[3+2]-Cycloaddition of α-Diazo carbonyl Compounds with Arenediazonium Salts Catalyzed by Silver Nitrate Delivers 2,5-Disubstituted Tetrazoles

Sergey Chuprun1
Dmitry Dar’in
Grigory Kantin
Mikhail Krasavin*2

Saint Petersburg State University, Saint Petersburg 199034, Russian Federation
m.krasavin@spbu.ru

Received: 25.06.2019
Accepted after revision: 22.07.2019
Published online: 12.08.2019

Abstract [3+2]-Cycloaddition of arenediazonium salts with diazo compounds (earlier exemplified only for trimethylsilyldiazomethane and 2,2,2-trifluorodiazoethane) has been developed to include a wide range of readily available α-diazo carbonyl compounds. The resulting 2-aryl-5-acyl-2H-tetrazoles are of high value in medicinal chemistry.

Key words α-diazo carbonyl compounds, arenediazonium tosylates, tetrazoles, [3+2]-cycloaddition, silver nitrate

Tetrazoles are important representatives of the azole family of heterocycles with much utility in medicinal chemistry.1 In particular, 5-substituted 1H-tetrazoles are considered classical carboxylic acid isosteres.2 Disubstituted tetrazoles can be considered suitable amide bond replacements.3 Moreover, replacement of other five-membered nitrogen heterocyclic cores with tetrazole may significantly alter such molecular characteristics as total polar surface area and hydrophilicity, thus transitioning a compound’s properties (in particular, solubility) into a more favorable range.4 In order to be able to exercise such scaffold-hopping options with facility, there must be a versatile arsenal of synthetic methods to construct tetrazoles with a broad substituent variation. Methods reported to date include azide–nitrile and azide–isocyanide cycloadditions, dimerization of α-diazo carbonyl compounds, diazotization–cyclization of imidohydrazides or amidines, cyclocondensation of acyl hydrazides with arenediazonium salts, and cyclization of amides or imidoyl compounds with azides.5 A novel approach to constructing 2-aryltetrazoles was presented in 2015/2016 by Ma5 and Kamenecka6 and their coworkers. It involves silver-catalyzed cycloaddition of arenediazonium salts with 2,2,2-trifluorodiazoethane (CF3CHN2)7 and trimethylsilyldiazomethane (Me3SiCHN2),8 respectively (Scheme 1). While the method displayed a broad scope with respect to the aromatic groups at N6, the substitution at position 5 attainable by this approach has so far been limited to either a trifluoromethyl group (in compounds 1) or hydrogen (in compounds 2). It is worth noting that while preparation of compounds 1 was achieved with a catalytic amount of the silver salt, more than a stoichiometric amount of the latter was required to prepare compounds 2. We thought it surprising this cycloaddition-based entry into tetrazoles has not been explored further to include other diazo compounds, which would dramatically broaden the range of substituents on the tetrazole carbon atom. Considering, in particular, the diversity of α-diazo ketones available, the resulting 2-aryl-5-acyltetrazoles 3 (EWG = RC(O)) would be a very valuable chemotype to access (Scheme 1). Such cores have been utilized in the design of mGluR5 receptor modulators,9 fatty acid amide hydrolase inhibitors,10 antiviral compounds,11 and compounds endowed with hypoglycemic activity.12 Thus, we became interested in the opportunity to fill the above-mentioned void in synthetic methodology toward 2,5-disubstituted tetrazoles. Herein, we present the results of our investigation in this regard.

For the initial optimization studies, we selected commercially available benzenediazonium tosylate (4a) and 2-diazo-4′-methylacetophenone (5a). Our preference for the tosylate counterion was motivated by the recently reported convenient preparation and use of arenediazonium tosylates.13 Not only are they more stable toward chemical decomposition and explosion compared to conventionally used tetrafluoroborates, they are more cleanly prepared by diazotization of the respective anilines in the presence of p-toluenesulfonic acid in a variety of polar organic solvents, and even water.14 As the silver catalyst, we initially selected the readily available silver nitrate. The initial testing of the...
conditions described by Ma and co-workers (employing a twofold excess of the diazo compound relative to the diazonium salt) gave, gratifyingly, a 48% yield of the anticipated product 3a (Table 1, entry 1). The yield of 3a was improved to 66% by altering the reagent ratio and doubling the amount of the catalyst (Table 1, entry 4).

