# Rearrangement of 3,3-Disubstituted 1-Aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium Tetrafluoroborates; Part 2. A Convenient Synthesis of 1,5-Annulated 1,2-Dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones

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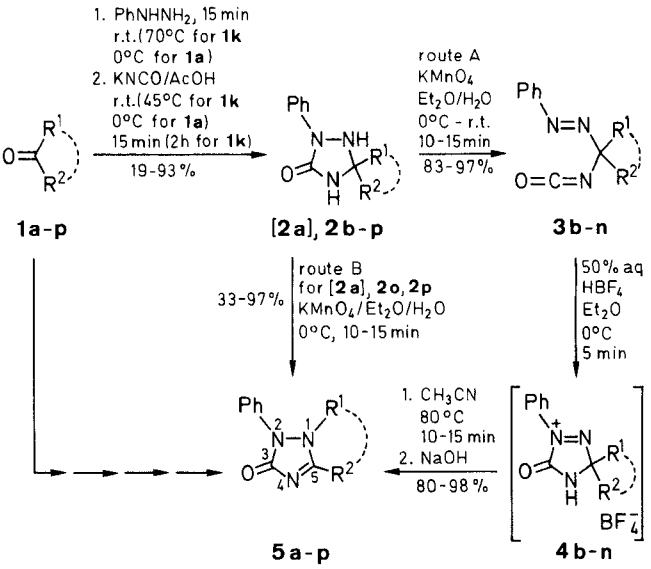
1-Isocyanato-1-(phenylazo)cycloalkanes **3** react with tetrafluoroboric acid to yield 3-spiro substituted 4,5-dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium tetrafluoroborates **4**. Compounds **4** rearrange with ring expansion in good yield to give, after basic workup, 1,5-annulated 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **5**.

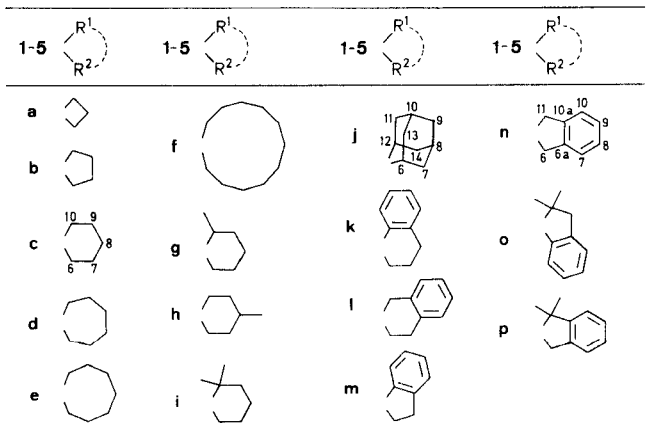
As described previously, 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones are easily accessible by acid-induced rearrangement of α-(arylazo)alkyl isocyanates.[2,3] Upon the action of acid, intramolecular ring closure of α-(arylazo)alkyl isocyanates affords first the 3,3-disubstituted 1-aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborates. Some of these compounds can be isolated,[2,3] the majority, however, exist only as short-lived intermediates.[2] The diazenium function in the 1,2,4-triazolium salts is a structural requirement for the 1,2-shift of an adjacent substituent. As the study showed,[2] if two different substituents compete, the rearrangement takes place with complete selectivity.

In continuation of our studies on substituted dihydro-1,2,4-triazol-3-ones,[2] we now report the synthesis of 1,5-annulated 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **5**. Starting from cyclic ketones **1**, 5-spiro substituted 1-phenyl-1,2,4-triazolidin-3-ones **2** were prepared (Table 1). The heterocyclic ring is then cleaved oxidatively by potassium permanganate to give 1-isocyanato-1-(phenylazo)cycloalkanes **3** (Table 2). The acid-induced rearrangement of compounds **3**, via intermediate 3-spiro substituted 4,5-dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium tetrafluoroborates **4**, takes place with ring expansion to yield, after basic workup, 1,5-annulated 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **5**. Thus, the application of this reaction concept opens a new ring expansion annulation method for cyclic ketones **1** of all commonly used ring sizes (Scheme **A**).

We were able to synthesize several annulated 1,2,4-triazoe derivatives **5** according to Scheme **A** (Table 3). The syntheses of **5b–n** follow the reaction sequence described above (route A, Scheme **A**). However, during the syntheses of **5a,o,p**, reaction anomalies, which may be connected with mechanistic aspects of certain reaction steps, were observed.

The 5-spiro substituted 2-phenyl-1,2,4-triazolidin-3-ones **2b–f,h–k,m** were prepared following well-documented literature methods.[4–9] The syntheses of compounds **5g,l,n–p**, however, raised difficulties (**5g**), or failed completely (**5l,n–p**). On prolonged contact with acetic acid, the respective phenylhydrazones of the ketones

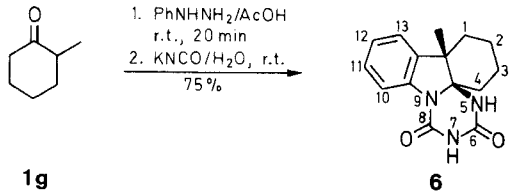



Scheme **A**

**1g,l,n–p** do not undergo the desired [3 + 2]-cycloaddition with isocyanic acid to form **2g,l,n–p**, but undergo a Fischer-indole synthesis.

When racemic 2-methylcyclohexanone (**1g**) was converted to its phenylhydrazone in acetic acid, and the reaction mixture was treated with an aqueous solution of potassium isocyanate, after 20 minutes, no 1,2,4-triazolidin-3-one **2g** was formed. Instead, (4a*RS*, 13b*RS*)-2,3,4,13b-tetrahydro-13b-methyl-1*H*-1,3,5-triazino-[6,1-*k*]carbazol-6,8-dione (**6**) was isolated in good yield (Scheme **B**). The stereochemical structure of **6** was established. A positive NOE for (5)-NH was obtained by irradiating the angular methyl group.




**1g** **6**

Scheme **B**

However, if acetic acid is the last reagent to be added to the reaction mixture (see experimental part, Method B), the formation of **6** can be avoided, and 6-methyl-2-phenyl-1,2,4-triazaspiro[4.5]decan-3-one (**5g**) is isolated in high yield. This method variant can also be applied to the syntheses of **5l,n–p**.

The oxidative ring cleavage[6,9–11] of the 5-spiro substituted 2-phenyl-1,2,4-triazolidin-3-ones **2b–n** to give the 1-isocyanato-1-(phenylazo)cycloalkanes **3b–n** succeeds in excellent yield, yet the compounds **3g,i,m** prove to be very unstable. Compounds **3i,m** rearrange during their isolation to the respective 1,5-annulated dihydro-1,2,4-triazol-3-ones **5i,m**. Compound **3g** can be kept at lower temperature (0 °C) for a couple of hours.

Attention must be paid to the potassium permanganate oxidation of the triazolidin-3-ones **2o,p**. In both cases, the intermediate occurrence of the isocyanates **3o,p** during the oxidation process could not be detected. The organic layer of the two-layered system diethyl ether/water remains colorless, even if the oxidation is carried out at 0 °C, and TLC control does not show any traces of a yellow isocyanate **3o,p**. The oxidation of **2o,p** immediately yield the respective rearranged products **5o,p** (route B, Scheme **A**). During the synthesis of **5a**, an analogous reaction behaviour discussed below, is noticed.

