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# Spiro ß-Lactam Thiadiazoline and Triazoline Systems. Comparison with the Chemistry of Spiro ß-Lactam Oxadiazolines

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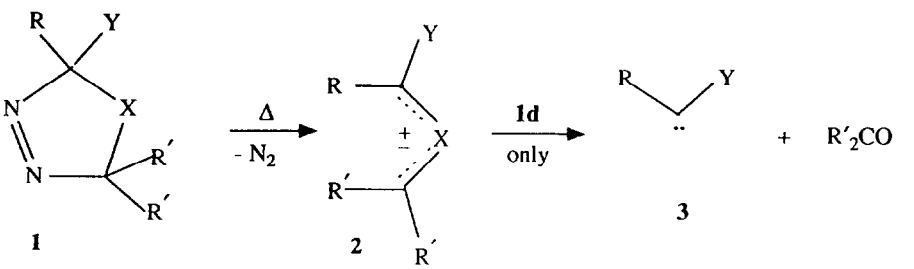
**Abstract:** Triazoline, oxadiazoline, and thiadiazoline ring systems spiro-fused to C4 of a ß-lactam ring undergo 1,3-dipolar cycloreversion to form azomethine-, carbonyl-, and thiocarbonyl ylides, respectively. The order of reactivities is triazoline > thiadiazoline > oxadiazoline.

## INTRODUCTION

Among the many 1,3-dipoles that have been generated and studied (1 - 4) are azomethine ylides (**2a**), carbonyl ylides (**2b**), and thiocarbonyl ylides (**2c**). An attractive route to those intermediates is the thermolysis of the appropriate diaza precursors, the $\Delta^1$-1,2,4-triazolines (**1a**), the $\Delta^3$-1,3,4-oxadiazolines (**1b**), and the $\Delta^3$-1,3,4-thiadiazolines (**1c**), Scheme 1.




( a : X= NR , Y= alkyl ; b : X= O , Y= alkyl ; c : X= S , Y= alkyl ;

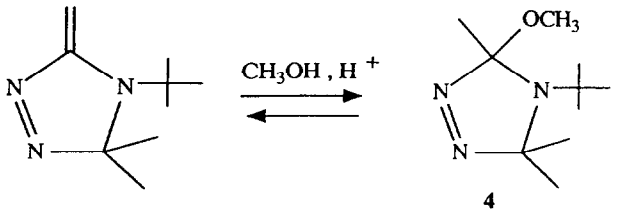
d : X= O , Y= NR , OAc , or OR )

Scheme 1

Apart from their utility for the synthesis of heterocyclic, five membered rings by ($4\pi + 2\pi$) cycloaddition and for the formation of three membered rings by electrocyclic ring closure, at least one member of the trio of intermediates can serve as a carbene source. Carbonyl ylides from oxadiazolines (**1d**) with an acetoxy (5), alkoxy (6), or amino (7) substituent have been shown to fragment to carbenes (**3**), Scheme 1, either cleanly or in competition with other processes.

In spite of the considerable interest in systems **1**, as precursors of azomethine ylides (8) the $\Delta^1$-1,2,4-triazoline family (**1a**) is very sparsely populated, consisting of one that is equilibrated (9) with its precursor

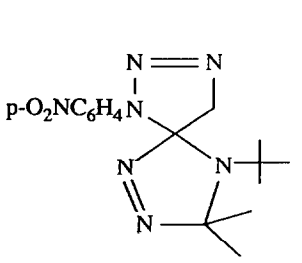
in methanol but not isolated from it (**4**, eq (1)), three spirocyclic compounds (**5, 6, 7**) (9) and two stable




4 (1)

perfluoroamino compounds (**8, 9**) reported (10) as components of a mixture. A seventh $\Delta^1$-1,2,4-triazole (**10**) reported in a review (11), is apparently the result of an error in transcription from the original literature (12). Triazolines **11 - 15** are presumed unstable intermediates (9, 13).

Given the paucity of stable compounds with the $\Delta^1$-1,2,4-triazoline structure, interest in a procedure for generating them, and in a reason for their apparently low stability, remains high. It was of particular interest to us to rank the reactivities of triazolines, oxadiazolines, and thiadiazolines with respect to the cycloreversion

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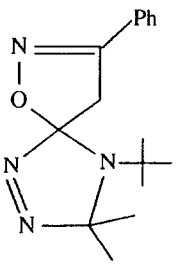


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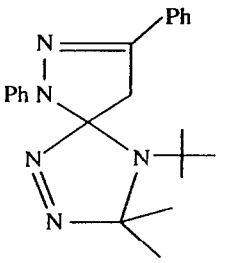


