accurate mass measurements can establish this point (see Table 6 for two examples).

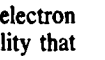
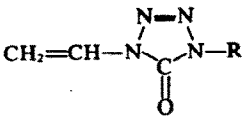
As expected, the mass spectra of α-styryltetrazolinones (**16** and **18**) are characterized by strong *m/e* 145 peaks for styrylisocyanate ion (including possibly styryl azide ion) and strong *m/e* 117 peaks for styrylnitrenium ion ($CH_2{=}C(Ph)N^{\cdot+}$) or phenylazirinium ion (). In these cases, conversion *m/e* 145 → 117 is proven by the presence of metastable ion peaks at *m/e* 94·4. Another significant peak in the spectra is observed at *m/e* 103 which can be attributed to the styryl

Table 6. Cycloelimination of Tetrazolinones **1** upon Electron Impact

Compound	R	R'	*m/e* (rel. intensity)	Assignment
	C_6H_5	H	119 (93)	Calcd for $C_6H_5NCO^{\cdot+}$: 119·0371. Obsd. 119·0375
			43 (16)	Calcd for $HNCO^{\cdot+}$: 43·0058. Obsd. 43·0060
3a	C_6H_5	$CH_2{=}CH$	119 (100)	Calcd for $C_6H_5NCO^{\cdot+}$: 119·0371. Obsd. 119·0369
			69 (< 2)	Calcd for $CH_2{=}CHNCO^{\cdot+}$: 69·0215. Obsd. 69·0216
				Calcd for $CH_2{=}CHN_3^{\cdot+}$: 69·0327. Obsd. 69·0327
				$(CH_2{=}CHNCO^{\cdot+})/(CH_2{=}CHN_3^{\cdot+}) = 4/7$
4a	C_6H_6	p-$ClC_6H_4SO_2$	119 (100)	Calcd for $C_6H_5NCO^{\cdot+}$: 119·0371. Obsd. 119·0372
				Calcd for $C_6H_5N_3^{\cdot+}$: 119·0483. Obsd. 119·0482
				$(C_6H_5NCO^{\cdot+})/(C_6H_5N_3^{\cdot+}) = 14$
			217 (2)	Calcd for p-$ClC_6H_4SO_2NCO^{\cdot+}$: 216·9590. Obsd. 216·9598
11b	$ClCH_2CH_2$	p-$ClC_6H_4SO_2$	105 (<2)	Calcd for $ClCH_2CH_2N_3^{\cdot+}$: 105·0084. Obsd. 105·0084
			217 (<2)	Calcd for p-$ClC_6H_4SO_2NCO^{\cdot+}$: 216·9590. Obsd. 216·9598
13	H	$CH_2{=}CH$	69 (100)	Calcd for $CH_2{=}CHNCO^{\cdot+}$: 69·0215. Obsd. 69·0212
				Calcd for $CH_2{=}CHN_3^{\cdot+}$: 69·0327. Obsd. 69·0323
				$(CH_2{=}CHNCO^{\cdot+})/(CH_2{=}CHN_3^{\cdot+}) = 16/5$
			43 (31)	Calcd for $HNCO^{\cdot+}$: 43·0058. Obsd. 43·0060

Table 7. Mass Spectra of Vinyltetrazolinones



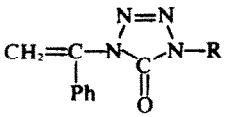
Compound	R	CH_2=CHNCO$^{+\cdot}$ *m/e* 69 Rel. intensity	RNCO$^{+\cdot}$ *m/e*	RNCO$^{+\cdot}$ Rel. intensity	RNCO$^{+\cdot}$ Metastable ion peak	CH_2=CHN$^{+\cdot}$, *m/e* 41 Rel. intensity
3a	C_6H_5	<2	119	100	75·3	9
3b	p-ClC_6H_4	<2	153	100	105·4	<2
3c	o,p-$Cl_2C_6H_3$	<2	187	100	136·6	9
3d	p-$CH_3C_6H_4$	<2	133	100	87·6	4
3e	$C_6H_5CH_2$	3	133	15	—	5
3f	n-C_4H_9	85	99	3	—	100
13	H	100	43	31	—	62
14a	CH_3SO_2	100	121	2	—	31
14b	p-$ClC_6H_4SO_2$	23	217	5	—	29
14c	p-$CH_3C_6H_4SO_2$	8	197	<2	—	32

ion CH_2=C(Ph)$^+$. Table 8 presents the relative abundances of these major peaks.

Cycloreversion reactions are not important for alkyl substituted tetrazolinones. The characteristic features of the spectra of n-butyltetrazolinones are peaks at [M$^{+\cdot}$ − 55], *m/e* 56 and [M$^{+\cdot}$ − 42], and their relative importance depends on the nature of the other N-substituent as shown in Table 9. To account for these fragments, processes can be depicted analogous to those established for succinimides[16] and maleimides[17] (see Scheme 6). The first two paths proposed in Scheme 6 involve N–C cleavage accompanied by transfer of one or two hydrogen atoms; processes which are substantiated by appropriate metastable peaks in some cases (see Table 9). The [M$^{+\cdot}$ − 42] peak arises from α-cleavage with transfer of a γ-hydrogen atom. If the n-butyl group is changed for an ethyl or β-chloroethyl group, this fragmentation path is impossible and, hence, the [M$^{+\cdot}$ − 42] peak is not observed.

