Rearrangement of 3,3-Disubstituted 1-Aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium Tetrafluoroborates; Part 1. A Versatile Synthesis of 1,5-Disubstituted 2-Aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-one Tetrafluoroborates

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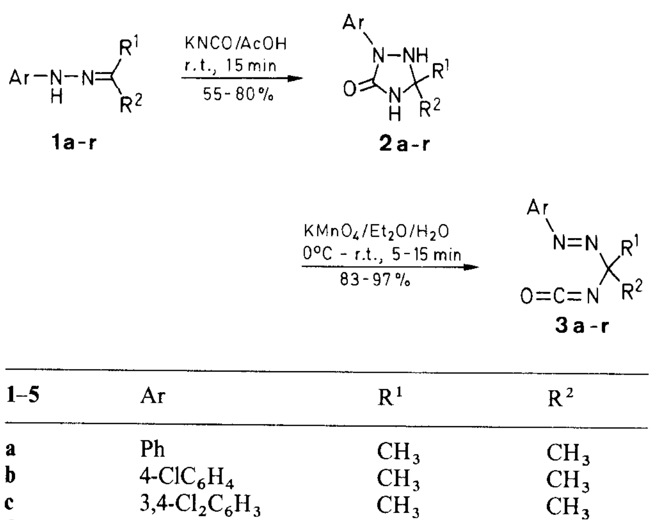
α-(Arylazo)alkyl isocyanates **3** react with tetrafluoroboric acid to yield 3,3-disubstituted 1-aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborates **4**. These compounds rearrange under mild conditions and in good yields to the tetrafluoroborates of 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones **5**. Our results show that the nature of the substituents determines their migratory aptitude for the rearrangement.

Only few methods for the preparation of 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones have been reported, e.g. the cyclization of 1,2-diaryl-4-benzoylsemicarbazides in hydrochloric acid, or the thermolysis of carbonyl azide derivatives of hydrazones.[2] Furthermore, good yields of these dihydro-1,2,4-triazol-3-ones have been reported to result from thermally induced rearrangement of α-(arylazo)alkyl isocyanates.[3] Here we present a new and convenient synthesis of 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-one tetrafluoroborates **5** by acid-induced rearrangement of α-(arylazo)alkyl isocyanates **3**.

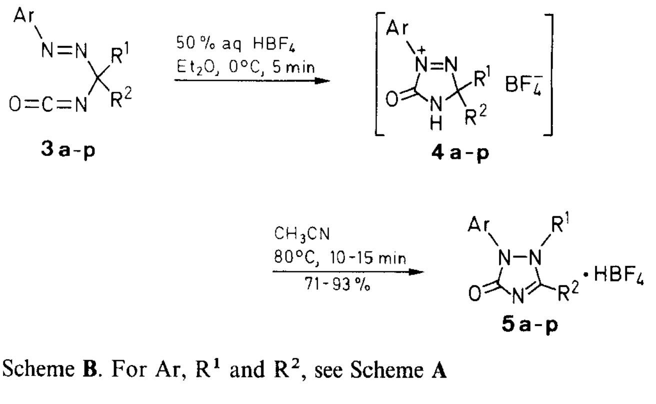


1-5	Ar	R^1	R^2
a	Ph	CH_3	CH_3
b	4-ClC_6H_4	CH_3	CH_3
c	3,4-$Cl_2C_6H_3$	CH_3	CH_3
d	4-$MeOC_6H_4$	CH_3	CH_3
e	4-$O_2NC_6H_4$	CH_3	CH_3
f	Ph	Et	CH_3
g	Ph	Pr	CH_3
h	Ph	*i*-Bu	CH_3
i	Ph	*i*-Pr	CH_3
j	Ph	*c*-Pr	CH_3
k	Ph	Ph	CH_3
l	Ph	Et	Ph
m	Ph	CH_2CH_2Ph	CH_3
n	Ph	Et	Et
o	Ph	*i*-Pr	Et
p	Ph	*c*-Pr	*c*-Pr
1-3, 6, 7			
q	Ph	*t*-Bu	CH_3
r	Ph	CH_2Ph	CH_3

Scheme A

Several well described procedures for the synthesis of the substrates **3** are reported in the literature.[5,6,8-11] We chose the 1,3-dipolar cycloaddition of isocyanic acid (generated *in situ*) to arylhydrazones **1** to give 5,5-disubstituted 2-aryl-1,2,4-triazolidin-3-ones **2** (Table 1),[4-9] followed by oxidation[8,9] with potassium permanganate (Scheme **A**) (Table 2).

