Monatshefte für Chemie 126: 431–437 (1995)

Monatshefte für Chemie
Chemical Monthly

Synthesis of 1,2,4-Triazolium Salts: Reaction of 1-Azo-2-azonia-allene Salts with Nitriles

A. M. Amer

Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt

Summary. Alkyl ketone hydrazones **1** are oxidized with *tert*-butylhypochlorite to give geminal chloro azo compounds **2**. These react with $SbCl_5$ to give 1-aza-2-azonia-allene salts **3** as reactive intermediates which are intercepted with nitriles to yield 3*H*-1,2,4-triazolium salts **5**. In most cases these salts rearrange spontaneously to form 1*H*-triazolium salts **6**. Hydrolysis of **6e–g** by NaOH provide bases **7a–c**, which react with picric acid to give 1*H*-pyrazolium picrates **8**.

Synthese von 1,2,4-Triazoliumsalzen: Reaktion von 1-Azo-2-azonia-allensalzen mit Nitrilen

Zusammenfassung. Alkylketonhydrazone **1** werden durch *tert*-Butylhypochlorit zu geminalen Chlorazoverbindungen **2** oxidiert. Diese reagieren mit $SbCl_5$ zu 1-Aza-2-azonia-allensalzen **3**, welche mit Nitrilen unter Bildung von 3*H*-1,2,4-Triazoliumsalzen **5** abgefangen werden. In den meisten Fällen lagern diese spontan zu 1*H*-Triazoliumsalzen **6** um. Hydrolyse von **6e–g** mit NaOH führt zu den Basen **7a–c**, welche mit Pikrinsäure 1*H*-Pyrazoliumpikrate **8** bilden.

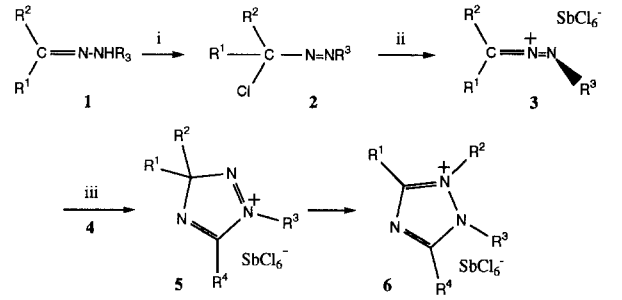
Keywords. Hydrazones; Heterocumulenes; Nitriles; Triazoles; Rearrangements.

Introduction

Rearrangement reactions provide a very useful tool in the field of organic chemistry. Among these, migrations to nitrogen are of particular importance for the synthesis of many industrial products [1]. Therefore we continue our research program directed towards the reaction of 1-aza-2-azonia-allene salts with multiple bonds [2–3]. 1-Aza-2-azonia-allene cations **3** (R^3 = aryl) have been postulated by *Huisgen* and *Koch* as intermediates in the reaction of aryl diazonium salts with diazoalkanes [4]. In fact, 1-aza-2-azonia-allene ions are generated as reactive intermediates in many oxidative processes of hydrazones. In a previous report [2] we described some reactions of cations **3** with several types of multiple bonds. In this paper we extend our study to the reaction of different nitriles **4** to explore the scope and limitations of this procedure as a synthetic method for the formation of 1,2,4-triazolium salts **6** and/or triazole derivatives **8**.

Results and Discussion

Hydrazones **1** are oxidized with *tert*-butylhypochlorite to give geminal chloro azo compounds **2**. When treated with the Lewis acid antimony pentachloride, they afford 1-aza-2-azonia-allen salts **3**. It was found that it is possible to intercept **3** with nucleophiles such as nitriles **4** ($R^4 = CH_3$, SMe, Ph, CH_2COOEt) to obtain triazolium salts **6**. To rationalize the formation of **6**, one has to assume the formation of an intermediate **5** which undergoes a 1,2-shift of the substituent R^2.