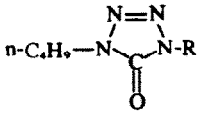
The 1 - (α - phenyl - β - iodoethyl)tetrazolinones (**15a-c**

Table 8. Relative abundances of the major fragments in the mass spectra of α-styryltetrazolinones



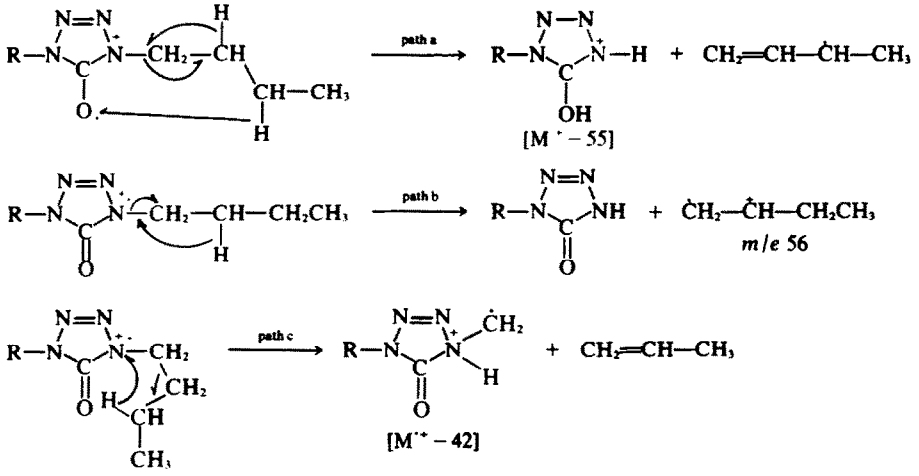
Compound	R	*m/e* 145	*m/e* 117	*m/e* 103
16a	$C_6H_5SO_2$	67	50	30
16b	p-$ClC_6H_4SO_2$	100	87	54
16c	p-$CH_3C_6H_4SO_2$	89	36	27
18	H	100	64	43

Table 9. Mass spectral data of n-butyltetrazolinones

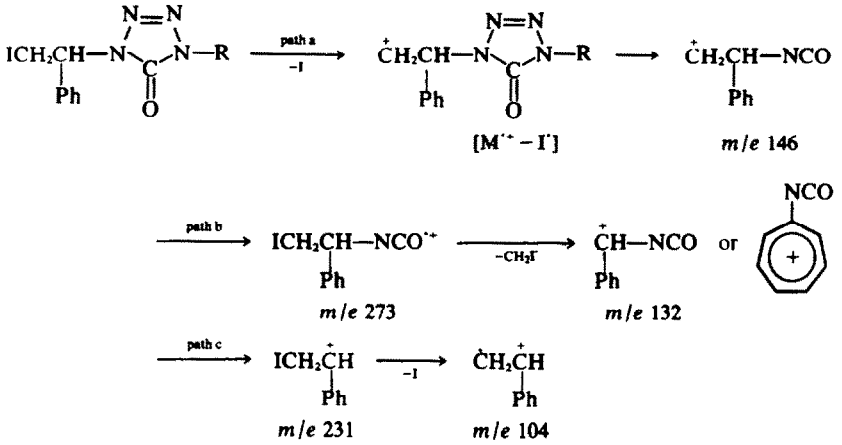


R	[M$^{+\cdot}$ − 55] *m/e*	[M$^{+\cdot}$ − 55] Rel. intensity	*m/e* 56 Rel. intensity	[M$^{+\cdot}$ − 42] *m/e*	[M$^{+\cdot}$ − 42] Rel. intensity
H	87	75	65[a]	100	27
CH_3	101	100	21	114	12
C_2H_5	115	100	18	128	9
$ClCH_2CH_2$	149	100	26	162	11
CH_2=CH	113	60	32	126	73
C_6H_5[d]	163	2	<2	176	<2
p-$NO_2C_6H_4$[d]	208	11[b]	11	221	<2
$C_6H_5SO_2$[d]	227	<2	3	240	<2
p-$ClC_6H_4SO_2$	261	<2	5	274	<2
p-$CH_3C_6H_4SO_2$[d]	241	<2[c]	<2	254	<2
p-$NO_2C_6H_4SO_2$[d]	272	9	12	285	<2

[a] Metastable peak at *m/e* 22·1; [b] Metastable peak at *m/e* 164·5; [c] Metastable peak at *m/e* 196·2; [d] This compound was prepared cf. ref. 1



SCHEME 6.



SCHEME 7.