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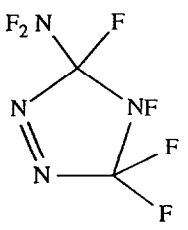


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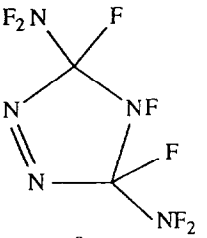


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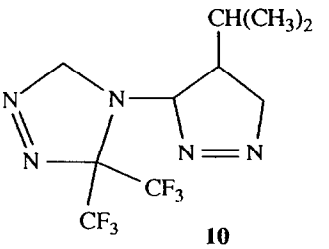


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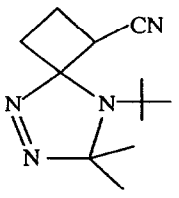


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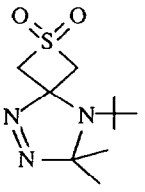


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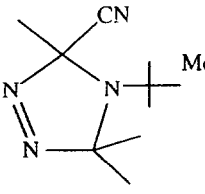


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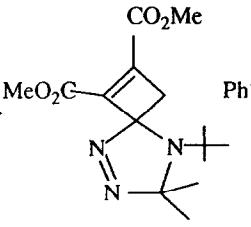


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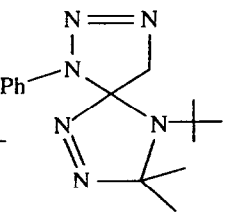


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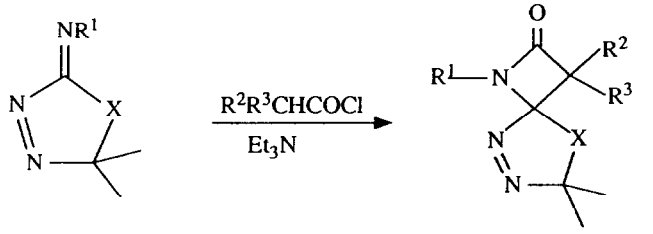
(Scheme 1) to afford an ylide and $N_2$. The choice of a common set of substituents was guided by the fact that we had recently studied the thermolysis of a set of spiro-fused ß-lactam oxadiazolines (**17b**) (14). It was

thought that the approach to those compounds, treatment of 2-imino-oxadiazolines (**16b**) with ketene equivalents (Scheme 2), might lend itself to the preparation of analogous triazolines and thiadiazolines. If successful, that approach would permit not only the desired comparison of cycloreversion rate constants but it would also afford potentially interesting products containing the ß-lactam moiety.




**16a** X= NR
**16b** X= O
**16c** X= S

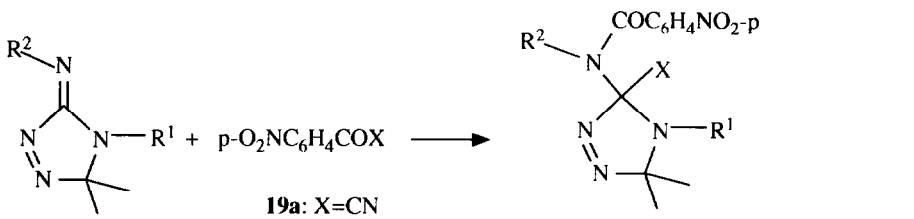
**17a** X= NR
**17b** X= O
**17c** X= S

Scheme 2

In this paper we report the preparation of members of the familes **17a** and **17c**, as short lived intermediates or moderately stable compounds. The relative cycloreversion reactivities of triazolines, oxadiazolines, and thiadiazolines was established, albeit only qualitatively, for one set of common substituents.

## METHODS, RESULTS AND DISCUSSION

In a first attempt at preparation of a compound to model **1a** and **17a**, phenyliminotriazoline (**18a**) (9) was treated with p-nitrobenzoyl cyanide **19a** (Scheme 3). The expected product **20a** was not obtained; most




**19a**: X=CN
**19b**: X=Cl

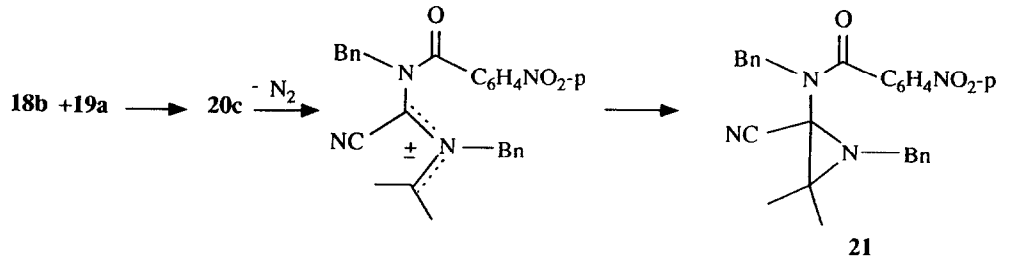
**18a**. $R^1=R^2=Ph$
**18b**: $R^1=R^2=Bn$