α-(Arylazo)alkyl isocyanates **3** were converted to 3,3-disubstituted 1-aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborates **4** by simply stirring with tetrafluoroboric acid[12] in diethyl ether for 5 minutes (Scheme **B**). The compounds **4a–f** could be isolated as crystals and characterized (Table 3). All triazolium tetrafluoroborates **4** rearrange under mild reaction conditions with a 1,2-shift of one of the substituents from position 3 to the nitrogen atom at position 2 to yield the salts of 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones **5** (Table 4). This opens a new synthetic route to the heterocycles **5** (Scheme **B**).



Scheme **B**. For Ar, R^1 and R^2, see Scheme A

The stability of the 3,3-disubstituted 1-aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborates **4a–p** depends strongly on the nature of the substituents R^1 and R^2, but to a lesser degree, it is also influenced by the substitution pattern of the aromatic ring. The compounds with geminal methyl substituents **4a–e** ($R^1 = R^2$ = methyl) are the most stable triazolium salts. Within these, the reaction leading to 1,2-shift of a methyl group, which needs 10 to 15 minutes to be performed in boiling acetonitrile for **4a–c**, is slowed down by the donor-substituted aryl group in **4d** to such a degree that the reaction time has to be prolonged to 6 hours. On the other hand, compound **4e**, with a 4-nitro substitution of the aromatic ring, shows a steep increase in the rate of the rearrangement reaction. Crystalline **4e** is always accompanied by impurities of **5e**, a result of rearrangement even at low temperatures. The 4-nitrophenyl substituent on the heterocyclic ring of **4e** does accelerate the rearrangement reaction, but it hinders the acid-promoted ring closure of the 1-(4-nitrophenylazo)-1-methylethyl isocyanate (**3e**) to the triazolium salt **4e**. This synthetic problem can be resolved by carrying out the reaction in pure aqueous tetrafluoroboric acid without previously dissolving the isocyanate **3e** in an organic solvent.

In the series of 3,3-disubstituted 4,5-dihydro-1-phenyl-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborates **4a,f–p** the influence of the substituents R^1 and R^2 on the rearrangement was studied, by following the course of the reaction by UV/Vis-spectroscopy. The yellow triazolium salts **4** show a broad, strong absorption at $\lambda = 336$–364 nm ($\log \varepsilon = 3.87$–3.98), which decreases with the progression of the rearrangement reaction. The colorless products **5** do not show any absorption above $\lambda = 300$ nm. Compound **4a** ($R^1 = R^2 =$ methyl) shows in acetonitrile at 22 °C a half-life of 22 h with regard to its rearrangement to **5a**. In compound **4j** ($R^1 =$ cyclopropyl, $R^2 =$ methyl) only the cyclopropyl substituent undergoes the 1,2-migration, but the half-life in acetonitrile at 21.5 °C decreases to 10.2 minutes. Compound **4f** ($R^1 =$ ethyl, $R^2 =$ methyl) can be isolated as crystals and kept at low temperature for a few minutes, but in acetonitrile at 22 °C the half-life is only 16 seconds, yielding **5f** with exclusive migration of the ethyl substituent. The considerable acceleration in the rate of the rearrangement reaction by replacing one of the methyl groups in **4a** with an ethyl group in **4f** [$t_{1/2}$ (methyl) : $t_{1/2}$ (ethyl) = 5000 : 1] can be associated with the presence of a strongly polarized transition state during the migration of one of the substituents.

The ease with which alkyl substituents larger than methyl undergo the 1,2-migration explains that only few of the triazolium salts **4f–p** can be isolated even at low temperatures and that most of the compounds **4f–p** exist only as short-lived intermediates. Furthermore, the important differences in the migration rates of the respective substituents ensures that, in the case of a rearrangement with two different substituents R^1 and R^2, the formation of mixtures of the two possible isomers is never observed. The tetrafluoroborates of 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones **5f–p** formed are the products of migration of only one substituent. Even the acid catalysed rearrangement of **3o** via **4o** shows a complete differentiation of the alkyl substituents. The exclusive migration of the isopropyl substituent generates only **5o**. If an alkyl and a phenyl substituent compete for the migration, the following observations can be made:

Table 1. 5,5-Disubstituted 2-Aryl-1,2,4-triazolidin-3-ones **2** Prepared

Product	Yield (%)	mp (°C) (solvent)	Molecular Formula[a] or Lit. mp (°C)	IR (KBr) $\nu_{N-H,C=O}$ (cm^{-1})	^1H-NMR ($CDCl_3$/TMS) δ, J(Hz)
2d	60	103–104.5 (MeOH)	$C_{11}H_{15}N_3O_2$ (221.3)	3170, 1713	1.42 (s, 6H, t-C_4H_9), 3.73 (s, 3H, CH_3O), 4.54 (br s, 1H, NNH), 6.09 (br s, 1H, CONH), 6.68, 6.82, 7.40, 7.55 (AA′BB′, 4H_{arom})
2f	73	109–111 (MeOH)	102–104[7]	3190, 1704	0.97 (t, 3H, $J = 7$, $C\underline{H}_3CH_2$), 1.39 (s, 3H, CH_3), 1.48–1.97 (m, 2H, $CH_3C\underline{H}_2$), 4.44 (s, 1H, NNH), 6.48 (br s, 1H, CONH), 6.70–7.77 (m, 5H_{arom})
2g	77	101–103 (crude)	98–100[7]	3165, 1698	0.60–1.13 (m, 3H, $C\underline{H}_3CH_2CH_2$), 1.13–1.86 (m, 4H, $CH_3C\underline{H}_2C\underline{H}_2$), 1.37 (s, 3H, CH_3), 4.44 (br s, 1H, NNH), 6.64 (br s, 1H, CONH), 6.74–7.78 (m, 5H_{arom})
2h	77	118–119 (crude)	118–120[7]	3215, 1695	0.95, 1.04 [2d, 3H each, $J = 7$, $(C\underline{H}_3)_2CH$], 1.41 (s, 3H, CH_3), 1.53–2.25 [m, 3H, $(CH_3)_2C\underline{H}C\underline{H}_2$], 4.45 (s, 1H, NNH), 6.45 (br s, 1H, CONH), 6.75–7.80 (m, 5H_{arom})
2i	81	142–143 (crude)	139–141[7]	3170, 1696	0.99 [d, 6H, $J = 7$, $(C\underline{H}_3)_2CH$], 1.34 (s, 3H, CH_3), 1.54–2.22 [sept, 1H, $J = 7$, $(CH_3)_2C\underline{H}$], 4.39 (s, 1H, NNH), 6.43 (br s, 1H, CONH), 6.75–7.85 (m, 5H_{arom})
2j	55	104–106 (crude)	98–100[7]	3185, 1694	0.20–0.76 (m, 4H, CH_2CH_2), 0.76–1.27 (m, 1H, CH), 1.43 (s, 3H, CH_3), 4.51 (s, 1H, NNH), 6.42 (br s, 1H, CONH), 6.66–7.80 (m, 5H_{arom})
2l	63	143–144 (MeOH)	$C_{16}H_{17}N_3O$ (267.3)	3165, 1687	0.85 (t, 3H, $J = 7$, $C\underline{H}_3CH_2$), 2.09 (q, 2H, $J = 7$, $CH_3C\underline{H}_2$), 4.76 (s, 1H, NNH), 6.85–7.90 (m, 11H, 10H_{arom} + CONH)
2m	77	110–111 (MeOH)	$C_{17}H_{19}N_3O$ (281.4)	3235, 1703	1.46 (s, 3H, CH_3), 1.75–2.15 (m, 2H, $C\underline{H}_2CH_2Ph$), 2.50–2.95 (m, 2H, $C\underline{H}_2Ph$), 4.45 (s, 1H, NNH), 6.45 (br s, 1H, CONH), 6.75–7.85 (m, 10H_{arom})
2n	80	132–134 (crude)	125–128[7]	3175, 1698	0.92 (t, 6H, $J = 7$, 2 × $C\underline{H}_3CH_2$), 1.40–1.93 (m, 4H, 2 × $CH_3C\underline{H}_2$), 4.39 (br s, 1H, NNH), 6.52 (br s, 1H, CONH), 6.70–7.80 (m, 5H_{arom})
2o	85	109–110 (MeOH)	$C_{13}H_{19}N_3O$ (233.3)	3175, 1700	0.75–1.20 [m, 9H, $C\underline{H}_3CH_2$, $(C\underline{H}_3)_2CH$], 1.50–2.15 [m, 3H, $CH_3C\underline{H}_2$, $(CH_3)_2C\underline{H}$], 4.35 (br s, 1H, NNH), 6.43 (br s, 1H, CONH), 6.65–7.75 (m, 5H_{arom})
2p	63	97–99 (PE)	$C_{14}H_{17}N_3O$ (243.3)	3190, 1697	0.23–0.84 (m, 8H, 2 × CH_2CH_2), 0.84–1.47 (m, 2H, 2 × CH), 4.41 (br s, 1H, NNH), 6.40 (br s, 1H, CONH), 6.65–7.88 (m, 5H_{arom})
2q	74	128 (dec) (MeOH)	$C_{13}H_{19}N_3O$ (233.3)	3210, 1697	1.02 (s, 9H, t-C_4H_9), 1.47 (s, 3H, CH_3), 4.45 (br s, 1H, NNH), 6.09 (br s, 1H, CONH), 6.90–7.83 (m, 5H_{arom})
2r	81	>108 (dec) (MeOH)	$C_{16}H_{17}N_3O$ (267.3)	3200, 1704	1.40 (s, 3H, CH_3), 2.70, 2.91, 2.95, 3.16 (AB, 2H, $J_{AB} = 12$, CH_2), 4.56 (br s, 1H, NNH), 6.06 (br s, 1H, CONH), 6.80–7.80 (m, 10H_{arom})

[a] Satisfactory microanalyses obtained: C ±0.13, H ±0.15, N ±0.21, except for **2r** which is unstable.