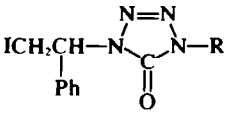
and **17**) were also synthesized in this work and exhibit some interesting features in the mass spectra which can be adequately described by fragmentation patterns shown in Scheme 7 (see also Table 10). Loss of an iodine radical from the molecular ion gives a $[M^{\cdot+} - I^{\cdot}]$ fragment which further degrades by cyclo-elimination to an isocyanate ion at *m/e* 146 (path a). The two steps of path a are established by metastable peaks. Direct cycloreversion of the molecular ion also occurs, but to a minor extent (path b). The isocyanate ion formed at *m/e* 273 probably loses $CH_2I^{\cdot}$ to give the important tropylium ion at *m/e* 132. (As already mentioned earlier, we do not in fact differentiate in Scheme 7 between isocyanate ions and azide ions since the composition of the fragments has not been established by high resolution mass spectrometry). A third and major path of fragmentation occurs via the ions at *m/e* 231 and *m/e* 104. The formation of a radical ion (at *m/e* 104) from an even-electron ion (at *m/e* 231) is uncommon. It is established in our case by the presence of a metastable ion peak at *m/e* 46·8

EXPERIMENTAL

All m.ps were obtained on a Leitz apparatus and are uncorrected. Ir spectra were taken on a Perkin-Elmer 521 spectrometer. Nmr Spectra were recorded with a Varian A-60 or XL-100 spectrometer using TMS as internal reference unless otherwise stated. Mass spectra were obtained with an AEI MS-12 instrument operating at an ionizing potential of 70 eV.

Synthesis of 1 - *vinyl* - 4 - *aryl* - Δ^2 - *tetrazolin* - 5 - *ones* **3a-c** *by Scheme* 1. A mixture of aryl isocyanate[18] (0·1 mole) and β-chloroethyl azide[3] (0·3 mole) was heated at 97° in the absence of solvent. After complete reaction (monitored by IR), the excess of azide was distilled off under reduced pressure, and the residual oil was dissolved in $CHCl_3$ and treated with activated charcoal. **2a** was purified by distillation (b.p. 146–147°/0·9 mm), pale yellow oil; IR (CCl_4) 1735 cm^{-1} (C=O); mass spectrum, *m/e* (%) 224 (11, M^+), 119 (100, $PhNCO^{\cdot+}$ and/or $PhN_3^{\cdot+}$) and 105 (2, $ClCH_2CH_2NCO^{\cdot+}$ and/or $ClCH_2CH_2N_3^{\cdot+}$ Found: C, 47·80; H, 3·90; Cl, 16·00; N, 25·05. Calc. for $C_9H_9ClN_4O$ (224): C, 48·12; H, 4·04; Cl, 15·78; N, 24·94% **2b** was crystallized from 1:1 toluene-ether, m.p. 65·0–65·5°; IR (KBr) 1732 cm^{-1}; mass spectrum, *m/e* (%) 258 (9, M^+), 153 (100, $ClC_6H_4NCO^{\cdot+}$ and/or $ClC_6H_4N_3^{\cdot+}$) and 125 (13, $ClC_6H_4N^{\cdot+}$) Found: C, 41·75; H, 3·00; Cl, 27·65; N, 21·80. Calc.

Table 10. Mass Spectral Data of 1-(α-Phenyl-β-iodoethyl)tetrazolinones **15** and **17**



Compound	R	$[M^{\cdot+} - I^{\cdot}]$ *m/e*	$[M^{\cdot+} - I^{\cdot}]$ Rel. intensity	$[M^{\cdot+} - I^{\cdot}]$ Metastable ion peak	*m/e* 146 Rel. intensity	*m/e* 146 Metastable ion peak	*m/e* 273 Rel. intensity	*m/e* 132 Rel. intensity	*m/e* 231 Rel. intensity	*m/e* 104 Rel. intensity
15a	$C_6H_5SO_2$	329	56	—	56	—	<2	29	71	100
15b	$p\text{-}ClC_6H_4SO_2$	363	33	—	63	58·7	<2	37	74	100
15c	$p\text{-}CH_3C_6H_4SO_2$	343	39	250·3	32	62·1	<2	19	58	90
17	H	189	100	113·0	53	112·7	<2	35	24	73

for $C_9H_8Cl_2N_4O$ (259): C, 41·72; H, 3·11; Cl, 27·37; N, 21·62%. **2e** was crystallized from cyclohexane-CH_2Cl_2, m.p. 71°; IR (KBr) 1737 cm^{-1}; mass spectrum, *m/e* (%) 292 (5, $M^{\cdot+}$), 187 (100, $Cl_2C_6H_3NCO^{\cdot+}$ and/or $Cl_2C_6H_3N_3^{\cdot+}$), 159 (8, $Cl_2C_6H_3N^{\cdot+}$) and 105 (2) (Found: C, 36·70; H, 2·35; Cl, 36·35; N, 19·20 Calc. for $C_9H_7Cl_3N_4O$ (293): C, 36·83; H, 2·40; Cl, 36·23; N, 19·09%).