**20a** : $R^1=R^2=Ph$ , X=CN
**20b** : $R^1=R^2=Ph$ ,X=Cl ( salt form )
**20c** ·$R^1=R^2=Bn$ ,X=CN

Scheme 3

of the starting materials were recovered. Use of p-nitrobenzoyl chloride (**19b**) led to a reaction, affording a hygroscopic product that was probably the salt **20b**, with strong absorption in the IR at 1720 $cm^{-1}$ (amidinium) and 1655 $cm^{-1}$ (amide carbonyl). Salt **20b** was readily hydrolyzed back to **18a** on exposure to the atmosphere. The failure of **18a** to react with **19a**, and the ion pair character of the product from **18a** and **19b**, suggested that the basicity of the iminotriazoline should be increased. Consequently the dibenzyl analogue (**18b**) was prepared and treated with **19a** in dry acetonitrile at room temperature. A slow reaction, with visible evolution

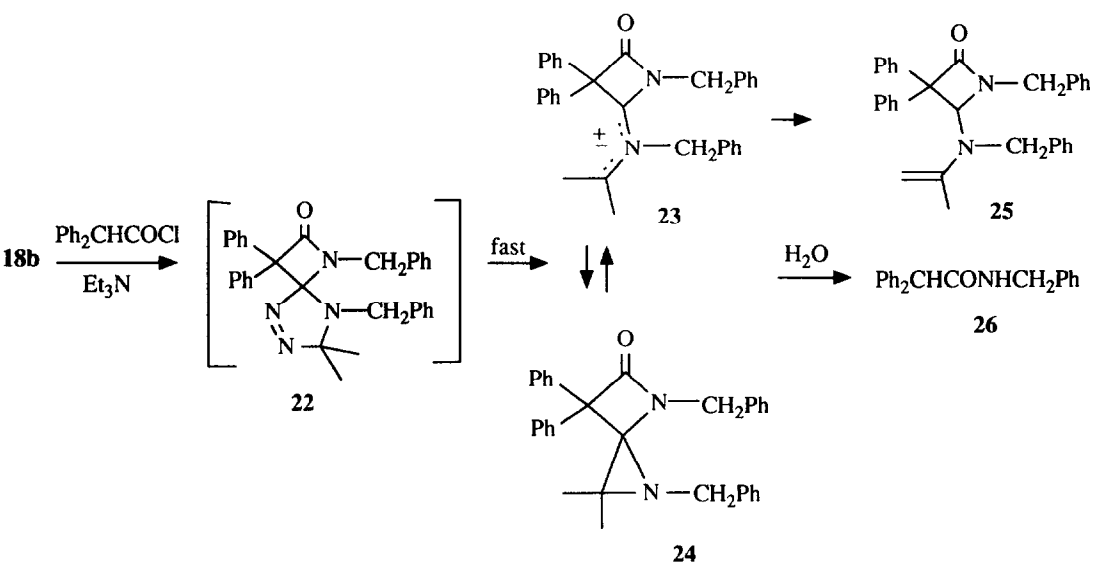
of a gas, affording aziridine **21** in 30% yield, is easily rationalized in terms of Scheme 4. That the product isolated was not **20c** was clear from the $^{13}C$ NMR spectrum, which lacked signals in the 100 - 110 ppm region that are diagnostic for the presence of the $\Delta^1$-1,2,4-triazoline ring. For example, C5 of the $\Delta^1$-1,2,4-triazoline rings of **5**, **6**, and **7** absorbs at 104.11, 104.68, and 102.68 δ, respectively, in the $^{13}C$ NMR spectra (9). Failure to observe the presumed intermediate (**20c**) indicates that it is much less stable than similar oxadiazolines. 2-Acetoxy and 2-alkoxy oxadiazolines decompose with rate constants near $10^{-5}$ $s^{-1}$ at 80 °C (5,6). The short




