Synthesis and alkylation reaction of 1-arylmethyleneamino- and 1-arylsulfonyl-5-hydroxy-1*H*-1,2,3-triazoles

Yury A. Rozin,[a] Elena A. Savel'eva,[a] Yury Yu. Morzherin,[a] Wim Dehaen,*[b] Suzanne Toppet,[b] Luc Van Meervelt[b] and Vasily A. Bakulev*[a]

[a] *The Urals State Technical University, 620002 Ekaterinburg, Russia. E-mail: VAB@htf.ustu.ru; Fax: +7 3432 420086*
[b] *Department of Chemistry, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

Received (in Cambridge, UK) 10th September 2001, Accepted 9th November 2001
First published as an Advance Article on the web 14th December 2001

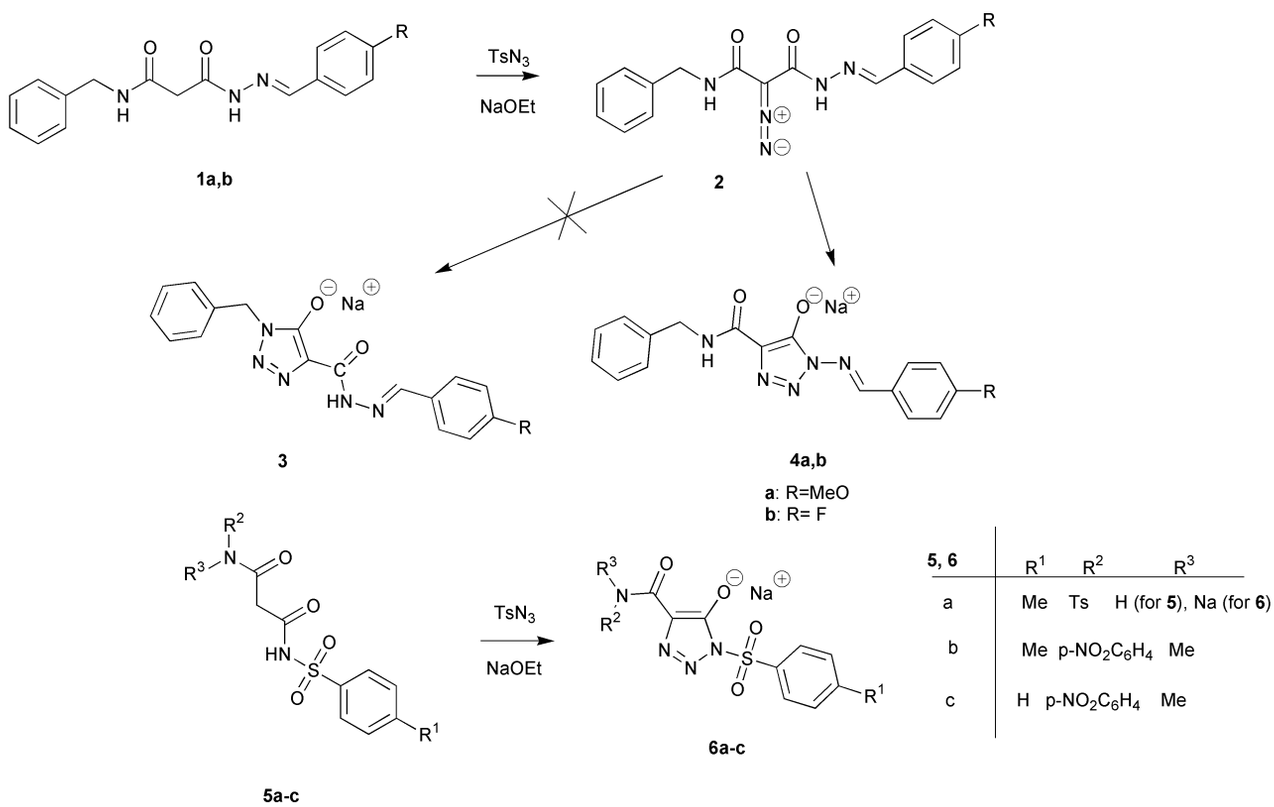
New derivatives of 1*H*-1,2,3-triazole **4**, **6**, **7** were prepared from malonic acid derivatives by a diazo group transfer reaction with *p*-tosyl azide. It was found that alkylation of sodium 1-aryl- and 1-arylmethyleneamino-1,2,3-triazol-5-olates **7**, **4** with methyl iodide, benzyl chloride or substituted phenacyl bromides results in 3-alkyltriazol-3-ium-5-olates **8**, **9** that are compounds of mesoionic structure. In contrast, alkylation of 1-arylsulfonyl-substituted triazoles **6** with methyl iodide leads to the 2-methyl-1,2-dihydro-1,2,3-triazol-5-ones **12**. Hydrolysis of azomethines **9** affords 1-aminotriazoles **10**, which in turn can be deaminated by nitrous acid or butyl nitrite to give 1-alkyl-4-hydroxytriazoles **11**.

