Rearrangement of 3,3-Disubstituted 1-Aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium Tetrafluoroborates; Part 3. An Efficient Synthesis of 1,5-Heteroannulated 1,2-Dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones

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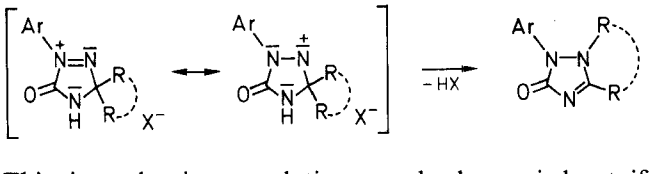
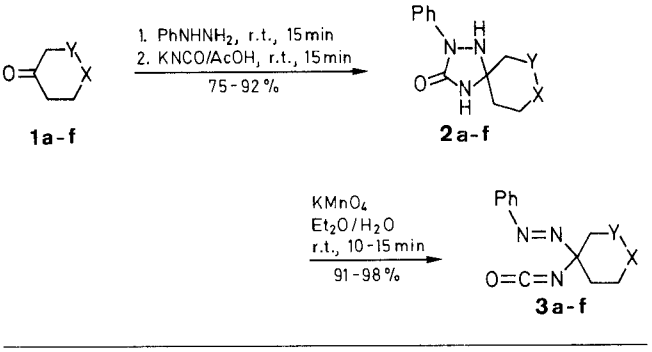
1-Isocyanato-1-(phenylazo)heterocycloalkanes **3a–f** react with tetrafluoroboric acid to yield the respective 3-spiro-substituted 4,5-dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium tetrafluoroborates **4a–f**. These compounds rearrange under ring enlargement in good yields to 1,5-heteroannulated 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **5a–f**. In two special cases, 4,5-heteroannulated 2,4-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **7g,h** are obtained.

Rearrangement reactions are a very useful tool in the field of organic chemistry. Among these, migrations to nitrogen are of a particular importance for the synthesis of many industrial products.[2] In these rearrangements, an electron-deficient nitrogen atom is created by loss of a leaving group, accompanied by the migration of a substituent adjacent to the electron-deficient species.

As we have reported earlier,[3,4] the migration of a carbon substituent to an electron-deficient nitrogen atom also occurs in 3,3-disubstituted 1-aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium salts. The heterocyclic ring of these salts contains, as a characteristic feature, a diazenium function,[5] in which the nitrogen atom in β-position to the aryl substituent shows a latent nitrenium character. This functional group enables the migration of a substituent adjacent to the nitrogen atom mentioned above. In the respective spiro compounds,[4] the migration takes place with simultaneous ring enlargement and insertion of the nitrogen atom into the carbon skeleton.



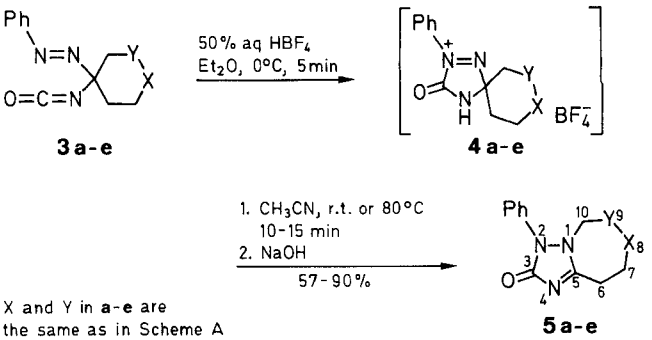
This ring enlarging annulation can also be carried out, if the spiro-ring contains heteroatoms. Starting from the six membered heterocyclic ketones **1a–f**, the 5-spiro-substituted 2-phenyl-1,2,4-triazolidin-3-ones **2a–f** (Table 1) were prepared.[4,6–11] Oxidative ring cleavage[8,11–13] of **2a–f** yields the 1-isocyanato-1-(phenylazo)heterocycloalkanes **3a–f** (Table 2) (Scheme **A**), which serve as substrates for the rearrangement reaction.