i = *t*-Bu-OCl/CH_2Cl_2 < 0 °C; ii = $SbCl_5$, < 0 °C; iii = R^4–CN;

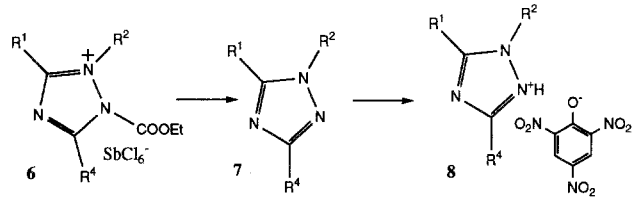
1–3	R^1	R^2	R^3	
a	CH_3	Ph	Ar	
b	CH_3	p-C_6H_4-Ph	Ar	
c	CH_3	4-Pyridyl	Ar	
d	CH_3	Ph	COOEt	
e		–$(CH_2)_5$–	COOEt	
5–6	R^1	R^2	R^3	R^4
a	CH_3	Ph	Ar	CH_2COOEt
b	CH_3	4-p-C_6H_4-Ph	Ar	CH_3
c	CH_3	4-p-C_6H_4Ph	Ar	Ph
d	CH_3	4-Pyridyl	Ar	CH_3
e	CH_3	Ph	COOEt	CH_3
f		–$(CH_2)_5$–	COOEt	CH_2COOEt
g		–$(CH_2)_5$–	COOEt	SCH_3

Ar = 2,4,6-Trichlorophenyl

Scheme 1

We found that the migratory aptitude of R^2 to form salts **6** from **5** paralleles the stabilities of the cations $(R^2)^+$. In most cases, the primary cyclization products **5** cannot be isolated because of their fast rearrangement to **6**. For $R^1 \neq R^2$ ($R^1 = CH_3$; R^2 = Ph, Ph-Ph, Py), the substituent forms the more stable carbenium ion **3**. Furthermore, migration occurs exclusively to N-2 (and not N-4) [6–9] except for compound **5d**. In this case the migration of the pyridyl group could not be achieved, even at elevated temperatures. This phenomenon is presently being studied in detail. The ^{13}C NMR resonance signals for compound **5d** appear at 29.24, 29.29 (CH_3), 94.69 (C-3), 118.0, 123.0, 126.7, 129.9, 134.5, 145.2, 148.3 (pyridyl, aryl), and 168 (C=N) ppm. The triazolium derivatives **5** and **6** can be easily distinguished by inspection of their ^{13}C NMR spectra. The ^{13}C NMR resonances of C-3 appear in

the range of $\delta = 94$ ppm for compound **5d** and in the range of $\delta = 153$ ppm for compounds **6**. The tendency to migrate paralleles the migratory aptitude of substituents, which has been observed for the *Beckmann* rearrangement of oximes [10]. Therefore it is likely that not a free cation but an electronic cloud of the heterocycle governs the rearrangement process. With regard to this hypothesis it seems most likely that compound **5d** (R^2 = Py) forms especially stable cations and can therefore escape from 5 without forming **6**.



7–8	R^1	R^2	R^3
a	CH_3	Ph	CH_3
b	$-(CH_2)_5-$		CH_2COOEt
c	$-(CH_2)_5-$		SCH_3

Scheme 2

Obviously, the reaction of the hydrazone esters **2d–e** (R^3 = COOEt) with nitriles afford triazolium salts **6e–g**. Treatment of **6e–g** with aqueous NaOH yielded the free bases **7a–c**. This method provides a possible starting point for the synthesis of many new triazole derivatives. Furthermore, treatment of triazoles **7a–b** with picric acid afford pure picrates **8a–b**. The structure of all newly synthesized compounds is confirmed by their elemental and spectroscopic data.

Experimental

All melting points are uncorrected. IR: Mattson Polaris Ft-IR Spectrometer; ^1H and ^{13}C NMR: Bruker WM 250 and AC 250 spectrometers: chemical shifts are given in δ units relative to internal *TMS* at 295 K. All experiments were carried out with exclusion of moisture. For all newly synthesized compounds satisfactory elemental analyses were obtained.

