OXIDATION AND REARRANGEMENT OF 5-SUBSTITUTED 5-ETHOXYCARBONYL[1,2,4]TRIAZOLIDINE-3-THIONES

Joachim G. Schantl,*[a] Sergius Lang,[a] and Klaus Wurst[b]

[a]Institut für Organische Chemie, [b]Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck,
Innrain 52a, A-6020 Innsbruck, Austria

Abstract – The reaction of ethyl 2-(phenylhydrazono)alkanoates (**1**) with potassium thiocyanate in acetic acid affords 5-ethoxycarbonyl-substituted [1,2,4]triazolidine-3-thiones (**3**). Oxidation ($KMnO_4$) converts **3** into 1-ethoxycarbonyl-2,3-dihydro-1*H*-[1,2,4]triazole-3-thiones (**9**) as evidenced by the X-Ray structure analysis of **9a**. Products (**9**) result from an oxidative conversion of **3** to the intermediates (**5**) and the cyclic valence isomers (**7**) followed by [1,5] sigmatropic rearrangement selectively involving the 5-ethoxycarbonyl group to migrate.

INTRODUCTION

Arylhydrazones of aliphatic and araliphatic ketones (**1**, R^1, R^2 = alkyl, aryl) react with potassium cyanate or thiocyanate in acetic acid yielding 5,5-disubstituted 2-aryl[1,2,4]triazolidin-3-ones (**2**) and 3-thiones (**3**), respectively (Scheme 1).[1] The formation of the heterocyclic ring is considered to occur by way of a [3 + 2] cycloaddition reaction of the prototropic isomer of the hydrazone (i.e. the azomethine imine form) with the *in situ* generated cyanic and thiocyanic acid.[2,3] Oxidation of **2** and **3** furnishes 1-arylazoalkyl-1-isocyanates (**4**) and 1-isothiocyanates (**5**), respectively.[1,4] The reactivity of 1-arylazoalkyl-1-isocyanates (**4**) is partly due to their cyclic valence isomers, i.e. 3,3-disubstituted 1-aryl-4,5-dihydro-5-oxo-3*H*-[1,2,4]triazol-1-ium-4-ides (**6**).[5,6] Compounds (**4**) undergo a thermally induced or acid catalyzed [1,5] or [1,2$^+$] sigmatropic rearrangement *via* the cyclic intermediates (**6**), one of the 3-substituents migrating to the neighboring nitrogen atom thus affording 1,5-disubstituted 2,3-dihydro-2-aryl-1*H*-[1,2,4]triazol-3-ones (**8**).[6,7] Similarly, 1-phenylazoalkyl-1-isothiocyanates (**5**) when treated with acid furnished 1,5-disubstituted 2,3-dihydro-2-aryl-1*H*-[1,2,4]triazole-3-thiones (**9**).[8] The intermediate involved in the acid

---

Dedicated to Professor Fritz Sauter on the occasion of his retirement.

induced rearrangement is presumed to be the 4,5-dihydro-5-thioxo-3*H*-[1,2,4]triazol-1-ium ion ($7 \cdot H^+$).[8] The rearrangement reaction is selective in respect of the migrating group, the order of preferred migration being tert. > sec. > prim. alkyl > methyl; aryl > alkyl.