Scheme 4

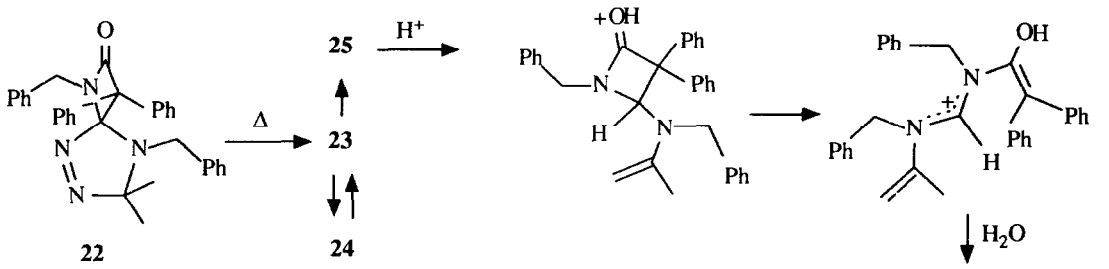
lifetime of **20c** could mean that $\Delta^1$-1,2,4-triazolines are inherently more prone to 1,3-dipolar cycloreversion than $\Delta^3$-1,3,4- oxadiazolines, or that the cyano substitutent, being small and strongly electron withdrawing, is particularly effective at stabilizing the transition state for loss of $N_2$ from **20c**.

The model systems (Schemes 3, 4) suggested that a spiro ß-lactam triazoline **17a** would undergo cycloreversion readily. Treatment of **18b** with diphenylacetyl chloride/triethylamine afforded a crude product showing ß-lactam carbonyl group absorption at 1765 $cm^{-1}$ in the infrared spectrum. It was not possible to get additional structural information about the β-lactam component(s) of the crude because attempted separation led to the disappearances of that infrared band and to the isolation of N-benzyl-2,2-diphenylacetamide (**26**) in 65% yield. We assume that **22** was formed as a transient (Scheme 5) that rapidly gave way to **23**, and that




Scheme 5

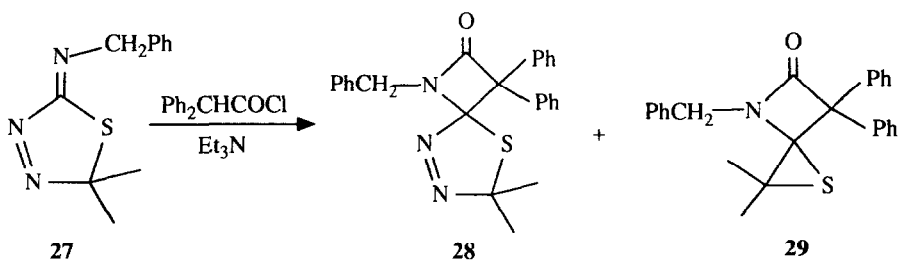
the β-lactam component of the initial crude material was the aziridine (**24**) from electrocyclic ring closure of (**23**) or an enamine (**25**) from a 1,4-sigmatropic hydrogen shift. Good precedent for hydrolytic ring opening of a ß-lactam *with C3-C4 bond cleavage*, comes from the work of Bose and coworkers (15) on 4-amino-2-azetidinones. As an alternative to their mechanism, which involves nucleophilic attack by water at C4 (15), we propose the mechanism illustrated in Scheme 6. Ring opening of the conjugate acid of an initial product (aziridine or enamine, the latter shown) to form an enol (Scheme 6) avoids the mechanistic problem associated




Scheme 6

with $S_N2$ attack by water at C4 of the neutral β-lactam molecule. The acid catalyst (Scheme 6) is presumably $Et_3\overset{+}{N}H$, formed in the step that generates diphenylketene (Scheme 5).

The evidence that **22** is short-lived at room temperature, relative to the family of oxadiazolines **17a**, led us to attempt the synthesis of the sulfur analog **28**, in order to rank it with respect to the others. 2-Benzylimino-5,5-dimethyl-$\Delta^3$-1,3,4-thiadiazoline (**27**), upon treatment with diphenylacetyl chloride/triethylamine afforded a mixture of spiro-β-lactam thiadiazoline (**28**) and spiro-β-lactam thiirane (**29**), Scheme 7. It was possible to isolate the β-lactam thiadiazoline, but it is unstable. In solution ($CDCl_3$) it decomposed slowly at room temperature, with evolution of gas, to form **29**. β-Lactam thiirane **29** appears to be only the second example of that ring system, Yamamoto and coworkers having reported the N-phenyl analogue (17).