1–3	X	Y	1–3	X	Y	1–3	X	Y
a	O	CH_2	**c**	CH_2	O	**e**	NCOPh	CH_2
b	S	CH_2	**d**	CH_2	S	**f**	NMe	CH_2
2e'		NH			CH_2			

Scheme **A**

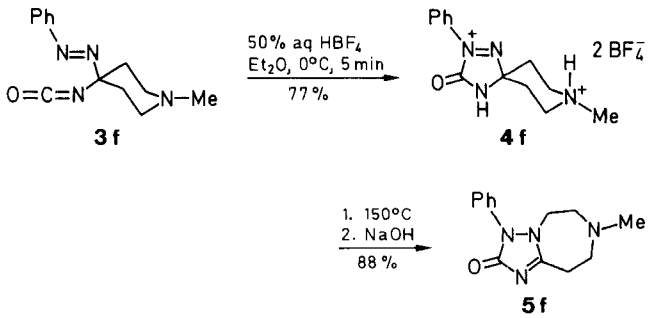
Treatment of **3a–e** with tetrafluoroboric acid in diethyl ether generates the 3-spiro-substituted 4,5-dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium tetrafluoroborates **4a–e**, which rearrange almost immediately into the salts of 1,5-heteroannulated 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **5a–e** · HBF_4. By basic work-up of these compounds, the free bases **5a–e** (Table 3) can easily be obtained (Scheme **B**). During the synthesis of **5a,b**, the unstable triazolium salts **4a,b** can be isolated as crystals, but they quickly rearrange to **5a,b** · HBF_4.



Scheme **B**

In the intermediate triazolium salts **4c,d**, derived from oxan-3-one **1c** and thian-3-one **1d**, the ring enlargement occurs exclusively with migration of the heterosubstituted methylene group. Evidence for this migration selectivity is furnished by the observed strong downfield-shift of the isolated methylene groups in the ^{1}H-NMR of the products **5c,d** (**5c**, $\delta = 5.03$; **5d**, $\delta = 4.73$) in comparison with their nonhetero-substituted analogues.[4]

Upon treatment with tetrafluoroboric acid, the isocyanate **3f** is converted into the bis(tetrafluoroborate) **4f**, which proves to be particularly stable. Obviously, the



Scheme **C**

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protonation of the tertiary amine function prevents the rearrangement at room temperature. The conversion of **4f** into the rearrangement product **5f** succeeds only when crystalline **4f** is heated to 150 °C without solvent (Scheme **C**). The structure of **5f** is established by X-ray structure analysis.[14] All attempts to rearrange **4f** in boiling acetonitrile generate, besides traces of **5f**, a complex product mixture.

A remarkable result is obtained when 7-methyl-2-phenyl-1,2,4,7-tetraazaspiro[4.5]decan-3-one (**2h**), available by reaction of 1-methylpiperidin-3-one (**1h**) with phenylhydrazine and potassium isocyanate in the presence of acetic acid, is submitted to potassium permanganate oxidation. In the course of this oxidation, no 3-isocyanato-1-methyl-3-(phenylazo)piperidine (**3h**) can be detected. Instead, a colourless crystalline product, 3-methyl-9-phenyl-1,3,8,9-tetraazabicyclo[5.3.0]dec-7-en-10-one (**7h**) is obtained as the sole product (Scheme **D**). The structure of **7h** is established by X-ray structure analysis.[14]

The fact, that this difference of the reaction pattern from the normal reaction behaviour of the 3-spiro-substituted 4,5-dihydro-5-oxo-1-phenyl-3*H*-1,2,4-triazolium salts **4a–f** is associated with the availability of the free electron pair of the tertiary amine-function in **2h**, can be proved by oxidizing the *N*-benzoyl derivative **2g**, derived from 1-benzoylpiperidin-3-one (**1g**). Like in the case of **2h**, no intermediate 1-benzoyl-3-isocyanato-3-(phenylazo)piperidine (**3g**) is detectable during the course of