Preparation of Hydrazones **1** [2]

A mixture of the ketone [acetophenone, 4-acetyl biphenyl, 4-acetyl pyridine and/or ethyl carbazate (100 mmol)] and the hydrazine (100 mmol) in ethanol (80 ml)/acetic acid (1 ml) was boiled under reflux for 5 h. Evaporation of the solvent and crystallization of the residue afforded the pure hydrazone. 1-Phenylethanone-2,4,6-trichlorophenylhydrazone (**1a**) and ethyl cyclohexylidenecarbazate (**1e**) were prepared according to Ref. [2].

N-(1-Biphenyl-4-yl-ethylidene)-N'-(2,4,6-trichlorophenyl)-hydrazine (**1b**; $C_{20}H_{15}Cl_3N_2$)

From 4-acetylbiphenyl (18.60 g, 100 mmol) and 2,4,6-trichlorophenyl-hydrazine (21.15 g, 100 mmol); crystallization from acetic acid gave colourless fine crystals (35.81 g, 92%); m.p.: 102–104 °C; IR (CH_2Cl_2): ν = 3352 br, 3040, 1620, 1490, 1460 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.31$ (s, 3H, CH_3), 7.32–7.61 (m, 11H, biphenyl and trichlorophenyl) ppm.

N-(1-Pyridin-4-yl-ethylidene)-N'-(2,4,6-trichlorophenyl)-hydrazine (**1c**; $C_{13}H_{10}Cl_3N_3$)

From 4-acetylpyridine (10.90 g, 100 mmol) and 2,4,6-trichlorophenyl-hydrazine (21.15 g, 100 mmol); crystallization from methanol gave colourless fine crystals (37.00 g, 95%); m.p.: 85–88 °C; IR (CH_2Cl): $\nu = 3360$ br, 2950 br, 1600, 1480, 1450, 1415 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.20$ (s, 3H, CH_3), 7.34 (s, 2H, trichlorophenyl), 7.53 (s, 1H, NH), 7.61 (d, 2H, pyridyl), 7.63 (d, 2H, pyridyl) ppm.

N-Ethoxycarbonyl-N'-(1-phenyl-ethylidene)-hydrazine (**1d**; $C_{11}H_{14}N_2O_2$)

From acetophenone (12,02 g, 100 mmol) and ethyl carbazäte 10.41 g, 100 mmol); crystallization from ethanol gave colourless fine crystals (17.55 g, 85%); m.p.: 85 °C; IR (CH_2Cl_2): $\nu = 3350$, 1740, 1690, 1500, 1450 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.22$ (t, 3H, CH_3), 2.10 (s, 3H, CH_3), 4.20 (q, 2H, CH_2), 7.26 (m, 6H, Ph and NH) ppm.

Preparation of the α-Chloroalkylazo Compounds **2**

The reaction was carried out in the dark; *tert*-butylhypochlorite (13.03 g, 120 mmol) was added dropwise to a cold (−10 °C) solution of the hydrazone (100 mmol) in $CHCl_3$ (120 ml). The mixture was stirred for 3 h at 0 °C. Evaporation of the solvent afforded the orange-yellow compound **2**. In most cases the oil thus obtained was used without further purification.

(1-Chloro-1-phenylethyl)-1azo-(2,4,6-trichlorobenzene) (**2a**; $C_{14}H_{10}Cl_4N_2$)

From **1a** (31.36 g, 100 mmol); yield 34.11 g (98%) as a yellow oil which solidified at −20 °C to give a yellow powder; m.p.: 38–40 °C; IR (CCl_4): $\nu = 3010$, 1450, 1440, 1425 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.34$ (s, 3H, CH_3), 7.35–7.54 (m, 7H, phenyl and trichlorophenyl) ppm.