If the cooled (0 °C) solution of the isolated 1-isocyanato-1-(phenylazo)cycloalkanes **3b–n** in diethyl ether are treated with aqueous tetrafluoroboric acid, a yellow crystalline precipitate forms in the cases of **3c–f,h,l,n**. The 3-spiro substituted 4,5-dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium tetrafluoroborates **4c–f,h,l,n** obtained in this manner can be characterized by IR spectroscopy and show carbonyl absorptions in the range of $\nu = 1848–1860\ cm^{-1}$. Only **4c** is pure according to the IR spectrum, but it rearranges during drying *in vacuo* at room temperature with strong evolution of heat to give **5c** · $HBF_4$. The compounds **4d–f,h,l,n** are obtained accompanied by the tetrafluoroborates of the respective rearrangement products **5d–f,h,l,n**. During the reaction of the isocyanates **3b,g,i–k,m** with tetrafluoroboric acid, the triazolium salts **4b,g,i–k,m** exist only as short-lived intermediates, and the rearrangement to **5b,g,i–k,m** · $HBF_4$ is complete within a few seconds to minutes.

The acid-induced rearrangement of the isocyanates **3g,i,k–m** derived from the asymmetric ketones **1g,i,k–m** permits the study of the migration aptitudes of the substituents in the 3-spiro substituted triazolium salts **4**. The analysis of the $^1$H-NMR-spectra[2] of the products **5g,i,k–m** allows the following observations to be made: In the intermediate triazolium salts **4g,i**, the ring expansion proceeds homogeneously with exclusive migration of the higher substituted side of the ring. The isocyanate **3l**, derived from β-tetralone (**1l**), rearranges via **4l** to 3-phenyl-3,5,10,11-tetrahydro-[1,2,4]triazolo[2,3-*b*]-[2]benzazepin-2-one (**5l**) with 1,2-shift of the benzyl substituent. The benzannulated derivatives **3k,m** undergo the ring expansion to **5k,m** with exclusive migration of the aromatic side of the ring. This 1,2-shift of the aryl substituent in the intermediate **4k,m** is remarkable, for the rearrangement of the open chain compound 4,5-dihydro-3-ethyl-5-oxo-1,3-diphenyl-3*H*-1,2,4-triazolium tetrafluoroborate, which itself exists only as intermediate, proceeds only with the migration of the ethyl substituent.[2]

The selectivity observed during the acid-induced rearrangement of **3k** via **4k** is lost with the attempt to produce 1-phenyl-1,4,5,6-tetrahydro-[1,2,4]triazolo[2,3-*a*]-[1]benzazepin-2-one (**5k**) by thermal rearrangement of **3k** at 120 °C. The $^1$H-NMR spectrum of the reaction product indicates undoubtedly the presence of a mixture of isomers, which is composed of **5k** (73%) and 3-phenyl-3,5,6,7-tetrahydro-[1,2,4]triazolo[2,3-*a*]-[2]benzazepin-2-one (27%). The chemical shift of the methylene protons of the isomer, due to migration of the aliphatic substituent, is in agreement with the data of suitable open chain compounds.[2] Separation of both isomers, thus far, failed.

The dihydro-1,2,4-triazol-3-ones **5o,p**, obtained directly during the oxidation of **2o,p** result from exclusive 1,2-shift of the tertiary substituents, which have a higher migration aptitude than the aryl or benzyl substituents.

The synthesis of 2-phenyl-1,2,4-triazabicyclo[3.3.0]oct-4-en-3-one (**5a**) is outlined in Scheme **C**. All attempts to isolate 6-phenyl-5,6,8-triazaspiro[3.4]octan-7-one (**2a**) failed. The formation of the open chain compound, 2,3-dihydro-2-phenyl-5-propyl-3*H*-1,2,4-triazol-3-one (**7**) obtained instead, shows analogies to the thermal decomposition of 2,2-disubstituted benzimidazolines.[12–14] Intermediate **2a** has to be generated at 0 °C and oxidized *in situ*. The presumption that the oxidative ring cleavage of **2a** should decrease the ring strain and thus produce a stable 1-isocyanato-1-(phenylazo)cyclobutane (**3a**) did not prove to be correct. The formation of **3a** could not be detected during the oxidation, the sole reaction products were **5a** and **7**. There is every reason to believe that, during the potassium permanganate oxidation of **2a**, a 3-