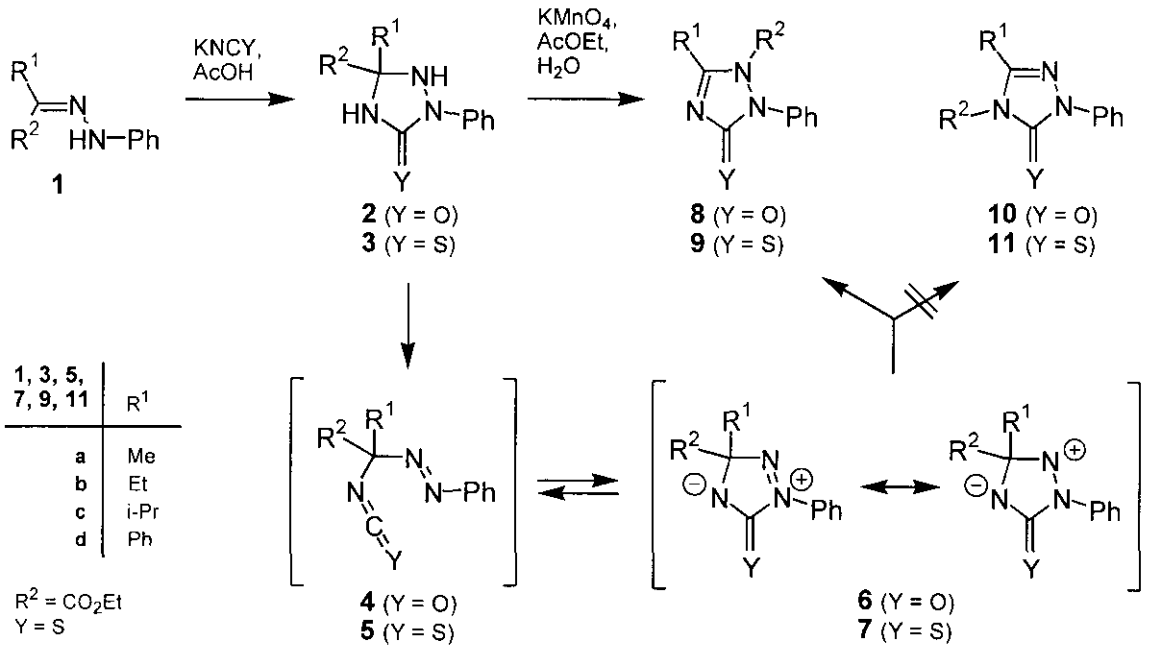
It deemed worthwhile to further explore this rearrangement reaction with respect to the migratory aptitude of functionalized substituents R^1 and R^2.

RESULTS AND DISCUSSION

The selectivity between migrating groups is expected to be more pronounced among substituents bearing different functional groups at the migrating carbon center. Thus, the competition between alkyl or phenyl groups (R^1) and the ethoxycarbonyl group (R^2) was investigated.

For this purpose, the preparation of 5-substituted 5-ethoxycarbonyl-2-phenyl[1,2,4]triazolidin-3-ones (**2a-d**, $R^2 = CO_2Et$) was attempted. However, the reaction of ethyl 2-(phenylhydrazono)alkanoates (**1a-d**) with potassium cyanate in acetic acid failed. By contrast, the reaction of **1a-d** with potassium thiocyanate in acetic acid succeeded in the formation of 5-substituted 5-ethoxycarbonyl-2-phenyl[1,2,4]triazolidine-3-thiones (**3a-d**) (Scheme 1).

Oxidation of 5-substituted 5-ethoxycarbonyl-2-phenyl[1,2,4]triazolidine-3-thiones (**3a-d**, $R^2 = CO_2Et$) was carried out with potassium permanganate in a two-phase system of water and ethyl acetate. The

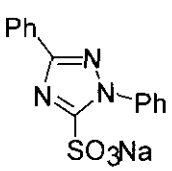


Scheme 1.

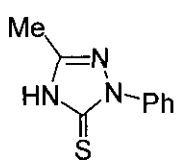
anticipated primary oxidation products 1-ethoxycarbonyl-1-phenylazoalkylisothiocyanates (**5**) were not isolated. Instead, 5-substituted 1-ethoxycarbonyl-2,3-dihydro-2-phenyl-1*H*-[1,2,4]triazole-3-thiones (**9**) were obtained in good yields (for structure proof *vide infra*) (Scheme 1).

The conversion of **3d** into **9d** was accompanied by the formation of traces of sodium 1,3-diphenyl-1*H*-[1,2,4]triazole-5-sulfonate (**12**) (Figure 1); obviously, this side-product (**12**) results from further oxidation of the sulfur function and the loss of the ester group (in the course of alkaline hydrolysis).