Having identified the optimal reagent and catalyst ratio, we screened for a possible better solvent, base or catalyst (Table 2). The only improvement, however, that we were able to achieve was the replacement of the base with equally workable (yet significantly less expensive and easier to dose) DABCO. THF/DMF mixture and silver nitrate were only confirmed to be the best catalysts for the transformation.

With the optimized reaction conditions at hand, we proceeded to investigate the scope of the tetrazole synthesis for a range of substituted arenediazonium tosylates (4a–k, prepared by diazotization of the respective anilines) and (hetero)aromatic (5a–g, 5i–k, 5n–q) and aliphatic (5h) diazo ketones, as well as diazo acetamides (5l, 5m), all of which are commercially available and can be conveniently prepared by the literature protocols (Figure 1).
particularly sensitive to substituent effects in the diazonium portion. However, the yields were markedly lower for \( \alpha \)-diazo acetamides (cf. 3r, 3s, 3x, 3y) compared to diazo ketones. Reassuringly, the yields for aromatic and heteroaromatic ketones were comparable, thus allowing access to intriguing combinations of three different aromatic motifs in a single molecule (e.g., benzene/tetrazole/pyridine in 3o).

To conclude, we have described a novel variant of the [3+2]-cycloaddition of arenediazonium tosylates with structurally diverse \( \alpha \)-diazocarbonyl compounds which employs the readily available silver nitrate as a catalyst and significantly expands the range of druglike tetrazoles accessible from a broader range of reagents than has been reported to date. We are in the process of investigating other diazo compounds as partners in these reactions and will report the results in due course.
All commercial reagents and solvents were used without further purification, unless otherwise noted. Diazacarbonyl compounds 5 were prepared according to the known methods. Analytical TLC was carried out on UV-254 silica gel plates using appropriate eluents. Compounds were visualized with short-wavelength UV light. NMR spectroscopic data were recorded with a 400 MHz spectrometer (400.13 MHz for 1H and 100.61 MHz for 13C) on solutions in CDCl3 and in DMSO-d6 and were referenced to residual solvent proton signals (δH = 7.26 and 2.50, respectively) and solvent carbon signals (δC = 77.0 and 39.5, respectively). All chemical shifts are reported in parts per million (ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (multiplet). Coupling constants (J) are quoted to the nearest 0.1 Hz. Melting points were determined in open capillary tubes with a Stuart SMP50 instrument. Mass spectra were recorded with a Bruker maXis HRMS-qTOF spectrometer (electrospray ionization mode).

### Diazonium Tosylates 4a–k; General Procedure

To a stirred ice-cooled solution/suspension of the corresponding aniline (15.0 mmol) in THF (5 mL), a solution of p-toluenesulfonic acid monohydrate (3.043 mg, 16.0 mmol) in glacial acetic acid (15 mL) was added. The resulting suspension was stirred for 5 min and t-BuONO (2.44 mL, 22.5 mmol) was added in one portion. The mixture was stirred at 0 °C for 20 min, then the ice bath was removed and stirring was continued for 50 min at ambient temperature. The resulting solution was poured into Et2O (150 mL) and the mixture was stirred for 30 min. The precipitate was collected by filtration, washed with Et2O (2 × 50 mL) and dried under reduced pressure at 30 °C. The obtained arenediazonium tosylates were used without any further purification.

### Benzenediazonium 4-Methylbenzenesulfonate (4a)

White solid; yield: 3.39 g (82%).

1H NMR (400 MHz, DMSO-d6): δ = 8.73–8.65 (m, 2 H), 8.30–8.21 (m, 1 H), 8.02–7.93 (m, 2 H), 7.50 (d, J = 8.1 Hz, 2 H), 7.13 (d, J = 7.8 Hz, 2 H), 2.30 (s, 3 H).