**Table 1.** 5-Spiro substituted 2-Phenyl-1,2,4-triazolidin-3-ones **2** Prepared

| Product | Method | Yield (%) | mp (°C) (solvent) | Molecular Formula[a] or Lit. mp (°C) | IR (KBr) $\nu_{N-H,C=O}$ ($cm^{-1}$) | $^1$H-NMR (TMS)[b] $\delta$, $J$(Hz) |
|---|---|---|---|---|---|---|
| **2b** | A | 79 | 140–141 (MeOH) | $C_{12}H_{15}N_3O$ (217.3) | 3195, 1700 | 1.55–2.05 (m, 8H, $CH_2$), 4.48 (br s, 1H, NNH), 6.19 (br s, 1H, CONH), 6.75–7.40 (m, $3H_{arom}$, H-3′, 4′, 5′), 7.50–7.75 (m, $2H_{arom}$, H-2′, 6′) |
| **2c** | A | 91 | 171–175 (crude) | 176–177[7] | 3205, 3165sh, 1700 | 1.30–2.00 (m, 10H, $CH_2$), 4.39 (br s, 1H, NNH), 5.94 (br s, 1H, CONH), 6.75–7.45 (m, $3H_{arom}$, H-3′, 4′, 5′), 7.55–7.85 (m, $2H_{arom}$, H-2′, 6′) |
| **2d** | A | 82 | 159–160 (MeOH) | $C_{14}H_{19}N_3O$ (245.3) | 3195, 1683 | 1.30–2.40 (m, 12H, $CH_2$), 4.35 (br s, 1H, NNH), 6.26 (br s, 1H, CONH), 6.75–7.45 (m, $3H_{arom}$, H-3′, 4′, 5′), 7.50–7.85 (m, $2H_{arom}$, H-2′, 6′) |
| **2e** | A | 69 | 153–155 (MeOH) | $C_{15}H_{21}N_3O$ (259.3) | 3235, 3170sh, 1677 | 1.30–2.50 (m, 14H, $CH_2$), 4.37 (br s, 1H, NNH), 6.33 (br s, 1H, CONH), 6.85–7.60 (m, $3H_{arom}$, H-3′, 4′, 5′), 7.60–7.95 (m, $2H_{arom}$, H-2′, 6′) |
| **2f** | A | 70 | 163–165 (DMSO) | $C_{19}H_{29}N_3O$ (315.5) | 3255, 3180sh, 1675 | 1.10–2.00 (m, 22H, $CH_2$), 5.76 (br s, 1H, NNH), 6.70–7.40 (m, $3H_{arom}$, H-3′, 4′, 5′), 7.43–7.75 (m, 3H, $2H_{arom}$, H-2′, 6′ + CONH) |
| **2g**[c] | B | 85 | 114–118 (crude) | 182–188[7] | 3200, 1695 | 0.93, 0.96 (2d, 3H, $J$ = 7, $CH_3$), 1.20–2.00 (m, 9H, $CH_2$ + CH), 4.37, 4.48 (2s, 1H, NNH), 6.72 (br s, 1H, CONH), 6.90–7.03 (m, $1H_{arom}$, H-4′), 7.20–7.36 (m, $2H_{arom}$, H-3′, 5′), 7.65–7.79 (m, $2H_{arom}$, H-2′, 6′) |
| **2h$_1$** | A | 93[d] | 190–192 | 154–160[e,7] | 3190, 1698 | 0.96 (d, 3H, $J$ = 7, $CH_3$), 1.08–1.24, 1.56–1.84, 1.84–1.97 (3m, 2H, 4H and 2H, $CH_2$), 1.39–1.56 (m, 1H, CH), 4.49 (s, 1H, NH), 6.56 (br s, 1H, CONH), 7.00 (dd, $1H_{arom}$, $J_1 = J_2$ = 7, H-4′), 7.30 (dd, $2H_{arom}$, $J_1 = J_2$ = 7, H-3′, 5′), 7.71 (d, $2H_{arom}$, $J$ = 7, H-2′, 6′) |
| **2h$_2$** | | – | 175–177 | | 3140, 1718 | 0.96 (d, 3H, $J$ = 7, $CH_3$), 1.18–1.75, 1.80–2.05 (2m, 7H and 2H, $CH_2$ + CH), 4.32 (s, 1H, NNH), 5.33 (br s, 1H, CONH), 7.00 (dd, $1H_{arom}$, $J_1 = J_2$ = 7, H-4′), 7.31 (dd, $2H_{arom}$, $J_1 = J_2$ = 7, H-3′, 5′), 7.72 (d, $2H_{arom}$, $J$ = 7, H-2′, 6′) |
| **2i** | A | 54 | 144–145 (dec) (EtOH) | $C_{15}H_{21}N_3O$ (259.3) | 3200, 1695 | 0.84 (s, 3H, $CH_3$), 0.88 (s, 3H, $CH_3$), 1.17–1.80 (m, 8H, $CH_2$), 5.77 (br s, 1H, NNH), 6.88 (dd, $1H_{arom}$, $J_1 = J_2$ = 7, H-4′), 7.26 (dd, $2H_{arom}$, $J_1 = J_2$ = 7, H-3′, 5′), 7.65 (d, $2H_{arom}$, $J$ = 7, H-2′, 6′), 7.80 (br s, 1H, CONH) |
| **2j** | A | 92 | 245–246 (EtOH) | $C_{17}H_{21}N_3O$ (283.4) | 3200, 1686 | 1.35–2.40 (m, $14H_{adamantyl}$), 5.87 (br s, 1H, NNH), 6.65–7.40 (m, $3H_{arom}$, H-3′, 4′, 5′), 7.45–7.75 (m, $2H_{arom}$, H-2′, 6′), 8.07 (br s, 1H, CONH) |
| **2k** | C | 51 | 177–179 (MeOH) | $C_{17}H_{17}N_3O$ (279.3) | 3375, 3185, 1687 | 1.40–3.05 (m, 6H, $CH_2$), 4.51 (br s, 1H, NNH), 5.85 (br s, 1H, CONH), 6.60–7.95 (m, 9H, $H_{arom}$) |
| **2l** | B | 78 | 165–167 (MeOH) | $C_{17}H_{17}N_3O$ (279.3) | 3170, 1718 | 1.85–2.25 (m, 2H, H-6), 2.80–3.25, 3.05 (m, s, 4H, H-7, 12), 4.54 (br s, 1H, NNH), 5.92 (br s, 1H, CONH), 6.85–7.45 (m, $7H_{arom}$, H-3′, 4′, 5′ + H-8-11), 7.45–7.80 (m, $2H_{arom}$, H-2′, 6′) |
| **2m** | A | 19 | 163–165 (MeOH) | $C_{16}H_{15}N_3O$ (265.3) | 3210sh, 3180, 1682 | 1.75–3.40 (m, 4H, $CH_2$), 4.55 (br s, 1H, NNH), 6.21 (br s, 1H, CONH), 6.65–7.75 (m, 9H, $H_{arom}$) |
| **2n** | B | 56 | 147–150 (MeOH) | $C_{16}H_{15}N_3O$ (265.3) | 3200, 1698 | 3.22 (s, 4H, $CH_2$), 4.68 (br s, 1H, NNH), 6.01 (br s, 1H, CONH), 6.75–7.45 (m, $7H_{arom}$, H-3′, 4′, 5′ + H-7-10), 7.45–7.75 (m, $2H_{arom}$, H-2′, 6′) |
| **2o** | B | 61 | >123 (dec) (EtOH) | $C_{18}H_{19}N_3O$ (293.4) | 3205, 1693 | 0.93 (s, 3H, $CH_3$), 1.05 (s, 3H, $CH_3$), 2.61, 2.66, 2.80, 2.85 (AB, 2H, $J_{AB}$ = 15, $CH_2$), 6.11 (br s, 1H, NNH), 6.91 (dd, $1H_{arom}$, $J_1 = J_2$ = 7, H-4′), 7.22–7.36 (m, $5H_{arom}$, H-3′, 5′ + 3H of $C_6H_4$), 7.46 (d, $1H_{arom}$, $J$ = 7, 1H of $C_6H_4$), 7.67 (d, $2H_{arom}$, $J$ = 7, H-2′, 6′), 8.08 (br s, 1H, CONH) |
| **2p** | B | 41 | >159 (dec) (EtOH) | $C_{18}H_{19}N_3O$ (293.4) | 3210, 1693 | 1.11 (s, 3H, $CH_3$), 1.18 (s, 3H, $CH_3$), 3.11, 3.16, 3.23, 3.28 (AB, 2H, $J_{AB}$ = 15, $CH_2$), 6.25 (br s, 1H, NNH), 6.90 (dd, $1H_{arom}$, $J_1 = J_2$ = 7, H-4′), 7.10–7.30 (m, $6H_{arom}$, H-3′, 5′ + H-7-10), 7.58 (d, $2H_{arom}$, $J$ = 7, H-2′, 6′), 8.00 (br s, 1H, CONH) |

[a] Satisfactory microanalyses obtained: C ±0.26, H ±0.19, N ±0.28.