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

Product	Method	Yield (%)	mp (°C) (solvent)	Molecular Formula[a]	IR (KBr) $\nu_{N-H,C=O}$ (cm^{-1})	^{1}H-NMR[b] δ, J (Hz)
2a	A	91	162–164 (MeOH)	$C_{12}H_{15}N_3O_2$ (233.3)	3195, 1695	1.75–2.15 (m, 4H, $CH_2CH_2OCH_2CH_2$), 3.70–4.05 (m, 4H, CH_2OCH_2), 4.57 (br s, 1H, NNH), 6.93 (br s, 1H, CONH), 7.05–7.65 (m, 3H_{arom}, H-3′, 4′, 5′), 7.65–8.00 (m, 2H_{arom}, H-2′, 6′)
2b	A	92	> 207 (dec) (MeOH)	$C_{12}H_{15}N_3OS$ (249.3)	3195, 1694	1.65–2.15 (m, 4H, $CH_2CH_2SCH_2CH_2$), 2.40–3.00 (m, 4H, CH_2SCH_2), 5.95 (br s, 1H, NNH), 6.70–7.40 (m, 3H_{arom}, H-3′, 4′, 5′), 7.45–7.85 (m, 3H, CONH + H_{arom}, H-2′, 6′)
2c	B	91	158–160 (MeOH)	$C_{12}H_{15}N_3O_2$ (233.3)	3185, 1700	1.62–1.92 (m, 4H, $CH_2CH_2CH_2O$), 3.31–3.64 (m, 4H, CH_2OCH_2), 6.09 (br s, 1H, NNH), 6.91 (dd, 1H_{arom}, J = 7,7, H-4′), 7.26 (dd, 2H_{arom}, $J_1 = J_2$ = 7, H-3′, 5′), 7.60 (d, 2H_{arom}, J = 7, H-2′, 6′), 7.75 (br s, 1H, CONH)
2d	B	86	165–166 (MeOH)	$C_{12}H_{15}N_3OS$ (249.3)	3205, 3170sh, 1700	1.55–2.35 (m, 4H, $CH_2CH_2CH_2S$), 2.35–2.65 (m, 2H, CH_2SCH_2C), 2.71 (s, 2H, CH_2SCH_2C), 4.52 (br s, 1H, NNH), 6.09 (br s, 1H, CONH), 6.75–7.45 (m, 3H_{arom}, H-3′, 4′, 5′), 7.50–7.80 (m, 2H_{arom}, H-2′, 6′)
2e′	A	82	173–175 (EtOH)	$C_{12}H_{16}N_4O$ (232.3)	3265, 3100–2400, 1681	1.50–1.74 (m, 4H, $CH_2CH_2NHCH_2CH_2$), 2.65–2.85 (m, 4H, CH_2NHCH_2), 3.05 (br s, 1H, $NHCH_2$), 5.96 (s, 1H, NNH), 6.92 (dd, 1H_{arom}, $J_1 = J_2$ = 7, H-4′), 7.28 (dd, 2H_{arom}, $J_1 = J_2$ = 7, H-3′, 5′), 7.65 (d, 2H_{arom}, J = 7, H-2′, 6′), 7.73 (s, 1H, CONH)
2e	C	75	205–209 (MeOH)	$C_{19}H_{20}N_4O_2$ (336.4)	3180, 1705, 1616	1.50–1.95 (br m, 4H, $CH_2CH_2NCH_2CH_2$), 3.40–3.60 (br m, 4H, CH_2NCH_2), 6.25 (s, 1H, NNH), 6.94 (dd, 1H_{arom}, $J_1 = J_2$ = 7, H-4′), 7.29 (dd, 2H_{arom}, $J_1 = J_2$ = 7, H-3′, 5′), 7.36–7.50 (m, 5H, COC_6H_5), 7.66 (d, 2H, J = 7, H-2′, 6′), 7.84 (s, 1H, CONH)
2f	A	86	167–169 (MeOH)	$C_{13}H_{18}N_4O$ (246.3)	3200, 1690	1.57–1.81 (m, 4H, $CH_2CH_2NCH_2CH_2$), 2.21 (s, 3H, NCH_3), 2.27–2.60 (m, 4H, CH_2NCH_2), 3.51 (br s, 1H, NNH), 5.95 (s, 1H, CONH), 6.89–6.99 (m, 1H_{arom}, H-4′), 7.22–7.37 (m, 2H_{arom}, H-3′, 5′), 7.59–7.73 (m, 2H_{arom}, H-2′, 6′)
2g	B	89	161–163 (MeOH)	$C_{19}H_{20}N_4O_2$ (336.4)	3190, 1700, 1622	1.60–2.10 (br m, 4H, $CH_2CH_2CH_2N$), 2.85–4.10 (br m, 4H, CH_2NCH_2), 6.26 (s, 1H, NNH), 6.82–7.74 (br m, 10H_{arom}), 7.74–8.25 (br m, 1H, CONH)
2h	B	73	150–152 (MeOH)	$C_{13}H_{18}N_4O$ (246.3)	3180, 1695	1.47–1.80 (m, 4H, $CH_2CH_2CH_2N$), 2.17 (s, 3H, NCH_3), 2.17–2.40, 2.36 (m and s, 4H, CH_2NCH_2), 5.98 (s, 1H, NNH), 6.90 (dd, 1H_{arom}, $J_1 = J_2$ = 7, H-4′), 7.25 (dd, 2H_{arom}, $J_1 = J_2$ = 7, H-3′, 5′), 7.61 (s, 1H, CONH), 7.62 (d, 2H_{arom}, J = 7, H-2′, 6′)

[a] Satisfactory microanalyses obtained: C ±0.12, H ±0.13, N ±0.27; exception **2e**: C −0.32.

[b] The NMR spectra were recorded at 60 and 300 MHz in different solvents.
60 MHz: **2a**, **d** ($CDCl_3$); **2b** (DMSO-d_6).
300 MHz: **2c**, **e**, **e′**, **g**, **h** (DMSO-d_6); **2f** (methanol-d_4).