A solution of **2** (0·1 mole) in methanol (100 ml) containing 0·2 mole of NaOH was stirred for 1 h and then heated at reflux for 1–3 h. After removal of solvent, water (100 ml) is added, the product is extracted with ether and the combined ether extracts are dried over $CaCl_2$. After evaporation of the ether, the crude product is chromatographed on Florisil using CH_2Cl_2 as the eluent. **3a** is crystallized from ether, m.p. 35·5°; IR (KBr) 1732 cm^{-1}; mass spectrum, $M^{\cdot+}$ (54%) at *m/e* 188, see also Table 7 (Found: C, 57·30; H, 4·10; N, 29·90. Calc. for $C_9H_8N_4O$ (188): C, 57·44; H, 4·28; N, 29·77%). **3b** is crystallized from ether, m.p. 82–83°; IR (KBr) 1726 cm^{-1}; mass spectrum, $M^{\cdot+}$ (26%) at *m/e* 222, see also Table 7. (Found: C, 48·60; H, 3·00; Cl, 16·10; N, 25·40. Calc. for $C_9H_7ClN_4O$ (222): C, 48·55; H, 3·17; Cl, 15·92; N, 25·17%). **3c** is crystallized from n-pentane-CH_2Cl_2, m.p. 93·5–94·5°; IR (KBr) 1724 cm^{-1}; mass spectrum, $M^{\cdot+}$ (11%) at *m/e* 256, see also Table 7 (Found: C, 42·00; H, 2·30; Cl, 27·60; N, 22·00. Calc. for $C_9H_6Cl_2N_4O$ (257): C, 42·04; H, 2·36; Cl, 27·58; N, 21·79%).

Synthesis of 1-*Vinyl*-4-*aryl* (*or alkyl*) - Δ^2 - *tetrazolin* - 5 - *ones* **3a, 3d-f** *by Scheme* 2. Equimolar mixtures of arylsulfonyl isocyanate[19] and azide were heated under the conditions given in Table 2. The reaction mixture is then dissolved in CH_2Cl_2 and cooled. Recrystallization from ether-CH_2Cl_2 gives the following products: **4a**: IR (KBr) 1760 cm^{-1}; mass spectrum, *m/e* (%) 336 (13, $M^{\cdot+}$), 175 (16, $ClC_6H_4SO_2^+$), see also Table 6 (Found: C, 46·15; H, 2·60; Cl, 10·70; N, 16·65. Calc. for $C_{13}H_9ClN_4O_3S$ (336): C, 46·37; H, 2·69; Cl, 10·53; N, 16·64%). **4d**: IR (KBr) 1760 cm^{-1}; mass spectrum, *m/e* (%) 350 (8, $M^{\cdot+}$), 175 (8, $ClC_6H_4SO_2^+$) and 133 (100, $CH_3C_6H_4NCO^{\cdot+}$ and/or $CH_3C_6H_4N_3^{\cdot+}$) (Found: C, 47·85; H, 3·05; Cl, 10·60; N, 16·05. Calc. for $C_{14}H_{11}ClN_4O_3S$ (350): C, 47·94; H, 3·16; Cl, 10·11; N, 15·97%). **4e**: IR (KBr) 1750 cm^{-1}; mass spectrum, *m/e* (%) 350 (5, $M^{\cdot+}$), 175 (59, $ClC_6H_4SO_2^+$) and 91 (100, $PhCH_2^+$) (Found: C, 47·75; H, 3·00; N, 15·80; S, 9·15. Calc. for $C_{14}H_{11}ClN_4O_3S$ (350): C, 47·94; H, 3·16; N, 15·97; S, 9·14%). **4f**: IR (KBr) 1754 cm^{-1}; mass spectrum, *m/e* (%) 316 (< 1, $M^{\cdot+}$), 175 (91, $ClC_6H_4SO_2^+$) and 111 (100).

Compound **4** (0·2 mole) in 1:2 water-alcohol (400 ml) containing KOH (0·4 mole) was heated during a period of 4 h. Then, β-chloroethanol (0·4 mole) is added and the mixture is heated for another 12 h. The solvent is removed and the residue is extracted with warm $CHCl_3$. The combined chloroform extracts are dried over $MgSO_4$ and then evaporated to give **6** as a viscous oil, IR ($CHCl_3$) 3410 (OH) and 1710 cm^{-1} (C=O). Compound **6** (0·13 mole) is dissolved in $CHCl_3$ (100 ml) and $SOCl_2$ (0·39 mole) is added dropwise with stirring. When SO_2 evolution slows down, the mixture is refluxed for 2–6 h. The excess of $SOCl_2$ is distilled off and the residue is treated with water and extracted with ether. After drying over $CaCl_2$, the ether is removed and the residue is subjected to fractional distillation. The first fractions are composed of **2** and **7** (NMR analysis) and the following fractions contain pure **2** (see Table 2 for yields and b.p.). In the case of R = n-Bu, compound **7** was isolated in the pure state. **2d** is obtained as a pale yellow oil and is crystallized from ether to give white needles, m.p. 58–59°; IR (KBr) 1731 cm^{-1}; mass spectrum, *m/e* (%) 238 (1, $M^{\cdot+}$), 133 (100, $CH_3C_6H_4NCO^{\cdot+}$ and/or $CH_3C_6H_4N_3^{\cdot+}$) and 105 (15, $ClCH_2CH_2NCO^{\cdot+}$ and/or $ClCH_2CH_2N_3^{\cdot+}$ and/or $CH_3C_6H_4N^{\cdot+}$) (Found: C, 50·30; H, 4·65; Cl, 14·65; N, 23·43. Calc. for $C_{10}H_{11}ClN_4O$ (238): C, 50·32; H, 4·65; Cl, 14·85; N, 23·47%). **2e** is obtained as a colourless viscous oil; IR (CCl_4) 1729 cm^{-1}; mass spectrum, *m/e* (%) 238 (1, $M^{\cdot+}$), 105 (3), 91 (85, $PhCH_2^+$) and 43 (100). (Found: C, 50·20; H, 4·60; N, 23·20. Calc. for $C_{10}H_{11}ClN_4O$ (238): C, 50·32; H, 4·65; N, 23·47%). **2f** is obtained as a colorless viscous oil; IR (CCl_4) 1729 cm^{-1}; mass spectrum, $M^{\cdot+}$ (16%) at *m/e* 204, see also Table 9 (Found: C, 40·85; H, 6·35; Cl, 17·55; N, 27·40. Calc. for $C_7H_{13}ClN_4O$ (204): C, 41·08; H, 6·40; Cl, 17·32; N, 27·38%). **7** (R=n-Bu, R'=Me) is obtained in 13% yield, b.p. 62–64°/0·2–0·3 mm; IR (CCl_4) 1718 cm^{-1}; mass spectrum, $M^{\cdot+}$ (34%) at *m/e* 156, see also Table 9. (Found: C, 46·25; H, 7·75; N, 35·65. Calc. for $C_6H_{12}N_4O$ (156): C, 46·14; H, 7·74; N, 35·87). **7** (R=n-Bu, R'=Et) is obtained in 12% yield, b.p. 66–70°/0·2–0·4 mm; IR (CCl_4) 1727 cm^{-1}; mass spectrum, $M^{\cdot+}$ (28%) at *m/e* 170, see also Table 9. (Found: C, 49·35; H, 8·60; N, 33·20. Calc. for $C_7H_{14}N_4O$ (170): C, 49·40; H, 8·29; N, 32·91%).