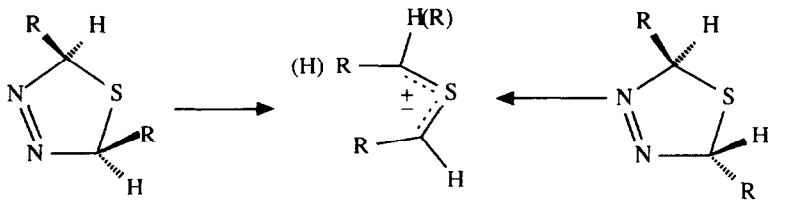

Scheme 7

It is clear, from the short lifetimes of **20c**, **22**, and **28** in solution at room temperature, and the relatively long lifetime of oxadiazolines **17b** in solution at 80 °C, that the former undergo 1,3-dipolar cycloreversion much more rapidly. The rate acceleration resulting from changing the heteroatom from oxygen (**17b**) to nitrogen (**17a**) can be estimated as follows. Taking $k = 10^{-4}$ $s^{-1}$ ($t_{1/2} = 6.9 \times 10^3$ s) as the rate constant for oxadiazoline **17b** ($R^1$ = Bn, $R^2 = R^3$ = Ph) at 100 °C (14) and a factor of 250 for the difference between 100 °C and room temperature, suggests that triazoline **22** would have a half life of *ca* $1.7 \times 10^6$ s (ca 470 h) at room temperature if it were of comparable stability. Assuming that 5% of triazoline **22** would have been

detectable at the time of workup (24 h), the fact that none was found suggests that 24 h corresponds to at least four half-lives of **22** at room temperature and that its half life is 6 h or less. Thus, the triazoline must be 80-fold or more faster than the corresponding oxadiazoline, in the 1,3-dipolar cycloreversion process.

The most likely cause of the higher reactivity of triazolines in the 1,3-dipolar cycloreversion process is the greater transition state stabilization when the center atom of the developing ylide is nitrogen (azomethine ylide) rather than oxygen (carbonyl ylide). Although the ground states are not directly comparable, of course, the assumption that transition state stabilization dominates is probably reasonable, given that conjugation is absent in the ground states and that CN bonds are typically only slightly longer (ca 0.06Å) than CO bonds. This latter feature makes it unlikely that steric effects influence the decompositions of triazolines significantly more than they affect decompositions of oxadiazolines.

The reactivity of thiadiazoline **28** falls between those of triazoline **22** and oxadiazoline **17b** ($R^1$ = Bn, $R^2$ = $R^3$ = Ph). That order is not the same as the order of $\sigma^+$ substituent constants of SMe(-0.60), $NMe_2$ (-1.70), and OMe (-0.78). The increased reactivity of the thiadiazoline, above expectation based on sulfur's ability to accept positive charge, can be attributed to steric effects. The carbon sulfur bond distance (1.82 Å) is *ca* 0.4 Å greater than the C-O bond distance (1.43 Å) (both values for $CH_3$-X, X= OH or SH) and this feature probably relieves crowding in the developing ylide, which must have eclipsed endo substituents for maximum π-bonding. That steric effects are important in determining rates of 1,3-dipolar cycloreversions has been demonstrated convincingly by Kellogg and coworkers (18). They prepared and thermolyzed a number of $\Delta^3$-1,3,4-thiadiazolines, including the *cis-trans* isomers **30a, b** and **31a, b** (Scheme 8). In each case the *cis* isomer decomposed much more rapidly than the *trans* isomer, as expected for loss of $N_2$ in a suprafacial,



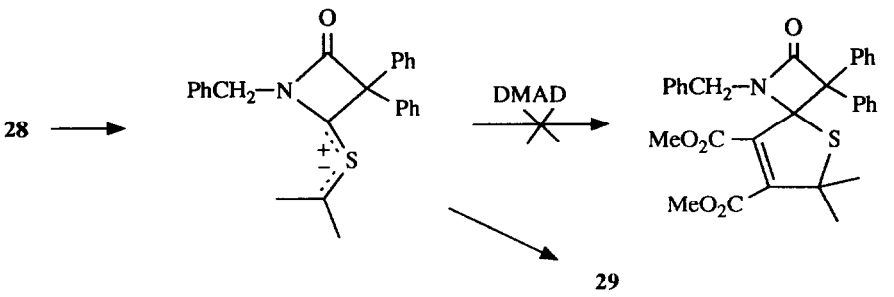
**30a**:R=$CMe_3$ **32** **30b**:R=$CMe_3$

**31a**:R=Et **31b**:R=Et

Scheme 8

suprafacial sense. That mechanism permits the *cis* isomers to go to that ylide (**32**) with both substituents *exo* (or both *endo*) whereas the *trans* isomers must place one substituent in the more crowded *endo* position of **32**. In the present cases, with identical methyl substituents at one ylide carbon and with substituents "tied back" at the other ylide carbon, the steric factors are probably small overall, and particularly small for the thio system with its longer C-S bonds.

In view of the fact that **28** affords **29**, without any evidence for fragmentation of the ylide intermediate, an attempt was made to intercept that ylide. A sample of **28** was dissolved in pure dimethyl acetylene dicarboxylate (DMAD) at room temperature. After 24 hours most of the thiadiazoline (**28**) had decomposed to form thiirane **29**. There was no evidence in the $^1$H NMR spectrum, either from additional methyl singlets at high field or from additional benzyl signals, for a cycloadduct of the pressured thiocarbonyl ylide intermediate and DMAD (Scheme 9).