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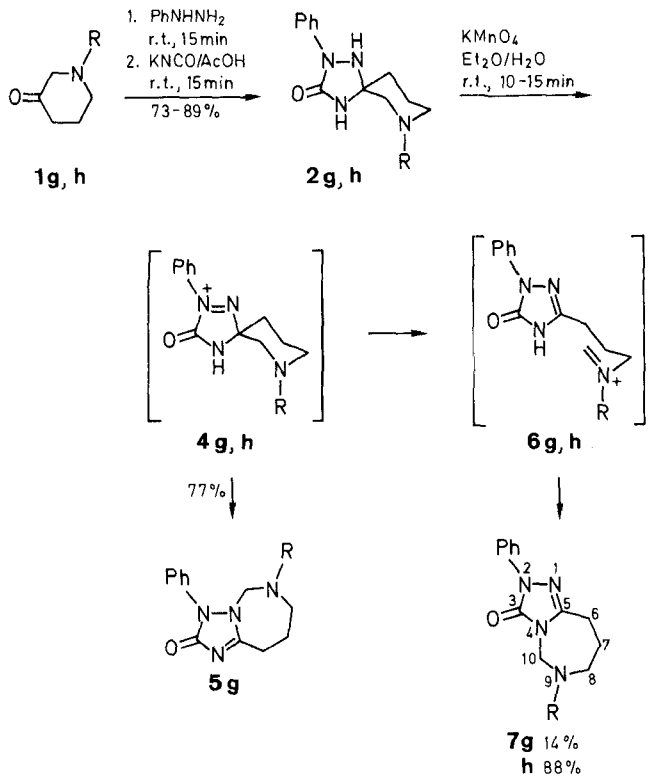

1,2,4-7	R
g	COPh
h	Me

Scheme **D**

the oxidation reaction. 1,5-Annulated 1,2,4-triazole derivative **5g** (77%) and the 4,5-annulated 1,2,4-triazole derivative **7g** (14%) can be isolated as rearranged reaction products (Scheme **D**). Compound **5g** is very sensitive to hydrolysis.

Both compounds are formed by an individual reaction path. The products are isomers, but cannot be converted into each other under the present reaction conditions, as demonstrated by TLC controlled experiments with isolated **5g** and **7g**. Thus, the unusual reaction path can be slowed by an acceptor substituent on the tertiary nitrogen atom, and the "normal" rearrangement process takes place again to a certain degree. The isomer triazolone derivatives **5** und **7** can be easily distinguished by inspection of their ^{13}C-NMR spectra. The resonance signals of the ^{13}C-atoms of the respective carbonyl functions appear in the range of $\delta = 162$ for compounds **5** and in the range of $\delta = 151$ for compounds **7**.

The formation of **7g,h** is closely related to the Beckmann fragmentation of 1-methylpiperidin-3-one oxime,[15] where only 4-methylaminobutyronitrile is obtained. Assuming that in the course of the oxidation of **2g,h** an intermediate triazolium salt **4g,h** is formed,[4] the formation of **7g,h** can be interpreted as follows: **4g,h** reacts in a first step with ring opening, and the resulting imminium ion **6g,h** closes a new ring to the 4,5-annulated triazoe derivative **7g,h** by a favoured 7-*endo-trig* attack.[16]

Melting points were determined on a Thermovar–Reichert Kofler melting point microscope and are uncorrected. ^{1}H-NMR spectra were obtained using a JEOL JNM-PMX-60 or a Bruker AM 300 spectrometer in various solvents with TMS as an internal standard.