The compounds **2d-f** are dehydrochlorinated by the procedure given for Scheme1 (see above). **3d** is crystallized from n-pentane-CH_2Cl_2, m.p. 68–69°; IR (KBr) 1730 cm^{-1}; mass spectrum, $M^{\cdot+}$ (40%) at *m/e* 202, see also Table 7 (Found: C, 59·60; H, 4·85; N, 27·70. Calc. for $C_{10}H_{10}N_4O$ (202): C, 59·40; H, 4·98; N, 27·71%). **3e** is crystallized from ether, m.p. 42·5–49°; IR (KBr) 1726 cm^{-1}; mass spectrum, *m/e* (%) 202 (30, $M^{\cdot+}$), 91 (100, $PhCH_2^+$), see also Table 7. (Found: C, 59·40; H, 4·90; N, 27·70. Calc. for $C_{10}H_{10}N_4O$ (202): C, 59·40; H, 4·98; N, 27·71%). **3f** is obtained as an oil, b.p. 72°/1·2–1·3 mm; IR (CCl_4) 1736 cm^{-1}; mass spectrum, $M^{\cdot+}$ (76%) at *m/e* 168, see also Tables 7 and 9. (Found: C, 50·00; H, 7·20; N, 33·30. Calc. for $C_7H_{12}N_4O$ (168): C, 49·99; H, 7·19; N, 33·31%).

Synthesis of 1,4 - *dibenzyl* - Δ^2 - *tetrazolin* - 5 - *one* **9**. A solution of **4e** (0·1 mole) and KOH (0·2 mole) in 1:2 water-EtOH (200 ml) was heated at reflux temperature for 8 h. After addition of benzyl bromide (0·2 mole), the solution is refluxed for another 24 h. The solvent is then removed and the residue is extracted with warm $CHCl_3$ (500 ml) and dried over $MgSO_4$. Removal of the solvent gives an oil (29·5 g) which is dissolved in ether and cooled to yield a white crystalline product **9** in 31% after recrystallization from ether, m.p. 103–104°; IR (KBr) 1718 cm^{-1}; mass spectrum, *m/e* (%) 266 (19, $M^{\cdot+}$), 133 (3, $PhCH_2NCO^{\cdot+}$ and/or $PhCH_2N_3^{\cdot+}$) and 91 (100, $PhCH_2^+$). (Found: C, 67·65; H, 5·30; N, 21·20. Calc. for $C_{15}H_{14}N_4O$ (266): C, 67·65; H, 5·30; N, 21·04%). The mother liquor is evaporated and the residual oil is fractionally distilled to give successively benzyl ethyl ether (3 ml), benzyl alcohol (2·5 ml) and 1 - benzyl - 4 - ethyl - Δ^2 - tetrazolin - 5 - one (5·5 g, b.p. 125–131°/0·7–0·8 mm). The latter is crystallized from ether to give a white crystalline product, m.p. 36–38·5°; IR (KBr) 1719 cm^{-1}; NMR ($CDCl_3$) τ2·64 (s, 5H), 4·94 (s, 2H), 6·06 (q, 2H, J = 7 Hz) and 8·62 (t, 2H, J = 7 Hz); mass spectrum, *m/e* (%) 204 (20, $M^{\cdot+}$) and 91 (100, $PhCH_2^+$) (Found: C, 58·80; H, 5·90; N, 27·75. Calc. for $C_{10}H_{12}N_4O$ (204): C, 58·81; H, 5·92; N, 27·43%).