(1-Biphenyl-4-yl-1-chloro-ethyl)-(2,4,6-trichlorobenzene) (**2a**; $C_{20}H_{14}Cl_4N_2$)

From **1b** (38.97 g, 100 mmol); yield 40.00 g, (94%) of a brownish oil; IR (CCl_4): $\nu = 3080$, 2950, 1700, 1615, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): 2.30 (s, 3H, CH_3), 7.30–7.73 (m, 11H, biphenyl and trichlorophenyl) ppm.

(1-Chloro-1-pyridin-4-yl-ethyl)-(2,4,6-trichlorophenyl)-diazene (**2c**; $C_{13}H_9Cl_4N_3$)

From **1c** (38.97, 100 mmol); yield 33.20 g (95%) as yellow powder which can be crystallized at −20 °C from ether to give yellow needles; m.p.: 54–55 °C; IR (CCl_4): $\nu = 3040$, 3020, 3000, 1950, 1710, 1590, 1440 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.30$ (s, 3H, CH_3), 7.42 (s, 2H, trichlorophenyl), 7.60 (d, 2H, pyridyl), 7.67 (d, 2H, pyridyl) ppm.

(1-Chloro-1-phenyl-ethyl)-ethoxycarbonyl-diazene (**2d**; $C_{11}H_{13}ClN_2O_2$)

From **1d** (20.62 g, 100 mmol); yield 22.88 g (95%) as yellow powder which can be crystallized at −20 °C from ethyl acetate to give fine yellow crystals; m.p.: 149–151 °C; IR (CCl_4): $\nu = 3015$, 2950, 1750, 1610, 1500 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.38$ (t, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.40 (q, 2H, CH_2) 7.35 (m, 5H, phenyl) ppm.

Ethyl (1-chlorocyclohexyl)-azocarboxylate (**2e**; $C_9H_{15}ClN_2O_2$)

From **1d** (18.42 g, 100 mmol); yield $\delta = 20.80$ (96%) of a yellow oil; IR (CCl_4): $\nu = 3015$, 2950, 1750, 1610, 1500 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.42$ (t, 3H, CH_3), 1.74–2.25 (m, 10H, $5CH_2$), 4.45 (q, 2H, OCH_2) ppm.

Reactions of the α-Chloroalkylazo Compounds With Nitrile Derivatives **4**

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (−60 °C) solution of the α-chloroalkylazo compound (10 mmol) and the nitriles (12 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at −60 °C for 2 h, then at 0 °C for 1 h, and finally at room temperature for 15 min. The solvent was evaporated under reduced pressure and the remaining salt was purified by crystallization.

3-Ethoxycarbonylmethyl-5-methyl-1-phenyl-2-(2,4,6-trichlorophenyl)-1 H-[1,2,4]triazolium hexachloroantimonate (**6a**; $C_{19}H_{17}Cl_9N_3O_2Sb$)

From **2a** (3.48 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and ethyl cyanoacetate (1.35 g, 12 mmol); the mixture was stirred at −60 °C for 2 h, then at 0 °C for 1 h, finally at 25 °C for 10 min. The solvent was evaporated and the residue was crystallized at −18 °C from CH_2Cl_2/ether to yield faint yellowish prisms (6.31 g, 83%); m.p.: 185–189 °C; IR (CH_2Cl_2): ν = 1730, 1600, 1550, 1520, 1480, 1450 cm^{-1}; ^1H NMR (CD_3CN): δ = 1.25 (t, 3H, CH_3), 2.8 (s, 3H, CH_3), 4.2 (q, 2H, OCH_2), 4.32 (s, 2H, CH_2CO), 7.70–7.93 (m, 7H, phenyl and trichlorophenyl) ppm; ^{13}C NMR (CD_3COCD_3): δ = 13.5, 13.9 (CH_3), 32.8 (CH_2), 62.2 (OCH_2), 123.5, 127.8, 128.3, 130.2, 130.7, 133.9, 136.0, 141.3, 157.4, 162.5, 164.2 (aryl, C=N), 205.6 (C=O) ppm.