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

Product	Yield (%)	mp (°C) (solvent) or n_D^{22}	Molecular Formula[a]	UV(CH_3CN) λ_{max} (nm) ($\log\varepsilon$)	IR (KBr or film) $\nu_{N=C=O}$ (cm^{-1})	^{1}H-NMR (60 MHz, $CDCl_3$/TMS) δ, J (Hz)
3a	96	79–80 (pentane)	$C_{12}H_{13}N_3O_2$ (231.3)	271 (4.02), 382 (2.25)	2260sh, 2215, 2145sh	1.35–1.90, 2.15–2.75 (2m, 2H each, $CH_2CH_2OCH_2CH_2$), 3.63–4.35 (m, 4H, CH_2OCH_2), 7.35–7.65 (m, 3H$_{arom}$, H-3′, 4′, 5′), 7.65–8.05 (m, 2H$_{arom}$, H-2′, 6′)
3b	98	67–69 (pentane)	$C_{12}H_{13}N_3OS$ (247.3)	272 (4.06), 383 (2.28)	2245sh, 2200, 2140sh	1.55–3.40 (m, 8H, CH_2), 7.30–7.60 (m, 3H$_{arom}$, H-3′, 4′, 5′), 7.65–8.00 (m, 2H$_{arom}$, H-2′, 6′)
3c[b]	–	–	$C_{12}H_{13}N_3O_2$ (231.3)	–	2240	–
3d	91	65–66 (pentane)	$C_{12}H_{13}N_3OS$ (247.3)	271 (4.08), 388 (2.31)	2215, 2185sh, 2150sh	1.55–1.75 (m, 1H, 1H of CH_2SCH_2C), 2.07–2.28 (m, 3H, 1H of CH_2SCH_2C + $CH_2CH_2CH_2S$), 2.37–2.51 (m, 1H, 1H of SCH_2C), 2.57–2.80 (m, 2H, $CH_2CH_2CH_2S$), 3.41 (d, 1H, J = 13, 1H of SCH_2C), 7.40–7.57 (m, 3H$_{arom}$, H-3′, 4′, 5′), 7.77–7.90 (m, 2H$_{arom}$, H-2′, 6′)[c]
3e	95	130–132 (Et_2O)	$C_{19}H_{18}N_4O_2$ (334.4)	272 (4.08), 372 (2.34)	2195, 2155sh, 1634[d]	1.30–1.85, 2.00–2.65 (2 br m, 2H each, $CH_2CH_2NCH_2CH_2$), 3.15–3.75, 3.75–4.65 (2 br m, 2H each, CH_2NCH_2), 7.20–7.55 (m, 8H$_{arom}$, H-3′, 4′, 5′ + COC_6H_5), 7.55–7.90 (m, 2H$_{arom}$, H-2′, 6′)
3f	94	1.5528	$C_{13}H_{16}N_4O$ (244.3)	270 (4.04), 381 (2.88)	2230, 2210, 2165sh	1.35–3.05, 2.38 (m and s, 11H, CH_2 + NCH_3), 7.25–7.60 (m, 3H$_{arom}$, H-3′, 4′, 5′), 7.60–7.95 (m, 2H$_{arom}$, H-2′, 6′)

[a] *Satisfactory microanalyses obtained:* C ±0.19, H ±0.20, N ±0.24, **3b**: S +0.09; compounds **3c** and **3f** are unstable.
[b] Compound **3c** rearranges within seconds at room temperature, and is therefore always contaminated with **5c**.
[c] 300 MHz spectra.
[d] C=O stretching vibration.

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^{13}C-NMR spectra were obtained on Bruker AM 300 spectrometer. IR spectra were recorded on a Beckman AccuLab 2 spectrophotometer and UV/Vis spectra on a Gilford 250 spectrophotometer. 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. Oxan-3-one (**1c**),[17,18] thian-3-one (**1d**),[19] 1-benzoylpiperidin-3-one (**1g**),[20] and 1-methylpiperidin-3-one (**1h**)[20] were prepared according to literature. Solvents were distilled before use. The boiling range of the petroleum ether was 40–60°C. 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 2a–h: General Procedures:

Method A, *for* **2a,b,f**: Phenylhydrazine (5.41 g, 50 mmol) is added to a solution of the appropriate ketone **1a,b,f** (50 mmol) in AcOH (60 mL). After stirring at r.t. for 10 to 15 min the hydrazone formation is completed (TLC control, Et_2O/PE, 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 **2a,b** formed (TLC control, Et_2O/PE, 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* over P_2O_5. In the case of **2f** the mixture is not diluted with water but made alkaline, while cooling on an ice bath, by adding KOH (50%) until a pH of 13–14 is obtained. The resulting suspension is extracted exhaustively with CH_2Cl_2 (50 mL portions, TLC control). The combined organic extracts are dried

Table 3. 1,5-Heteroannulated 1,2-Dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **5** Prepared