Table 2. α-(Arylazo)alkyl Isocyanates **3** Prepared

Product	Yield (%)	n_D(°C)	Molecular Formula[a] or Lit. Data	UV (CH_3CN) λ_{max}(nm) (log ε)	IR (film) $\nu_{N=C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
3d	97	1.5508 (25)	$C_{11}H_{13}N_3O_2$ (219.2)	304 (4.14), 370 (2.58)	2220, 2165sh, 2125sh	1.55 (s, 6H, t-C_4H_9), 3.82 (s, 3H, CH_3O), 6.83, 6.98, 7.69, 7.84 (AA'BB', 4H_{arom})
3f	90	1.5275 (22)	bp 80–81/0.2[10]	268 (4.01), 382 (2.25)	2220, 2155sh	0.82 (t, 3H, J = 7, $C\underline{H}_3CH_2$), 1.54 (s, 3H, CH_3), 1.76–2.24 (m, 2H, $CH_3C\underline{H}_2$), 7.20–7.92 (m, 5H_{arom})
3g	90	1.5230 (23)	$C_{12}H_{15}N_3O$ (217.3)	268 (4.02), 382 (2.26)	2220, 2160sh	0.50–2.20, 1.53 (m, s, 10H, $CH_3CH_2CH_2$, CH_3), 7.15–7.98 (m, 5H_{arom})
3h	84	1.5191 (24)	$C_{13}H_{17}N_3O$ (231.3)	269 (4.10), 380 (2.28)	2220, 2140sh	0.79, 0.90 [2d, 3H each, $(C\underline{H}_3)_2CH$], 1.50 (s, 3H, CH_3), 1.62–2.10 [m, 3H, $(CH_3)_2C\underline{H}C\underline{H}_2$], 7.10–7.92 (m, 5$H_{arom}$)
3i	90	1.5298 (20)	$C_{12}H_{15}N_3O$ (217.3)	268 (3.96), 381 (2.24)	2220, 2170sh	0.80, 1.04 [2d, 3H each, J = 7, $(C\underline{H}_3)_2CH)$], 1.49 (s, 3H, CH_3), 2.07–2.60 [m, 1H, $(CH_3)_2C\underline{H}$], 7.16–7.87 (m, 5H_{arom})
3j	94	1.5422 (20)	$C_{12}H_{13}N_3O$ (215.3)	268 (4.08), 379 (2.26)	2220, 2160sh	0.10–0.80 (m, 4H, CH_2CH_2), 1.25–1.80 (m, 1H, CH), 1.65 (s, 3H, CH_3), 7.13–7.90 (m, 5H_{arom})
3l	97	1.5784 (22)	$C_{16}H_{15}N_3O$ (265.3)	273 (4.09), 382 (2.30)	2220	0.83 (t, 3H, J = 7, CH_3), 2.27 (q, 2H, J = 7, CH_2), 7.10–8.05 (m, 10H_{arom})
3m	88	1.5688 (22)	$C_{17}H_{17}N_3O$ (279.3)	268 (4.16), 380 (2.29)	2225	1.60 (s, 3H, CH_3), 2.02–2.85 (m, 4H, $C\underline{H}_2C\underline{H}_2C_6H_5$), 6.90–7.20 (m, 5H, $CH_2C_6\underline{H}_5$), 7.30–7.95 (m, 5H, $C_6H_5N{=}N$)
3n	83	1.5258 (23)	$C_{12}H_{15}N_3O$ (217.3)	271 (4.11), 381 (2.26)	2220, 2125sh	0.78 (t, 6H, J = 7, 2 × $C\underline{H}_3CH_2$), 1.78–2.30 (m, 4H, 2 × $CH_3C\underline{H}_2$), 7.18–7.85 (m, 5H_{arom})
3o	94	1.5254 (24)	$C_{13}H_{17}N_3O$ (231.3)	269 (4.01), 385 (2.23)	2210, 2150sh	0.55–1.15 [m, 9H, $C\underline{H}_3CH_2$, $(C\underline{H}_3)_2CH$], 1.70–2.80 [m, 3H, $CH_3C\underline{H}_2$, $(CH_3)_2C\underline{H}$], 7.20–7.90 (m, 5H_{arom})
3p	88	1.5531 (20)	$C_{14}H_{15}N_3O$ (241.3)	269 (4.06), 380 (2.27)	2220	0.10–0.92 (m, 8H, 2 × CH_2CH_2), 1.38–2.10 (m, 2H, 2 × CH), 7.21–7.95 (m, 5H_{arom})
3q	–	–	$C_{13}H_{17}N_3O$ (231.3)	–	2200, 2145sh	–
3r	–	–	$C_{16}H_{15}N_3O$ (265.3)	–	2215, 2155sh	–

