MOLECULAR REARRANGEMENTS IN HETEROCYCLIC SYNTHESIS. A GENERALIZED SYNTHESIS OF 1,2,4-THIADIAZOLES FROM 3-ACYLAMINO-1-OXA-2-AZOLES

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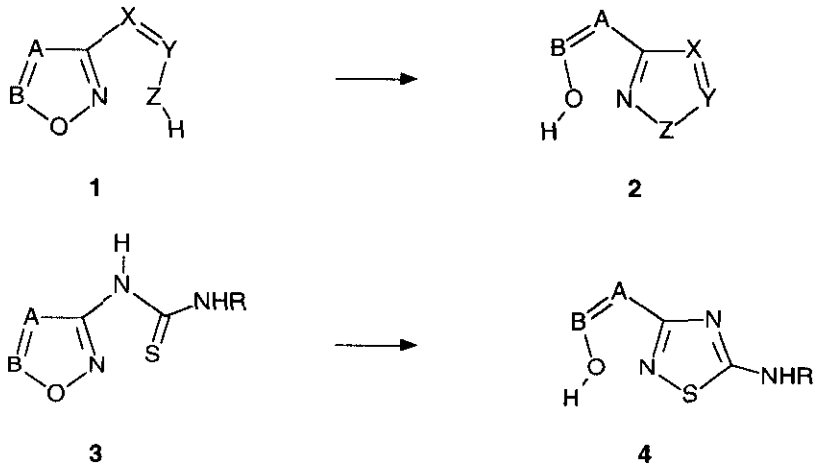
Abstract - The sulfurization reaction of some 3-acylamino-1-oxa-2-azoles (1,2,4-oxadiazoles, isoxazoles and 1,2,5-oxadiazoles) with the Lawesson reagent has been investigated. A generalized methodology for the synthesis of 5-aryl-/alkyl-3-substituted 1,2,4-thiadiazoles *via* molecular rearrangement of the corresponding thioamides has been pointed out.

One of the most intriguing interest in heterocyclic chemistry area is to provide generalized and efficient methodologies for the synthesis of target heterocycles. Undoubtly, ring-transformations of suitably substituted azoles constitute widely used reactions to this aim, particularly to the synthesis of five-membered heterocycles.[1] Among the enormous variety of ring-transformations, a general pattern can be recognised in molecular rearrangements of 1-oxa-2-azoles (1,2,4-oxadiazoles, isoxazoles and 1,2,5-oxadiazoles) containing a heteroallyl fragment at C-3 (**1** ⟶ **2**; Scheme 1).[2,3] Scope and restrictions of these reactions have been reviewed,[3] and significant features recognised in the nucleophilic character of the attacking Z atom in one hand, and in the leaving group *ability of the ABO sequence of the rearranging ring, in the other.*[3] Following this general scheme, and in combining different XYZ atoms, many syntheses have been realised and are being emphasized in the current literature.[3] In this context, we have reported[4-6] that a sulfur atom as an attacking nucleophile (*i.e.*, Z = S in **1**) greatly enhances the reactivity of substituted azoles (**1**). In fact, thioureas (**3**), which were obtainable from 3-amino-1-oxa-2-azoles and

isothiocyanates, easily rearranged into the corresponding 1,2,4-thiadiazoles (**4**) (even spontaneously as it was formed, as it was the case of 1,2,4-oxadiazole derivatives).



1 **2**

3 **4**

AB = NC; CC; CN
R = Ph; COOEt

Scheme 1

In pursuit our researches in providing methodologies in heterocyclic synthesis by molecular rearrangements of five-membered heterocycles, we became interested at generalized synthesis of 5-aryl-/alkyl-1,2,4-thiadiazoles. It is well known[7] that 1,2,4-thiadiazoles are generally obtained by intramolecular ring closures of appropriate intermediates, and one of the widely used synthesis involves oxidative ring closure of thioacylamidines.[7] Synthesis of 1,2,4-thiadiazoles by transformations of other heterocycles appears little exploited.[7] To this aim we have now considered the reactivity of 1-oxa-2-azoles containing a thioamide group as a participating side chain. Unfortunately, at variance with the corresponding 3-acylamino compounds, direct thioacylation does not appear easily practicable since thioacyl chlorides or thioacyl anhydrides are unstable and/or hardly accessible.[8] For this reasons, the formation of thioamides is generally achieved by the reaction of the corresponding carbonyl compounds with an O/S exchange reagent. With this in mind, we have considered the sulfurization reaction of some 3-acylamino-1-oxa-2-azoles, such as 3-acylamino-5-phenyl-1,2,4-oxadiazole (**5a-b**), 3-aroylamino-5-methylisoxazoles (**9a-b**) and 3-acylamino-1,2,5-oxadiazoles (furazans) (**12a-d**). To our pourpose we thought to use the Lawesson