### 4-Fluorobenzenediazonium 4-Methylbenzenesulfonate (4b)

White solid; yield: 4.01 g (91%).

1H NMR (400 MHz, DMSO-d6): δ = 8.84 (dd, J = 9.4, 4.5 Hz, 2 H), 7.89 (dd, J = 9.3, 8.3 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 7.9 Hz, 2 H), 2.29 (s, 3 H).

### 4-Methoxybenzenediazonium 4-Methylbenzenesulfonate (4c)

Pale purple solid; yield: 4.15 g (86%).

1H NMR (400 MHz, DMSO-d6): δ = 8.64 (d, J = 9.4 Hz, 2 H), 7.52–7.44 (m, 4 H), 7.11 (d, J = 7.8 Hz, 2 H), 4.04 (s, 3 H), 2.29 (s, 3 H).

### 4-Nitrobenzenediazonium 4-Methylbenzenesulfonate (4d)

White solid; yield: 4.15 g (86%).

1H NMR (400 MHz, DMSO-d6): δ = 8.96 (d, J = 9.2 Hz, 2 H), 8.70 (d, J = 9.1 Hz, 2 H), 7.47 (d, J = 7.9 Hz, 2 H), 7.11 (d, J = 7.7 Hz, 2 H), 2.29 (s, 3 H).

### (Methoxycarbonyl)benzenediazonium 4-Methylbenzenesulfonate (4e)

White solid; yield: 4.81 g (96%).

1H NMR (400 MHz, DMSO-d6): δ = 8.82 (d, J = 9.0 Hz, 2 H), 8.42 (d, J = 9.0 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 7.9 Hz, 2 H), 3.96 (s, 3 H), 2.29 (s, 3 H).

### 2-Methoxybenzenediazonium 4-Methylbenzenesulfonate (4f)

Pale beige solid; yield: 3.86 g (84%).

1H NMR (400 MHz, DMSO-d6): δ = 8.55 (dd, J = 8.4, 1.6 Hz, 1 H), 8.22 (dd, J = 9.0, 7.5, 1.7 Hz, 1 H), 7.69 (d, J = 8.8 Hz, 1 H), 7.48 (d, J = 7.9 Hz, 2 H), 7.44 (dd, J = 8.3, 7.4, 0.7 Hz, 1 H), 7.12 (d, J = 7.8 Hz, 2 H), 4.18 (s, 3 H), 2.29 (s, 3 H).

### 4-(Trifluoromethyl)benzenediazonium 4-Methylbenzenesulfonate (4g)

White solid; yield: 4.9 g (95%).

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**Table 2** Solvent, Base and Catalyst Screening for the Preparation of 3a

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<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>Catalyst</th>
<th>Yield (%) of 3a</th>
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<td>AgNO3</td>
<td>56</td>
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<td>AgNO3</td>
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1H NMR (400 MHz, DMSO-d$_6$): δ = 8.93 (d, $J$ = 8.6 Hz, 2 H), 8.41 (d, $J$ = 8.8 Hz, 2 H), 7.48 (d, $J$ = 8.0 Hz, 2 H), 7.11 (d, $J$ = 7.9 Hz, 2 H), 2.29 (s, 3 H).

2-(4-Fluorobenzyl)-2H-tetrazol-5-yl)(p-toly)methanone (3b)
Prepared from 2-diazo-1-(p-toly)ethan-1-one (5a)$^{14}$ and 4-fluorobenzeneziodiazonium tosylate (4b).
Yellow solid; yield: 49 mg (58%); mp 122.7–123.9 °C.
1H NMR (400 MHz, CDCl$_3$): δ = 8.38–8.30 (m, 2 H), 8.30–8.21 (m, 2 H), 7.38 (d, $J$ = 8.0 Hz, 2 H), 7.35–7.27 (m, 2 H), 2.49 (s, 3 H).
13C NMR (101 MHz, CDCl$_3$): δ = 181.8, 164.8, 162.7, 162.3, 145.6, 133.0, 132.7, 130.9, 129.4, 122.5, 122.4, 117.1, 116.8, 21.9.
HRMS-ESI: m/z calcd for C$_6$H$_5$F$_2$N$_4$ONA [M + Na]: 305.0809; found: 305.0814.

