

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

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Abstract
[3+2]-Cycloaddition of arenediazonium salts with diazo compounds (earlier exemplified only for trimethylsilyldiazomethane and 2,2,2-trifluorodiazoethane (CF₃CHN₂)) has been developed to include a wide range of readily available α-diazo carbonyl compounds. The resulting 2-aryl-5-acyltetrazoles 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. In particular, 5-substituted 1H-tetrazoles are considered classical carboxylic acid isosteres. Disubstituted tetrazoles can be considered suitable amide bond replacements. 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. 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–cyclocondensation of acyl hydrazides with arenediazonium salts, and cyclization of amides or imidoyl compounds with azides. A novel approach to constructing 2-aryltetrazoles was presented in 2015/2016 by Ma² and Kamenecka¹ and their co-workers. It involves silver-catalyzed cycloaddition of arenediazonium salts with 2,2,2-trifluorodiazoethane (CF₃CHN₂) and trimethylsilyldiazomethane (Me₃SiCHN₂) respectively (Scheme 1). While the method displayed a broad scope with respect to the aromatic groups at N², 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, fatty acid amide hydrolase inhibitors, antiviral compounds, and compounds endowed with hypoglycemic activity. 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. 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. As the silver catalyst, we initially selected the readily available silver nitrate. The initial testing of the
conditions described by Ma and co-workers\(^7\) (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 \(\alpha\)-diazo acetamides (\(5l, 5m\)), all of which are commercially available and can be conveniently prepared by the literature protocols (Figure 1).

![Scheme 1](image)

**Scheme 1** Cycloaddition-based routes from diazo compounds to tetrazoles reported previously and investigated in this work.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equiv of (4a)</th>
<th>Equiv of Cs(_2)CO(_3)</th>
<th>Equiv of AgNO(_3)</th>
<th>Yield (%) of (3a)</th>
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<td>0.05</td>
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<td>2</td>
<td>2.0</td>
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<td>5</td>
<td>1.1</td>
<td>1.2</td>
<td>0.1</td>
<td>59</td>
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</tbody>
</table>

**Table 1** Reagent Ratio Screening for the Preparation of \(3a\)

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 \(\alpha\)-diazo acetamides (\(5l, 5m\)), all of which are commercially available and can be conveniently prepared by the literature protocols (Figure 1).

As follows from the results presented in Scheme 2, the silver-catalyzed, DABCO-promoted cycloaddition of diazo compounds 5 with arenediazonium salts 4 (likely analogous, from the mechanistic perspective, to the earlier described cycloaddition of diazo compounds with isocyanides\(^15\)) gave moderate to good yields of the diversely substituted tetrazoles \(3a–y\). The reaction did not appear to be
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.
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%).

\( ^1 \text{H NMR (400 MHz, DMSO-} \text{d}_6 \text{): } \delta = 7.83–7.65 \text{ (m, 2 H), 8.30–8.21 (m, 1 H), 8.02–7.93 (m, 2 H), 7.50 (d, } J = 8.1 \text{ Hz, 2 H), 7.13 (d, } J = 7.8 \text{ Hz, 2 H), 2.30 (s, 3 H).} \)

4-Fluorobenzenediazonium 4-Methylbenzenesulfonate (4b)

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

\( ^1 \text{H NMR (400 MHz, DMSO-} \text{d}_6 \text{): } \delta = 8.84 \text{ (dd, } J = 9.4, 4.5 \text{ Hz, 2 H), 7.89 (dd, } J = 9.3, 8.3 \text{ Hz, 2 H), 7.49 (d, } J = 8.0 \text{ Hz, 2 H), 7.11 (d, } J = 7.9 \text{ Hz, 2 H), 2.29 (s, 3 H).} \)

4-Methoxybenzenediazonium 4-Methylbenzenesulfonate (4c)

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

\( ^1 \text{H NMR (400 MHz, DMSO-} \text{d}_6 \text{): } \delta = 8.64 (d, } J = 9.4 \text{ Hz, 2 H), 7.52–7.44 (m, 4 H), 7.11 (d, } J = 7.8 \text{ Hz, 2 H), 4.04 (s, 3 H), 2.29 (s, 3 H).} \)