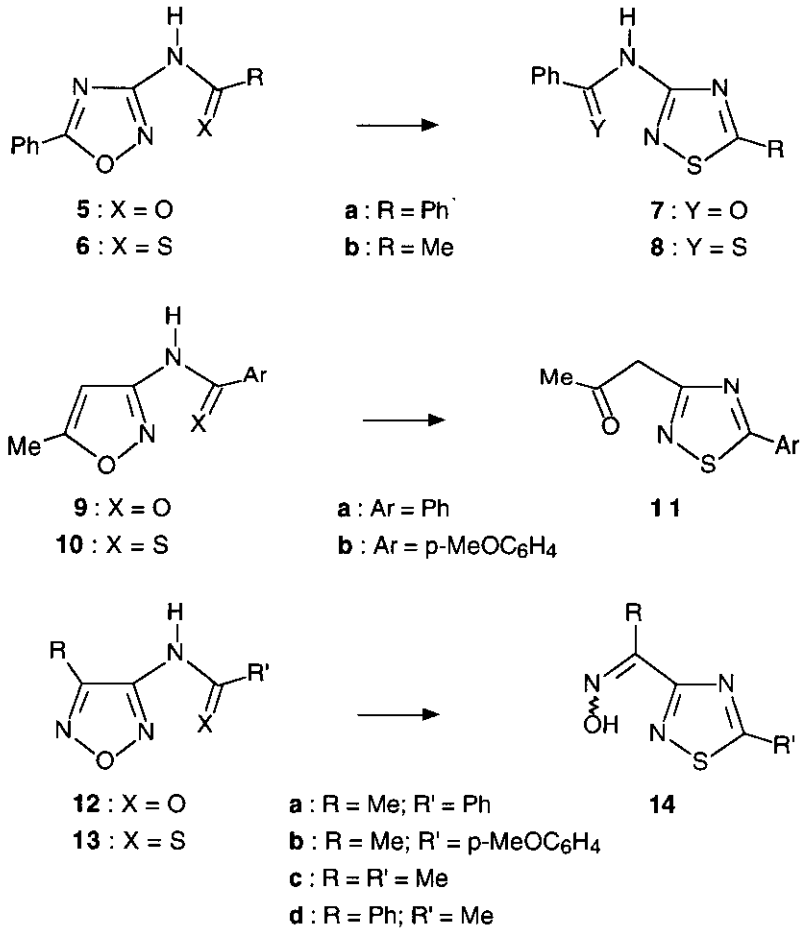
reagent,[9] which turned out well cut in pointing out a methodology for the direct synthesis of 1,2,4-thiadiazoles.

As expected on the basis of both the high tendency to rearrange of 1,2,4-oxadiazole and isoxazole heterocycles[3] and the marked reactivity of a sulfur-attacking side chain,[5] the sulfurization of compounds (**5**) and (**9**) directly gave the rearranged 1,2,4-thiadiazoles, clearly through the unisolated thioamides (**6**) and (**10**), respectively. In the case of the reaction on the 3-benzoylamino-1,2,4-oxadiazole (**5a**) , the firstly formed 3-benzoylaminothiadiazole (**7a**), under the used experimental conditions which required an excess of the reagent in refluxing toluene, underwent subsequent sulfurization into the final compound (**8a**). This obvious pattern is substantiated by a separate reaction of compound (**7a**) with the same reagent. On the other hand, sulfurization of the 3-acetylamino-5-phenyl-1,2,4-oxadiazole (**5b**) in refluxing benzene allowed to isolate the benzoylaminothiadiazole (**7b**) (through the rearrangement of firstly formed **6b**), and this result must be ascribed to the different reactivity of a benzoylamino and an acetylamino group, *respectively, towards the Lawesson reagent.*[10] Yelds of the isolated thiadiazoles (which were in the range of 40-50%, non optimized) were not excellent, and this probably because of some decomposition of both the reagent and the products in reaction conditions.[11]