(2-(4-Methoxybenzyl)-2H-tetrazol-5-yl)(p-toly)methanone (3c)
Prepared from 2-diazo-1-(p-toly)ethan-1-one (5a)$^{14}$ and 4-methoxybenzenediazonium tosylate (4c).
Orange solid; yield: 53 mg (60%); mp 107.0–109.0 °C.
1H NMR (400 MHz, CDCl$_3$): δ = 8.38–8.32 (m, 2 H), 8.16 (d, $J$ = 9.1 Hz, 2 H), 7.38 (d, $J$ = 8.0 Hz, 2 H), 7.09 (d, $J$ = 9.1 Hz, 2 H), 3.92 (s, 3 H), 2.49 (s, 3 H).
13C NMR (101 MHz, CDCl$_3$): δ = 182.0, 162.5, 161.2, 145.4, 133.1, 130.9, 129.9, 124.1, 114.8, 55.7, 21.9.
HRMS-ESI: m/z calcd for C$_6$H$_5$N$_4$O$_2$Na [M + Na]: 317.1009; found: 317.1014.

(2-(4-Nitrophenyl)-2H-tetrazol-5-yl)(p-toly)methanone (3d)
Prepared from 2-diazo-1-(p-toly)ethan-1-one (5a)$^{14}$ and 4-nitrobenzenediazonium tosylate (4d).
Orange solid; yield: 36 mg (39%); mp 147.4–148.2 °C (dec).
1H NMR (400 MHz, CDCl$_3$): δ = 8.51 (s, 4 H), 8.35–8.28 (m, 2 H), 7.40 (d, $J$ = 8.0 Hz, 2 H), 2.50 (s, 3 H).
13C NMR (101 MHz, CDCl$_3$): δ = 181.4, 163.1, 148.5, 146.0, 140.1, 132.7, 130.9, 129.6, 125.6, 121.0, 21.9.
HRMS-ESI: m/z calcd for C$_6$H$_5$N$_4$O$_2$Na [M + Na]: 332.0754; found: 332.0755.

Methyl 4-(5-(4-Methylbenzyl)-2H-tetrazol-2-yl)benzoate (3e)
Prepared from 2-diazo-1-(p-toly)ethan-1-one (5a)$^{14}$ and 4-methoxybenzenediazonium tosylate (4e).
Pale yellow solid; yield: 49 mg (51%); mp 160.8–161.6 °C (dec).
1H NMR (400 MHz, CDCl$_3$): δ = 8.46–8.28 (m, 6 H), 7.40 (d, $J$ = 8.1 Hz, 2 H), 4.01 (s, 3 H), 2.50 (s, 3 H).
13C NMR (101 MHz, CDCl$_3$): δ = 181.7, 165.6, 162.8, 145.8, 139.2, 132.9, 132.0, 131.4, 130.9, 129.5, 126.4, 52.6, 21.9.
HRMS-ESI: m/z calcd for C$_6$H$_5$N$_4$O$_2$Na [M + Na]: 345.0958; found: 345.0957.