Product	Method	Yield (%)	mp (°C) (solvent)	Molecular Formula[a]	IR (KBr) $\nu_{C=O}$	^{1}H-NMR[b] ($CDCl_3$/TMS, 300 MHz) δ, J(Hz)	^{13}C-NMR[b] ($CDCl_3$/TMS, 75.473 MHz) δ
5a	A	70	213–215 (MeOH)	$C_{12}H_{13}N_3O_2$ (231.3)	1682	3.08–3.17 (m, 2H, H-6), 3.72–3.80 (m, 2H, H-10), 3.86–4.02 (m, 4H, H-7, 9), 7.22–7.39 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.39–7.50 (m, 2H$_{arom}$, H-3′, 5′)	32.5 (C-6), 51.1 (C-10), 67.1, 68.8 (C-7, 9), 124.5 (NPh, C-2′, 6′), 127.8 (NPh, C-4′), 129.6 (NPh, C-3′, 5′), 133.8 (NPh, C-1′), 162.3 (C-5), 168.9 (C=O)
5b	A	90	172.5–174.5 (MeOH/Et_2O)	$C_{12}H_{13}N_3OS$ (247.3)	1688	2.68–2.76, 2.83–2.90 (m, 2H each, H-7, 9), 3.32–3.40 (m, 2H, H-6), 4.05–4.13 (m, 2H, H-10), 7.24–7.40 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.40–7.51 (m, 2H$_{arom}$, H-3′, 5′)	26.2, 28.5, 33.4 (C-6, 7, 9), 51.6 (C-10), 124.8 (NPh, C-2′, 6′), 127.9 (NPh, C-4′), 129.6 (NPh, C-3′, 5′), 133.6 (NPh, C-1′), 162.2 (C-5), 168.4 (C=O)
5c	A	72	>150 (dec) (MeOH)	$C_{12}H_{13}N_3O_2$ (231.3)	1684	1.83–1.93 (m, 2H, H-7), 2.98–3.06 (m, 2H, H-6), 3.95–4.04 (m, 2H, H-8), 5.03 (s, 2H, H-10), 7.24–7.37 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.37–7.46 (m, 2H$_{arom}$, H-3′, 5′)	25.5 (C-7), 27.4 (C-6), 74.9 (C-8), 78.3 (C-10), 123.6 (NPh, C-2′, 6′), 127.4 (NPh, C-4′), 129.5 (NPh, C-3′, 5′), 134.0 (NPh, C-1′), 162.1 (C-5), 169.7 (C=O)
5d	A	57	215–217 (MeOH)	$C_{12}H_{13}N_3OS$ (247.3)	1682	1.98–2.07 (m, 2H, H-7), 2.94–3.04 (m, 4H, H-6, 8), 4.73 (s, 2H, H-10), 7.28–7.37 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.42–7.50 (m, 2H$_{arom}$, H-3′, 5′)	25.6, 28.4, 35.2 (C-6, 7, 8), 50.0 (C-10), 123.8 (NPh, C-2′, 6′), 127.4 (NPh, C-4′), 129.5 (NPh, C-3′, 5′), 133.8 (NPh, C-1′), 162.3 (C-5), 171.8 (C=O)
5e	A	75	191–193 (MeOH)	$C_{19}H_{18}N_4O_2$ (334.4)	1671, 1614	2.95–3.25 (br m, 2H, H-6), 3.65–4.10 (br m, 6H, H-7, 9, 10), 7.24–7.55 (m, 10H$_{arom}$)	31.0 (br, C-6), 41.2–51.9 (br, C-7, 9, 10), 124.7 (NPh, C-2′, 6′), 126.6 (COPh, C-2′, 6′), 128.0 (NPh, C-4′), 128.6 (COPh, C-3′, 5′), 129.7 (NPh, C-3′, 5′), 130.3 (COPh, C-4′), 133.5, 134.9 (NPh, COPh, C-1′), 161.8 (C-5), 166.0–170.0 (br, COPh), 171.4 (C=O)
5f	B	88	175–177 (MeOH)	$C_{13}H_{16}N_4O$ (244.3)	1678	2.46 (s, 3H, CH_3), 2.70–2.81 (m, 4H, H-9, 1H of H-6 and H-7), 3.02–3.09 (m, 2H, 1H of H-6 and H-7), 3.72–3.79 (m, 2H, H-10), 7.24–7.37 (m, 3H$_{arom}$, H-2′, 4′, 6′), 7.42–7.50 (m, 2H$_{arom}$, H-3′, 5′)	29.6 (C-6), 46.9 (CH_3), 48.3 (C-10), 53.5 (C-7), 55.8 (C-9), 124.3 (NPh, C-2′, 6′), 127.5 (NPh, C-4′), 129.5 (NPh, C-3′, 5′), 134.0 (NPh, C-1′), 162.3 (C-5), 169.2 (C=O)
5g	C	77	>72 (dec)	$C_{19}H_{18}N_4O_2$ (334.4)	1696, 1650	1.85–2.18 (br m, 2H, H-7), 3.03–3.12 (m, 2H, H-6), 3.57–3.92 (br m, 2H, H-8), 5.34 (s, 2H, H-10), 7.05–7.45 (m, 10H$_{arom}$)	23.5–25.9 (br, C-7), 27.7 (C-6), 48.7–53.1 (br, C-8), 56.0–61.6 (br, C-10), 123.2–126.0 (br), 126.8, 127.6, 128.7, 129.2, 130.6 (NPh, COPh, C-2′–6′), 133.6, 133.8 (NPh, COPh, C-1′), 162.1 (C-5), 169.0 (br, COPh), 171.3 (C=O)

[a] Satisfactory microanalyses obtained: C ±0.13, H ±0.12, N ±0.26; **5b**: S +0.13. Exception: **5b**, C −0.22; **5g** is unstable.
[b] For numbering see Scheme **B**.