2-Biphenyl-4-yl-3,5-dimethyl-1-(2,4,6-trichlorophenyl)-1 H-[1,2,4]triazolium hexachloroantimonate (**6b**; $C_{22}H_{17}Cl_9N_3Sb$)

From **2b** (4.24 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and acetonitrile (0.50 g, 12 mmol) as described for **6a**; the residue was crystallized at −18 °C from acetonitrile/ether to yield greenish prisms (5.36 g, 70%); m.p.: 231–233 °C; IR (CH_2Cl_2): ν = 1610, 1560, 1530, 1485, 1440 cm^{-1}; ^1H NMR (CD_3CN): δ = 2.61 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.43–7.86 (m, 11H, biphenyl and trichlorophenyl) ppm; ^{13}C NMR (CD_3CN) at 278 K: 13.4, 14.7 (CH_3), 110.0, 120.03, 120.04, 124.5, 127.7, 127.9, 130.0, 131.1, 136.5, 142.0, 146.7, 153.3, 161.9, 162.7 (aryl, C=N) ppm.

2-Biphenyl-4-yl-3-methyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1 H-[1,2,4]-triazolium hexachloroantimonate (**6c**; $C_{27}H_{19}Cl_9N_3Sb$)

From **2b** (4.24 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and benzonitrile (1.24 g, 12 mmol) as described for **6a**. The residue was crystallized at −18 °C from acetonitrile/ether to yield faint brown fine crystals (4.20 g, 51%); m.p.: 218–220 °C (dec.); IR (CH_2Cl_2): ν = 1620, 1560, 1520, 1480, 1440 cm^{-1}; ^1H NMR (CD_3CN):S = 2.5 (s, 3H, CH_3), 7.35–7.85 (m, 16H, phenyl, biphenyl, and trichlorophenyl) ppm.

3,5-Dimethyl-3-pyridyl-4-yl-1-(2,4,6-trichlorophenyl)-3 H-[1,2,4]triazolium hexachloroantimonate (**5d**; $C_{16}H_{12}Cl_9N_4Sb$)

From **2c** (3.49 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and acetonitrile (0.50 g, 12 mmol); after stirring at −60 °C for 1H, a yellow-orange solid precipitated. Stirring was continued for 1 h at −60 °C, for 1h at −0 °C, and finally at room temperature for 10 min (note that there is no change in the colour or ^1H NMR spectrum for the solid formed by increasing the time of stirring). Filtering afforded an orange-yellow powder (5.77 g, 82%) which was recrystallized from acetonitrile; m.p.: 208–210 °C; IR (CH_2Cl_2): ν = 1600, 1550, 1530, 1485, 1450, 1390 cm^{-1}; ^1H NMR (CD_3CN): δ = 2.34 (s, 3H, CH_3) 2.50 (s, 3H, CH_3), 7.75 (s, 2H, trichlorophenyl), 8.0 (d, 2H, pyridyl), 9.0 (d, 2H, pyridyl) ppm; ^{13}C NMR (CD_3CN: DMSO = 1:1) at 295 K: δ = 29.24, 29.29 (CH_3), 94.69 (C-3), 118.0, 123.0, 126.7, 129.9, 134.5, 145.2, 148.3 (pyridyl, aryl), 168 (C=N) ppm.

1-Ethoxycarbonyl-3,5-dimethyl-3,5-dimethyl-2-phenyl-2-phenyl-1H-[1,2,4]triazolium hexachloroantimonate (**6e**; $C_{13}H_{16}Cl_6N_3O_2Sb$)

From **2d** (2.40 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and acetonitrile (0.50 g, 12 mmol) as described for **6a**. The residue was crystallized at −18 °C from CH_2Cl_2/ether to yield colourless fine crystals (3.65 g, 63%); m.p.: 210–215 °C (dec.); IR (CH_2Cl_2): $\nu = 1720$, 1610, 1540, 1475 cm^{-1}; ^1H NMR (CD_3CN): 1.31 (t, 3H, CH_3), 2.62 (s, 3H, CH_3), 4.2 (q, 2H, OCH_2), 7.45 (m, 5H, phenyl) ppm.