1,2,3-Triazoles are well known as compounds exhibiting interesting chemical and biological properties and their chemistry has been well studied. On the other hand, 1-amino and 1-arylsulfonyl derivatives of this heterocycle have been less extensively studied. Only a few reactions for this type of compound have been previously reported.[1]

Recently we have developed a new synthetic access to 1-arylmethyleneamino-1,2,3-triazol-5-olates based on the diazo group transfer reaction of acetic acid derivatives bearing a hydrazide moiety, followed by subsequent cyclization of the intermediate diazo compounds.[2]

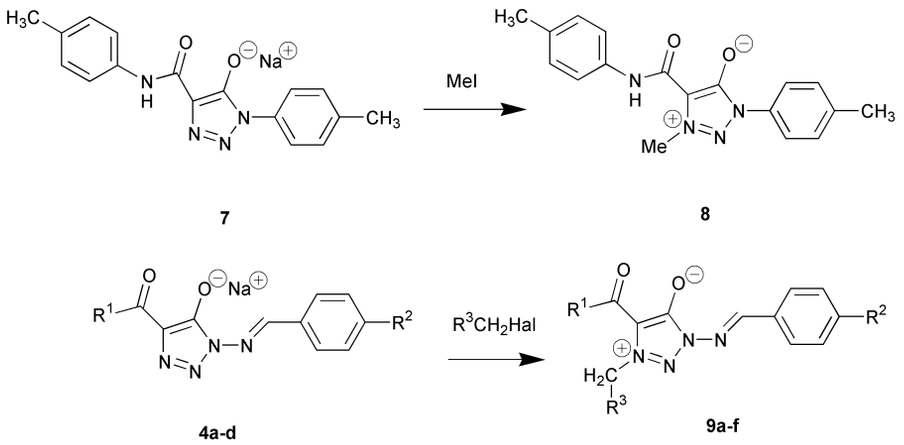
We now report the data on the diazo group transfer to α-(benzylcarbamoyl)acetohydrazides **1** and *N*-tosylmalonamide derivatives **5** and the alkylation reaction of 1-amino and 1-arylsulfonyl-1,2,3-triazole derivatives with methyl iodide, benzyl chloride and α-bromoacetophenones.

Reactions of benzyl amides **1a**,**b** with *p*-tosyl azide generate the intermediate diazo compounds **2**, which may cyclize involving either the amide or hydrazide moiety to form, respectively, triazoles **3** and **4** (Scheme 1). Our results show that the hydrazide group in compounds **2** is more reactive than the amide towards cyclization onto the diazo group. Thus, 1-amino-1,2,3-triazole



Scheme 1

DOI: 10.1039/b108202g



4	R^1	R^2
a	$PhCH_2NH$	MeO
b	$PhCH_2NH$	F
c	EtO	H
d	EtO	MeO

9	R^1	R^2	R^3
a	$PhCH_2NH$	MeO	H
b	$PhCH_2NH$	MeO	Ph
c	$PhCH_2NH$	F	p-$MeOC_6H_4CO$
d	EtO	H	H
e	EtO	MeO	Ph
f	EtO	H	p-BrC_6H_4CO

Scheme 2

derivatives **4a**,**b** (Table 1) were selectively prepared. The downfield shifts of the signals for the CH ylidene moiety in the ^{1}H NMR spectra (Tables 2, 3) of the reaction products **4a**,**b** in comparison with the starting hydrazones **1** are in agreement with the proposed structures. On the other hand, the signals of the methylene groups of compounds **4a**,**b** are similar to those of the starting compounds **1**, which is in contrast with structure **3**.

The *N*-arylsulfonylmalonamides **5** can also be involved in diazo group transfer reactions with tosyl azide to form sodium 1-arylsulfonyl-1,2,3-triazol-5-olates **6** in good yields. Most probably this reaction goes *via* intermediate diazoimidates. The latter spontaneously cyclize to the final products **6**.