Alkaline hydrolysis followed by acidification brought about removal of the ethoxycarbonyl function of the rearranged product (**9a**), thus proving the migration of the ethoxycarbonyl group to one of the neighboring ring nitrogen atoms. The product obtained was 4,5-dihydro-3-methyl-1-phenyl-1*H*-[1,2,4]triazoline-5-thione (**13**)[9] but it remains undecided which tautomeric structure (**13**) or (**14**) is prevalent (Figure 2).

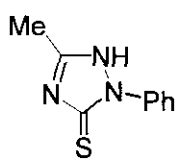


12



13

or



14

Figure 1.

Figure 2.

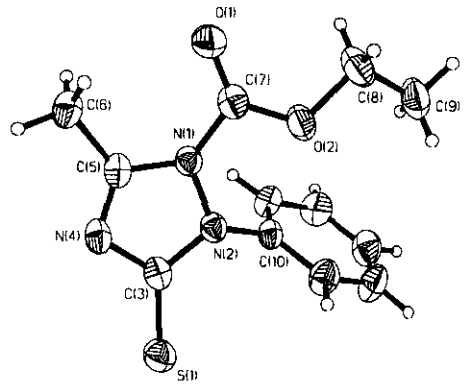


Figure 3. ORTEP Drawing of **9a**.

Generally, in the course of the rearrangement reaction of compounds (**4**) and (**5**) (*via* **6** and **7**) the migrating group R^2 is found in 1-N position of the rearranged 2,3-dihydro-1*H*-[1,2,4]triazoles (**8**) and (**9**), respectively.[6-8] In one case, a product of structure (**10**) resulting from the migration of R^2 to the neighboring ring position 4-N has been encountered.[10] The ultimate structure proof of the product derived from the oxidation of **3a** is provided by X-Ray structure analysis (Figure 3) and confirms structure (**9a**) ruling out the conceivable alternative structure (**11a**).

Formation of products (**9**) is envisaged to occur *via* the putative intermediates 1-ethoxycarbonyl-1-phenylazoalkylisothiocyanates (**5**) and their cyclic valence isomers, 3,3-disubstituted 1-phenyl-4,5-dihydro-5-thioxo-3*H*-[1,2,4]triazol-1-ium-4-ides (**7**). Since this rearrangement reaction takes place in the absence of acid (in the course of the oxidation with potassium permanganate the aqueous solution turns alkaline) **7** is considered the intermediate undergoing the rearrangement reaction (rather than the conjugate acid **7**•H^+). The ethoxycarbonyl group is known to preferentially migrate in similar rearrangement reactions,[11] and the high migrating tendency of the ethoxycarbonyl group appears to be the driving force also in the formation of **9** making **5** and **7** short lived and non-detectable intermediates.

Table 1: ^{1}H-NMR Data of 5-Substituted 5-Ethoxycarbonyl-2-phenyl[1,2,4]triazolidine-3-thiones (**3**) and 1-Ethoxycarbonyl-2,3-dihydro-2-phenyl-1*H*-[1,2,4]triazole-3-thiones (**9**). (Solvent DMSO-d_6).

	5-R[1]	R[2] = $CO_2CH_2CH_3$[a]	2-C_6H_5[b]	1-NH	4-NH
3a	1.59 (s)	4.15, 4.13 (AB, ^2J = 11.0 Hz; q), 1.17 (dd)	7.89 (d), 7.34 (dd), 7.13 (t)	7.23 (s)	9.67 (s)
3b	1.94 (dq, J = 3.0, 7.0 Hz), 1.87 (dq, J = 3.0, 7.0 Hz), 0.92 (dd, J = 7.0, 7.0 Hz)	4.18 (q), 1.20 (t)	7.90 (d), 7.34 (dd), 7.13 (t)	7.15 (s)	9.76 (s)
3c	2.17 (qq, J = 7.0, 7.0 Hz), 0.92 (d, J = 7.0 Hz), 0.91 (d, J = 7.0 Hz)	4.21 (q), 1.23 (t)	7.93 (d), 7.34 (dd), 7.13 (t)	7.06 (s)	9.75 (br s)
3d	7.5-7.4 (m), 7.7-7.5 (m)	4.16 (q), 1.14 (t)	7.94 (d), 7.35 (dd), 7.15 (t)	[c]	10.49 (s)
9a	2.63 (s)	4.14 (q), 0.95 (t)	7.6 – 7.3 (m)	–	–
9b	3.03 (q, J = 7.2 Hz), 1.30 (t, J = 7.2 Hz)	4.13 (q), 0.93 (t)	7.6 – 7.3 (m)	–	–
9c	3.55 (sept, J = 7.0 Hz), 1.34 (d, J = 7.0 Hz)	4.13 (q), 0.90 (t)	7.6 – 7.3 (m)	–	–
9d	7.93 (d),[b] 7.7 – 7.4 (m)	3.97 (q), 0.71 (t)	7.7 – 7.4 (m)	–	–