Scheme 9

Presumably the rate constant for electrocyclization of the ylide to **29** is very large relative to that for cycloaddition to DMAD.

Surprisingly, the N-phenyl analogue of **28** was not obtained under the conditions that afforded **28** itself (Scheme 7). Instead, only the N-phenyl analogue (17) of **29** was found, suggesting that the thermolysis rate constant for **28** is smaller than that for the N-phenyl analogue. In the series of spiro-fused ß-lactam oxadiazolines (**17 b**), which are stable enough for convenient measurement of decomposition kinetics, the N-benzyl member is indeed slower than its N-phenyl analogue, in the 1,3-dipolar cycloreversion reaction (14). However, the rate factor is less than three in the oxadiazoline series (14); it is probably larger in the thiadiazoline series.

In summary, the order of reactivities in 1,3-dipolar cycloreversions is $\Delta^1$-1,2,4-triazolines > $\Delta^3$-1,3,4-thiadiazolines > $\Delta^3$-1,3,4-oxadiazolines, at least for the substituents that were present in the compounds used for this study. The ylides formed in the cycloreversions show substantially different chemistry, the carbonyl ylide fragmenting cleanly to ß-lactam-4-ylidene and acetone (14) while the azomethine ylide and thiocarbonyl ylide undergo electrocyclization primarily, to form aziridine (**21**) and thiirane (**29**) systems. Although it is likely that azomethine ylide **23** also affords some of the expected aziridine, that product could not be confirmed probably because it is very easily hydrolyzed.

## EXPERIMENTAL SECTION

*3-Benzylimino-4-benzyl-5,5-dimethyl-$\Delta^1$-1,2,4-triazoline 18b.* This compound was prepared according to the literature procedure (19) for the 3-phenylimino-4-phenyl analogue. It was obtained as a yellow oil, in 20% yield based on the starting material, $Me_2C$=NNHC(S)NHCH$_2$Ph(20); IR (film), cm$^{-1}$: 1685 (C=N); $^1$H NMR (200 MHz, $CDCl_3$) δ:1.36 (s, 6 H), 4.51 (s, 2 H), 5.32 (s, 2 H), 7.20-7.43 (m, 10 H); $^1$H NMR (90 MHz, $CCl_4$) δ: 1.27 (s, 6 H), 4.40 (s, 2 H), 5.17 (s, 2 H), 7.03-7.43 (m, 10 H); $^{13}$C NMR (125.8 MHz, $CDCl_3$, ref. $CDCl_3$ at δ 77.2 ppm) δ 23.73 (2 x $CH_3$), 44.61 ($CH_2$), 52.58 ($CH_2$), 101.01 (C5), 126.49, 127.62, 128.02, 128.39, 128.51, 128.54, 128.57, 128.63, (8 x CH, aryl), 137.72 (C1, aryl), 141.99 (C1, aryl), 159.34 (C=N).

*1-Benzyl-2-cyano-2 (1-benzyl) p-nitrobenzoylamino-3,3-dimethylaziridine, 21.* To a solution of triazoline **18b** (0.499 g, 1.71 mmol) in dry acetonitrile (1 mL) was added a solution of freshly prepared (21) p-nitrobenzoyl cyanide (0.301 g, 1.71 mmol) in dry acetonitrile (1 mL). Stirring, and an atmosphere of $N_2$, were maintained

during addition and for 2 days after. The solvent was pumped out and the viscous, oily residue was triturated with ether (3 parts) in petroleum ether (2 parts). Purification of the extract by centrifugal chromatography (Chromatotron, Model 17924T, 2 mm silica plate) gave unreacted starting material **18b** and aziridine **21** as a thick yellow oil in 30 % yield, based on unrecovered starting material **18b**; IR (film, $cm^{-1}$): 2240 (C≡N), 1670 (C=O), 1525 ($NO_2$, asymm. str.), 1348 ($NO_2$, symm. str.); $^1H$ NMR (500 MHz, $CDCl_3$) δ: 1.55 (s, 3 H), 1.71 (s, 3 H), 4.09 (d, J=15.2 Hz, 1H), 4.43 (d, J=15.2 Hz, 1H), 4.59 (d, J=15.1 Hz, 1H), 5.05 (d, J=15.1 Hz, 1H), 6.99-7.50 (m,10 H), 7.81 (d, J = 8.7 Hz, 2 H), 8.32 (d, J = 8.7 Hz, 2 H), $^{13}C$ NMR (125.8 MHz, $CDCl_3$, ref. $CDCl_3$ at 96.7 ppm) δ: 26.10 (neg), 28.67 (neg), 46.42 (pos), 53.07 (pos), 75.54 (C3, pos), 97.62 (C2, pos), 116.01 (C≡N, pos), 124.62, 126.85, 127.22, 128.04, 128.35, 128.84, 129.10 (7 CH, aryl, neg), 138.61 (C1, aryl, pos), 140.15 (C1, aryl, pos), 141.67 (C1, aryl, pos), 149.37 (C4 of $C_6H_4NO_2$, pos); MS (ei) m/z: 440 ($M^+$, 3 %), 324 (4 %), 173 (13 %), 149 (22 %), 91 (100 %); MS (ci, $NH_3$) m/z: 441 ($M^+$ +1,100 %), 369(13 %), 353(29 %), 326(7 %), 91(5 %); MS (high resolution) m/z: 440.1840, calcd for $C_{26}H_{24}N_4O_3$ 440.1848.