In the case of 3-acylamino-4-methylfurazans (**12a-c**), owing to the lower reactivity of the ring towards rearrangements,[3,5,6] the reaction with the Lawesson reagent should have allowed isolation of thioamides (**13a-c**). However, it resulted rather troublesome to draw-out these compounds from the reaction mixture, and we did not mind that. On the other hand, since the best work-up procedure implied treatment of the sulphurised mixture with aqueous sodium hydroxide,[12] final products were the rearranged 1,2,4-thiadiazole oximes (**14a-c**) (yields in the range of 50-60%, non optimized[11]); that is, the initially formed thioamides (**13**) rearranged (even at room temperature) in the presence of bases which enhances the actual nucleophilic character of the sulfur atom of the side chain. Of course, this behaviour was expected on the basis of the reactivity of a thiourea side chain linked to a furazan ring (see **3**; AB = CN).[5,6]

Spectroscopic evidences (^{13}C nmr), as well as the expected higher stability of the **E** geometry for *aryl methyl ketoximes suggest the* **E** *configuration* for the isolated compounds.[13,14] Accordingly, ^{13}C nmr spectra showed the C-Me signal at about δ 12 which well fits with the corresponding values observed in the case of model *E*-oximes (**E-15**) (see Scheme 3). In turn, the model *Z*-isomers (**Z-15**) showed the C-Me signal at about δ 19.8. Furthermore, Beckmann rearrangement

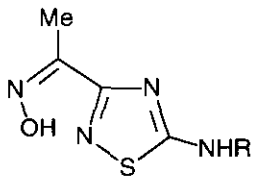
carried out representatively on **E-14a** gave the expected 3-acetylamino-5-phenyl-1,2,4-thiadiazole.



Scheme 2

Taking into account our previous results on rearrangement of substituted furazans with bases at room temperature,[5,6] the expected oximes should have the **Z** configuration, *i.e.*, with conservation of the geometry present in the starting ring; however, our opinion is that work-up procedures used for the isolation of the final products cause the configurational isomerization towards the more stable isomer. Likewise, in the sulfurization reaction of the 3-acetylamino-4-phenylfurazan (**12d**), the usual work-up gave the *E*-isomer (**E-14d**) as the predominant component. However, a careful chromatography allowed to obtain also some amounts of the *Z*-isomer (**Z-14d**), the *E/Z* ratio being

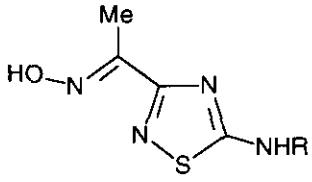
highly dependent from experimental manipulations. As for configuration of the isolated oximes, here a reasonable assignement can be based on the δ values of OH signals in the ^{1}H nmr spectra.[14] In the *Z*-isomer, the OH proton resonates at δ 11.93 (DMSO-d_6) and 11.41 ($CDCl_3$). Differently, the *E*-isomer shows the OH proton resonance at δ 12.02 (DMSO-d_6) and 8.69 ($CDCl_3$). Furthermore, Beckmann rearrangement of the *E*-isomer (**E-14d**) gave the expected benzoylamino compound (**7b**).