4-Nitrobenzenediazonium 4-Methylbenzenesulfonate (4d)

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

\( ^1 \text{H NMR (400 MHz, DMSO-} \text{d}_6 \text{): } \delta = 8.96 (d, } J = 9.2 \text{ Hz, 2 H), 8.70 (d, } J = 9.1 \text{ Hz, 2 H), 7.47 (d, } J = 7.9 \text{ Hz, 2 H), 7.11 (d, } J = 7.7 \text{ Hz, 2 H), 2.29 (s, 3 H).} \)

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

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

\( ^1 \text{H NMR (400 MHz, DMSO-} \text{d}_6 \text{): } \delta = 8.82 (d, } J = 9.0 \text{ Hz, 2 H), 8.42 (d, } J = 9.0 \text{ Hz, 2 H), 7.48 (d, } J = 8.0 \text{ Hz, 2 H), 7.11 (d, } J = 7.9 \text{ Hz, 2 H), 3.96 (s, 3 H), 2.29 (s, 3 H).} \)

2-Methoxybenzenediazonium 4-Methylbenzenesulfonate (4f)

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

\( ^1 \text{H NMR (400 MHz, DMSO-} \text{d}_6 \text{): } \delta = 8.55 (dd, } J = 8.4, 1.6 \text{ Hz, 1 H), 8.22 (dd, } J = 9.0, 7.5, 1.7 \text{ Hz, 1 H), 7.69 (d, } J = 8.8 \text{ Hz, 1 H), 7.48 (d, } J = 7.9 \text{ Hz, 2 H), 7.44 (dd, } J = 8.3, 7.4, 0.7 \text{ Hz, 1 H), 7.12 (d, } J = 7.8 \text{ Hz, 2 H), 4.18 (s, 3 H), 2.29 (s, 3 H).} \)

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

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

All commercial reagents and solvents were used without further purification, unless otherwise noted. Diazocarbonyl 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 \(^1\)H and 100.61 MHz for \(^13\)C) on solutions in CDCl₃ and in DMSO-\(d₆\) and were referenced to residual solvent proton signals (δ₁H = 7.26 and 2.50, respectively) and solvent carbon signals (δ₁₃C = 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-ESIQTOF spectrometer (electrospray ionization mode).

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

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<th>Catalyst</th>
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(2-(4-Fluorophenyl)-2H-tetrazol-5-yl)(p-tolyl)methanone (3b)
Prepared from 2-diazo-1-(p-tolyl)ethan-1-one-1 (5a)\textsuperscript{14} and 4-fluorobenzediazonium tosylate (4b).

(2-(4-Methoxyphenyl)-2H-tetrazol-5-yl)(p-tolyl)methanone (3c)
Prepared from 2-diazo-1-(p-tolyl)ethan-1-one-1 (5a)\textsuperscript{14} and 4-methoxybenzediazonium tosylate (4c).

(2-(4-Nitrophenyl)-2H-tetrazol-5-yl)(p-tolyl)methanone (3d)
Prepared from 2-diazo-1-(p-tolyl)ethan-1-one-1 (5a)\textsuperscript{14} and 4-nitrobenzediazonium tosylate (4d).

Methyl 4-(5-(4-Methylbenzoyl)-2H-tetrazol-2-yl)benzoate (3e)
Prepared from 2-diazo-1-(p-tolyl)ethan-1-one-1 (5a)\textsuperscript{14} and 4-(methoxy carbonyl)benzediazonium tosylate (4e).

(2-(2-Methoxyphenyl)-2H-tetrazol-5-yl)(p-tolyl)methanone (3f)
Prepared from 2-diazo-1-(p-tolyl)ethan-1-one-1 (5a)\textsuperscript{14} and 2-methoxybenzediazonium tosylate (4f).
HRMS-ESI: m/z calcd for C_{16}H_{11}F_{3}N_{4}ONa [M + Na]: 355.0777; found: 355.0786.

1H NMR (400 MHz, CDCl_3): δ = 8.26–8.16 (m, 2 H), 7.76–7.72 (m, 1 H), 7.67–7.52 (m, 5 H), 7.46 (ddd, J = 7.7, 6.5, 2.2 Hz, 1 H).