*Reaction of triazoline **18b** with diphenylketene.* Freshly prepared diphenylacetyl chloride (mp 55 - 57 °C, petroleum) (0.69 g, 3.0 mmol) in dry $CH_2Cl_2$ (10 mL) was added, drop by drop and with stirring, to a solution of triazoline **18b** (0.73 g, 2.5 mmol) and triethylamine (6.0 mmol) in dry $CH_2Cl_2$ (20 mL) under $N_2$ at *ca* -23 °C. The cold bath was removed and stirring was maintained overnight before the reaction mixture was washed with saturated bicarbonate solution and with brine. Each aqueous layer was back-washed twice with $CH_2Cl_2$ and the combined organic extract was dried over $MgSO_4$. Filtration and evaporation of the solvent afforded an oily residue which, upon addition of ether in hexane, formed a white solid. Recrystallization from ethyl acetate/hexane gave N-benzyl-2,2-diphenylacetamide in 65 % yield as a white solid; mp 126 °C, lit (22) mp 125 °C; IR (KBr) ($cm^{-1}$): 3260 (NH), 1639 (C=O); $^1H$ NMR (90 MHz, $CDCl_3$) δ 4.48 (d, 2 H), 4.94 (s, 1H), 5.95 (s, br, 1H), 7.25 - 7.55 (m, 15 H); $^{13}C$ NMR (125.8 MHz, $CDCl_3$) δ: 44.03 ($CH_2$), 59.45 (CH), 127.50, 127.70, 127.82, 128.87, 128.99, 129.11 (6 CH, aryl), 138.83 (C1, aryl), 139.58 (2 C1, aryl), 171.93 (C=O); MS (ei) m/z: 301 ($M^+$, 17 %), 167 ($Ph_2CH$, 100 %), 152 (13 %), 91 ($PhCH_2$, 29 %); MS (CI, $NH_3$) m/z: 319 ($M^+$ + $NH_4$, 3 %), 302 ($M^+$ - H, 100 %), 226 (5 %), 167 (7 %), 106 (5 %).

*5,5-Dimethyl-2-benzylimino-$\Delta^3$-1,3,4-thiadiazoline, **27**.* Acetone-4-benzyl-thiosemicarbazone was prepared from 0.10 mol of 4-benzyl-thiosemicarbazide (20) by refluxing with acetone (40 mL) in 95 % ethanol (95 mL) until all the solid had dissolved. On cooling, pure thiosemicarbazone crystallized out in 82 % yield, mp 145-146 °C, lit (20) mp 147-148 °C.

Oxidation of the thiosemicarbazone was based on the method of Landquist (23). To a sample (11 g, 0.05 mol) in dry benzene (800 mL) was added all at once, active manganese dioxide (109 g, 1.25 mol), prepared as described in the literature (24). The reaction mixture was stirred during the addition and for 2 hours thereafter. Filtration, washing of the filtrate with benzene, and evaporation of the benzene afforded a product that was separated by flash chromatography (30 % ether in hexane) into 2-benzylimino-5,5-dimethyl-$\Delta^3$-1,3,4-thiadiazoline **27** (59 % yield) and 4-benzyl-5,5-dimethyl-$\Delta^1$-1,2,4-triazoline-3-thione (6 % yield). Spectroscopic data for **27**; IR (film, $cm^{-1}$): 1640 (C=N); $^1H$ NMR (90 MHz, $CDCl_3$) δ: 1.85 (s, 6 H) 4.64 (s, 2 H), 7.20-7.55 (5H). Data for the thione; IR (film, $cm^{-1}$): 1300 (C=S); $^1H$ NMR (90 MHz, $CDCl_3$) δ: 1.45 (s, 6 H). 4.97 (s, 2 H), 7.37 (s, 5H).