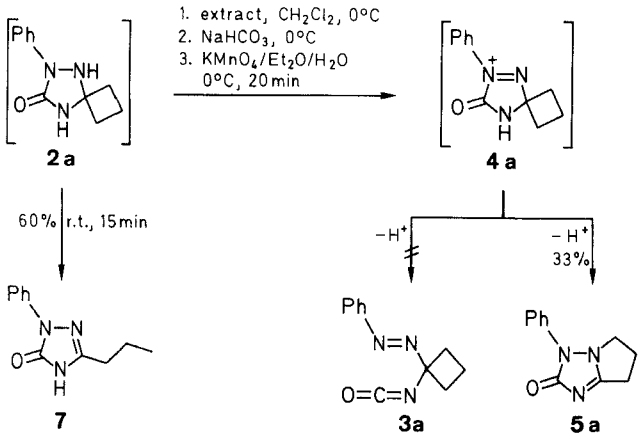
[b] $^1$H-NMR were recorded at 60 MHz for **2b–e**, **k–n** (solvent: $CDCl_3$) and for **2f**, **j** (solvent: DMSO-$d_6$), and at 300 MHz for **2g**, **h$_1$**, **h$_2$** (solvent: $CDCl_3$) and for **2i**, **o**, **p** (solvent: DMSO-$d_6$). For numbering see Scheme A.

[c] Mixture of 2 diastereoisomers.

[d] Combined yield of both isomers **2h$_1$** + **2h$_2$**. The isomers were separated by chromatography. **2h$_1$**: TLC, $Et_2O$, $R_f$ 0.73; **2h$_2$**: TLC, $Et_2O$, $R_f$ 0.57.

[e] Melting point of the isomeric mixture of **2h$_1$** and **2h$_2$**.

spiro substituted triazolium salt **4a** is produced, which possesses, with its diazenium function, the structural requirement for the 1,2-shift of a substituent. All available evidence indicates, that **4a** rearranges directly into **5a** with ring expansion, instead of deprotonating and opening the ring to give the isocyanate **3a**.




Scheme C

In conclusion, our synthetic method is a further example of rearrangement of compounds containing a diazenium function. The transformation of diazenes (azo compounds) to diazenium derivatives seems to be necessary for the migration of a carbon substituent to the nitrogen of this functional group.[21,22] Important information can be obtained by the action of the described reaction sequence upon (–)-menthone, an optically active ketone with a chiral migrating group. The results of these investigations will be presented at a later date.

Melting points were determined on a Thermovar-Reichert Kofler melting point microscope and are uncorrected. $^1$H-NMR spectra were performed on a JEOL JNM-PMX-60 or a Bruker AM 300 spectrometer in various solvents using TMS as an internal standard. $^{13}$C-NMR spectra were obtained on Bruker AM 300. IR-spectra were recorded on a Beckman AccuLab 2 spectrophotometer and UV/VIS spectra on a Gilford 250 spectrophotometer. MS-spectra were obtained using a Varian MAT 44S with EI ionisation. Microanalyses were performed by Dr. J. Zak at the Institute of Physical Chemistry of the University of Vienna.

Most reagents are available commercially and were purchased from Fluka, Merck or Aldrich. They were used without further purification. 2,2-Dimethylcyclohexanone (**1i**)[15], 2,2-dimethyl-1-indanone (**1o**)[16] and 1,1-dimethyl-2-indanone (**1p**)[17] were prepared according

**Table 2.** 1-Isocyanato-1-(phenylazo)cycloalkanes **3** Prepared

| Product | Yield (%) | mp (°C) (solvent) or $n_D$ (°C) | Molecular Formula[a] or Lit. mp (°C) | UV($CH_3CN$) $\lambda_{max}$(nm) (log ε) | IR (KBr or film) $\nu_{N=C=O}$(cm$^{-1}$) | $^1$H-NMR ($CDCl_3$/TMS/60 MHz) δ, J(Hz) |
|---|---|---|---|---|---|---|
| **3b** | 93 | 38–39 (PE) | $C_{12}H_{13}N_3O$ (215.3) | 269 (4.02) 379 (2.28) | 2205, 2140sh | 1.70–2.50 (m, 8H, $CH_2$), 7.20–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.95 (m, 2$H_{arom}$, H-2′, 6′) |
| **3c** | 93 | 47–50 (crude) | 49–51[10] | 272 (4.04) 384 (2.32) | 2225, 2145sh | 1.25–2.40 (m, 10H, $CH_2$), 7.25–7.60 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.60–7.95 (m, 2$H_{arom}$, H-2′, 6′) |
| **3d** | 94 | 1.5532 (22) | $C_{14}H_{17}N_3O$ (243.3) | 270 (3.99) 382 (2.27) | 2225 | 1.35–2.45 (m, 12H, $CH_2$), 7.20–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.90 (m, 2$H_{arom}$, H-2′, 6′) |
| **3e** | 93 | 1.5543 (21) | $C_{15}H_{19}N_3O$ (257.3) | 270 (4.02) 381 (2.28) | 2215 | 1.15–2.40 (m, 14H, $CH_2$), 7.25–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.90 (m, 2$H_{arom}$, H-2′, 6′) |
| **3f** | 97 | 86–87 ($Et_2O$) | $C_{19}H_{27}N_3O$ (313.4) | 270 (4.04) 385 (2.28) | 2245sh, 2175, 2150sh | 1.15–2.20 (m, 22H, $CH_2$), 7.30–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.65–7.90 (m, 2$H_{arom}$, H-2′, 6′) |
| **3g**[b] | 92 | 1.5469 (22) | $C_{14}H_{17}N_3O$ (243.3) | 271 (4.02) 388 (2.21) | 2220 | 0.55–0.95 (m, 3H, $CH_3$), 1.00–2.30 (m, 9H, $CH_2$ + CH), 7.25–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.90 (m, 2$H_{arom}$, H-2′, 6′) |
| **3h**[c] | 95 | 1.5414 (23) | $C_{14}H_{17}N_3O$ (243.3) | 271 (4.02) 382 (2.27) | 2225, 2165sh | 0.85–1.25 (m, 3H, $CH_3$), 1.25–2.60 (m, 9H, $CH_2$ + CH), 7.25–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–8.00 (m, 2$H_{arom}$, H-2′, 6′) |
| **3i**[d] | – | – | $C_{15}H_{19}N_3O$ (257.3) | – | 2210 | – |
| **3j** | 95 | 78–80 ($Et_2O$) | $C_{17}H_{19}N_3O$ (281.4) | 245 (3.82) 391 (2.00) | 2215 | 1.55–2.80 (m, 14H, $CH_2$ + CH), 7.22–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.90 (m, 2$H_{arom}$, H-2′, 6′) |
| **3k** | 94 | 45–47 (pentane) | $C_{17}H_{15}N_3O$ (277.3) | 274 (4.10) 381 (2.38) | 2225 | 1.80–2.65 (m, 4H, $CH_2CH_2$), 2.75–3.20 (m, 2H, $CH_2$), 6.65–7.25 (m, 4$H_{arom}$), 7.25–7.60 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.60–8.00 (m, 2$H_{arom}$, H-2′, 6′) |
| **3l** | 95 | 75–77 (pentane) | $C_{17}H_{15}N_3O$ (277.3) | 273 (4.10) 381 (2.39) | 2230, 2160sh | 1.55–3.30 (m) and 2.68, 2.97, 3.41, 3.70 (AB, $J_{AB}$ = 17) (6H, $CH_2$), 6.90–7.20 (m, 4$H_{arom}$), 7.25–7.50 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.90 (m, 2$H_{arom}$, H-2′, 6′) |
| **3m**[d] | 83 | – | $C_{16}H_{13}N_3O$ (263.3) | 282 | 2215 | 2.50–3.60 (m, 4H, $CH_2$), 6.70–7.90 (m, 9H, $H_{arom}$) |
| **3n** | 93 | 86–88 (chrom.) | $C_{16}H_{13}N_3O$ (263.3) | 268 (4.11) 274 (4.11) 378 (2.39) | 2225, 2175sh, 2145sh | 3.10, 3.36, 3.46, 3.72 (AA′BB′, 4H, $CH_2$), 7.05–7.25 (m, 4$H_{arom}$), 7.25–7.55 (m, 3$H_{arom}$, H-3′, 4′, 5′), 7.55–7.90 (m, 2$H_{arom}$, H-2′, 6′) |

[a] Satisfactory microanalyses obtained: C ±0.18, H ±0.23, N ±0.21, except for **3g**, **i**, **m** which are unstable.
[b] Mixture of 2 diastereoisomers.
[c] Mixture of 2 isomers.
[d] Compounds **3i**, **m** rearrange to **5i**, **m** within minutes.