[a] Satisfactory microanalyses obtained: C ±0.39, H ±0.15, N ±0.22, except for **3i**, **l**, **m**, **o**, **q**, **r** which are unstable.

Table 3. New Isolable 3,3-Disubstituted 1-Aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium Tetrafluoroborates **4** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	UV (CH_3CN) λ_{max}(nm) (log ε)	IR (KBr) $\nu_{C=O}$ (cm^{-1})
4c	91	120 (rear.)	$C_{10}H_{10}BCl_2F_4N_3O$ (345.9)	357 (3.93)	1874
4e	–	–	$C_{10}H_{11}BF_4N_4O_3$ (322.0)	–	1872
4f	–	–	$C_{11}H_{14}BF_4N_3O$ (291.0)	–	1865
4m	–	–	$C_{17}H_{18}BF_4N_3O$ (367.2)	–	1845

[a] Microanalysis obtained for **4c**: C −0.53, H +0.01, N −0.21; **4e**, **f**, **m** are unstable and accompanied by **5e**, **f**, **m**.

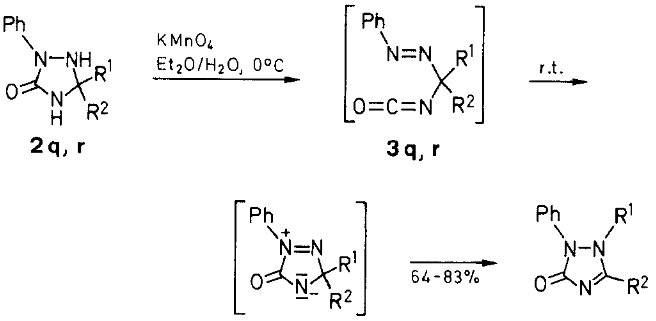
compound **4k** is converted into **5k** with the exclusive migration of the phenyl group, but **4l** yields **5l** with only the ethyl group undergoing the 1,2-shift.

The proof, which substituent has migrated during the rearrangement from **4** to **5** can be furnished simply by the analysis of the ^{1}H-NMR spectra of **5**. Compared to the respective chemical shifts in the substrates **3** and **4**, the α-protons of the substituent, which has migrated to the nitrogen atom show a strong shift downfield of about 2 ppm in the products **5**. The α-protons of the group, which did not migrate reflect the same tendency, but the shift downfield is only 0.5–1 ppm.

The scope of the acid-induced rearrangement reaction of α-(arylazo)alkyl isocyanates **3** for the synthesis of the tetrafluoroborates of 1,5-disubstituted 2-aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones **5** is broad. However, the synthesis of some of the compounds **5** fails at the step of the 1,2,4-triazolidin-3-ones **2**. Thus, for example, the arylhydrazones of 2,2,4-trimethyl-3-pentanone, 1,1,1-trifluoracetone and also diarylketones fail to add isocyanic acid to form **2**.

In the course of further investigations on the rearrangement of **4**, problems arose in attempts to synthesize the tetrafluoroborates of 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones with 1-*tert*-butyl- **5q** or 1-benzyl-substituent **5r**. The respective α-(phenylazo)alkyl isocyanates **3q,r** tend to rearrange to the 1,5-disubstituted 1,2-dihydro-2-phenyl-3*H*-1,2,4-triazol-3-ones **7q,r** during their synthesis, even if the oxidation is carried out at 0 °C. These examples show that the known, thermally induced rearrangement of the isocyanates 3[3] is influenced also strongly by the substitution pattern.

As the experience with the rearrangement of the triazolium salts 4 suggests, the presence of an aryldiazenium function is absolutely essential to induce the migration of an alkyl or aryl group to the nitrogen atom. For this reason the thermal rearrangement of 3 to 7 should proceed via the cyclic zwitterionic isomer 6 (Scheme C).