[a] ^3J = 7.0 – 7.3 Hz. [b] Under the assumption of first order multiplets ^3J ~ 7.0 Hz. [c] Obscured by C_6H_5 signals.

Table 2: ^{13}C-NMR Data of 5-Substituted 5-Ethoxycarbonyl-2-phenyl[1,2,4]triazolidine-3-thiones (**3**) and 1-Ethoxycarbonyl-2,3-dihydro-2-phenyl-1*H*-[1,2,4]triazole-3-thiones (**9**). (Solvent DMSO-d_6).

	5-R[1]	R[2] = $CO_2CH_2CH_3$	3-C	2-C_6H_5[a]	5-C
3a	20.1	170.3, 61.5, 14.0	176.8	139.5, 128.0, 124.6, 121.7	76.0
3b	27.7, 7.5	170. 0,61.5, 14.0	176.5	139.6, 127.9, 124.6, 121.8	79.6
3c	33.6, 16.0, 15.9	169.6, 61.6, 14.0	175.5	139.5, 128.0, 124.6, 121.8	82.0
3d	136.7, 129.2, 128.6, 125.9[b]	168.8, 62.0, 13.8	176.3	139.2, 128.0, 124.9, 122.1	80.2
9a	16.4	162.9, 65.3, 13.2	182.9	137.8, 128.9, 128.8, 126.8	144.9
9b	22.7, 10.1	166.7, 65.3, 13.1	183.0	137.8, 128.9, 128.8, 126.8	144.9
9c	28.1, 20.4	170.1, 65.4, 13.0	182.8	137.7, 128.9, 128.8, 126.6	144.7
9d	132.3, 131.0, 127.7, 127.1[c]	163.7, 65.3, 12.8	182.4	138.0, 128.8, 128.4, 126.5	144.9

[a-c] Order of phenyl signals: [a] 1-C, 3,5-C, 4-C, 2,6-C; [b] 1-C, 4-C, 3,5-C, 2,6-C; [c] 1-C, 3,5-C, 2,6-C, 4-C.

EXPERIMENTAL

Spectroscopic data were recorded on the following instruments: MATTSON Galaxy Series GL-3020 (IR), Hewlett-Packard HP-8452 (UV-Vis), Varian Gemini 200 (^{1}H-NMR, 200 MHz; ^{13}C-NMR 50 MHz) using solvent signals for calibration with reference to tetramethylsilane; Finnigan MAT 95 (EI-MS 70 eV; FAB-MS Cs gun, 20 KeV, 0.2 μA), Reichert Kofler hot stage microscope (mp). TLC was carried out on silica gel (Polygram Sil G/UV_{254}, Macherey-Nagel), silica gel filtration (230-400 mesh, Merck) was performed using a sintered glass funnel (5 cm length, 3.5 cm I.D.). Petroleum ether (PE) refers to the fraction with boiling range 40-60 °C.