It is known that alkylation of 1-substituted-5-hydroxy-1*H*-1,2,3-triazoles may give a mixture of *N*-2, *N*-3 and *O*-alkyl derivatives, with a preference for the 3-alkylated 1,2,3-triazoles.[1,3] Reactions of sodium 1-alkyl (or aryl)-1*H*-1,2,3-triazol-5-olates with methyl iodide occur more selectively to afford 3-alkylated 1,2,3-triazoles of mesoionic structure.[1,3] On the other hand, alkylation of 5-(benzoyloxy)-1*H*-1,2,3-triazoles with diazomethane can give *N*-2 substituted compounds.[4] Thus, the direction for the alkylation reaction depends on the nature of the substituents on the triazole ring. So far there have been no data reported in the literature on the alkylation of 1-amino- and 1-arylsulfonyl-1,2,3-triazoles. We wished to investigate whether the introduction of substituents containing heteroatoms at position 1 of the ring would change the reactivity of the 1,2,3-triazole moiety.

First we studied the alkylation of 1-arylmethyleneamino-1,2,3-triazol-5-olates **4**. For the purpose of comparison we also studied the methylation of 1-(*p*-tolyl)-1,2,3-triazol-5-olate **7** with methyl iodide (Scheme 2). The methylation of 1-(*p*-tolyl)-1,2,3-triazoles **7**, prepared from the bis-tolylamide of malonic acid by a diazo group transfer reaction similar to that of triazoles **4** and **6**, and 1-arylmethyleneamino-1,2,3-triazoles **4** was carried out with methyl iodide. This gave compounds of mesoionic structure **8** and **9**, respectively, with the alkyl group attached to N-3 of the ring. IR spectra of these compounds do not exhibit stretching bands in the range of 2100–2200 cm^{-1}, therefore diazo compounds, which can be formed under these conditions, were ruled out. The ^{1}H NMR spectra of the methylated products **8** and **9a**,**d** included signals of CH_3 groups at *ca.* 4.3 ppm (see Tables 2, 3 and the Experimental section). These values are similar to the data (3.80–4.07 ppm) published for similar compounds[5] and are shifted slightly downfield because of the presence of the electron-accepting carbonyl group at position 4 of the ring. These data are different from the structure with alkyl groups attached to N-2, because in this case the triazole ring loses its aromaticity and one should expect the appearance of the methyl group proton signals in such compounds at 3.2–3.5 ppm.

The data of the ^{13}C NMR spectra for compound **8** are also in a good agreement with a mesoionic structure. They include signals at 40.8, 112.5 and 156.8 ppm corresponding to the carbon atom of the NMe group (not MeO, for which one expect signal shifted downfield) and to C-4 and C-5 of the ring, respectively (Table 4). In addition, there is splitting of the C-4 signal (q, ^3J = 1.6 Hz) due to coupling with the protons of the methyl group attached to the position 3 of the ring. Indeed, the data for signals of Me group in both proton and carbon NMR spectra could be diagnostic in the analysis of the structure of the alkylation products.

The alkylation of **4** with benzyl chloride and phenacyl bromides followed a similar course, occurring at the position 3 of the ring, to form compounds **9b**,**c**,**e**,**f**. The ^{1}H NMR spectra (Tables 2 and 3) confirmed the presence of the aryl rings and the methylene groups of the benzyl (δ_H *ca.* 5.9 ppm) or phenacyl (δ_H *ca* 6.3 ppm) moieties. These signals are shifted downfield in comparison with 4-alkyl derivatives of similar structure,[5] again due to the effect of the carbonyl group in compounds **9**. The structure of **9** is also confirmed by the ^{13}C NMR spectra of their derivatives **10a**–**c** and **11a** (see below).

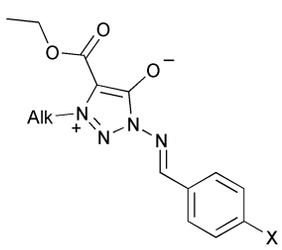
We have found that treatment of imines **9d**–**f** either with an excess of hydrazine or with aqueous acetic acid (Scheme 3) leads to mesoionic 1-amino-1,2,3-triazoles **10a**–**c** with a free amino group. In their turn, 1-amino-1,2,3-triazoles **10a**–**c**, after treatment either with sodium nitrite in hydrochloric acid or with butyl nitrite in acetic acid, afford 1-alkyl-4-hydroxy-1,2,3-triazoles **11a**–**c**. The ^{1}H and ^{13}C NMR spectra of **10a**–**c** (Table 4 and Experimental section) confirm the proposed structures (and thus also the structure of **9**) since the shift values of the triazole ring carbon atoms (106.5–109.8 ppm for C-4 and