**Table 3.** Compounds **5** Prepared

| Product | Method | Yield (%) | mp (°C) (solvent) | Molecular Formula[a] or Lit. mp (°C) | IR (KBr) $\nu_{C=O}$ ($cm^{-1}$) | $^1$H-NMR ($CDCl_3$/TMS/300 MHz)[b] $\delta$, $J$(Hz) | $^{13}$C-NMR ($CDCl_3$/TMS/75.473 MHz)[b] $\delta$ |
|---|---|---|---|---|---|---|---|
| **5a** | A | 33 | 166–167 (MeOH) | $C_{11}H_{11}N_3O$ (201.2) | 1682 | 2.52 (tt, 2H, $J$ = 7, H-7), 2.90 (t, 2H, $J$ = 7, H-6), 3.70 (t, 2H, $J$ = 7, H-8), 7.22–7.33 (m, 1H$_{arom}$, H-4′), 7.35–7.50 (m, 4H$_{arom}$, H-2′, 3′, 5′, 6′) | 20.9 (C-7), 23.5 (C-6), 48.7 (C-8), 121.3 (2′,6′-C$_{arom}$), 126.3 (4′-C$_{arom}$), 129.2 (3′,5′-C$_{arom}$), 135.6 (1′-C$_{arom}$), 165.7 (C-5), 173.3 (C-3) |
| **5b** | B | 92 | 148–149.5 (MeOH/$Et_2O$) | $C_{12}H_{13}N_3O$ (215.3) | 1671 | 1.98–2.25 (m, 4H, H-7, 8), 2.92 (t, 2H, $J$ = 7, H-6), 3.64 (t, 2H, $J$ = 7, H-9), 7.35–7.46 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.46–7.60 (m, 2H$_{arom}$, H-3′, 5′) | 20.2, 22.1 (C-8, 7), 24.9 (C-6), 47.2 (C-9), 125.1 (2′,6′-C$_{arom}$), 127.8 (4′-C$_{arom}$), 129.3 (3′,5′-C$_{arom}$), 133.6 (1′-C$_{arom}$), 162.0 (C-5), 163.2 (C-3) |
| **5c** | B | 89 | 152–153.5 (MeOH/$Et_2O$) | 150–152[20] | 1685 | 1.68–1.92 (m, 6H, H-7-9), 2.83–2.94 (m, 2H, H-6), 3.65–3.75 (m, 2H, H-10), 7.24–7.35 (m, 3H$_{arom}$, H-2′,4′,6′), 7.40–7.50 (m, 2H$_{arom}$, H-3′,5′) | 23.8, 26.4, 28.7, 29.1 (C-6-9), 48.2 (C-10), 124.0 (2′,6′-C$_{arom}$), 127.0 (4′-C$_{arom}$), 129.0 (3′,5′-C$_{arom}$), 133.9 (1′-C$_{arom}$), 162.1 (C-5), 169.4 (C-3) |
| **5d** | B | 93 | 163–165 (MeOH) | $C_{14}H_{17}N_3O$ (243.3) | 1684 | 1.26–1.37, 1.56–1.73, 1.96–2.08 (3m, 2H, 4H, 2H, H-7-10), 2.81–2.91 (m, 2H, H-6), 3.94–4.03 (m, 2H, H-11), 7.35–7.44 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.44–7.58 (m, 2H$_{arom}$, H-3′,5′) | 22.7, 25.2, 27.0, 29.0 (C-7-10), 30.9 (C-6), 43.2 (C-11), 124.9 (2′,6′-C$_{arom}$), 127.7 (4′-C$_{arom}$), 129.3 (3′,5′-C$_{arom}$), 134.1 (1′-C$_{arom}$), 163.1 (C-5), 169.6 (C-3) |
| **5e** | B | 95 | 132–134 (MeOH) | $C_{15}H_{19}N_3O$ (257.3) | 1694 | 1.05–1.16, 1.43–1.57, 1.66–1.78, 1.80–2.02 (4m, 2H, 4H, 2H, 2H, H-7-11), 2.76–2.86 (m, 2H, H-6), 3.93–4.02 (m, 2H, H-12), 7.26–7.38 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.41–7.51 (m, 2H$_{arom}$, H-3′, 5′) | 19.3, 25.6, 26.6, 27.1, 27.7 (C-7-11), 28.8 (C-6), 45.1 (C-12), 124.6 (2′,6′-C$_{arom}$), 127.5 (4′-C$_{arom}$), 129.1 (3′,5′-C$_{arom}$), 133.7 (1′-C$_{arom}$), 162.9 (C-5), 169.7 (C-3) |
| **5f** | B | 94 | 157.5–159 (MeOH) | $C_{19}H_{27}N_3O$ (313.4) | 1698sh, 1683 | 1.15–1.59, 1.92–2.04 (2m, 16H, 2H, H-7-15), 2.73 (t, 2H, $J$ = 7, H-6), 3.78 (t, 2H, $J$ = 7, H-16), 7.27–7.43 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.43–7.52 (m, 2H$_{arom}$, H-3′, 5′) | 23.7, 24.4, 24.4, 25.5, 25.6, 25.7, 25.8, 26.2, 26.6 (C-6-15), 45.6 (C-16), 125.6 (2′,6′-C$_{arom}$), 128.1 (4′-C$_{arom}$), 129.5 (3′,5′-C$_{arom}$), 134.3 (1′-C$_{arom}$), 163.0 (C-5), 166.3 (C-3) |
| **5g** | B | 87 | 185–186 (MeOH) | $C_{14}H_{17}N_3O$ (243.3) | 1677 | 1.20 (d, 3H, $J$ = 7, $CH_3$), 1.52–2.12 (m, 6H, H-7-9), 2.55–2.70 (m, 1H, H-6), 3.13–3.28 (m, 1H, H-6), 4.01–4.13 (m, 1H, CH), 7.27–7.41 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.41–7.53 (m, 2H$_{arom}$, H-3′, 5′) | 15.4 ($CH_3$), 22.8, 24.1, 29.6 (C-7-9), 31.6 (C-6), 54.4 (C-10), 124.3 (2′,6′-C$_{arom}$), 127.2 (4′-C$_{arom}$), 129.0 (3′,5′-C$_{arom}$), 134.1 (1′-C$_{arom}$), 162.4 (C-5), 169.4 (C-3) |
| **5h** | B | 89 | 139–140 (MeOH) | $C_{14}H_{17}N_3O$ (243.3) | 1681 | 1.03 (d, 3H, $J$ = 7, $CH_3$), 1.29–1.46 (m, 2H, H-7, 9), 1.73–1.89 (m, 2H, H-7, 9), 1.90–2.02 (m, 1H, H-8), 2.61–2.74 (m, 1H, H-6), 3.04–3.16 (m, 1H, H-6), 3.57–3.82 (m, 2H, H-10), 7.26–7.36 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.40–7.51 (m, 2H$_{arom}$, H-3′, 5′) | 22.2 ($CH_3$), 27.1, 31.4 (C-9, 7), 33.9 (C-6), 35.1 (C-8), 46.6 (C-10), 123.8 (2′,6′-C$_{arom}$), 126.8 (4′-C$_{arom}$), 128.9 (3′,5′-C$_{arom}$), 133.7 (1′-C$_{arom}$), 162.0 (C-5), 169.0 (C-3) |