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($MgSO_4$), the solvent is removed under reduced pressure and the crude product is dried *in vacuo* over $CaCl_2$.

Method B, *for* **2c,d,g,h**: Phenylhydrazine (5.41 g, 50 mmol) is added to a solution of the appropriate ketone **1c,d,g,h** (50 mmol) in MeOH (50 mL). After stirring at r.t. for 10 to 15 min the hydrazone formation is completed (TLC control, Et_2O/PE, 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 triazolidinones **2c,d,g** formed (TLC-control, Et_2O/PE, 1:1) is induced by careful addition of ice cold water (500 mL) to the mixture. The resulting suspension of **2c,d** resp. **2h** are worked up as described in Method A for **2a,b** resp. **2f**. Compound **2g** tends to separate 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 basic reaction of the aqueous layer occurs) and water (2 × 25 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure and the product is recrystallized from MeOH.

Method C, *for 8-Benzoyl-2-phenyl-1,2,4,8-tetraazaspiro[4.5]decan-3-one* (**2e**): First, 2-phenyl-1,2,4,8-tetraazaspiro[4.5]decan-3-one (**2e'**) is prepared according to the procedure for **2f** described above (Method A), starting from piperidin-4-one hydrochloride hydrate and phenylhydrazine. Compound **2e'** (6.97 g, 30 mmol) is then suspended in pyridine (40 mL), and a solution of benzoyl chloride (4.22 g, 30 mmol) in CH_2Cl_2 is added dropwise within 25 min with stirring and cooling, a process during which the triazolidinone **2e'** slowly dissolves. Stirring is continued at r.t. for 5 min and the mixture is diluted with water (250 mL). The layers are separated, and the aqueous layer is extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts are washed with 2 N HCl (2 × 100 mL) and water (2 × 100 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure and the crystalline **2e** is dried *in vacuo* over $CaCl_2$; yield. 7.58 g (75%).

1-Isocyanato-1-(phenylazo)heterocycloalkanes 3a–f:

Prepared by oxidative ring cleavage of 5-spiro-substituted 2-phenyl-1,2,4-triazolidin-3-ones **2a–f** according to Ref. 11. Compound **3c** rearranges to **5c** within min, even at r.t. so that the oxidation has to be carried out in an ice-bath. Compound **2b** is very insoluble in Et_2O and must be suspended in a mixture of Et_2O and CH_2Cl_2 (1:1) before the oxidation. Before the separation of the layers, the MnO_2 formed is removed by filtration with diatomaceous silica to prevent the formation of emulsions during the extraction process. Should a further purification of the product be necessary, it is performed best, if the product is crystalline, by recrystallization from pentane or Et_2O, or if the product is liquid, by column chromatography on a short column of silica gel at normal pressure (10–15 cm, Et_2O/PE, eluent ratio must be varied according to the product and the impurities). At elevated temperatures spontaneous rearrangement to **5** may occur, therefore distillation of the compounds **3** should be avoided.

3-Spiro-substituted 1-Phenyl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium Tetrafluoroborates 4a,b,f:

Prepared according to Ref. 5 by reacting 1-isocyanato-1-(phenylazo)heterocycloalkanes **3a,b,f** with HBF_4. Compound **4a** can be kept at 0°C for a few hours, while **4b** is very unstable and rearranges to **5b** · HBF_4 within a few min. Only **4f** can be kept at low temperatures for some months.

4a: yield: 33%; mp 84°C (rear).

IR (KBr): ν = 1866 sh; 1852 cm^{-1} (C=O).

UV (CH_3CN): λ_{max} (log ε) = 359 (3.51), 271 nm (3.87).

4b: yield: 57% (see above).

IR (KBr): ν = 1857 cm^{-1} (C=O).

4f: yield: 77%; mp 135°C (rear).

$C_{13}H_{18}B_2F_8N_4O$	calc.	C 37.18	H 4.32	N 13.34
(419.9)	found	36.86	4.35	13.25

IR (KBr): ν = 1847 cm^{-1} (C=O).

UV (CH_3CN): λ_{max} (log ε) = 367 (2.92), 275 nm (4.06).