Table 1 Physical and analytical data

Compound	Yield (%)	Mp/°C	Molecular formula	Analysis (%), Calcd./Found C	H	N
4a	52	>250	$C_{18}H_{16}N_5NaO_3$	57.91	4.32	18.76
				57.81	4.20	18.81
4b	82	275 decomp.	$C_{17}H_{13}FN_5NaO_2$	56.51	3.63	19.38
				56.02	3.37	19.12
6a	63	>250 decomp.	$C_{17}H_{14}N_4NaO_6S_2{\cdot}2H_2O$	39.54	3.51	10.85
				39.87	3.17	10.15
6b	68	>250 decomp.	$C_{17}H_{14}N_5NaO_6S{\cdot}2H_2O$	42.95	3.82	14.73
				42.88	3.64	14.32
6c	62	>250 decomp.	$C_{16}H_{12}N_5NaO_6S{\cdot}2H_2O$	41.65	3.50	15.18
				41.97	3.45	15.00
7	76	>300	$C_{17}H_{15}N_4NaO_2$	61.81	4.58	16.96
				61.69	4.63	17.00
8	80	212–214	$C_{18}H_{18}N_4O_2$	67.07	5.63	17.38
				66.88	5.76	17.69
9a	78	203–206	$C_{19}H_{19}N_5O_3$	62.46	5.24	19.17
				62.04	5.22	19.54
9b	64	116–118	$C_{25}H_{23}N_5O_3$	68.01	5.25	15.86
				67.79	5.21	16.05
9c	75	107–109	$C_{26}H_{22}FN_5O_4$	64.06	4.55	14.37
				64.28	4.67	14.11
9d	69	155–157	$C_{13}H_{14}N_4O_3$	56.93	5.14	20.43
				56.73	5.10	20.15
9e	57	160–163	$C_{20}H_{20}N_4O_4$	63.15	5.30	14.73
				62.78	5.42	14.56
9f	72	215–217	$C_{20}H_{17}BrN_4O_4$	52.53	3.75	12.25
				52.69	3.79	12.28
10a	61–76	169–171	$C_6H_{10}N_4O_3$	38.71	5.41	30.09
				38.75	5.55	30.40
10b	50	191–193	$C_{12}H_{14}N_4O_3$	54.96	5.38	21.36
				54.67	5.44	21.83
10c	62	243–245	$C_{13}H_{13}BrN_4O_4$	42.29	3.55	15.18
				42.18	3.42	14.97
11a	71	149–151	$C_6H_9N_3O_3$	42.10	5.30	24.55
				42.24	5.48	25.07
11b	71	156–158	$C_{12}H_{13}N_3O_3$	58.29	5.30	16.99
				58.02	5.18	17.13
11c	85	195–201	$C_{13}H_{12}BrN_3O_4$	44.09	3.42	11.86
				44.10	3.41	12.17
12a	59	132–134	$C_{19}H_{20}N_4O_6S_2$	49.13	4.34	12.06
				49.28	4.17	12.06
12b	71	197–198	$C_{18}H_{17}N_5O_6S{\cdot}H_2O$	48.10	4.26	15.58
				47.85	4.03	15.38
12c	58	126–128	$C_{17}H_{15}N_5O_6S{\cdot}H_2O$	46.89	7.36[a]	16.08
				47.16	7.49[a]	16.12

[a] Sulfur analysis instead of hydrogen.

Table 2 ^{1}H NMR chemical shifts



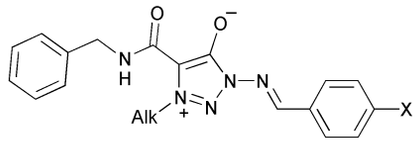
Compd.	N=C*H* s	CH_3CH_2 q	CH_3CH_2 t	Alk[a] s	ArH	MeO s
9d	9.62	4.29	1.29	4.23	7.90, 7.55	
9e	9.55	4.24	1.23	5.86	7.86, 7.09, 7.37	3.85
9f	9.71	4.15	1.14	6.34	8.02, 7.86, 7.59, 7.94	

[a] CH_3 or CH_2.

153.3–160.1 ppm for C-5) are close to those for similar compounds **B**[6] (Table 4) and are different from compounds **A**[6] and **C**. Furthermore, there is broadening ($\omega_{½}$ = 4.5 Hz) of the C-4 peak for **10a** and splitting of the C-5 peak for **11a** (q, ^3J = 1.5 Hz) because of spin–spin coupling with the 3-CH_3N^+ group.