Synthesis of 1 - *vinyl* - 4*H* - Δ^2 - *tetrazolin* - 5 - *one* **13**. Equimolar mixtures of arylsulfonyl isocyanate and β-chloroethyl azide are heated at 88° in the absence of solvent for 24 h. The mixtures are then crystallized from CH_2Cl_2 and recrystallized from ether-CH_2Cl_2 to give pure **11a-c** (see Table 3 for yields and m.p.).

11a: ir (KBr) 1745 cm^{-1}; mass spectrum, *m/e* (%) 288 (1, $M^{\cdot+}$), 141 (31, $PhSO_2^+$) and 77 (100) (Found: C, 37·40; H, 3·05; Cl, 12·30; N, 19·70. Calc. for $C_9H_9ClN_4O_3S$ (288): C, 37·44; H, 3·14; Cl, 12·28; N, 19·40%. **11b**: IR (KBr) 1747 cm^{-1}; mass spectrum, *m/e* (%) 323 (3, $M^{\cdot+}$), 175 (100, $ClC_6H_4SO_2^+$), see also Table 6 (Found: C, 33·45; H, 2·40; Cl, 21·95; N, 17·65. Calc. for $C_9H_8Cl_2N_4O_3S$ (323): C, 33·45; H, 2·49; Cl, 21·94; N, 17·33%). **11c**: IR (KBr) 1750 cm^{-1}; mass spectrum, *m/e* (%) 302 (2, $M^{\cdot+}$), 155 (89, $CH_3C_6H_4SO_2^+$) and 91 (100). (Found: C, 39·90; H, 3·55; Cl, 11·10; N, 18·40. Calc. for $C_{10}H_{11}ClN_4O_3S$ (302): C, 39·67; H, 3·66; Cl, 11·71; N, 18·51%).

Compound **11b** (15·3 g) was heated in methanol (200 ml) at reflux temp. for 4 days. The solvent was removed and the residue is treated with water (150 ml) and extracted with $CHCl_3$. The combined chloroform extracts are dried over $MgSO_4$ and then evaporated. After two crystallizations from toluene, white needles

of **12** are obtained in 44·5%, m.p. 77–78°; IR (KBr) 1710 cm^{-1}; mass spectrum, *m/e* (%) 148 (22, M^{+}) and 113 (100) (Found: C, 24·15; H, 3·40; Cl, 23·80; N, 37·70. Calc. for $C_3H_5ClN_4O$ (148): C, 24·26; H, 3·39; Cl, 23·87; N, 37·72%).

A methanol soln (250 ml) of **12** (0·1 mole) and KOH (0·5 mole) is stirred at room temp. for 1 h and then refluxed for 7 h. After removal of the solvent, the residue is acidified with a 4N soln of HCl and then extracted several times with $CHCl_3$. The combined chloroform extracts are dried over $MgSO_4$ and treated with activated charcoal. After several crystallizations from $CHCl_3$, a white product **13** is obtained in 55–70% yield, m.p. 112–115°; IR (KBr) 3400–2500 (br, NH), 1745, 1690 and 1650 cm^{-1}; mass spectrum, M^{+} (31) at *m/e* 112, see also Tables 6 and 7. (Found: C, 32·15; H, 3·50; N, 50·05. Calc. for $C_3H_4N_4O$ (112): C, 32·15; H, 3·60; N, 49·98%).

Synthesis of 1 - *vinyl* - 4 - *sulfonyl* - Δ^2 - *tetrazolin* - 5 - *ones* **14a-c**. A soln of the appropriate sulfonyl chloride (0·03 mole) in acetonitrile (15 ml) is added with stirring to a solution of **13** (0·03 mole) and NEt_3 (0·03 mole) in acetonitrile (15 ml). This results in the formation of a white precipitate. The mixture is stirred over-night and then heated for 1 h. After removal of the solvent, water (100 ml) is added and the reaction product is extracted with CH_2Cl_2. The extracts are dried over $MgSO_4$ and evaporated. Crystallization from CH_2Cl_2 yields white crystalline products (**14a-c**). **14a** is obtained in 46%, m.p. 142–144°; IR (KBr) 1751 and 1652 cm^{-1}; mass spectrum, *m/e* (%) 190 (24, M^{+}), 79 (30, $CH_3SO_2^{+}$), see also Table 7. Found: C, 25·20; H, 3·20; H, 29·40; S, 16·80. Calc. for $C_4H_6N_4O_3S$ (190): C, 25·26; H, 3·18; N, 29·46; S, 16·86%). **14b** is obtained in 50%, m.p. 151–152°; IR (KBr) 1749 and 1651 cm^{-1}; mass spectrum, *m/e* (%) 286 (27, M^{+}), 175 (77, $ClC_6H_4SO_2^{+}$), 111 (100), see also Table 7 (Found: C, 37·70; H, 2·40; N, 19·45; S, 11·20. Calc. for $C_9H_7ClN_4O_3S$ (286): C, 37·71; H, 2·46; N, 19·54; S, 11·18%). **14c** is obtained in 50%, mp 118–120°; IR (KBr) 1767, 1652 and 1641 cm^{-1}; mass spectrum, *m/e* (%) 266 (19, M^{+}), 155 (73, $CH_3C_6H_4SO_2^{+}$), 91 (100), see also Table 7. (Found: C, 44·45; H, 3·75; N, 21·25. Calc. for $C_{10}H_{10}N_4O_3S$ (266): C, 45·11; H, 3·79; N, 21·04%).