(2-(2-Methoxyphenyl)-2H-tetrazol-5-yl)(p-toly)methanone (3f)
Prepared from 2-diazo-1-(p-toly)ethan-1-one (5a)$^{14}$ and 2-methoxybenzenediazonium tosylate (4f).
Light yellow solid; yield: 64 mg (73%); mp 97.6–98.9 °C.
1H NMR (400 MHz, CDCl$_3$): δ = 8.35 (d, $J$ = 8.3 Hz, 2 H), 7.66–7.51 (m, 2 H), 7.36 (d, $J$ = 8.1 Hz, 2 H), 7.21–7.08 (m, 2 H), 3.89 (s, 3 H), 2.46 (s, 3 H).
13C NMR (101 MHz, CDCl$_3$): δ = 182.0, 162.4, 153.6, 145.4, 133.1, 132.6, 130.9, 129.4, 127.0, 125.9, 120.7, 112.8, 56.3, 21.8.
(4-Methoxyphenyl)(2-phenyl-2H-tetrazol-5-yl)methanone (3b)
Prepared from 2-diazo-1-(4-methoxyphenyl)ethan-1-one (4b) and benzenediazonium tosylate (4a).
Beige solid; yield: 66 mg (78%); mp 94.6–97.2 °C.
1H NMR (400 MHz, CDCl3): δ = 8.65–8.44 (m, 2 H), 8.34–8.20 (m, 2 H), 7.70–7.56 (m, 3 H), 7.35–7.22 (m, 2 H).
13C NMR (101 MHz, CDCl3): δ = 130.5, 129.8, 128.6, 126.8, 120.3, 114.0, 55.6.

(2-Chlorophenyl)(2-phenyl-2H-tetrazol-5-yl)methanone (3k)
Prepared from 1-(2-chlorophenyl)-2-diazoethan-1-one (5d) and benzenediazonium tosylate (4a).
Light yellow solid; yield: 49 mg (57%); mp 104.3–105.8 °C.
1H NMR (400 MHz, CDCl3): δ = 8.26–8.16 (m, 2 H), 7.76–7.72 (m, 1 H), 7.67–7.52 (m, 5 H), 7.46 (dd, J = 7.7, 6.5, 2.2 Hz, 1 H).
13C NMR (101 MHz, CDCl3): δ = 183.8, 162.5, 136.3, 136.8, 133.0, 132.7, 130.70, 130.69, 129.9, 126.9, 120.4.

(3,4-Dimethoxyphenyl)(2-phenyl-2H-tetrazol-5-yl)methanone (3i)
Prepared from 2-diazo-1-(3,4-dimethoxyphenyl)ethan-1-one (4i) and benzenediazonium tosylate (4a).
Pale yellow solid; yield: 30 mg (43%); mp 117.0–118.2 °C (dec).
1H NMR (400 MHz, CDCl3): δ = 8.45–8.33 (m, 2 H), 8.32–8.19 (m, 2 H), 7.70–7.56 (m, 3 H), 7.45–7.33 (m, 1 H).
13C NMR (101 MHz, CDCl3): δ = 179.5, 162.0, 154.6 (dd, J = 259.7, 12.9 Hz), 150.4 (dd, J = 251.1, 13.0 Hz), 136.3, 132.3 (dd, J = 5.0, 3.6 Hz), 130.8, 130.0, 128.2 (dd, J = 7.7, 3.6 Hz), 120.4, 120.1 (dd, J = 18.9, 1.9 Hz), 117.8 (d, J = 17.9 Hz).
HRMS-ESI: m/z calcd for C15H14N4O3Na [M + Na]: 333.0958; found: 333.0961.

(2,2-Dimethyl-1-(2-phenyl-2H-tetrazol-5-yl)propan-1-one (3n)
Prepared from 1-diazo-3,3-dimethylbutan-2-one (4n) and benzenediazonium tosylate (4a).
Yellow solid; yield: 30 mg (43%); mp 117.0–118.2 °C (dec).
1H NMR (400 MHz, CDCl3): δ = 8.22 (d, J = 7.8 Hz, 2 H), 7.72–7.53 (m, 3 H), 1.52 (s, 9 H).
13C NMR (101 MHz, CDCl3): δ = 196.5, 161.3, 136.5, 130.5, 129.8, 120.3, 44.7, 26.5.
HRMS-ESI: m/z calcd for C12H14N4ONa [M + Na]: 253.1060; found: 253.1065.