Scheme C

Table 4. Compounds 5 Prepared

Product	Method	Yield (%)	mp (°C) (solvent)[a]	Molecular Formula[b]	IR (KBr) $\nu_{C=O}$(cm^{-1})	^{1}H-NMR (TMS)[c] δ, J(Hz)
5a	A	91	>185 (dec) (MeOH)	$C_{10}H_{12}BF_4N_3O$ (277.0)	1750, 1775sh	2.56 (s, 3H, CH_3), 3.42 (s, 3H, NCH_3), 7.27–7.76 (m, 5H_{arom}), 10.06 (br s, 1H, NH)
5b	A	82	>180 (dec) (MeOH)	$C_{10}H_{11}BClF_4N_3O$ (311.5)	1755, 1797sh	2.56 (s, 3H, CH_3), 3.41 (s, 3H, NCH_3), 7.31, 7.45, 7.51, 7.66 (AA′BB′, 4H_{arom}), 10.21 (br s, 1H, NH)
5c	A	83	>205 (dec) (MeOH/Et_2O)	$C_{10}H_{10}BCl_2F_4N_3O$ (345.9)	1760, 1795sh	2.60 (s, 3H, CH_3), 3.48 (s, 3H, NCH_3), 6.96 (br s, 1H, NH), 7.24–7.85 (m, 3H_{arom})
5d	A	83	73–75 (CH_3CN/Et_2O)	$C_{11}H_{14}BF_4N_3O_2$ (307.0)	1751	2.52 (s, 3H, CH_3), 3.39 (s, 3H, NCH_3), 3.80 (s, 3H, CH_3O), 7.00, 7.14, 7.30, 7.44 (AA′BB′, 4H_{arom}), 9.56 (br s, 1H, NH)
5e	B	71	>208 (dec) (MeOH/TBME)	$C_{10}H_{11}BF_4N_4O_3$ (322.0)	1754	2.48 (s, 3H, CH_3), 3.44 (s, 3H, NCH_3), 7.50, 7.64, 8.18, 8.33 (AA′BB′, 4H_{arom}), 12.31 (br s, 1H, NH)
5f	C	93	>130 (dec) (CH_3CN/Et_2O)	$C_{11}H_{14}BF_4N_3O$ (291.0)	1756	1.07 (t, 3H, J = 7, $NCH_2C\underline{H}_3$), 2.56 (s, 3H, CH_3), 3.95 (q, 2H, J = 7, NCH_2), 7.35–7.77 (m, 5H_{arom}), 11.09 (br s, 1H, NH)
5g	C	85	>135 (dec) (MeOH/TBME)	$C_{12}H_{16}BF_4N_3O$ (305.1)	1746	0.72 (t, 3H, J = 7, $NCH_2CH_2C\underline{H}_3$), 1.05–1.65 (m, 2H, $NCH_2C\underline{H}_2$), 2.55 (s, 3H, CH_3), 3.87 (t, 2H, J = 7, $NC\underline{H}_2$), 7.48 (s, 6H, 5H_{arom} + NH)
5h	C	85	>148 (dec) (MeOH/TBME)	$C_{13}H_{18}BF_4N_3O$ (319.1)	1748	0.73 [d, 6H, J = 7, $CH(C\underline{H}_3)_2$], 1.30–1.90 [m, 1H, $C\underline{H}(CH_3)_2$], 2.57 (s, 3H, CH_3), 3.78 (d, 2H, J = 7, $NC\underline{H}_2$), 6.78 (s, 1H, NH), 7.47 (s, 5H_{arom})
5i	C	76	>180 (dec) (MeOH/TBME)	$C_{12}H_{16}BF_4N_3O$ (305.1)	1768	1.31 [d, 6H, J = 7, $NCH(C\underline{H}_3)_2$], 2.59 (s, 3H, CH_3), 4.04–4.67 [m, 1H, $NC\underline{H}(CH_3)_2$], 7.46 (s, 5H_{arom}), 10.64 (br s, 1H, NH)
5j	C	74	>155 (dec) (MeOH/Et_2O)	$C_{12}H_{14}BF_4N_3O$ (303.1)	1750	0.70–1.05 (m, 4H, CH_2CH_2), 2.52 (s, 3H, CH_3), 2.92–3.51 (m, 1H, NCH), 7.44 (s, 5H_{arom}), 9.91 (s, 1H, NH)
5k	C	83	>104 (dec) (MeOH/TBME)	$C_{15}H_{14}BF_4N_3O$ (339.1)	1752	2.29 (s, 3H, CH_3), 7.05 (br s, 1H, NH), 7.22 (s, 5H, H_{arom}), 7.38 (s, 5H_{arom})
5l	C	89	>205 (dec) (MeOH/Et_2O)	$C_{16}H_{16}BF_4N_3O$ (353.1)	1750	0.92 (t, 3H, J = 7, CH_3), 4.05 (q, 2H, J = 7, CH_2), 7.55–8.20 (m, 10H_{arom}), 9.04 (s, 1H, NH)
5m	C	74	80–95 (MeOH/TBME)	$C_{17}H_{18}BF_4N_3O$ (367.2)	1750	2.25 (s, 3H, CH_3), 2.78 (t, 2H, J = 7, $NCH_2C\underline{H}_2C_6H_5$), 4.19 (t, 2H, J = 7, $NC\underline{H}_2$), 6.85–7.40 (m, 5H, $CH_2C_6\underline{H}_5$), 7.40–7.80 (m, 5H, C_6H_5N), 8.58 (s, 1H, NH)
5n	C	71	>145 (dec) (MeOH/Et_2O)	$C_{12}H_{16}BF_4N_3O$ (305.1)	1748	1.06 (t, 3H, J = 7, $NCH_2C\underline{H}_3$), 1.32 (t, 3H, J = 7, $CH_2C\underline{H}_3$), 2.96 (q, 2H, J = 7, $C\underline{H}_2CH_3$), 3.98 (q, 2H, J = 7, $NC\underline{H}_2CH_3$), 7.51 (s, 5H_{arom}), 10.60 (s, 1H, NH)
5o	C	76	>185 (dec) (MeOH)	$C_{13}H_{18}BF_4N_3O$ (319.1)	1758	1.27 [d, 6H, J = 7, $NCH(C\underline{H}_3)_2$], 1.31 (t, 3H, J = 7, $CH_2C\underline{H}_3$), 2.97 (q, 2H, J = 7, $C\underline{H}_2CH_3$), 4.44 [sept, 1H, J = 7, $NC\underline{H}(CH_3)_2$], 7.55–7.85 (m, 6H, 5H_{arom} + NH)
5p	C	75	>185 (dec) (CH_3CN/TBME)	$C_{14}H_{16}BF_4N_3O$ (329.1)	1762	0.87–1.78 (m, 8H 2 × CH_2CH_2), 2.17–2.70 (m, 1H, CH), 3.08–3.51 (m, 1H, NCH), 7.10 (br s, 1H, NH), 7.47 (s, 5H_{arom})

