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(9) (a) For example, the yield of **8** using Jones reagent was 39% and using Collins reagent was 56%. (b) The use of a volatile ketone such as acetone required long reaction times and furnished **8** in low yield (44% after 60 h).
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(14) Filtration of the hot acetone solution was often necessary in order to remove small amounts of ammonium salts.
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Synthesis of 1,4-Disubstituted Tetrazoline-5-thiones

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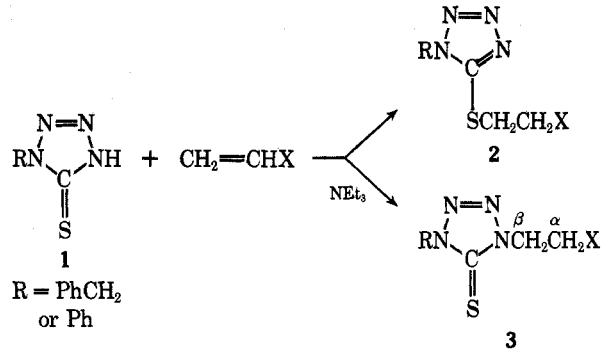
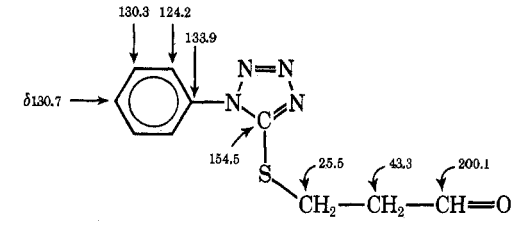
1,4-Disubstituted tetrazoline-5-thiones (**3**) may be considered as potential precursors for the hitherto unknown diaziridinethiones[1] which are of current interest in our laboratory.[2] We have already reported that alkylation, acylation, and sulfonylation of 1-benzyl-4*H*-tetrazoline-5-thione (**1**, R = $PhCH_2$) in the presence of triethylamine resulted in S-substitution in all cases except with phenylacetyl chloride, which furnished the N derivative.[3] Sulfenylations of 1-substituted 4*H*-tetrazoline-5-thiones in the presence of pyridine also occurred at sulfur as was shown by Stajer et al.[4]

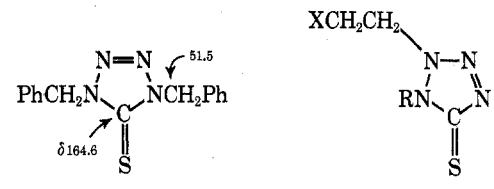
Very recently, Lippmann and Reifegerste[5] carried out Michael additions of 1-phenyl-4*H*-tetrazoline-5-thione onto α,β-unsaturated aldehydes, maleic anhydride, and methyl acrylate in the absence of base and concluded (correctly) from their ^1H NMR spectra that S-addition products (**2**) were formed. Independently, we have carried out Michael additions with 1-benzyl- (or phenyl-) 4*H*-tetrazoline-5-thione (**1**) under slightly modified experimental conditions (THF/NEt_3) which resulted in the formation of N derivatives (**3**) in all cases (see Table I). The structures of **3a–f** are fully supported by the ^{13}C NMR data recorded in Table II. That N-addition occurred instead of S-addition is apparent from the absorptions at δ 164 and 42–44 ppm which are attributed to the C=S and the β-CH_2 carbon atoms. If addition would have occurred at sulfur to give **2**, the C=N and β-CH_2 carbon resonances would be found at δ 154 and 25 ppm, respectively. This is shown below for structure **2a** prepared by the method of Lippmann and Reifegerste.[5] The assignment of the absorption peak at δ 164





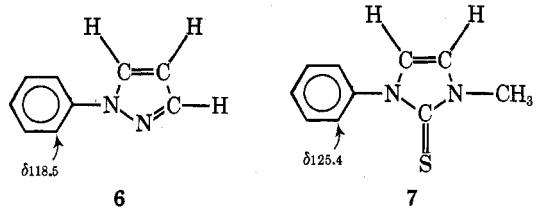
2a

ppm to the C=S carbon atom[3] is confirmed by the ^{13}C NMR spectrum of 1,4-dibenzyltetrazoline-5-thione (**4**) (C=S at δ 164.6 ppm). This compound was obtained in our laboratory