Synthesis of 1 - (α - *Styryl*) - 4 - *sulfonyl* - Δ^2 - *tetrazolin* - 5 - *ones* **16a-c**. Equimolar amounts of arylsulfonyl isocyanate and α-azido-β-iodostyrene[20] are heated at 55°. The solidified product is dissolved in CH_2Cl_2 and decolorized with a sodium thiosulfate solution (5%). The organic layer is isolated, dried over $CaCl_2$ and evaporated. Crystallization from ether-CH_2Cl_2 yields a white crystalline product of **15** (see Table 4). **15a**: IR (KBr) 1760 cm^{-1}; mass spectrum, *m/e* (%) 456 (1, M^{+}), 141 (32, $PhSO_2^{+}$), see also Table 10. (Found: C, 39·50; H, 2·80; I, 27·65; N, 12·15. Calc. for $C_{15}H_{13}IN_4O_3S$ (456): C, 39·49; H, 2·87; I, 27·81; N, 12·28%). **15b**: IR (KBr) 1750 cm^{-1}; mass spectrum, *m/e* (%) 490 (< 1, M^{+}), 175 (40, $ClC_6H_4SO_2^{+}$), see also Table 10. (Found: C, 36·69; H, 2·53; I, 26·03; N, 11·35; S, 6·48. Calc. for $C_{15}H_{12}ClIN_4O_3S$ (490): C, 36·72; H, 2·46; I, 25·86; N, 11·42; S, 6·53%). **15c**: IR (KBr) 1750 cm^{-1}; mass spectrum, *m/e* (%) 470 (1, M^{+}), 155 (50, $CH_3C_6H_4SO_2^{+}$), 91 (100), see also Table 10. (Found: C, 40·65; H, 3·05; I, 26·55; N, 11·85. Calc. for $C_{16}H_{15}IN_4O_3S$ (470): C, 40·86; H, 3·21; I, 26·98; N, 11·91%).

An acetonitrile solution (100 ml) of **15** (0·02 mole) and NEt_3 (0·02 mole) is stirred at room temp. for 1 day and then heated at 55° for 1 h. After removal of solvent, the red-brown residue was dissolved in CH_2Cl_2 and decolorized by treatment with a solution of sodium thiosulfate (5%). The organic layer is dried over $CaCl_2$ and then evaporated to dryness. The crude product is crystallized from ether-CH_2Cl_2 to give white crystals of **16a-c**. **16a**: IR (KBr) 1760 and 1631 cm^{-1}; mass spectrum, *m/e* (%) 328 (13, M^{+}), 141 (17, $PhSO_2^{+}$), 77 (100), see also Table 8. (Found: C, 54·60; H, 3·40; N, 16·85. Calc. for $C_{15}H_{12}N_4O_3S$ (328): C, 54·87; H, 3·68; N, 17·06%). **16b**: IR (KBr) 1760 and 1624 cm^{-1}; mass spectrum, *m/e* (%) 362 (6, M^{+}), 175 (28, $ClC_6H_4SO_2^{+}$), see also Table 8. (Found: C, 49·65; H, 3·05; Cl, 10·0; N, 15·40. Calc. for $C_{15}H_{11}ClN_4O_3S$ (362) C, 49·66; H, 3·06; Cl, 9·77; N, 15·44%). **16c**: IR (KBr) 1760 and 1625 cm^{-1}; mass spectrum, *m/e* (%) 342 (10, M^{+}), 155 (52, $CH_3C_6H_4SO_2^{+}$), 91 (100), see also Table 8. (Found: C, 56·15; H, 3·90; N, 16·40; S, 9·25. Calc. for $C_{16}H_{14}N_4O_3S$ (342): C, 56·13; H, 4·12; N, 16·36; S, 9·37%). The NMR spectra ($CDCl_3$) of **16a-c** show typical AB-patterns for the vinyl protons with absorptions at τ4·28 and 4·36 (J_{AB} = 1·5 Hz).