[a] TBME = *tert*-Butyl methyl ether.

[b] Satisfactory microanalyses obtained: C ± 0.36, H ± 0.19, N ± 0.32, exceptions: **5m** C + 0.71, **5n** C + 0.45; **5d**, **k**, **l** were analysed as free bases: C ± 0.18, H ± 0.23, N ± 0.18.

[c] Solvent: CD_3CN for **5a**–**c**, **p**; DMSO-d_6 for **5d**–**o**.

Taking into account these facts, the 3,3-disubstituted 1-aryl-5-oxo-4,5-dihydro-3*H*-1,2,4-triazolium tetrafluoroborates **4** may be considered as zwitterionic isomer **6** of α-(arylazo)alkyl isocyanates **3** stabilized by protonation,[12] even if up to this day no spectroscopic or chemical proof for the existence of **6** can be furnished. The cyclic intermediate **6** is probably only a transition state in the reaction pathway of the rearrangement of **3**.

Virtually all α-(arylazo)alkyl isocyanates **3a–p** can also be rearranged to **7a–p** thermally, but colored products are formed. In the case of **3o**, the ^{1}H-NMR spectrum of the crude reaction mixture shows that the selectivity of the reaction is affected and a mixture of the two possible isomers are produced.

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 spectrometer in various solvents with TMS as an internal standard. 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.

All reagents are available commercially and were purchased from Fluka, Merck, or Aldrich and used without further purification. Solvents were distilled before use. Petroleum ether (40–60 °C) was used. 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.

5,5-Disubstituted 2-aryl-1,2,4-triazolidin-3-ones **2a–r** were prepared from arylhydrazones **1** and KNCO in AcOH according to literature.[7–9] Care must be taken concerning the synthesis and storage of 5-benzyl-5-methyl-2-phenyl-1,2,4-triazolidin-3-one (**2r**). This compound is sensitive to air and should always be handled under a N_2 atmosphere, since it is slowly oxidized in contact with air to yield 2,3-dihydro-5-methyl-2-phenyl-3*H*-1,2,4-triazol-3-one and benzaldehyde.