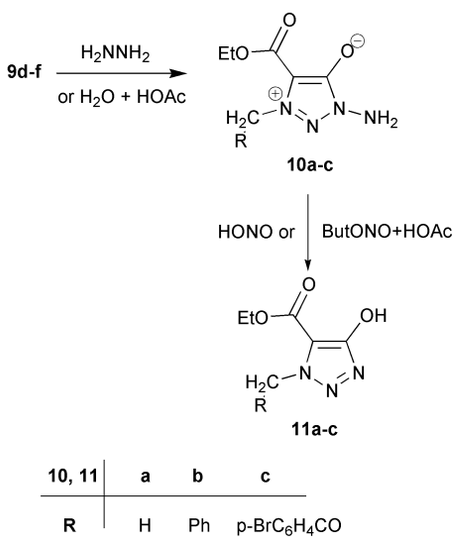
The reaction sequence **1** ⟶ **4** ⟶ **9** ⟶ **10** ⟶ **11** represents a new strategy for the preparation of 1-alkyl-4-hydroxy-1,2,3-triazoles. Thus, we have shown that alkylation of 1-aryl- and

Table 3 ^{1}H NMR chemical shifts

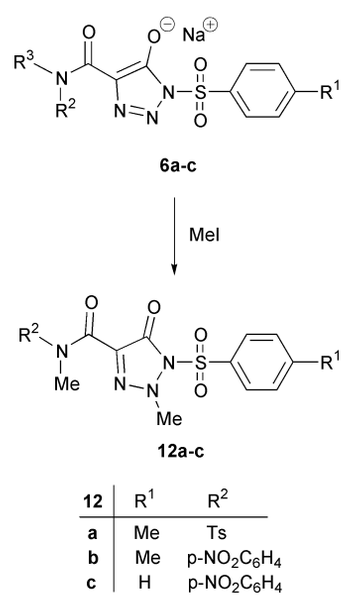


compd.	N=CH s	$PhCH_2$ d	NH	Alk[a]	$C_6H_5CH_2$ m	ArH	MeO s
9a	9.44	4.53	8.60	4.30	7.33	7.10 7.87	3.85
9b	9.49	4.54	8.68	5.99	7.46–7.26	7.86 7.09	3.84
9c	9.64	4.45	8.49	6.30	7.32	*ca.* 8.5, 7.4, 7.1	3.88

[a] CH_3 or CH_2.



Scheme 3



Scheme 4

1-arylmethyleneamino-1,2,3-triazoles takes place at position 3 of the 1,2,3-triazole ring to form the corresponding mesoionic 3-alkyl-1,2,3-triazol-3-ium-5-olates **8**, **9**.

We envisaged that the introduction of an electron-withdrawing arylsulfonyl group at position 1 of the triazole ring might change the direction of the alkylation reaction. Indeed, methylation of sodium salts of 1-arylsulfonyl-1,2,3-triazoles **6a**–**c** with methyl iodide took place exclusively at position 2 of the ring to form 1-arylsulfonyl-2-methyl-1,2-dihydro-1,2,3-triazol-5-ones **12a**–**c** in good yields (Scheme 4). The ^{1}H NMR spectra of these compounds, in comparison with the starting materials, contain new three-proton signals at 3.14–3.19 ppm. These values are very close to those reported for the methyl group in 2-methyl-1,2-dihydro-1,2,3-triazol-5-ones (3.22–3.53 ppm) and are different from the values for the methyl group attached to the ring N-3 (3.75–4.09 ppm) of 1,3-disubstituted-1*H*-1,2,3-triazolium-5-olates and the 5-methoxy group (3.75–4.02 ppm) of 1,4-disubstituted-5-methoxy-1*H*-1,2,3-triazoles studied earlier.[7] Alkylation of triazole **6a** occurs at both N-2 and the nitrogen of the tosylamide group to afford **12a** of which the ^{1}H NMR spectrum includes a signal corresponding to two *N*-methyl groups at 3.14 ppm.

The change of the direction for the alkylation reaction after the replacement of the imino function by an arylsulfonyl moiety can be rationalized by the displacement of the π-electrons of the heteroaromatic ring to N-2 when a strong electron-withdrawing group is placed at position 1. This is in accordance with the well known upfield shift of α-carbon atom signals in NMR spectra after introduction of an electron acceptor at the nitrogen atom of an aromatic heterocycle.

Experimental

The NMR spectra of all substances were recorded for DMSO-d_6 solutions either on a Bruker WM-250 (^{1}H NMR) or Bruker WM-400 NMR spectrometer (^{13}C NMR at 100 MHz), with *J*-values given in Hz. IR spectra were run on a UR-20 spectrometer for KBr pellets.