1,5-Heteroannulated 1,2-Dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones 5a–g and 4,5-Heteroannulated 2,4-Dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones 7g,h; General Procedures:

Method A, *for* **5a–e**: A 1-isocyanato-1-(phenylazo)heterocycloalkane **3a–e** (5 mmol) is dissolved in Et_2O (40 mL), and the solution is cooled to 0°C. Aq HBF_4 (50%, 5 mL) is added dropwise with stirring 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 the cases of **5b–d**, the colour of the solution fades during this step, indicating a completed rearrangement. The solutions of **5a,e** are refluxed for 10 min to accomplish the same task. The major part of the CH_3CN is removed under reduced pressure, and 2 N NaOH is added to the remaining solution until it becomes basic. Water is added (50–100 mL) to prevent the formation of emulsions, and the resulting basic reaction 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 colourless crystalline product is dried *in vacuo* over $CaCl_2$.

Method B, *for 4-Methyl-10-phenyl-1,4,8,10-tetraazabicyclo[5.3.0]dec-7-en-9-one* (**5f**): Compound **4f** (3.01 g, 7.02 mmol) is finely crushed and heated to 150°C until the initially bright yellow colour has faded (~ 10 min), during which time partial melting can be observed. After cooling to r.t., the solidified product is crushed in a mortar and extracted with CH_2Cl_2 (2 × 10 mL). The extracts are discarded, and the crude product is treated with 2 N NaOH (40 mL). The suspension formed is extracted exhaustively with CH_2Cl_2 (10 mL portions, TLC control). The combined organic extracts are dried ($MgSO_4$), the solvent is removed under reduced pressure, and the crystalline **5f** is purified by column chromatography (Et_2O/MeOH/Et_3N, 6:3:1, R_f 0.31); yield: 1.55 g (88%).

Method C, *for* **5g; 7g,h:** Compounds **2g,h** are oxidized in a mixture of Et_2O/CH_2Cl_2 (1:1) according to the procedure for isocyanates **3** mentioned above. After filtration of the 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 are dried *in vacuo* over $CaCl_2$. Compound **2g** yields a mixture of **5g** and **7g**, which is separated by column chromatography (Et_2O/MeOH/Et_3N, 6:3:1, R_f **5g**: 0.31; **7g**: 0.80).

7g: yield: 14%; mp 165–168°C.

$C_{19}H_{18}N_4O_2$	calc.	C 68.25	H 5.43	N 16.76
(334.4)	found	68.25	5.55	16.41

IR (KBr): ν = 1706, 1640 cm^{-1} (C=O).

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): 1.75–2.15 (br m, 2H, H-7), 2.85–2.96 (m, 2H, H-6), 3.70–3.95 (br m, 2H, H-8), 5.20–5.45 (br s, 2H, H-10), 7.18 (dd, 1 H_{arom}, $J_1 = J_2$ = 8, H-4'), 7.22–7.50 (m, 7 H_{arom}, H-3', 5' + COC_6H_5), 7.92 (d, 2 H_{arom}, J = 8, H-2', 6').

^{13}C-NMR (75.473 MHz, $CDCl_3$/TMS): δ = 26.2 (br, C-7), 26.6 (C-6), 50.5 (br, C-8), 55.3 (br, C-10), 118.2 (NPh, C-2',6'), 124.9 (NPh, C-4'), 126.7 (COPh, C-2', 6'), 128.5 (COPh, C-3', 5'), 128.7 (NPh, C-3', 5'), 130.2 (COPh, C-4'), 134.2 (COPh, C-1'), 137.6 (NPh, C-1'), 147.4 (C-5), 150.2 (C-3), 171.4 (COPh).

7h: yield: 88%; mp 92–93°C.

$C_{13}H_{16}N_4O$	calc.	C 63.91	H 6.60	N 22.93
(244.3)	found	63.72	6.64	22.87

IR (KBr): ν = 1692 cm^{-1} (C=O).

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 1.67–1.79 (m, 2H, H-7), 2.31 (s, 3H, CH_3), 2.70–2.78 (m, 2H, H-6), 3.03–3.12 (m, 2H, H-8), 4.69 (s, 2H, H-10), 7.16 (dd, 1 H_{arom}, $J_1 = J_2$ = 8, H-4'), 7.38 (dd, 2 H_{arom}, J = 8, 8, H-3', 5'), 7.96 (d, 2 H_{arom}, J = 8, H-2', 6').

^{13}C-NMR (75.473 Hz, $CDCl_3$/TMS): δ = 21.1 (C-7), 27.1 (C-6), 36.6 (CH_3), 57.5 (C-8), 62.9 (C-10), 118.3 (C_{arom}, C-2', 6'), 124.9 (C_{arom}, C-4'), 128.8 (C_{arom}, C-3', 5'), 138.1 (C_{arom}, C-1'), 149.0 (C-5), 152.2 (C=O).

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