Ethyl 2-phenylhydrazonoalkanoates (1). General Procedure: To a stirred solution of ethyl 2-oxo-alkanoate (15 mmol) in ethanol (20 mL) and acetic acid (1 mL) was added dropwise a solution of phenyl-hydrazine (1.78 g, 16.5 mmol) in ethanol (5 mL) under a nitrogen atmosphere. After completion of the reaction (checked by TLC) the solvents were evaporated under reduced pressure at 40 °C. The residue was either crystalline: **1a** (30%; mp 116-120 °C ($CHCl_3$), lit.,[12] 118-120 °C) or an oil which slowly crystallized: **1b** (77%: mp 79-83 °C, lit.,[13] 86 °C) or remained an oil: **1c** (70%; n_D^{20} 1.5758). **1d** separated from the reaction mixture as crystals (88%; mp 91.5 °C, lit.,[14] 94 °C).

5-Substituted 5-Ethoxycarbonyl-2-phenyl[1,2,4]triazolidine-3-thiones (3). General Procedure: To a solution or suspension of ethyl 2-(phenylhydrazono)alkanoates (**1**) (10 mmol) in formic acid (30 mL) was added a solution of KNCS (2.8 g, 30 mmol) in formic acid (10 mL). The reaction mixture was kept at 50 °C, the reaction time was determined by TLC-monitoring the consumption of the starting material (**1**). Work-up was as follows: (a) After 100 h the reaction mixture was poured into water (75 mL), the sticky yellow oil formed was removed by filtration, and from the filtrate the crude product (**3a**) separated; (b) after 18 h the reaction mixture was concentrated *in vacuo* to two thirds of its volume whereupon crystallization of the product (**3b**) was induced; (c) after 69 h the reaction mixture was cooled to rt to initiate separation of product (**3c**); (d) similarly, **3d** was obtained after 22 h. Products **3a-d** were isolated as analytically pure compounds (TLC); recrystallization, in particular prolonged heating in a solvent may induce decomposition.

5-Ethoxycarbonyl-5-methyl-2-phenyl[1,2,4]triazolidine-3-thione (3a): Colorless crystals (31%); mp 96-103 °C (cyclohexane); R_f 0.17 (PE/ether 1:1); IR (KBr): ν 3225 (NH), 3132(NH), 2937 (CH_3), 1735 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 265 (3, $M^{\bullet+}$), 218 (10, M – OC_2H_5), 192 (25, M – $CO_2C_2H_5$), 175 (91, M – $HCO_2C_2H_5$ – CH_4), 132 (31, C_6H_5N-N=C-CH_3), 91 (100, C_6H_5N), 77 (31, C_6H_5). Anal. Calcd for $C_{12}H_{15}N_3O_2S$: C, 54.32; H, 5.70; N, 15.84; S, 12.08. Found: C, 54.21; H, 5.80; N, 16.23; S, 11.75.

5-Ethoxycarbonyl-5-ethyl-2-phenyl[1,2,4]triazolidine-3-thione (3b): Colorless crystals (25%); mp 117-119 °C (ethanol/water); R_f 0.47 (PE/ether 1:1); IR (KBr): ν 3220 (NH), 3135(NH), 2964 (CH_3), 2931 CH_3 (CH_2), 2875 (CH_2), 1735 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 279 (18, $M^{\bullet+}$), 220 (M – HNCS), 206 (100,

M – $CO_2C_2H_5$), 146 (21, M – $HCO_2C_2H_5$ – HNCS), 91 (58, C_6H_5N), 77 (17, C_6H_5). Anal. Calcd for $C_{13}H_{17}N_3O_2S$: C, 55.89; H, 6.13; N, 15.04; S, 11.48. Found: C, 56.05; H, 6.32; N, 15.22; S, 11.07.

5-Ethoxycarbonyl-5-(1-methylethyl)-2-phenyl[1,2,4]triazolidine-3-thione (3c): Colorless crystals (68%); mp 118-120 °C (ethanol); R_f 0.41 (PE/ether 1:1); IR (KBr): ν 3228 (NH), 3148(NH), 2969 (CH_3), 2929 (CH_2), 1735 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 293 (9, $M^{\bullet+}$), 234 (M – HNCS), 220 (100, M – $CO_2C_2H_5$), 160 (56, M – $HCO_2C_2H_5$ – HNCS), 91 (85, C_6H_5N), 77 (38, C_6H_5). Anal. Calcd for $C_{14}H_{19}N_3O_2S$: C, 57.31; H, 6.53; N, 14.32; S, 10.93. Found: C, 57.68; H, 6.89; N, 14.59; S, 10.67.