α-(Arylazo)alkyl isocyanates **3** were prepared by oxidative ring cleavage of 2-aryl-1,2,4-triazolidin-3-ones **2** according to literature.[9] Before the separation of the layers, the MnO_2 formed may be filtered with diatomaceous silica to prevent the formation of emulsions during the extraction process. If further purification of the product is necessary, it is best performed by short column chromatography on silica gel (10–15 cm, eluent: Et_2O/petroleum ether (40–60 °C), eluent ratio must be varied according to the product and the impurities). Bulb to bulb distillation *in vacuo* is possible with some of the products **3**, but at elevated temperatures spontaneous rearrangement to **7** may occur, therefore distillation of these compounds should be avoided. Compounds **3i,l,m,o,q,r** rearrange to **7i,l,m,o,q,r** even at r.t., so that the oxidation is best carried out in an ice bath.

3,3-Disubstituted 1-Aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium Tetrafluoroborates 4; General Procedure:

The appropriate α-(Arylazo)alkyl isocyanate **3** (10 mmol) is dissolved in Et_2O (75 mL), and the solution is cooled to 0 °C. A 50% aq HBF_4 (10 mL) is added dropwise within 10 min with stirring, whereupon the yellow crystalline product **4** (red in the case of **4m**) precipitates (crystallization of **4c** needs cooling to −40 °C). Stirring is continued for 5 min, the product is filtered, washed with a small quantity of ice cold Et_2O, and dried *in vacuo* over $CaCl_2$.

1,5-Disubstituted 2-Aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-one Tetrafluoroborates 5; General and Typical Procedures:

Method A, *for* **5a–d**: A solution of the appropriate 1-aryl-4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborate **4** (5 mmol) in CH_3CN (10 mL) is refluxed for 10–15 min (6 h for **4d**), during which time the initially bright yellow color fades. The solvent is removed under reduced pressure, and the crystalline residue is dissolved in a minimum quantity of CH_3CN. Precipitation is induced by careful addition of Et_2O, or better *t*-BuOMe, and the colorless crystalline product **5** is dried *in vacuo* over $CaCl_2$.

Method B, *for 1,5-dimethyl-1,2-dihydro-2-(4-nitrophenyl)-3H-1,2,4-triazol-3-one tetrafluoroborate* (**5e**): A suspension of **3e** (1.17 g, 5 mmol) in 50% aq HBF_4 (10 mL) is stirred at r.t., for 10 min. The nearly colorless suspension is heated at 90 °C for 10 min when it becomes homogeneous. This solution is filtered, cooled to r.t., diluted with Et_2O (100 mL) and cooled to 0 °C for 2–3 h. The colorless crystalline product **5e** is filtered and dried *in vacuo* ($CaCl_2$); yield: 1.15 g (71%).

Method C, for **5f–p**: To a stirred solution of the appropriate α-(arylazo)alkyl isocyanate **3** (5 mmol) in Et_2O (40 mL) at 0 °C is added dropwise 50% aq HBF_4 (5 mL) within 5 min. The mixture becomes only slightly turbid without formation of any crystalline precipitate of **4**. 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 the CH_3CN is removed under reduced pressure, and the colorless crystalline product **5** is precipitated by careful addition of Et_2O, or better *t*-BuOMe, filtered, and dried *in vacuo* ($CaCl_2$).

1,5-Disubstituted 2-Aryl-1,2-dihydro-3*H*-1,2,4-triazol-3-ones 7; General Procedure:

The α-(arylazo)alkyl isocyanates **3q,r** are synthesized starting from **2q,r** (10 mmol) at 0 °C following the general procedure above, but they rearrange to **7q,r** even at r.t., within minutes. After filtration of MnO_2 and separation of the layers, 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 at a bath temperature of 40 °C to give colorless solid **7q**, and in the case of **7r** a strongly impure dark red solid. The impurities are washed out with Et_2O, and the, now colorless products **7q,r** are recrystallized from MeOH or MeOH/Et_2O and dried *in vacuo* ($CaCl_2$).

7q; yield: 83%; mp 122–124 °C (MeOH/Et_2O, dec).

$C_{13}H_{17}N_3O$	calc.	C 67.51	H 7.41	N 18.17
(231.3)	found	67.57	7.48	17.97

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

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 1.37$ (s, 9H, NBu-*t*), 2.61 (s, 3H, CH_3), 7.20–7.40 (m, 5H_{arom}).

7r; yield: 64%; mp 127–128 °C (MeOH/Et_2O (Lit.[3] mp 142–144 °C).

IR (KBr): $\nu = 1664\ \mathrm{cm}^{-1}$ (C=O).

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 2.41$ (s, 3H, CH_3), 4.88 (s, 2H, CH_2), 6.70–7.50 (m, 10H_{arom}).

Support of this work by the "Fonds zur Förderung der wissenschaftlichen Forschung" through grant P 6804-CH (project leadership: H. Gstach) is gratefully acknowledged.

Received: January 11, 1990

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