Reductive Removal of the Pivaloyl Protecting Group from Tetrazoles by a Naphthalene-Catalysed Lithiation Process

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Received: The date will be inserted once the manuscript is accepted.

Abstract: The reaction of different tetrazoles protected with a pivaloyl group, with an excess of lithium and a catalytic amount of naphthalene (8 mol%) led, after treatment with methanol, to the corresponding free tetrazoles through a reductive carbon-nitrogen bond cleavage. This methodology represents a reasonable alternative to other non-reductive protocols.

Keywords: tetrazoles, pivaloyl, lithium.

The pivaloyl group has been widely used in organic synthesis to protect alcohols, amines and thiols, due to its easy introduction, its stability under a variety of reaction conditions and its relatively easy removal to give the corresponding depivalated compounds.¹ Among the different methodologies reported to achieve the deacylation of protected alcohols and amines, we can find hydrolysis under basic or acidic conditions,² reduction with alkali metals in liquid ammonia,³ reductive cleavage using an arene-catalysed lithiation,⁴ reaction with hydride sources,⁵ electrolysis,⁶ and enzymatic methods.⁷

On the other hand, the tetrazole moiety is present in several biologically active compounds, such as sartans, which are pharmaceuticals that have proved to be efficient for the treatment of hypertension, kidney damage caused by diabetes and heart failure. Usually, the synthesis of sartans involves steps of protection and deprotection of the tetrazole ring.⁸ The effective protection caused by the high steric demand of the pivaloyl group, together with the ease of its introduction into and its removal from the nitrogen atom, are features that could make the pivaloyl group to become a very useful tool for the preparation of such an interesting family of drugs. Thus, the development of procedures that could remove the pivaloyl protecting group without affecting the tetrazole ring would be very interesting.⁸

In the last years our research group has been using an arene-catalysed lithiation to perform metallations under very mild reaction conditions.^{9–12} This lithiation methodology has been applied to the reductive cleavage of trityl ethers¹³ and amines,¹⁴ for the desilylation of silylated alcohols, amines and thiols,¹⁵ for the cleavage of carbonates, carbamates and thiocarbonates,¹⁶ and for the deacylation of esters, thioesters and amides.¹⁷

In this paper we wish to report the use of a naphthalene-catalysed lithiation to perform the removal of the pivaloyl protecting group from tetrazoles under very mild conditions.

The reaction of different N-pivaloyl tetrazoles **1a–1f** with an excess of lithium powder (1:9 molar ratio) and a catalytic amount of naphthalene (1:0.16 molar ratio) in THF at 0 °C for 3 h led, after quenching with methanol, to the corresponding free tetrazoles **2a–2f** (Table 1, entries 1–6).

Equation 1

The deprotected tetrazoles were isolated generally in good yields (Equation 1 and Table 1). In general, moderate to good yields were obtained in the deprotection of N-pivaloyl tetrazoles bearing aromatic (Table 1, entries 1 and 2), aliphatic (Table 1, entries 3 and 5) or benzylic (Table 1, entry 6) R groups. Interestingly, a substituent functionalized with a carbonyl group, which could undergo reduction under these reaction conditions, was not altered and the depivalated product was obtained in 62% yield (Table 1, entry 4). All the lithiation processes were complete in a reaction time of 3 h.

The starting tetrazoles were prepared by reaction of sodium azide with the corresponding nitriles in the presence of an amine. The isolated tetrazoles were then pivalated on the N1 by reaction with pivaloyl chloride, giving the expected protected tetrazoles **1** in good yields.

In conclusion, we have reported in this paper an efficient method to remove the pivaloyl protecting group from different tetrazoles bearing aliphatic, aromatic or benzylic substituents on the carbon atom of the ring, under very mild reaction conditions. This procedure is a reasonable alternative to other methodologies, especially those involving hydrolysis, which usually require harsh reaction conditions.

FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer using KBr plates (for solid compounds). NMR spectra were recorded on a Bruker spectrometer (400 MHz for ¹H and 100 MHz for ¹³C) using CDCl₃, DMSO-d₆, MeOD-d₄ as solvents and TMS (0.00

ppm, ^1H) and CDCl_3 (77.0 ppm, ^{13}C), $\text{DMSO}-d_6$ (2.50 ppm, ^1H and 39.75 ppm, ^{13}C), $\text{MeOD}-d_4$ (4.87 ppm, ^1H and 49.0 ppm, ^{13}C) as internal standards; chemical shifts are given in δ (ppm) and coupling constants (J) in Hz. Elemental analysis were measured by the Technical Services at the University of Alicante. Column chromatography was performed using silica gel 60 (35-70 mesh) or basic aluminium oxide (50-160 micrometres particle

size). Lithium powder was prepared according to the procedure described in reference.¹⁸ Commercially available *n*-butyllithium was titrated with a 1M solution of *sec*-butanol in xylene using 1,10-phenanthroline as indicator.¹⁹ Commercially available anhydrous THF (99.9%, water content $\leq 0.006\%$, Acros) was used as solvent in all the lithiation reactions.

Table 1 Reductive Removal of the Pivaloyl Group from Protected Tetrazoles **1**

Entry	Substrate	Time	Product	Yield (%) ^a
1	1a	3 h	2a	63
2	1b	3 h	2b	56
3	1c	3 h	2c	55
4	1d	3 h	2d	62
5	1e	3 h	2e	61
6	1f	3 h	2f	61

^a Yield of isolated product after extraction and recrystallization, based on the starting material **1**

All reagents used for the synthesis of substrates **1** and naphthalene were commercially available (Acros, Aldrich) and were used without further purification. All glassware was dried in an oven at 100°C and cooled to room temperature under argon before use.

Synthesis of tetrazoles. General Procedure²⁰

The mixture of a nitrile (50 mmol), NaN₃ (65 mmol) and an amine salt Et₃N·HCl (150 mmol) in toluene (100 mL) was heated to 110°C with stirring for 24 h for nitriles with aromatic R groups (**2a** and **2f**) and for 17 and 30 h, respectively, in the case of nitriles bearing aliphatic groups (**2c** and **2d**). After cooling to room temperature, the mixture was extracted with water (100 mL). 36% HCl was added dropwise to the aqueous layer till pH was acidic. After filtration, the solid was dried under reduced pressure, yielding the expected tetrazoles **2**. The corresponding physical and spectroscopic data for all tetrazoles **2** follow.

5-phenyl-1H-tetrazole (**2a**)

White solid; yield: 95%; mp: 215–216°C.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.55–7.62 (m, 3H), 8.01–8.07 (m, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 124.2 (2×CH), 127.0 (C), 129.4 (CH), 131.3 (2×CH), 155.3 (C).

5-(4'-methyl-[1,1'-biphenyl]-2-yl)-1H-tetrazole (**2b**)²¹

Brown solid; yield: 78%; mp: 149–151°C.

IR (KBr): 3336, 2974, 2900, 1080, 1046, 879, 755 cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.28 (s, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.55 (ddd, *J* = 10.3, 5.8, 1.9 Hz, 2H), 7.63–7.69 (m, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 20.7 (CH₃), 123.4 (CH), 127.5 (CH), 128.7 (2×CH), 128.9 (CH), 130.5 (2×CH), 130.6 (CH), 131.1 (C), 136.3 (C), 136.8 (C), 141.5 (C), 155.1 (C).

Anal. Calcd for C₁₄H₁₂N₄: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.19; H, 5.10; N, 23.74.

5-(*tert*-butyl)-1H-tetrazole (**2c**)²¹

White solid; yield: 90%; mp: 208–210°C.

IR (KBr): 2986, 2977, 2869, 1717, 1558, 1366, 1066, 1045, 1008 cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.35 (s, 9H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 28.9 (3×CH₃), 30.3 (C), 163.4 (C).

3,3-dimethyl-1-(1H-tetrazol-5-yl)butan-2-one (**2d**)

Orange solid; yield: 85%; mp: 152–154°C.