5-Ethoxycarbonyl-2,5-diphenyl[1,2,4]triazolidine-3-thione (3d): Colorless crystals (55%); mp 130-132 °C;[15] R_f 0.32 (PE/ether 1:1); IR (KBr): ν 3224 (NH), 3106(NH), 2977 (CH_3), 2896 (CH_2), 1714 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 327 (9, $M^{\bullet+}$), 268 (19, M – HNCS), 254 (100, M – $CO_2C_2H_5$), 194 (33, M – $HCO_2C_2H_5$ – HNCS), 151 (18, C_6H_5N-C(=S)NH_2), 91 (31, C_6H_5N), 77 (19, C_6H_5). Anal. Calcd for $C_{17}H_{17}N_3O_2S$: C, 62.37; H, 5.23; N, 12.83; S, 9.79. Found: C, 62.24; H, 5.37; N, 13.01; S, 9.45.

1-Ethoxycarbonyl-2,3-dihydro-2-phenyl-1*H*-[1,2,4]triazole-3-thiones (9). General Procedure: To a stirred, ice-cooled solution of **3** (1.4 mmol) in ethyl acetate (10 mL) was added dropwise (during 2 – 3 min) a solution of $KMnO_4$ (0.216 g, 1.4 mmol) in water (10 mL). After 30 min MnO_2 was filtered off and washed with ethyl acetate. The aqueous layer of the filtrate was separated and repeatedly extracted with ethyl acetate. The combined organic extracts were washed with satd. sodium chloride solution (3 x 20 mL) and dried ($MgSO_4$). Removal of the solvent furnished **9**.

1-Ethoxycarbonyl-2,3-dihydro-5-methyl-2-phenyl-1*H*-[1,2,4]triazole-3-thione (9a): Slightly yellow crystals (73%), mp 122-124 °C (ethanol); R_f 0.01 (PE/ether 1:1); R_f 0.56 (ethyl acetetate); IR (KBr): ν 3009 (HC_{arom}), 2933 (CH_2), 1763 (C=O) cm^{-1}; FAB-MS (glycerol) (*m/z* (%)): 264 (100, $M^{\bullet+}$), 232 (6, M – S), 220 (10, M – OC_2H_5), 192 (33, M – $CO_2C_2H_5$). Anal. Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.74; H, 4.98; N, 15.96; S, 12.18. Found: C, 54.94; H, 5.08; N, 16.26; S, 11.84.

Crystal Data for **9a**: Dimensions 0.65 x 0.25 x 0.2 mm, monoclinic, a = 13.546(2), b = 5.830(1), c = 16.732(2) Å, β = 104.46(1)°, U = 1279.5(3) $Å^3$, space group $P2_1/c$ (No. 14), Z = 4, $F(000)$ = 552, ω – scans were made at a speed of 4.0° min^{-1} in ω at 218(2) K: 1793 reflections were collected in the range $5° < 2\theta < 42°$; of these, 1365 were independent, 1198 having $I > 2\sigma(I)$. The data were collected on a Siemens P4 diffractometer using graphite monochromated Mo-Kα radiation, and corrected for *LP*. No absorption correction was applied. The structure was solved by direct methods and structure refinement on F^2 was carried out with the program SHELXL-93.[17] Anisotropic temperature factors were applied for all non-hydrogen atoms. Hydrogen atoms were inserted at idealized positions and were refined riding with the atoms to which they were bonded. The final full-matrix-least-squares refinement varied 165 parameters and used all 1327 independent reflections weighted by $w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.6865P]$ where $P = F_o^2 + 2F_c^2)/3$. Final $R1$ = 0.0278, $wR2$ = 0.0655 and S = 1.062 for 1198 reflections with $I > 2\sigma(I)$. The final difference Fourier map showed minimum and maximum values of 0.126 and