The sodium salts of benzylamides of 1-arylmethylenamino-5-hydroxy-1*H*-1,2,3-triazole-4-carboxylic acid (**4a**,**b**) were prepared by a diazo group transfer reaction with tosyl azide in the presence of sodium ethoxide similarly to a reported procedure.[2] The analogous esters **4c**,**d** were obtained earlier.[2]

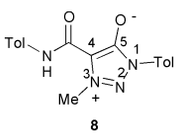
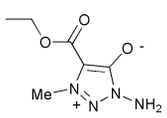
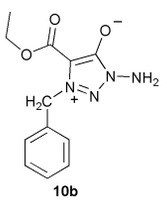
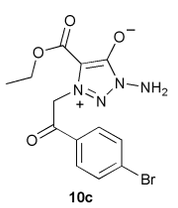
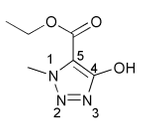
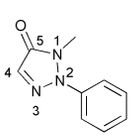
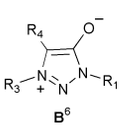
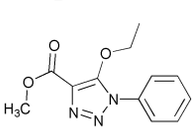
1-(*p*-Methoxyphenylmethyleneamino)-*N*′-benzyl-5-hydroxy-1*H*-1,2,3-triazole-4-carboxamide sodium salt (4a)

The α-(benzylcarbamoyl)acetylhydrazone **1a** (0.002 mol) was suspended in a solution of sodium ethoxide (0.136 g, 0.002 mol) in 12 ml of ethanol, and tosyl azide (0.40 g, 0.002 mol) was added in a dropwise manner at 0–5 °C. The reaction mixture was stirred for 2 h after which the precipitate **4a** was filtered off and dried. ^{1}H NMR: δ_H 9.29 (1H, s, N=CH), 8.47 (1H, t, J = 5.8 Hz, NH), 7.79 and 7.04 (each 2H, d, J = 8.7 Hz, HAr), 7.25–7.28 (5H, m, Ph), 4.47 (2H, d, J = 5.8 Hz, CH_2), 3.82 (3H, s, MeO).

1-(*p*-Fluorophenylmethyleneamino)-*N*′-benzyl-5-hydroxy-1*H*-1,2,3-triazole-4-carboxamide sodium salt (4b)

This was prepared similarly to **4a** from hydrazone **1b**. ^{1}H NMR:

Table 4 ^{13}C NMR (at 100 MHz) chemical shifts and coupling constants (*J*/Hz)

Structures of compounds[a]	Triazole				Ar			
	C-4	C-5	CO	3-Alk (Me or CH_2)	*i*	*o*	*m*	*p*
 **8**	112.5 q, ^3J = 1.6	156.8 s	155.4 d, ^2J = 1.3	40.8 s	135.2 132.2	119.2 121.0	129.7 129.3	138.2 132.9
 **10a**	107.5 br s, $\omega_{1/2}$ = 4.5 Hz	153.6 s	158.8 t, ^3J = 3.5	41.1 q ^1J = 146	—	—	—	—
 **10b**	106.7	153.6	158.6	55.9	134.5	128.7	128.4	127.7
 **10c**	107.0	153.3	158.7	60.0	132.9	132.1	130.2	128.6
 **11a**	160.1 s	109.8 q, ^3J = 1.5	158.5 t, ^3J = 7.0	38.5 q	—		—	—
 **A**[6]	130.1	160.1						
 **B**[6]	103.6–115.8	154.1–159.3						
 **C**	119.7	155.5						

[a] The values for model compounds A–C were calculated by the L′abbé method[9] or obtained from literature data.[10]

δ_H 9.36 (1H, s, N=CH), 8.45 (1H, t, *J* = 6.1 Hz, NH), 7.95–7.86 (2H, m, ArH), 7.37–7.18 (7H, m, ArH), 4.47 (2H, d, *J* = 6.1 Hz, CH_2).

Sodium 1-(*p*-tolyl)-4-(*p*-tolylcarbamoyl)-1*H*-1,2,3-triazol-5-olate (7)

This was prepared similarly to a reported procedure.[8] Yield 76%, mp >300 °C; ^1H NMR: δ_H 10.58 (1H, s, NH), 7.94 and 7.23 (4H, each d, *J* = 8.4 Hz, HAr), 7.51 and 7.08 (4H, each d, *J* = 8.2 Hz, HAr), 2.29 and 2.25 (each 3H, s, Me).

General procedure for the alkylation of sodium triazol-5-olates 4, 7

A solution of 10 mmol of the sodium salt **4** (or **7**) and 1.56 g (0.65 ml, 11 mmol) of CH_3I in 7.5 ml of DMF was kept at room temperature for 48 h, then heated at 50 °C for 1 h, and the product was precipitated with 50 ml of water. After 1 h the solid **9** (or **8**) was filtered off, washed with water, dried at 50–70 °C and crystallized from ethanol and then from toluene.