(2-Phenyl-2H-tetrazol-5-yl)(pyridin-3-yl)methanone (3o)
Prepared from 2-diazo-1-(pyridin-3-yl)ethan-1-one (5o) and benzenediazonium tosylate (4a).
Pale orange solid; yield: 48 mg (64%); mp 74.6–77.6 °C.
1H NMR (400 MHz, CDCl3): δ = 9.66 (d, J = 2.2 Hz, 1 H), 8.90 (dd, J = 4.9, 1.7 Hz, 1 H), 8.72 (dt, J = 8.0, 2.0 Hz, 1 H), 8.32–8.16 (m, 2 H), 7.70–7.47 (m, 4 H).
13C NMR (101 MHz, CDCl3): δ = 181.0, 161.9, 154.3, 151.8, 137.8, 136.3, 131.2, 130.8, 129.9, 123.6, 120.4.
HRMS-ESI: m/z calcd for C13H18N4O [M + H]: 252.0880; found: 252.0886.
(2-Phenyl-2H-tetrazol-5-yl)(thiophen-2-yl)methanone (3p)
Prepared from 2-diazo-1-(thiophen-2-yl)ethan-1-one (5j)18 and benzenediazonium tosylate (4a).
Beige solid; yield: 20 mg (18%); mp 110.8–110.0 °C.

1H NMR (400 MHz, CDCl3): δ = 8.59 (dd, J = 3.9, 1.1 Hz, 1 H), 3.82–3.84 (m, 2 H), 7.89 (dd, J = 4.9, 1.2 Hz, 1 H), 7.68–7.56 (m, 3 H), 7.30 (dd, J = 5.0, 3.9 Hz, 1 H).
11C NMR (101 MHz, CDCl3): δ = 173.7, 162.1, 141.8, 137.1, 136.7, 136.4, 130.7, 129.9, 128.8, 120.4.

HRMS-ESI: m/z calcd for C15H12BrF3N5O2Na [M + Na]: 405.8554; found: 405.8551.

Naphthalen-1-yl(2-(2,3-dihydrobenzo[b]1,4]dioxin-6-yl)-2H-tetrazol-5-yl)methanone (3u)
Prepared from 2-diazo-1-(naphthalen-1-yl)ethan-1-one (5o)18 and 2,3-dihydrobenzo[b][1,4]dioxin-6-yl)benzenediazonium tosylate (4g).
Beige solid; yield: 110 mg (72%); mp 184.1–184.3 °C (dec).

1H NMR (400 MHz, CDCl3): δ = 8.68 (s, 1 H), 7.78–7.69 (m, 2 H), 7.56–7.45 (m, 2 H).
13C NMR (101 MHz, CDCl3): δ = 186.6, 140.7, 128.8, 128.7, 128.4, 124.9, 124.2, 123.0, 121.4, 120.7.

HRMS-ESI: m/z calcd for C31H11F8N5O3Na [M + Na]: 519.7505; found: 519.7507.
N,N-Diethyl-2-phenyl-2H-tetrazole-5-carboxamide (3y)

Prepared from 2-diazotetrazole-5-carboxamide (3y)23 and benzene-diazonium tosylate (4a).

Yellow oil; yield: 22 mg (30%).

1H NMR (400 MHz, CDCl3): δ = 8.22–8.11 (m, 2 H), 7.64–7.50 (m, 3 H), 3.97–3.86 (m, 4 H), 3.83 (dd, J = 5.9, 4.0 Hz, 2 H), 3.78 (dd, J = 5.6, 4.0 Hz, 2 H).

13C NMR (101 MHz, CDCl3): δ = 159.9, 157.4, 136.4, 130.4, 129.8, 120.2, 66.9, 66.7, 47.5, 43.0.


Funding Information

This research was supported by the Russian Science Foundation (project grant 19-75-30008).

Acknowledgment

We thank the Research Centre for Magnetic Resonance and the Center for Chemical Analysis and Materials Research of Saint Petersburg State University Research Park for obtaining the analytical data.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690159.

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(1) Address correspondence to this author at the Laboratory of Pharmaceutical Chemistry, Institute of Chemistry, Saint Petersburg State University, 26 Universitetskiy prospekt, Peterhof 198504, Russian Federation.

(2) Current address: Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St., Miami, FL 33199, USA.


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