-0.175 e $Å^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

1-Ethoxycarbonyl-5-ethyl-2,3-dihydro-2-phenyl-1*H*-[1,2,4]triazole-3-thione (9b): Yellow crystals (90%), mp 106-109 °C (cyclohexane); R_f 0.08 (PE/ether 1:1); IR (KBr): ν 2987 (CH_3), 1776 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 277 (36, $M^{\bullet+}$), 232 (24, M – OC_2H_5), 204 (100, M – $CO_2C_2H_5$), 91 (97, C_6H_5N), 77 (52, C_6H_5). Anal. Calcd for $C_{13}H_{15}N_3O_2S$: C, 56.30; H, 5.45; N, 15.15; S, 11.56. Found: C, 56.50; H, 5.37; N, 15.26; S, 11.35.

1-Ethoxycarbonyl-2,3-dihydro-5-(1-methylethyl)-2-phenyl-1*H*-[1,2,4]triazole-3-thione (9c): Yellow crystals (90%), mp 111-117 °C (decomp, cyclohexane); R_f 0.18 (PE/ether 1:1); IR (KBr): ν 2977 (CH_3), 1768 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 291 (22, $M^{\bullet+}$), 246 (16, M – OC_2H_5), 232 (22, M – HNCS), 218 (100, M – $CO_2C_2H_5$), 91 (73, C_6H_5N), 77 (38, C_6H_5). Anal. Calcd for $C_{14}H_{17}N_3O_2S$: C, 57.71; H, 5.88; N, 14.42; S, 11.00. Found: C, 57.94; H, 6.06; N, 14.49; S, 10.71.

1-Ethoxycarbonyl-2,3-dihydro-2,5-diphenyl-1*H*-[1,2,4]triazole-3-thione (9d) and **sodium 1,3-diphenyl-1*H*-[1,2,4]triazole-5-sulfonate (12):** The reaction furnished a mixture of two products. Fractional silica gel filtration (17 g) of a 0.500 g portion with ethyl acetate provided (**9d**), a yellow powder (78%), mp 129-130 °C (ethanol/water); R_f 0.10 (PE/ether 1:1), R_f 0.70 (ethyl acetate); IR (KBr): 2975 (CH_3), 1783 (C=O) cm^{-1}; EI-MS (*m/z* (%)): 325 (27, $M^{\bullet+}$), 281 (39, M – OC_2H_4), 280 (37, M – OC_2H_5), 252 (57, M – $CO_2C_2H_5$ – HNCS), 91 (100, C_6H_5N), 77 (66, C_6H_5). Anal. Calcd for $C_{17}H_{15}N_3O_2S$: C, 62.75; H, 4.65; N, 12.91; S, 9.85. Found: C, 62.61; H, 4.64; N, 13.02; S, 9.68.

Further elution with ethyl acetate afforded the salt (**12**), colorless crystals (4%), mp > 330 °C (ethanol); R_f 0.05 (ethyl acetate); IR (KBr): ν 3500 (br), 3068, 1255, 1230, 1062 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 7.4 – 7.6 (m, 6H, 3,4,5-H 1,3-C_6H_5), 7.82 (dd, 2H, *J* = 8.0, 2.0 Hz, 2,6-H, 1-(or 3-)C_6H_5), 8.06 (dd, 2H, *J* = 7.0, 2.0 Hz, 2,6-H, 3-(or 1-)C_6H_5); ^{13}C-NMR (DMSO-d_6): δ 158.8 (3- or 5-C), 158.3 (5- or 3-C), 138.5, 129.5, 128.8, 128.5, 126.1, 125.2 (1,3-C_6H_5); FAB-MS (NOBA) (*m/z* (%)): 346 (100, M + Na^+), 324 (69, M + H^+). Anal. Calcd for $C_{14}H_{10}N_3O_3NaS•0.5\ H_2O$: C, 50.60; H, 3.34; N, 12.64; Na 6.92; O, 16.85; S, 9.65. Found: C, 50.99; H, 3.72; N, 12.78; S, 9.30.