Hydrolysis of **6e–g** *and Formation of 1H-pyrazolium Picrates* **8**

A solution of NaOH (2.80 g, 70 mmol) in H_2O (10 ml) was added dropwise at −10 °C to the solution of compounds **6e–g** (10 mmol) in CH_3CN (10 ml). After stirring at −10 °C for 1 h the solvent was evaporated and the residue was extracted with $CHCl_3$ (2 × 30 ml). The combined $CHCl_3$ extracts were dried over Na_2SO_4 and the solvent was evaporated. The residue was crystallized to afford **7a–c**. The compounds **7a, b** were dissolved in a saturated solution of picric acid (2.75 g, 12 mmol) in ethanol/H_2O (10 ml). Crystallization at −18 °C afforded the picrates **8a, b**.

3,5-Dimethyl-2-phenyl-1H-[1,2,4]triazolium picrate (**8a**; $C_{16}H_{14}N_6O_7$)

From the base **7a** (1.74 g, 10 mmol) and picric acid (2.75 g, 12 mmol); yield: 2.20 g (54%) which was recrystallized at −18 °C from $CHCl_3$ to yield faint yellow prisms; m.p.: 137–140 °C; IR (CH_2Cl_2): $\nu = 3673$, 1609, 1547, 1500, 1420 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.69$ (s, 3H, CH_3), 2.84 (s, 3H, CH_3), 7.47–7.66 (m, 5H, Ph), 8.62 (br, 1H, NH), 8.95 (s, 2H, trinitrophenyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 11.6$, 11.8 (CH_3), 124.7, 126.4, 130.2, 130.0, 134.8, 140.9, 151.2 (aryl), 154.2, 160.1 (C=N) ppm.

(6,7,8,9-Tetrahydro-5H-[1,2,4]triazolo[1,5-a]azepin-2-yl)-acetic acid ethyl ester (**7b**; $C_{11}H_{17}N_3O_2$) *and picrate* (**8b**; $C_{16}H_{18}N_6O_9$)

The salt **6f** was prepared from **2e** (2.19 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and ethyl cyanoacetate (1.35 g, 12 mmol). The precipitate formed during stirring at 0 °C was separated to yield pure **6f** as colourless fine crystals (4.27 g, 68%) which can be recrystallized at −18 °C from CH_2Cl_2/ether (note: the filtrate of the reaction mixture was evaporated under reduced pressure and crystallized at −18 °C from CH_2Cl_2/ether to yield a mixture of **6f** and *nor*-carbethoxy **6f** ($R^3 = H$)); m.p.: 212–215 °C; IR (CH_2Cl_2): $\nu = 1745$, 1710, 1590, 1530, 1470 cm^{-1}; ^1H NMR (CD_3CN): $\delta = 1.30$ (m, 6H, $2CH_3$), 1.90 (m, 6H, $3CH_2$), 3.17 (m, 2H, CH_2), 4.0 (s, 2H, CH_2CO), 4.25 (m, 4H, $2OCH_2$), 4.43 (m, 2H, CH_2) ppm. The base **7b** was prepared from **6f** (6.31 g, 10 mmol) and C 2.80 g, 70 mmol) NaOH; yield: 2.02 g (90%) as colourless oil; IR (CCl_4): $\nu = 1715$, 1600, 1580, 1520, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.27$ (t, 3H, CH_3), 1.64–1.90 (m, 6H, $3CH_2$), 2.95 (m, 2H, CH_2), 3.7 (s, 2H, CH_2CO), 4.18 (q, 2H, OCH_2), 4.37 (m, 2H, CH_2) ppm. The base **7b** was transformed into the picrate **8b** with a saturated solution of picric acid in ethanol/H_2O. Crystallization at −18 °C from chloroform (2.65 g, 60%) gave yellow fine crystals; m.p.: 144–146 °C; IR (CH_2Cl_2): $\nu = 3677$, 1700, 1615, 1600, 1530, 1480, 1420 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.2$ (t, 3H, CH_3), 1.93–2.03 (m, 6H, $3CH_2$), 3.35 (m, 2H, CH_2), 4.0 (s, 2H, CH_2CO), 4.11 (q, 2H, OCH_2), 4.4 (m, 2H, CH_2), 8.75 (s, 2H, trinitrophenyl), 9.35 (br, 1H, NH) ppm.