Z-15

δ_C(Me): 19.83

δ_C(Me): 19.82



E-15

R = Ph: δ_C(Me): 11.64

R = $COOC_2H_5$: δ_C(Me): 11.67

Scheme 3

As a conclusive comment, our results show that the sulfurization reaction of 3-acylamino-1-oxa-2-azoles (through molecular rearrangement of the corresponding thioamides) can really constitute a procedure for the synthesis of 5-aryl-/alkyl-1,2,4-thiadiazoles, especially for the synthesis of target thiadiazoles of type **11** or **14** which do not appear easily accessible by conventional methods.[7]

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus; ir spectra (nujol mulls) were determined with a Perkin-Elmer 257 instrument, ^{1}H and ^{13}C nmr spectra with a Bruker AC 250 E (tetramethylsilane as internal standard) spectrometer and mass spectra with a RMU-60 instrument. Flash chromatography was performed on Merck silica gel by using mixtures of light petroleum and ethyl acetate in varying ratios. Light petroleum boils in the range 40-60°C. Lawesson reagent was obtained from Aldrich Chemical Co. Compounds (**5b**,[15] **7a**,[16] **9ab**,[17] **12a**,[18] **12b**,[19] **12c**,[20] and **12d**[21]) (which were used for sulfurization reactions) and thiadiazoles (**Z-15**)[5,6] and (**E-15**)[5,6] (which were used as model compounds) were prepared as reported.

3-Benzoylamino-5-phenyl-1,2,4-oxadiazole (**5a**) was prepared by reacting 3-amino-5-phenyl-1,2,4-oxadiazole[22] (1.6 g, 10 mmol) with benzoyl chloride (2.1 g, 15 mmol) in anhydrous benzene (100 ml) containing equimolar amounts of pyridine (1.2 ml, 15 mmol) at reflux (20 h), and then working as usual.[15] Yield 1.8 g (70%); mp 136-138°C (benzene); ir: 3240 (NH) and 1675 cm^{-1} (CO); ^1H nmr (DMSO-d_6) δ: 7.51-8.13 (m, 10H, 2 Ph); 11.68 (s, 1H, NH). *Anal.* Calcd for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.80; H, 4.30; N, 15.70.

Sulfurization reaction of 3-benzoylamino-5-phenyl-1,2,4-oxadiazole (5a). To a solution of compound (**5a**) (0.55 g, 2.1 mmol) in anhydrous toluene (40 ml), the Lawesson reagent (1.2 g, 3 mmol) wad added and the mixture was refluxed for 3 h. Monitoring of the reaction by tlc analysis showed the intermediate formation of the thiadiazole (**7a**). To avoid chromatography of the very crude reaction, a standard procedure for drawing-out thioamides was adopted.[12] Thus, the solution was extracted with aqueous 1N sodium hydroxide (3 x 50 ml), the aqueous layer acidified (to pH 5) with 15% hydrochloric acid and then extracted with ethyl acetate, which was dried over anhydrous sodium sulfate and evaporated. Chromatography of the residue gave the *N*-(5-phenyl-1,2,4-thiadiazol-3-yl)thiobenzamide (**8a**) (0.25 g, 40%), mp 174-176°C (ethanol); ir: 3200 cm^{-1}(NH); ^1H nmr (DMSO-d_6) δ: 7.41-8.02 (m, 10H, 2 Ph);12.70 (s, 1H, NH). *Anal.* Calcd for $C_{15}H_{11}N_3S_2$: C, 60.58; H, 3.73; N, 14.13. Found: C, 60.65; H, 3.90; N, 14.20.
Similarly, sulfurization of compound (**7a**) (0.5 g, 1.8 mmol) with the Lawesson reagent (0.5 g, 1.2 mmol) in refluxing toluene (40 ml, 3 h) also gave **8a** (0.3 g, 60%).

Sulfurization reaction of 3-acetylamino-5-phenyl-1,2,4-oxadiazole (5b). To a solution of compound (**5b**) (0.6 g, 3 mmol) in anhydrous benzene (40 ml), the Lawesson reagent (0.8 g, 2 mmol) was added and the mixture was refluxed for 2 h. By adopting the previous procedure, chromatography of the residue gave 3-benzoylamino-5-methyl-1,2,4-thiadiazole (**7b**) (0.3 g, 50%), mp 124-126°C (aqueous ethanol) (lit.,[23] mp 126°C).

Sulfurization reaction of 3-Aroylamino-5-methylisoxazoles (9a-b). To a solution of compound (**9**) (2.5 mmol) in anhydrous toluene (40 ml), the Lawesson reagent (1.0 g, 2.5 mmol) was added and the mixture was refluxed for 2 h. After removing of the solvent, chromatography of the residue gave the rearranged thiadiazoles (**11a-b**) (45% yield).