Benzylation of sodium triazol-5-olates **4** was carried out as described above. The sodium salts were heated in DMF with an equivalent amount of benzyl chloride for 15 h at 70–80 °C.

The reaction of sodium triazol-5-olates **4** with substituted α-bromoacetophenones was carried out by the general method for 2–3 h at 70–80 °C. Characteristics of **8** and **9** can be found in Tables 1–4.

1-Amino-3-methyl-4-ethoxycarbonyl-1*H*-1,2,3-triazol-3-ium-5-olate (10a)

Method A. A mixture of azomethine **9d** (1.1 g, 4 mmol), and 0.14 g (4.4 mmol) 100% H_2NNH_2 was refluxed in 20 ml of ethanol for 3 h and evaporated to dryness. The residue was washed with diethyl ether and crystallized from ethanol. Yield 83%. ^{1}H NMR: δ_H 6.16 (2H, s, NH_2), 4.24 (2H, q, J = 7.0 Hz, CH_3CH_2), 4.10 (3H, s, MeN^+), 1.26 (3H, t, J = 7.0 Hz, CH_3CH_2).

Method B. Azomethine **9d** (0.82 g, 3 mmol) was refluxed in 220 ml of 10% HOAc for 3–5 h with azeotropic removal of benzaldehyde. After cooling and filtration, the liquid was evaporated under vacuum to dryness. The residue was recrystallized from ethanol. Yield of **10a** 61%.

1-Amino-3-benzyl-4-ethoxycarbonyl-1*H*-1,2,3-triazol-3-ium-5-olate (10b)

This was prepared by method B from azomethine **9e**. ^{1}H NMR: δ_H 7.32–7.36 (5H, m, Ph), 6.24 (2H, s, NH_2), 5.75 (2H, s, $PhCH_2$), 4.21 (2H, q, J = 7.1 Hz, CH_3CH_2), 1.20 (3H, t, J = 7.1 Hz, CH_3). ^{13}C NMR: see Table 4.

1-Amino-3-(4-bromobenzoylmethyl)-4-ethoxycarbonyl-1*H*-1,2,3-triazol-3-ium-5-olate (10c)

This was prepared by method B from **9f**. ^{1}H NMR: δ_H 7.98 and 7.83 (each 2H, d, J = 7.8 Hz, HAr), 6.35 (2H, s, NH_2), 6.17 [2H, s, $C(O)CH_2$], 4.10 (2H, q, J = 7.1 Hz, CH_3CH_2), 1.10 (2H, t, J = 7.1 Hz, CH_3CH_2). ^{13}C NMR: see Table 4.

1-Methyl-4-hydroxy-5-ethoxycarbonyl-1*H*-1,2,3-triazole (11a)

To a solution of 0.5 g (2.7 mmol) of the amine **10a** in 10 ml water and 0.5 ml (5.4 mmol) HCl (conc.) was added in a dropwise manner, at 0–5 °C, a solution of 0.2 g (3.0 mol) $NaNO_2$ in 5 ml of water and this was kept for 15 min at the same temperature. The resulting solid was filtered off and washed with water. ^{1}H NMR: δ_H 11.30 (1H, br s, OH), 4.28 (2H, q, J = 7.1 Hz, CH_2), 4.11 (3H, s, MeN), 1.29 (3H, t, J = 7.1 Hz, CH_3CH_2).

Deamination of compounds 10b,c: general procedure

To a solution (or suspension) of 0.4 mmol amine **10b** (or **10c**) in 1 ml HOAc and 1 ml EtOH at 0–5 °C was added with stirring *n*-butyl nitrite (45 mg, 0.44 mmol). The mixture was kept for 1 h at 0–5 °C and 1 h at room temperature and diluted with 20 ml of water. The solid **11b** (or **11c**) was filtered off and washed with water.

1-Benzyl-4-hydroxy-5-ethoxycarbonyl-1*H*-1,2,3-triazole (11b). ^{1}H NMR: δ_H 11.23 (1H, br s, OH), 7.35–7.19 (5H, m, Ph), 5.73 (2H, s, $PhCH_2$), 4.25 (2H, q, J = 7.2, CH_3CH_2), 1.27 (3H, t, J = 7.2, CH_3CH_2).