13C NMR (101 MHz, CDCl_3): δ = 138.1, 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 C_{16}H_{14}N_{4}O_{2}Na [M + Na]: 317.1009; found: 307.0371.

(3,4-Dimethoxyphenyl)(2-phenyl-2H-tetrazol-5-yl)methanone (3i)
Prepared from 2-diazo-1-(3,4-dimethoxyphenyl)ethan-1-one (4a) and benzenediazonium tosylate (4a).
Pale yellow solid; yield: 53 mg (62%); mp 120.7–121.3 °C (dec).

HRMS-ESI: m/z calcd for C_{16}H_{14}N_{4}O_{2}Na [M + Na]: 333.0958; found: 333.0961.

(3,4-Difluorophenyl)(2-phenyl-2H-tetrazol-5-yl)methanone (3m)
Prepared from commercially available 2-diazo-1-(3,4-difluorophenyl)ethan-1-one (5g) and benzenediazonium tosylate (4a).
Beige solid; yield: 53 mg (62%); mp 106.0–107.5 °C.

HRMS-ESI: m/z calcd for C_{14}H_{9}ClN_{4}ONa [M + Na]: 307.0357; found: 307.0358.

2,2-Dimethyl-1-(2-phenyl-2H-tetrazol-5-yl)propan-1-one (3n)
Prepared from 1-diazo-3,3-dimethylbutan-2-one (5h) and benzenediazonium tosylate (4a).
Yellow solid; yield: 30 mg (43%); mp 117.0–118.2 °C (dec).

HRMS-ESI: m/z calcd for C_{12}H_{14}N_{4}O_{2}Na [M + Na]: 253.0558; found: 253.0559.

(2-Phenyl-2H-tetrazol-5-yl)(pyridin-3-yl)methanone (3o)
Prepared from 2-diazo-1-(pyridin-3-yl)ethan-1-one (5i) and benzenediazonium tosylate (4a).
Pale orange solid; yield: 48 mg (64%); mp 74.6–77.6 °C.

HRMS-ESI: m/z calcd for C_{12}H_{14}N_{4}O_{2}Na [M + Na]: 253.1060; found: 253.1065.
(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 benzzenediazonium tosylate (4a).
Beige solid; yield: 54 mg (70%); mp 109.5–110.8 °C.
1H NMR (400 MHz, CDCl3): δ = 8.88 (dd, J = 3.9, 1.1 Hz, 1 H), 8.32–8.24 (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).
13C NMR (101 MHz, CDCl3): δ = 137.3, 162.1, 141.8, 137.1, 136.7, 136.4, 130.7, 129.9, 128.8, 120.4.
HRMS-ESI: m/z calcd for C14H10N4O2Na [M + Na]: 334.0550; found: 334.0556.

Naphthalen-1-yl(2-(4-(trifluoromethyl)phenyl)-2H-tetrazol-5-yl)methanone (3u)
Prepared from 2-diazo-1-(naphthalen-1-yl)ethan-1-one (5o)18 and 4-(trifluoromethyl)benzenediazonium tosylate (4g).
Beige solid; yield: 91 mg (82%); mp 148.8–146.6 °C (dec).
1H NMR (400 MHz, CDCl3): δ = 8.75 (d, J = 8.5 Hz, 1 H), 8.41 (d, J = 8.5 Hz, 2 H), 8.28–8.12 (m, 2 H), 7.98 (dd, J = 8.1, 1.5 Hz, 1 H), 7.90 (d, J = 8.5 Hz, 2 H), 7.70 (dd, J = 8.5, 6.8, 1.5 Hz, 1 H), 7.66–7.59 (m, 2 H).
13C NMR (101 MHz, CDCl3): δ = 184.3, 163.9, 138.7, 134.7, 133.9, 132.7, 132.5, 123.4, 131.0, 128.8, 128.7, 127.2 (q, J = 3.7 Hz), 126.9, 125.4, 124.7, 142.3, 123.3 (q, J = 276.2 Hz), 120.6.
HRMS-ESI: m/z calcd for C26H16F3N3O4 [M + Na]: 439.0777; found: 439.0795.