*Reaction of thiadiazoline **27** with diphenylketene.* Diphenylacetyl chloride (0.65 g, 3.0 mmol), mp 55 - 57 °C,

in dry $CH_2Cl_2$ (10 mL) was added drop by drop, with stirring, to a solution of thiadiazoline **27** (0.55 g, 2.5 mmol) and triethylamine (6.0 mmol) in dry $CH_2Cl_2$ (20 mL), under nitrogen at *ca* -23 °C. When addition was complete, the flask was allowed to reach room temperature, and stirring was maintained overnight. The reaction solution was washed with saturated aqueous sodium bicarbonate solution and with brine. Both aqueous layers were extracted twice with $CH_2Cl_2$ and the combined organic extract was dried with $MgSO_4$. Filtration and evaporation of the solvent afforded an oily residue consisting of spiro β-lactam thiadiazoline **28** (2.4 parts) and spiro β-lactam thiirane **29** (1.0 part), as determined by $^1H$ NMR spectroscopy ($CDCl_3$ solvent). The sample in the NMR tube lost $N_2$ slowly (bubbles), as **28** decomposed to **29**. Addition of ether (20 %) in hexane to a portion of the crude sample caused selective precipitation of thiadiazoline **28** as a white solid. Chromatography (Chromatotron plate, 20% ether in hexane) of the main portion afforded thiadiazoline **28**, followed by thiirane **29**.

*1,7,8-Triaza-1-benzyl-6,6-dimethyl-2-oxo-3,3-diphenyl-5-thiaspiro [3.4] oct-7-ene or spiro β-lactam thiadiazoline 28*. Unstable white solid; IR (KBr): 1765 $cm^{-1}$ (C = O); $^1H$ NMR (500 MHz, $C_6D_6$) δ: 1.63 (s, 3 H), 1.75 (s, 3 H), 4.40 (s, 2 H), 7.2 - 7.4 (m,15 H); $^{13}C$ NMR (125.8 MHz, $CDCl_3$) δ: 29.12, 29.83, 43.57, 77.56, (C3), 106.77 (C6), 127.66, 127.74, 127.81, 128.11, 128.18, 128.51, 128.59, 129.00 (8 CH, aryl), 134.56 (C4), 135.02 (C1, aryl), 138.36 (2 C1, aryl), 168.59 (C = O); Ms (ei) m/z: 385 ($M^+$ -$N_2$, 3 %), 353 ($M^+$ -$N_2$ - S, 5 %), 262 (11%), 237 (11%), 220 (97 %), 205 (85 %), 194 ($Ph_2CCO$, 15 %), 165 ($C_{13}H_9$ = 9-fluorenyl, 35 %), 129 (10 %), 91 ($PhCH_2$, 100 %), 65 (15 %); MS (ci, $NH_3$) m/z: 386 (M - $N_2$, 6 %), 354 (M - $N_2$ - S, 100 %), 220 (9 %), 144 (20 %), 91 (10 %).

*4-Aza-4-benzyl-2,2-dimethyl-6,6-diphenyl-1-thiaspiro [2.3] hexan-5-one, or spiro β-lactam thiirane 29*. Oil; IR (film) 1765 $cm^{-1}$ (C = O); $^1H$ NMR (500 MHz, $CDCl_3$) δ: 1.14 (s, 3 H), 1.46 (s, 3 H), 4.16 (d, J = 16.1 Hz, 1H), 4.86 (d, J = 16.1 Hz, 1H), 7.17 - 7.44 (m, 15H);$^{13}C$ NMR (125.8 MHz, $CDCl_3$) δ: 26.76, 29.23, 44.57, 46.00 (C2), 72.17 (C6), 87.45 (C3), 127.41, 127.61, 127.73, 127.81, 128.16, 128.70, 129.61 (7 CH, aryl), 135.78 (C1, aryl), 137.13 (C1, aryl), 138.21 (C1, aryl), 171.15 (C = O); MS (ei) m/z: 385 ($M^+$, 5 %), 353 ($M^+$ - S, 5 %), 262 (11%), 237 (11%), 220 (97 %), 205 (85 %), 194 ($Ph_2CCO$, 15 %), 165 ($C_{13}H_9$ = 9-fluorenyl, 35 %), 129 (10 %), 91($PhCH_2$, 100%), 65 (15%); MS (ci, $NH_3$) m/z: 386 ($M^+$+H, 6 %), 354 ($M^+$+H-S, 100 %), 220 (9 %), 144 (20 %), 91 (10 %); MS (high resolution) m/z: 385.1504, calcd for $C_{25}H_{23}NOS$ 385.1500.

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*References and Notes*

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