1-(*p*-Bromobenzoylmethyl)-4-hydroxy-5-ethoxycarbonyl-1*H*-1,2,3-triazole (11c). ^{1}H NMR: δ_H 11.23 (1H, br s, OH), 8.00 and 7.74 (4H, 2d, J = 8.5 Hz, C_6H_4), 6.10 (2H, s, $COCH_2$), 4.18 (2H, q, J = 7.1, CH_3CH_2), 1.21 (3H, t, J = 7.1, CH_3CH_2).

1,*N*′-Di-(*p*-tosyl)-5-hydroxy-1*H*-1,2,3-triazole-4-carboxamide disodium salt (6a)

This was prepared from *N,N*′-di(*p*-tosyl)malonamide as for **4** using 2 equivalents of NaOEt. ^{1}H NMR: δ_H 7.85, 7.70, 7.29 and 7.22 (each 2H, d, HAr), 2.36 (3H, s, Me), 2.24 (3H, s, Me).

1-(*p*-Tosyl)-*N*′-methyl-*N*′-(*p*-nitrophenyl)-5-hydroxy-1*H*-1,2,3-triazole-4-carboxamide sodium salt (6b)

^{1}H NMR: δ 8.08, 7.67, 7.53, 7.23 (each 2H, d, HAr), 3.22 (3H, s, NMe), 2.36 (3H, s, $ArCH_3$).

1-Phenylsulfonyl-*N*′-methyl-*N*′-(*p*-nitrophenyl)-5-hydroxy-1*H*-1,2,3-triazole-4-carboxamide sodium salt (6c)

^{1}H NMR: δ 8.08 (2H, d, HAr), 7.60–7.70 (2H, m, Ph), 7.54 (2H, d, HAr), 7.30–7.40 (3H, m, Ph), 3.22 (3H, s, NCH_3).

1,*N*′-Di-(*p*-tosyl)-2,*N*′-dimethyl-5-oxo-1,2-dihydro-1,2,3-triazole-4-carboxamide (12a)

This was prepared by alkylation of **6a** with 2 equivalents of MeI. ^{1}H NMR: δ 7.75 and 7.42 (each 4H, d, HAr), 3.14 (6H, s, 2-Me and SO_2NMe), 2.39 (6H, s, MeC_6H_4).

1-(*p*-Tosyl)-2,*N*′-dimethyl-*N*′-(*p*-nitrophenyl)-5-oxo-1,2-dihydro-1,2,3-triazole-4-carboxamide (12b)

^{1}H NMR: δ 8.21 and 7.58 (each 2H, d, J = 9.0 Hz, $O_2NC_6H_4$), 7.76 and 7.42 (each 2H, d, J = 7.9 Hz, $SO_2C_6H_4$), 3.25 (3H, s, NMe), 3.15 (3H, s, 2-Me), 2.40 (3H, s, MeAr).

1-Phenylsulfonyl-2,*N*′-dimethyl-*N*′-(*p*-nitrophenyl)-5-oxo-1,2-dihydro-1,2,3-triazole-4-carboxamide (12c)

^{1}H NMR: δ 8.23 (2H, d, J = 9.2 Hz, HAr), 7.93–7.50 (7H, m, HAr), 3.26 (3H, s, MeN), 3.19 (3H, s, 2-Me).

References

1 J. A. Montgomery, *Triazoles: 1, 2, 3*, John Wiley & Sons, Chichester, 1980.
2 Yu. A. Rozin, E. A. Vorob'eva, Yu. Yu. Morzherin, A. S. Yakimov, W. Dehaen and V. A. Bakulev, *Mendeleev Commun.*, 1998, 240.
3 M. Begtrup, K. Hansen and C. Pedersen, *Acta Chem. Scand.*, 1967, **21**, 1234.
4 M. Begtrup, *Acta Chem. Scand.*, 1969, **23**, 2025.
5 M. Begtrup and C. Pedersen, *Acta Chem. Scand.*, 1967, **21**, 633.
6 M. Begtrup, *Acta Chem. Scand., Ser. B*, 1974, **28**, 61.
7 M. Begtrup and C. Pedersen, *Acta Chem. Scand.*, 1969, **23**, 1091.
8 V. A. Bakulev, Yu. Yu. Morzherin, A. T. Lebedev, E. F. Dankova, M. Yu. Kolobov and Yu. M. Shafran, *Bull. Soc. Chim. Belg.*, 1993, **102**, 493.
9 G. L'abbe, P. Delbeke, G. Van Essche, I. Luyten, K. Vercauteren and S. Toppet, *Bull. Soc. Chim. Belg.*, 1990, **99**, 1007.
10 R. W. Saalfrank, B. Weiss, V. Wirth, K. Peters and H. G. von Schering, *Z. Naturforsch., Teil B*, 1989, **44**, 587.