4,5-Dihydro-3-methyl-1-phenyl-1*H*-[1,2,4]triazoline-5-thione (13):[9] A solution of **3a** (0.1 g, 0.4 mmol) in 20% KOH (10 mL) was heated under reflux for 110 min. After cooling to rt the reaction mixture was extracted with ethyl acetate (2 x 10 mL). The aqueous phase was neutralized by dropwise addition of conc. HCl, and the precipitate formed was filtered off and dried to yield 0.04 g (55%) colorless crystals (**13**), mp 178-181 °C (toluene), lit.,[9] 182 °C; R_f 0.36 (ethyl acetate); IR (KBr): ν 3100-2700 (br), 1602, 1496, 1477, 1431, 1380 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 13.00 (br, NH), 7.95 (d, *J* = 7 Hz, 2,6-H C_6H_5), 7.48 (d,d, *J* = 7 Hz, 3,5-H C_6H_5), 7.36 (d, *J* = 7 Hz, 4-H C_6H_5), 2.27 (s, CH_3); ^{13}C-NMR (DMSO-d_6): δ 165.2 (5-C=S), 148.8 (3-C), 137.9 (1-C 1-C_6H_5), 128.6 (3,5-C 1-C_6H_5), 127.4 (4-C 1-C_6H_5), 123.4 (2,6-C 1-C_6H_5), 10.9 (CH_3).

ACKNOWLEDGEMENTS

The measurement of MS spectra by Prof. K.-H. Ongania, Institut für Organische Chemie, Universität Innsbruck, is gratefully acknowledged. The authors appreciate the preparation of hydrazones and the experimental help by Mrs. C. Prevedel. Elemental analyses were determined by J. Theiner, Institut für Physikalische Chemie, Universität Wien.

This work has received financial support by the Fonds zur Förderung der Wissenschaftlichen Forschung (FWF), Vienna (Project Nr. MOB 10462).

REFERENCES AND NOTES

1. J.G. Schantl and P. Hebeisen, L. Minach, *Synthesis*, **1984**, 315.
2. R. Grigg, J. Kemp, and N. Thompson, *Tetrahedron Lett.*, **1978**, *31*, 2827.
3. R. Grigg, *Chem. Soc. Rev.*, **1987**, *16*, 89.
4. P. Hebeisen, *Sci. Pharm.*, **1983**, *51*, 379.
5. J.G. Schantl and H. Gstach, *Monatsh. Chem.*, **1985**, *116*, 1051.
6. P. Seil, J.G. Schantl, A. Gieren, T. Hübner, and J. Wu, *Angew. Chem.*, **1986**, *98*, 1111; *Angew. Chem., Int. Ed. Engl.*, **1986**, *25*, 1132.
7. H. Gstach and P. Seil, *Synthesis*, **1990**, 803; 808.
8. B. Klötzer, Diploma Thesis, University of Innsbruck, **1989**.
9. G.F. Duffin, J.D. Kendall, and H.R.J. Waddington, *J. Chem. Soc.*, **1959**, 3799.
10. H. Gstach and P. Seil, *Synthesis*, **1990**, 1048.
11. D. Berner, D.P. Cox, and H. Dahn, *J. Am. Chem. Soc.*, **1982**, *104*, 2631, and references cited therein.
12. L.J. Simon, *C. R. Hebd. Seances Acad. Sci.*, **1900**, *131*, 682.
13. R. Rambaud and M.L. Dondon, *C. R. Hebd. Seances Acad. Sci.*, **1946**, *223*, 381.
14. S. Goldschmidt and W. Beuschel, *Liebig's Ann. Chem.*, **1926**, *447*, 197.
15. The attempt to recrystallize **3d** from ether/cyclohexane gave rise to decomposition and furnished 3,4-dihydro-2,5-diphenyl-2*H*-[1,2,4]triazole-3-thione.[16]
16. G. Barnikow and D. Richter, Z. Chem., **1980**, *20*, 97.
17. G.M. Sheldrick, SHELXL-93, computer program for crystal structure refinement, University of Göttingen, **1993.**

Received, 29th June, 1998