4 **5**

from the corresponding ketone[6] upon treatment with P_2S_5. Thus far, we have only interpreted our results in terms of S vs. N_4 addition. The alternative structure for the N adduct, namely **5**, can be excluded on the basis of the position of the ortho phenyl carbon absorption in compounds **3a,c,e**. According to Begtrup[7] the chemical shift value of this ortho carbon atom is strongly dependent on the extent of interannular conjugation between the two rings, resulting in a downfield shift as the steric hindrance increases. This is illustrated for three compounds, **6**, **7**, and **8**, taken from the work of Begtrup.[7] In our phenyl substituted compounds **3a,c,e** (as well as in **2a**) the ortho phenyl carbon absorptions are found at ca. δ 124 ppm in accordance with the value noted on model compound **7** which has only one neighboring sub-



6 **7**

Table I. 1,4-Disubstituted Tetrazoline-5-thiones

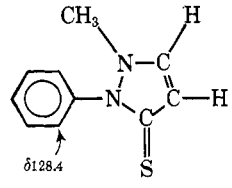
Compd	R	X	Yield, %	^1H NMR, δ values[a]		
				$PhCH_2N$	NCH_2CH_2X	X
3a	Ph	CHO	43		4.60, 3.18	9.84
3b	$PhCH_2$	COMe	85	5.38	4.45, 3.07	2.14
3c	Ph	COMe	76		4.56, 3.18	2.24
3d	$PhCH_2$	CO_2Me	70	5.56	4.56, 2.92	3.61
3e	Ph	CO_2Me	57		4.70, 3.10	3.70
3f	$PhCH_2$	CN	72.5	5.43	4.50, 2.98	

[a] All the spectra were recorded in $CDCl_3$ with Me_4Si as internal reference. The aromatic proton absorptions are omitted.

Table II. ^{13}C Chemical Shifts[a] for the Michael Adducts 3

Compd	C=S	NCH_2CH_2X	Other shift values
3a	163.7	42.1, 40.9	CHO at 198.6
3b	164.2	43.2, 40.2	$COCH_3$ at 204.9 and 29.9
3c	163.6	43.3, 40.2	$COCH_3$ at 205 and 30
3d	164.4	44, 31.7	CO_2CH_3 at 170.5 and 52
3e	163.6	44, 31.7	CO_2CH_3 at 170.6 and 52.2
3f	164.4	43.6, 16.3	CN at 116.4

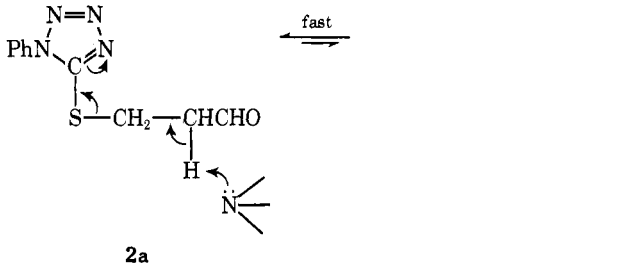
[a] All the spectra were recorded in $CDCl_3$ with Me_4Si as internal reference. The benzyl methylene carbons in **3b,d,f** absorbed at 51.1–51.4 ppm. For compounds **3a,c,e** the phenyl carbon atoms resonated at 135.1, 124 (ortho), 129.6 (meta), and 130 ppm (para).



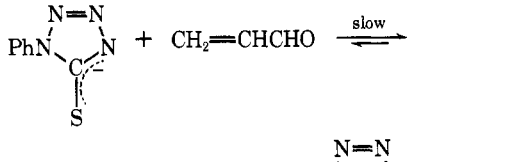
8

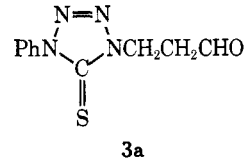
stituent. For compound **5** (R = Ph), the two substituents adjacent to the phenyl group would impede interannular conjugation to such an extent that a chemical shift of about δ 128 ppm would be expected for the carbon atom under discussion (see model 8).