| **5i** | B | 92 | 138–140 (MeOH) | $C_{15}H_{19}N_3O$ (257.3) | 1700 | 1.29 (s, 6H, $CH_3$), 1.88–2.04 (m, 6H, H-7-9), 3.05–3.13 (m, 2H, H-6), 7.28–7.38 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.38–7.49 (m, 2H$_{arom}$, H-3′, 5′) | 24.0, 24.2 (C-8, 7), 28.1 (2 × $CH_3$), 30.9 (C-6), 41.2 (C-9), 66.5 (C-10), 124.2 (2′,6′-C$_{arom}$), 127.1 (4′-C$_{arom}$), 129.0 (3′,5′-C$_{arom}$), 141.4 (1′-C$_{arom}$), 167.0 (C-5), 177.2 (C-3) |
| **5j** | B | 87 | 238–239 (MeOH) | $C_{17}H_{19}N_3O$ (281.4) | 1680 | 1.73–2.38 (m, 12H, H-7-11, 13, 14), 3.31–3.41 (m, 1H, H-6), 3.90–3.98 (m, 1H, H-12), 7.28–7.38 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.45–7.53 (m, 2H$_{arom}$, H-3′, 5′) | 26.0, 26.2 (C-8, 10), 31.7, 33.2, 34.1 (C-7, 9, 11, 14, 13), 32.3 (C-6), 52.3 (C-12), 123.9 (2′,6′-C$_{arom}$), 127.1 (4′-C$_{arom}$), 129.3 (3′,5′-C$_{arom}$), 134.5 (1′-C$_{arom}$), 163.0 (C-5), 173.8 (C-3) |
| **5k** | B | 80 | 202–203 (MeOH) | $C_{17}H_{15}N_3O$ (277.3) | 1708 | 2.36 (tt, 2H, $J$ = 7, H-7), 2.70 (t, 2H, $J$ = 7, H-8), 3.00 (t, 2H, $J$ = 7, H-6), 6.80 (d, 1H$_{arom}$, $J$ = 8), 7.10–7.43 (m, 8H$_{arom}$) | 24.9 (C-7), 27.6, 29.5 (C-6, 8), 122.7 (2′,6′-C$_{arom}$), 128.9 (3′,5′-C$_{arom}$), 120.5, 126.6, 127.3, 127.6, 130.2 (C-9-12, 4′-C$_{arom}$), 133.1, 134.8, 134.9 (C-8a, 12a, 1′-C$_{arom}$), 162.6 (C-5), 164.7 (C-3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **5l** | B | 89 | 224–225 (chrom.) | $C_{17}H_{15}N_3O$ (277.3) | 1670 | 3.19 (s, 4H, H-6, 7), 4.73 (s, 2H, H-12), 7.03–7.58 (m, $9H_{arom}$) | 28.5, 29.4 (C-7, 6), 51.0 (C-12), 124.5 (2′,6′-$C_{arom}$), 127.4, 127.6, 128.9, 129.3, 129.8 (C-8-11, 4′-$C_{arom}$), 129.5 (3′,5′-$C_{arom}$), 132.3, 134.1, 140.4 (C-7a, 11a, 1′-$C_{arom}$), 161.9 (C-5), 167.3 (C-3) |
| **5m** | B | 98 | 177–179 (MeOH) | $C_{16}H_{13}N_3O$ (263.3) | 1708 | 3.12 (s, 4H, H-6, 7), 6.54–6.62 (m, $1H_{arom}$), 7.05–7.16 (m, $2H_{arom}$), 7.26–7.49 (m, $6H_{arom}$) | 24.1, 24.9 (C-6, 7), 114.6, 125.0, 126.8, 127.6, 128.5 (C-8-11, 4′-$C_{arom}$), 122.1 (2′,6′-$C_{arom}$), 129.2 (3′,5′-$C_{arom}$), 125.3, 132.9, 137.0 (C-7a, 11a, 1′-$C_{arom}$), 164.2 (C-5), 167.6 (C-3) |
| **5n** | B | 88 | 195–197 (MeOH) | $C_{16}H_{13}N_3O$ (263.3) | 1687 | 4.18–4.25 (AA′, 2H, H-6), 4.73–4.80 (BB′, 2H, H-11), 7.16 (d, $1H_{arom}$, $J = 8$), 7.27–7.45 (m, $6H_{arom}$), 7.45–7.55 (m, $2H_{arom}$) | 29.0 (C-6), 48.5 (C-11), 124.9 (2′,6′-$C_{arom}$), 126.4, 127.4, 128.0, 128.5, 128.6 (C-7-10,4′-$C_{arom}$), 127.1, 128.2 (C-6a, 10a), 129.5 (3′,5′-$C_{arom}$), 133.7 (1′-$C_{arom}$), 162.3, 162.5 (C-5, 3) |
| **5o** | C | 97 | 192.5–193.5 (MeOH) | $C_{18}H_{17}N_3O$ (291.4) | 1706 | 1.14 (s, 6H, $CH_3$), 3.16 (s, 2H, H-10), 7.24–7.57 (m, $8H_{arom}$), 8.29 (d, $1H_{arom}$, $J = 8$) | 25.4 (2 × $CH_3$), 42.5 (C-10), 65.6 (C-11), 123.0, 135.1 (C-9a, 5a), 125.7 (2′,6′-$C_{arom}$), 129.2 (3′,5′-$C_{arom}$), 127.7, 128.0, 128.1, 128.3, 133.3 (C-6-9, 4′-$C_{arom}$), 139.5 (1′-$C_{arom}$), 166.7 (C-5), 167.5 (C-3) |
| **5p** | C | 15 | 167–169 (MeOH/$Et_2O$) | $C_{18}H_{17}N_3O$ (291.4) | 1692 | 1.49 (s, 6H, $CH_3$), 4.29 (s, 2H, H-6), 7.28–7.46 (m, $9H_{arom}$) | 28.0 (2 × $CH_3$), 30.3 (C-6), 66.3 (C-11), 124.1, 127.8, 128.1, 128.4, 128.5 (C-7-10, 4′-$C_{arom}$), 125.7 (2′,6′-$C_{arom}$), 129.2 (3′,5′-$C_{arom}$), 127.4, 139.0, 140.1 (C-6a, 10a, 1′-$C_{arom}$), 166.9 (C-5), 171.5 (C-3) |

[a] Satisfactory microanalyses obtained: C ± 0.28, H ± 0.19, N ± 0.31, exception **5g**: N + 0.54.
[b] For numbering see, Scheme A.

to literature. Solvents were distilled before use. The reactions were monitored, and the purity of the compounds was checked by TLC on Polygram SIL G/$UV_{254}$ plates purchased from Macherey-Nagel. Column chromatographies were run at a pressure of 2 bar using Merck silica gel 60 (particle size 0.040–0.063 mm; 230–400 mesh ASTA).