3-Acetonyl-5-phenyl-1,2,4-thiadiazole (**11a**) had mp 56-58°C (light petroleum); ir: 1710 cm^{-1} (CO); ^1H nmr ($CDCl_3$) δ: 2.30 (s,3H, Me), 4.16 (s, 2H, CH_2), 7.45-7.54 and 7.92-7.96 (2m, 3H + 2H, Ph); ^{13}C nmr ($CDCl_3$) δ: 29.97, 47.86, 127.52-132.16 (6C), 170.54, 188.87, 203.04; *m/z*: 218 (M^+). *Anal.* Calcd for $C_{11}H_{10}N_2OS$: C, 60.53; H, 4.62; N, 12.83. Found: C, 60.60; H, 4.50; N, 12.70.

3-Acetonyl-5-(*p*-methoxyphenyl)-1,2,4-thiadiazole (**11b**) had mp 76-78°C (light petroleum); ir: 1705 cm^{-1} (CO); ^1H nmr (DMSO-d_6) δ: 2.30 (s, 3H, C-Me), 3.91 (s, 3H, O-Me), 4.27 (s, 2H, CH_2), 7.15-7.19 and 7.99-8.03 (2m, 2H + 2H, Aromatic); ^{13}C nmr (DMSO-d_6) δ: 20.99, 47.26, 55.76, 115.12 (2C), 122.56, 129.36 (2C), 162.60, 170.88, 187.49, 203.71; *m/z*: 248 (M^+). *Anal* Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87; N, 11.28. Found: C, 58.10; H, 4.80; N, 11.20.

Sulfurization reaction of 3-Acylaminofurazans (12a-d). To a solution of compound (**12**) (2.5 mmol) in anhydrous toluene (40 ml), the Lawesson reagent (1.0 g, 2.5 mmol) was added and the mixture was refluxed for 2 h (in the case of **12a-b**) or 30 min (in the case of **12c-d**). After cooling, the mixture was extracted with 1N sodium hydroxide (3 x 50 ml) and the aqueous layers were left at room temperature (1 h) in order to complete the rearrangement. The alkaline solution was then acidified (to pH 5) with 15% hydrochloric acid and extracted with ethyl acetate. The extract was dried over anhydrous sodium sulfate and evaporated. A proper work-up of the residue gave the rearranged thiadiazoles (**14a-d**).

(*E*)-3-Acetyl-5-phenyl-1,2,4-thiadiazol oxime (**E-14a**). By addition of the minimum amount of ethanol and filtration, compound (**12a**) gave the *E*-oxime (**E-14a**) (50%), mp 206-208°C (ethanol); ir: 3180 cm^{-1} (br, OH); ^1H nmr (DMSO-d_6) δ: 2.37 (s, 3H, Me), 7.62-7.70 and 8.09-8.12 (2m, 3H + 2H, Ph), 12.01 (s, 1H, OH); δ_{OH}($CDCl_3$): 8.68 (br); ^{13}C nmr (DMSO-d_6) δ: 12.10, 127.63-132.75 (6C), 149.30, 171.29, 187.83; *m/z*: 219 (M^+). *Anal.* Calcd for $C_{10}H_9N_3OS$: C, 54.78; H, 4.14; N, 19.16. Found: C, 54.70; H, 4.30; N, 19.10.

To a sample of the *E*-oxime (**E-14d**) (0.22 g, 1.0 mmol) in anhydrous chloroform (30 ml) cooled in an ice bath, phosphorus pentachloride (0.31 g, 1.5 mmol) was added and the mixture was left at room temperature for 3 h. The solvent was then allowed to evaporate spontaneously, the residue taken-up with water and then neutralized with aqueous 30% ammonium hydroxide. Extraction with chloroform and chromatography of the residue gave some amounts of the 3-amino-5-phenyl-1,2,4-

thiadiazole, mp 132-134°C (water), (lit.,[16] mp 132-134°C) and then the 3-acetylamino-5-phenyl-1,2,4-thiadiazole (90 mg, 40%), mp 146-148°C (water), (lit.,[16] mp 147-149°C).