Synthesis of 1 - (α - *Styryl*) - 4*H* - Δ^2 - *tetrazolin* - 5 - *one* **18**. An equimolar mixture (0·2 mole) of p-chlorophenylsulfonyl isocyanate and α - azido - β - iodo-styrene is allowed to react at 55° for 4 weeks. Then MeOH (700 ml) is added and the solution is heated at reflux temp. for 5 days. After removal of the solvent, the residue is treated with water (250 ml) and extracted three times with $CHCl_3$. The combined chloroform extracts are dried over $MgSO_4$ and treated with activated charcoal. Crystallization of the crude product from $CHCl_3$ yields a white crystalline product **17** in 57%, m.p. 162°; IR (KBr) 3500–2500 (br, NH), 1727 and 1688 cm^{-1}; mass spectrum, M^{+} (6%) at *m/e* 316, see also Table 10 (Found: C, 34·75; H, 2·70; I, 39·60; N, 17·85. Calc. for $C_9H_9IN_4O$ (360): C, 34·20; H, 2·87; I, 40·15; N, 17·72%). Compound **17** (26 g) is dissolved in MeOH (125 ml) and treated with NaOH (0·2 mole) at reflux temp. for 3 h. After removal of the solvent, the residue is dissolved in water (400 ml) and acidified with conc. HCl which results in the formation of a white precipitate. This is collected by filtration, washed several times with water and dried. Crystallization from MeOH or ether yields pure **18** in 90%, m.p. 173–175°; IR (KBr) 3400–2600 (br, NH), 1740, 1727, 1713 and 1689 cm^{-1}; NMR (100 MHz, DMSO-d_6) τ2·67 (s, 5H), 4·33 and 4·37 (AB quartet, 2H, J = 1 Hz); mass spectrum, M^{+} (29%) at *m/e* 188, see also Table 8. (Found: C, 57·50; H, 4·30; N, 30·05. Calc. for $C_9H_8N_4O$ (188): C, 57·44; H, 4·28; N, 29·77%).

Synthesis of 1 - *n* - *butyl* - 4*H* - Δ^2 - *tetrazolin* - 5 - *one*. This compound was prepared by the method of Horwitz *et al.*[21] as follows. To a suspension of NaN_3 (0·3 mole) in dry THF (20 ml) containing n-butyl isocyanate (0·1 mole) is added a solution of $AlCl_3$ (0·11 mole) in THF (100 ml). The reaction mixture is refluxed for 24 h and then acidified with HCl aqu. After removal of the insoluble material, the solution is evaporated to dryness. The residue is treated with water and extracted with $CHCl_3$. The combined chloroform extracts are dried over $MgSO_4$ and treated with activated charcoal. The resulting oil is distilled *in vacuo* (b.p. 132–135°/0·5–0·7 mm, yield 70%) and crystallized from toluene to give the pure adduct, m.p. 40·5–41°; IR (KBr) 3500–2400 (br, NH) and 1724 cm^{-1}; mass spectrum, *m/e* (%) 142 (22, M^{+}), 99 (6, $BuNCO^{+}$ and/or BuN_3^{+}), 41 (100), see also Table 9. (Found: C, 42·20; H, 7·15; N, 39·50. Calc. for $C_5H_{10}N_4O$ (142): C, 42·24; H, 7·09; N, 39·41%).

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REFERENCES

[1]J.-M. Vandensavel, G. Smets and G. L'abbé, *J. Org. Chem.* **38**, 675 (1973).
[2]G. Denecker and G. Smets, to be published.
[3]R. H. Wiley and J. Moffat, *J. Org. Chem.* **22**, 995 (1957).
[4]G. R. Clemo and W. H. Perkin, *J. Chem. Soc.* **125**, 1804 (1924).
[5]W. G. Finnegan and R. A. Henry, *J. Org. Chem.* **24**, 1565 (1959).
[6]H. Hopff, *Kunststoffe* **53**, 593 (1963).
[7]K. Hattori, E. Lieber and J. P. Horwitz, *J. Am. Chem. Soc.* **78**, 411 (1956).

[8]W. S. Wadsworth, *J. Org. Chem.* **34**, 2994 (1969).
[9]R. Raap and J. Howard, *Can J. Chem.* **47**, 813 (1969).
[10]U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, *Tetrahedron* **25**, 691 (1969).
[11]S. W. Tobey, *J. Org. Chem.* **34**, 1281 (1969).
[12]G. Descotes, Y. Bahurel, M. Bourillot, G. Pingeon and R. Rostaing, *Bull. Soc. Chim. Fr.* 282 (1970).
[13]Y. Tanaka and S. I. Miller, *Tetrahedron* **29**, 3285 (1973).
[14]Y. Nomura, F. Furusaki and Y. Takeuchi, *J. Org. Chem.* **37**, 502 (1972); S. Hammerum and P. Wolkoff, *Ibid.* **37**, 3965 (1972).
[15]For a discussion of the fragmentation patterns of arylnitrenium ions, see R. A. Abramovitch, E. P. Kyba and E. F. V. Schriven, *J. Org. Chem.* **36**, 3796 (1971).
[16]A. M. Duffield, H. Budzikiewicz and C. Djerassi, *J. Am. Chem. Soc.* **87**, 2913 (1965).
[17]W. J. Feast, J. Put, F. C. De Schryver and F. C. Compernolle, *Org. Mass Spectrometry* **3**, 507 (1970).
[18]The aryl isocyanates were prepared according to the procedure of R, L. Shriner, W. H. Horne and R. F. B. Cox, *Organic Synthesis*, Coll. Vol. 2, Wiley, New York (1946) p. 453.
[19]H. Ulrich and A. A. R. Sayigh, *Angew. Chem.* **78**, 761 (1966); *Angew. Chem. Int. Ed. Engl.* **5**, 704 (1966).
[20]F. W. Fowler, A. Hassner and L. A. Levy, *J. Am. Chem. Soc.* **89**, 2077 (1967).
[21]J. P. Horwitz, B. E. Fisher and A. J. Tomasewski, *J. Am. Chem. Soc.* **81**, 3076 (1959).