**5-Spiro substituted 2-Phenyl-1,2,4-triazolidin-3-ones 2b–p: General Procedures:**

Method A, *for* **2b–f,h–j,m**: Phenylhydrazine (5.41 g, 50 mmol) is added to a solution of the appropriate ketone **1** (50 mmol) in AcOH (60 mL). After stirring at r.t. for 10 to 15 min the hydrazone formation is complete (TLC control, $Et_2O$/petroleum ether (40–60 °C) 1:1), and a solution of KNCO (5.07 g, 62.5 mmol) in water (15 mL) is added dropwise within 2 to 3 min. Stirring is continued for a further 15 min, and the crystallization of the triazolidinone **2** formed (TLC control, $Et_2O$/petroleum ether (40–60 °C) 1:1) is induced by careful addition of ice-cold water (125 mL) to the mixture. The resulting suspension is stirred for 30 min, the product is filtered, washed with water until neutral, and dried *in vacuo* ($P_2O_5$). In some cases, however, the product separates as an oil and has to be extracted with $CH_2Cl_2$ (5 × 25 mL). The combined organic extracts are washed with 2 N NaOH (25 mL portions until the aqueous layer is basic) and water (2 × 25 mL), and dried ($MgSO_4$). The solvent is removed under reduced pressure and the product is recrystallized from MeOH.

Method B *for* **2g,l,n–p**: Phenylhydrazine (5.41 g, 50 mmol) is added to a solution of the appropriate ketone **1** (50 mmol) in MeOH (50 mL). After stirring at r.t. for 10 to 15 min the hydrazone formation is complete (TLC control, $Et_2O$/petroleum ether (40–60 °C) 1:1), and a solution of KNCO (5.07 g, 62.5 mmol) in water (15 mL) is added in one portion, followed immediately by the addition of AcOH (150 mL). Stirring is continued for further 15 min, and the crystallization of the triazolidinone **2** formed (TLC control, $Et_2O$/petroleum ether (40–60 °C) 1:1) is induced by careful addition of ice-cold water (500 mL) to the mixture. The resulting suspension is worked up as described in Method A.

Method C, *for 2′-Phenylspiro[1,2,3,4-tetrahydronaphthalin-1,5′-[1′,2′,4′]-triazolidin]-3′-one* (**2k**): A stirred mixture of **1k** (14.6 g, 100 mmol), phenylhydrazine (10.8 g, 100 mmol) and AcOH (2 mL) is kept at 70 °C for 10 min, diluted with AcOH (200 mL), and cooled to 45 °C. After the addition of water (15 mL), solid KNCO (40.5 g, 500 mmol) is added in 5 g portions within 2 h, and the mixture is stirred for a further 90 min at r.t. The crystallization process, which starts during this time, is completed by careful addition of ice-cold water (150 mL), and the resulting suspension is kept at 0 °C for 1 h. The crude product is filtered, washed with water until neutral, and dried *in vacuo* ($P_2O_5$). The impurity, α-tetralonephenylhydrazone, present is removed by refluxing a suspension of the crude product in $Et_2O$ (200 mL) for 15 min. The desired triazolidinone **2k**, which is very insoluble in $Et_2O$ is filtered, washed with $Et_2O$ (2 × 50 mL), and dried *in vacuo* ($CaCl_2$); yield: 14.22 g (51%).

**1-Isocyanato-1-(phenylazo)cycloalkanes 3b–n:**

These are prepared by oxidative ring cleavage of 5-spiro substituted 2-phenyl-1,2,4-triazolidin-3-ones **2** with $KMnO_4$ according to literature.[9] Compounds **3g,i** rearrange even at r.t. within min, so that the oxidation of **2g,i** has to be carried out at 0 °C. Compounds **2f,j,k** are very insoluble in $Et_2O$ and must be dissolved or suspended in a mixture of $Et_2O/CH_2Cl_2$ (1:1) before oxidation. Before the separation of the layers, the $MnO_2$ formed is filtered with diatomaceous silica to prevent the formation of emulsions during the extraction process. If a further purification of the product is necessary, it is performed best, if the product is crystalline, by recrystallization from pentane, petroleum ether (40–60 °C) or $Et_2O$, or, if the product is liquid, by a short column chromatography at normal pressure (10–15 cm, silica gel, $Et_2O$/petroleum ether (40–60 °C) eluent ratio must be varied according to the product and the impurities). At elevated temperatures spontaneous rearrangement to **5** may occur, therefore distillation should be avoided.

**3-Spiro substituted 4,5-Dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium Tetrafluoroborates 4c–f,h,l,n:**

These are prepared according to literature[3] by the action of $HBF_4$ upon 1-isocyanato-1-(phenylazo)cycloalkanes **3** in $Et_2O$ at 0°C. Only **4c** can be isolated pure and stored for a short while; the other compounds **4d–f,h,l,n** always separate accompanied by **5d–f,h,l,n** · $HBF_4$ and their rearrangement is completed within a few min.

**4c**; yield: 89%, rearranges spontaneously to **5c** with strong evolution of heat during drying *in vacuo*.

IR (KBr): $\nu_{C=O}$, **4c** = 1860, **4d** = 1851, **4e** = 1853, **4f** = 1858, **4h** = 1853, **4l** = 1854, and **4n** = 1848 $cm^{-1}$.

**1,5-Annulated 1,2-Dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones 5a–p; Typical and General Procedures:**

Method A, *for 2-Phenyl-1,2,4-triazabicyclo[3.3.0]oct-4-en-3-one* (**5a**):

Cyclobutanone (**1a**; 1.10 g, 15.7 mmol) and phenylhydrazine (1.70 g, 15.7 mmol) are mixed at r.t. under $N_2$ atmosphere. After the addition of one drop of AcOH the mixture crystallizes completely within 10 sec. The cyclobutanone phenylhydrazone formed is crushed in a mortar and dried *in vacuo* ($CaCl_2$).