2-Methylsulfanyl-6,7,8,9-tetrahydro-5H-[1,2,4]triazolo[1,5-a]azepine (**7c**; $C_7H_{13}N_3S$)

The salt **6g** was prepared from **2e** (2.19 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and CH_3SCN (0.88 g, 12 mmol) as described for **6f**. Yield 4.33 g (73%) which was recrystallized at −18 °C from CH_2Cl_2/Et_2O; m.p.: 200–205 °C (dec.) as greenish prisms; IR (CH_2Cl_2): $\nu = 1751$, 1610–1590, 1535, 1450 cm^{-1}; ^1H NMR (CD_3CN): $\delta = 1.40$ (t, 3H, CH_3), 1.82–1.97 (m, 6H, 3 CH_2), 2.6 (s, 3H, SCH_3), 3.0–3.1 (m, 2H, CH_2), 4.36–4.40 (m, 2H, CH_2), 4.48–4.54 (q, 2H, OCH_2) ppm. The crude product **6f** was dissolved in

acetonitrile (25 ml). At −10 °C, a solution of NaOH (2.80 g, 70 mmol) in H_2O (10 ml) was added. Stirring at −10 °C for 1 h, evaporation of the solvent, and extraction of the residue with $CHCl_3$ (2 × 30 ml) afforded after usual work up **7c** a yellow solid (1.50 g, 82%). It was crystallized from ethyl acetate; m.p.: 93 °C; IR (CCl_4): ν = 1610, 1580, 1540, 1480, 1390 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.70–1.89 (m, 6H, $3CH_2$), 2.55 (s, 3H, SCH_3), 2.88–2.93 (m, 2H, CH_2), 4.19–4.22 (m, 2H, CH_2) ppm.

Acknowledgements

The author is indebted to his colleagues in the *Institut für Chemie, Johannes Kepler Universität Linz* for their kind assistance during a fellowship sponsored by the *Austrian Academic Exchange Service*, Vienna, Austria.

References

[1] Gstach H., Seil P. Synthesis 1990: 1048, and references therein
[2] Wang Q., Amer A., Mohr S., Ertel E., Jochims J. C. (1993) Tetrahedron **49**: 9973
[3] Wang Q., Amer A., Troll C., Fischer H., Jochims J. C. (1993) Chem. Ber. **126**: 2519
[4] Huisgen R., Koch H. J. (1955) Liebigs Ann. Chem. **591**: 200
[5] Wang Q., Jochims J. C., Köhlbrandt S., Dahlenburg I., Al-Talib M., Hamed A., Ismail E. A. Synthesis 1992: 710
[6] Gstach H., Seil P. Synthesis 1990: 803, 808
[7] Majchrzak M. W., Jefferson E., Warkentin J. (1990) J. Am. Chem. Soc. **112**: 2449
[8] De Kimpe N., Stanoeva E. (1991) Bull. Soc. Chim. Belg. **100**: 195
[9] Sammes M. P., Katritzky A. R. (1983) Adv. Hetetocycl. Chem. **34**: 35

Received August 25, 1994. Accepted (revised) October 3, 1994