(*E*)-3-Acetyl-5-*p*-methoxyphenyl-1,2,4-thiadiazol oxime (**E-14b**). Likewise, compound (**12b**) gave the *E*-oxime (**E-14b**) (50%), mp 190-192°C (ethanol); ir: 3280 cm^{-1} (br, OH); ^1H nmr (DMSO-d_6) δ: 2.35 (s, 3H, C-Me), 3.91 (s, 3H, O-Me), 7.16-7.19 and 9.03-8.06 (2m, 2H + 2H, Aromatic), 11.96 (s, 1H, OH); ^{13}C nmr (DMSO-d_6) δ: 12.08, 55.79, 115.14 (2C), 122.63, 129.47 (2C), 149.33, 162.71, 171.06, 187.31; *m/z*: 249 (M^+). *Anal.* Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.00; H, 4.45; N, 16.86. Found: C, 53.10; H, 4.50; N, 16.90.

(*E*)-3-Acetyl-5-methyl-1,2,4-thiadiazol oxime (**E-14c**). By working with the minimum amount of benzene and filtration (or by chromatographic purification), compound (**12c**) gave the *E*-oxime (**E-14c**) (60%), mp 159-161°C (benzene); ir: 3160 cm^{-1} (br, OH); ^1H nmr (DMSO-d_6) δ: 2.29 and 2.86 (2s, 6H, 2 Me), 11.84 (s, 1H, OH); $\delta_{OH}(CDCl_3)$: 9.13 (br); ^{13}C nmr (DMSO-d_6) δ: 12.09, 17.02, 149.35, 170.26, 187.43; *m/z*: 157 (M^+). *Anal.* Calcd for $C_5H_7N_3OS$: C, 38.21; H, 4.49; N, 26.73. Found: C, 38.30; H, 4.40; N, 26.60.

(*E*)- And (*Z*)- 3-benzoyl-5-methyl-1,2,4-thiadiazol oximes (**E-14d**) and (**Z-14d**). (a) By working with the minimum amount of ethanol and filtration, compound (**12d**) gave **E-14d** (45%), mp 205-208°C (ethanol); ir: 3260 cm^{-1} (br, OH); ^1H nmr (DMSO-d_6) δ: 2.80 (s, 3H, Me), 7.42-7.48 (m, 5H, Ph), 12.02 (s, 1H, OH); $\delta_{OH}(CDCl_3)$: 8.69 (br); ^{13}C nmr (DMSO-d_6) δ: 16.98, 128.01-132.22 (6C), 150.29, 169.93, 187.38; *m/z*: 219 (M^+). *Anal.* Calcd for $C_{10}H_9N_3OS$: C, 54.78; H, 4.14; N, 19.16. Found: C, 54.90; H, 4.10; N, 19.30.

(b) The crude residue was rapidly chromatographed. Elution with light petroleum-ethyl acetate (1:1) gave at first **Z-14d** (10%), mp 138-140°C (benzene); ir: 3160 cm^{-1} (br, OH); ^1H nmr (DMSO-d_6) δ: 2.93 (s, 3H, Me), 7.38-7.47 (m, 5H, Ph), 11.93 (s, 1H, OH); $\delta_{OH}(CDCl_3)$: 11.41 (br); ^{13}C nmr (DMSO-d_6) δ: 16.86, 126.16-134.18 (6C), 149.83, 166.33, 187.20; *m/z*: 219 (M^+). *Anal.* Calcd for $C_{10}H_9N_3OS$: C, 54.78; H, 4.14; N, 19.16. Found: C, 54.70; H, 4.10; N, 19.20. Further elution gave **E-14d** (35%). The *E/Z* ratio of the isolated oximes highly depended on the work-up procedures. Melting of pure **E-14d** or **Z-14d** produced mixtures containing almost equimolar amounts of both isomers. By adopting the procedure previously described, Beckmann rearrangement of the *E*-oxime

(**E-14d**) (0.22 g, 1.0 mmol) in anhydrous chloroform (30 ml) and phosphorus pentachloride (0.42 g, 2.0 mmol) (at room temperature for 12 h), gave the benzoylaminothiadiazole **7b** (0.11 g, 50%).

ACKNOWLEDGEMENTS

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