To a stirred solution of cyclobutanone phenylhydrazone (1.55 g, 9.7 mmol) in cold MeOH (30 mL, 0°C), a solution of KNCO (0.98 g, 12.1 mmol) in a minimum of water is added, followed immediately by the addition of AcOH (10 mL). After 15 min the formation of **2a** is completed (TLC control, $Et_2O$/petroleum ether (40–60°C) 4:1). The mixture is diluted with ice water (100 mL) and extracted with ice-cold $CH_2Cl_2$ (5 × 20 mL). The combined organic extracts are poured into an ice-cold solution of 5% $NaHCO_3$ (100 mL). To this vigorously stirred two-layered mixture, a solution of $KMnO_4$ (1.91 g, 12.1 mmol) in water (50 mL) is added portionwise within 5 min at 0°C. After 20 min the oxidation is completed (TLC control, $Et_2O$/petroleum ether (40–60°C) 4:1). The $MnO_2$ formed is filtered over diatomaceous silica, the layers are separated, and the aqueous layer is extracted exhaustively with $CH_2Cl_2$ (20 mL portions, TLC control). The combined organic extracts are dried ($MgSO_4$), and the solvent is removed under reduced pressure to give a dark red oil. Crystallization can be induced by treatment with *t*-BuOMe. The slightly yellowish crystals of **5a** are filtered and dried *in vacuo* ($CaCl_2$); yield: 0.65 g (33%).

Method B, *for* **5b–n**: To a stirred solution of an appropriate 1-isocyanato-1-(phenylazo)cycloalkane **3** (5 mmol) in $Et_2O$ (40 mL) at 0°C is added dropwise 50% aq $HBF_4$ (5 mL) within 5 min. Disregarding an occasional precipitate or turbidity, the mixture is diluted with $CH_3CN$ (10 mL) and the $Et_2O$ is removed under reduced pressure. In most cases the color of the solution fades during this step, but to make sure that the rearrangement is complete, the solution is refluxed for 10 min. The major part of $CH_3CN$ is removed under reduced pressure, and 2 N NaOH is added until a permanent basic reaction occurs. Water is added (50–100 mL) to prevent the formation of emulsions, and the resulting basic mixture is extracted exhaustively with $CH_2Cl_2$ (20 mL portions, TLC control). The combined organic extracts are dried ($MgSO_4$), the solvent is removed under reduced pressure, and the remaining colorless crystalline product is dried *in vacuo* ($CaCl_2$).

Method C, *for* **5o,p**: Compounds **2o,p** are oxidized in a mixture of $Et_2O/CH_2Cl_2$ (1:1) according to the procedure for compounds **3** mentioned above. After filtration of $MnO_2$ formed, the layers are separated and the aqueous layer is extracted exhaustively with $CH_2Cl_2$ (20 mL portions, TLC control). The combined organic extracts are dried ($MgSO_4$), the solvent is removed under reduced pressure, and the remaining crystalline products **5o,p** are dried *in vacuo* ($CaCl_2$). Compound **5o** separates to a high degree of purity, but **5p** has to be purified by column chromatography on silica gel ($Et_2O$, $R_f$ 0.11)

**(4a*RS*,13b*RS*)-13b-Methyl-2,3,4,13b-tetrahydro-1*H*-1,3,5-triazino[6,1-*k*]carbazol-6,8-dione (6):**

Phenylhydrazine (10.82 g, 100 mmol) is added to a solution of 2-methylcyclohexanone (11.22 g, 100 mmol) in AcOH (120 mL). After stirring at r.t. for 20 min, a solution of KNCO (18.25 g, 225 mmol) in water (50 mL) is added dropwise within 5 min. Compound **6** precipitates almost immediately, and crystallization is completed by addition of water (250 mL) to the resulting suspension. The product is filtered, washed with water until neutral, and dried *in vacuo* ($P_2O_5$); yield: 20.25 g (75%); colorless crystals; mp 325–326°C ($Et_2O$).

| | | | | |
|---|---|---|---|---|
| $C_{15}H_{17}N_3O_2$ | calc. | C 66.40 | H 6.32 | N 15.48 |
| (271.3) | found | 66.29 | 6.33 | 15.92 |

IR (KBr): $\nu$ = 3170, 3055 (NH), 1704, 1680 $cm^{-1}$ (C=O).

$^1$H-NMR (300 MHz, DMSO-$d_6$): $\delta$ = 1.04 (s, 3H, $CH_3$), 1.00–1.17 (m, 1H, H-2), 1.25–1.52 (m, 3H, H-3 + H-4), 1.52–1.65 (m, 1H, H-2), 1.75–1.91 (m, 1H, H-1), 1.91–2.01 (m, 1H, H-4), 2.14–2.29 (m, 1H, H-1), 7.09 (dd, 1 $H_{arom}$, $J_1 = J_2$ = 7 Hz), 7.20–7.27 (m, 2 $H_{arom}$), 7.76 (d, 1 $H_{arom}$, $J$ = 7 Hz), 8.85, 9.85 (2s, 1H each, NH).

$^{13}$C-NMR (75.473 MHz, DMSO-$d_6$): $\delta$ = 20.0 (C-3), 21.7 (C-2), 26.2 ($CH_3$), 29.2 (C-1), 34.9 (C-4), 47.5 (C-13b), 78.3 (C-4a), 114.7, 121.9, 123.7, 127.7 (C-10, 11, 12, 13), 137.4, 138.2 (C-9a, 13a), 148.2, 152.9 (C-6, 8).

MS (EI, 70 eV): $m/z$ (%) = 271 ($M^+$, 44), 256 (6), 228 (41), 215 (100), 185 (19), 171 (14), 158 (9), 144 (26), 130 (20), 129 (22), 117 (20), 116 (19), 115 (18), 77 (18).

**2,4-Dihydro-2-phenyl-9-propyl-3*H*-1,2,4-triazol-3-one (7):**

Compound **7** formed during the attempt to isolate 6-phenyl-5,6,8-triazaspiro[3.4]octan-7-one (**2a**); reaction scale: 14.3 mmol; yield: 1.74 g (60%); colorless crystals; mp 143.5–144.5°C (EtOH) (Lit.[18] mp 145–146°C, Lit.[19] mp 146°C).

IR (KBr): $\nu$ = 3125 (NH), 1698 $cm^{-1}$ (C=O).

$^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 1.02 (t, 3H, $J$ = 7 Hz, $CH_3CH_2CH_2$), 1.78 (qt, 2H, $J_1 = J_2$ = 7 Hz, $CH_3CH_2CH_2$), 2.59 (t, 2H, $J$ = 7 Hz, $CH_3CH_2CH_2$), 7.21 (dd, 1 $H_{arom}$, $J_1 = J_2$ = 8 HZ, H-4'), 7.42 (dd, 2 $H_{arom}$, $J_1 = J_2$ = 8 Hz, H-3', 5'), 7.94 (d, 2 $H_{arom}$, $J$ = 8 Hz, H-2', 6'), 12.10 (br s, 1H, NH).

$^{13}$C-NMR (75.473 MHz, $CDCl_3$): $\delta$ = 13.5 ($CH_3CH_2CH_2$), 20.0 ($CH_3CH_2CH_2$), 28.6 ($CH_3CH_2CH_2$), 119.1 (3',5'-$C_{arom}$), 125.4 (4'-$C_{arom}$), 128.9 (2',6'-$C_{arom}$), 137.7 (1'-$C_{arom}$), 147.9 (C-5), 154.6 (C-3).

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