From the mechanistic point of view, it is worth mentioning that **2a** isomerizes into **3a** when heated at 70 °C for 1 h in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco, monitored by NMR in $CDCl_3$). In the absence of base, no isomerization occurred at 70 °C within 1 h, whereas 20% conversion into **3a** was observed at room temperature after a period of 2 months. When the reaction of 1-phenyl-4*H*-tetrazoline-5-thione and acrolein in the presence of Dabco was followed by NMR ($CDCl_3$ as solvent), the S derivative **2a** (triplet at δ 3.5 for the β-CH_2) was formed first, but underwent further isomerization into the N derivative **3a** (triplet at δ 4.6 for the β-CH_2). A mechanism which accounts for the amine-catalyzed isomerization of **2a** into **3a** is given below.[8]



2a





3a

In conclusion, the Michael additions of 1-substituted 4*H*-tetrazoline-5-thiones 1 onto electrophilic olefins can be carried out either under kinetic or thermodynamic controlled conditions. Until now the 1,4-disubstituted tetrazoline-5-thiones **3** could not be transformed into diaziridinethiones. They remained unchanged when heated at 120–150 °C for 2 days (monitored by ir), thereby resembling the corresponding ketones[6,9] in their thermal stability. Also photolysis did not produce the three-membered ring but, instead, furnished a carbodiimide after loss of nitrogen and sulfur.[10]

Experimental Section

The starting materials 1 (R = $PhCH_2$, mp 144 °C; R = Ph, mp 151 °C) were prepared by the procedure of Lieber and Ramachandran.[11] Adduct **2a** (oil) was synthesized in 41% yield by the method of Lippmann and Reifegerste.[5] The ^{13}C NMR spectra were taken with a XL-100 spectrometer equipped with a device for pulsed Fourier transform operation.

General Procedure for the Synthesis of 1,4-Disubstituted Tetrazoline-5-thiones. Compound 1 (0.03 mol) was allowed to react with 2 equiv of olefin and 1 equiv of triethylamine in dry THF (100 ml) at reflux temperature (ca. 80 °C) for the appropriate reaction time. The solvent (including Et_3N and the excess of olefin) was removed in vacuo and the residue was chromatographed on silica gel using CCl_4–EtOAc as the eluent. Compound **3a** was obtained as a colorless oil, reaction time 1 h, ir (neat) 1717 cm^{-1}. Anal. Calcd for $M\cdot^+$ (determined by high-resolution exact-mass measurements): 234.05748. Found: 234.05654.

Compound **3b** was obtained as a colorless, viscous oil, reaction time 1 day, ir (neat) 1720 cm^{-1}. Anal. Calcd for $M\cdot^+$: 262.08828. Found: 262.08744. Compound **3c** was obtained from the reaction residue by crystallization from CCl_4, mp 73–74 °C, reaction time 3 days, ir (KBr) 1700 cm^{-1}. Anal. Calcd for $M\cdot^+$: 248.07317. Found: 248.07238.

Compound **3d** was obtained as a colorless, viscous oil, reaction time 3 weeks, ir (neat) 1730 cm^{-1}. Anal. Calcd for $M\cdot^+$: 278.08374. Found: 278.08175.

Compound **3e** was obtained as a viscous oil, reaction time 16 days, ir (neat) 1735 cm^{-1}. Anal. Calcd for $M\cdot^+$: 264.06808. Found: 264.06785.

Compound **3f** was obtained as white needles, mp 59 °C (ether–*n*-hexane), reaction time 3 weeks, ir (KBr) 2255 cm^{-1}. Anal. Calcd for $M\cdot^+$: 245.07351. Found: 245.07262.

Synthesis of 1,4-Dibenzyltetrazoline-5-thione (4). 1,4-Dibenzyltetrazolinone (1 g)[6] and P_2S_5 (2 g) were heated in dry toluene (10 ml) at reflux temperature for 2 days. After addition of 50 ml of CCl_4, the reaction mixture was filtered and the filtrate was chromatographed on silica gel using CCl_4–1.5% EtOAc as the eluent. Compound **4** was obtained in 57% yield and was crystallized from ether–petroleum ether to give white needles: mp 109–109.5 °C; ^1H NMR ($CDCl_3$) δ 5.38 (s, 4 H) and 7.2–7.5 (m, 10 H). Anal. Calcd for $M\cdot^+$ (determined by high-resolution exact-mass measurements): 282.09391. Found: 282.09386.

Registry No.—1 (R = $PhCH_2$), 33898-72-5; 1 (R = Ph), 86-93-1; **3a**, 58408-31-4; **3b**, 58408-32-5; **3c**, 58408-33-6; **3d**, 58408-34-7; **3e**, 58438-25-8; **3f**, 58408-35-8; **4**, 58408-36-9; P_2S_5, 1314-80-3; 1,4-dibenzyltetrazolinone, 20628-50-6; acrolein, 107-02-8; methyl vinyl ketone, 78-93-3; methyl acrylate, 96-33-3; acrylonitrile, 107-12-0.

References and Notes

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