Beno[d][1,3]dioxol-5-yl(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2H-tetrazol-5-yl)methanone (3v)
Prepared from 1-(benzo[d][1,3]dioxol-5-yl)-2-diazoethan-1-one (5p)18 and 2,3-dihydrobenzo[b][1,4]dioxin-6-diazotzoyl (4i).
Light orange solid; yield: 79 mg (75%); mp 151.2–151.9 °C (dec).
1H NMR (400 MHz, CDCl3): δ = 8.19 (dd, J = 8.3, 1.8 Hz, 1 H), 7.88 (d, J = 1.8 Hz, 1 H), 7.77 (d, J = 2.6 Hz, 1 H), 7.72 (dd, J = 8.8, 2.6 Hz, 1 H), 7.05 (d, J = 8.8 Hz, 1 H), 6.96 (d, J = 8.3 Hz, 1 H), 6.12 (s, 2 H), 4.36 (s, 2 H).
13C NMR (101 MHz, CDCl3): δ = 180.3, 162.4, 153.1, 148.3, 145.5, 144.2, 130.2, 130.1, 128.3, 118.2, 113.6, 110.0, 109.9, 108.2, 102.1, 64.5, 64.4.
HRMS-ESI: m/z calcd for C26H17F3N4O4 [M + Na]: 375.0700; found: 375.0728.

(4-(3-Nitrobenzoyl)-2H-tetrazol-2-yl)phenyl(piperidin-1-yl)methanone (3w)
Prepared from 2-diazo-1-(3-nitrophenyl)ethan-1-one (5q)18 and 4-(piperidin-1-ylcarbonyl)benzenediazonium tosylate (4j).
Yellow solid; yield: 82 mg (67%); mp 132.1–134.3 °C (dec).
1H NMR (400 MHz, CDCl3): δ = 9.36 (t, J = 2.0 Hz, 1 H), 8.81 (dt, J = 7.8, 1.4 Hz, 1 H), 8.57 (dd, J = 8.3, 2.1, 1.1 Hz, 1 H), 8.39–8.27 (m, 2 H), 7.83 (t, J = 8.0 Hz, 1 H), 7.73–7.65 (m, 2 H), 3.76 (br s, 2 H), 3.40 (br s, 2 H), 1.91–1.49 (m, 6 H).
13C NMR (101 MHz, CDCl3): δ = 179.9, 168.3, 161.8, 148.5, 139.2, 136.6, 136.5, 136.1, 130.1, 128.7, 128.5, 125.7, 120.5, 48.8, 43.3, 26.6, 25.6, 24.5.
HRMS-ESI: m/z calcd for C26H23N2O4 [M + H]: 407.1462; found: 407.1481.

Morpholin(2-phenyl-2H-tetrazol-5-yl)methanone (3x)
Prepared from 2-diazo-1-morpholinooetan-1-one (5l)23 and benzenediazonium tosylate (4a).
Beige solid; yield: 32 mg (41%); mp 88.5–89.6 °C.
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, 157.5, 136.5, 130.4, 129.8, 120.6, 66.9, 66.7, 47.5, 43.0.

HRMS-ESI: m/z calcd for C₁₂H₁₃N₅O₂Na [M + Na]: 282.0961; found: 282.0967.

**N,N-Diethyl-2-phenyl-2H-tetrazole-5-carboxamide (3y)**

Prepared from 2-diazo-N,N-diethylacetamide (5m) and benzene-diazonium tosylate (4a).

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

1H NMR (400 MHz, CDCl₃): δ = 8.23–8.16 (m, 2 H), 7.65–7.51 (m, 3 H), 3.60 (q, J = 7.1 Hz, 2 H), 7.1 Hz, 6 H).

13C NMR (101 MHz, CDCl₃): δ = 160.6, 158.5, 136.5, 130.2, 129.8, 120.1, 43.4, 40.9, 14.6, 12.7.

HRMS-ESI: m/z calcd for C₁₂H₁₃NONa [M + Na]: 268.1182; found: 268.1189.

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**Supporting Information**

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**References**

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