IR (KBr): 2973, 2322, 1716, 1365, 1048, 1007, 728 cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.18 (s, 9H), 4.41 (s, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 25.8 (3×CH₃), 32.2 (CH₂), 44.0 (C–C=O), 128.2 (C), 209.3 (C=O).

Anal. Calcd for C₇H₁₂N₄O: C, 49.99; H, 7.19; N, 33.31. Found: C, 49.97; H, 7.16; N, 33.28.

5-methyl-1H-tetrazole (**2e**)

White solid; yield: 93%; mp: 138–140°C.

IR (KBr): 3005, 2879, 2605, 1578, 1565, 1112, 1052, 899, 683 cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.46 (s, 3H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 8.4 (CH₃), 152.2 (C).

Anal. Calcd for C₂H₄N₄: C, 28.57; H, 4.80; N, 66.64. Found: C, 28.60; H, 4.78; N, 66.165.

5-benzhydryl-1H-tetrazole (**2f**)

White solid; yield: 72%; mp: 165–166°C.

IR (KBr): 3264, 2917, 1560, 1446, 743, 695, 632 cm⁻¹.

¹H NMR (400 MHz, MeOD-*d*₄): δ = 5.85 (s, 1H), 7.14–7.30 (m, 10H).

¹³C NMR (100 MHz, MeOD-*d*₄): δ = 40.8 (CH), 128.6 (2×CH), 129.6 (4×CH), 129.9 (4×CH), 140.8 (C), 160.0 (2×C).

Anal. Calcd for C₁₄H₁₂N₄: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.14; H, 5.16; N, 23.74.

Synthesis of the Protected Tetrazoles **1**. General Procedure

n-BuLi (4 mL of a 2.5 M solution in hexane, 10.0 mmol) was dropwise added to a stirred solution of the corresponding tetrazole (10.0 mmol) in anhydrous THF (10 mL) under Ar at 0 °C. 10 Minutes after the addition had been completed, pivaloyl chloride (1.23 mL, 10.0 mmol) was added during *ca.* 5 min. After stirring at room temperature overnight, the reaction was quenched with H₂O (5 mL) and extracted with EtOAc (3 × 15 mL) and the combined organic phases were washed with brine (5 mL) and dried (Na₂SO₄). After filtration and evaporation of the solvents, the resulting residue was purified by recrystallisation (hexane–EtOAc) affording the expected N-pivaloyltetrazoles **1** in pure form. Their corresponding physical, spectroscopic and analytical data follow.

2,2-dimethyl-1-(5-phenyl-1H-tetrazol-1-yl)propan-1-one (**1a**)

White solid; yield: 65% (1.49 g); mp: 218–220°C.

IR (KBr): 1701, 1608, 1562, 1484, 1409, 1256, 685.

^1H NMR (400 MHz, MeOD- d_4): δ = 1.06 (s, 9H), 7.45–7.90 (m, 5H).

^{13}C NMR (100 MHz, MeOD- d_4): δ = 27.6 ($3\times\text{CH}_3$), 39.3 (C), 125.6 (C), 128.2 ($2\times\text{CH}$), 130.5 ($2\times\text{CH}$), 132.5 (CH), 157.7 (C).

Anal for $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}$: C, 62.69; H, 6.13; N, 24.33. Found: C, 62.66; H, 6.15; N, 24.37.

2,2-dimethyl-1-[5-(4'-methyl-1,1'-biphenyl-2-yl)-1H-tetrazol-1-yl]propan-1-one (1b)

Yellow solid; yield: 62% (0.072 g).

IR (KBr): 1712, 1482, 1244, 1078, 823, 754 cm^{-1} .

^1H NMR (400 MHz, MeOD- d_4): δ = 0.92 (s, 9H), 2.27 (s, 3H), 6.93–7.08 (m, 4H), 7.45–7.63 (m, 4H).

^{13}C NMR (100 MHz, MeOD- d_4): δ = 21.1 (CH_3), 27.6 ($3\times\text{CH}_3$), 124.2 (C), 128.7, 129.9, 130.2, 131.6, 131.8, 132.5 ($8\times\text{CH}$), 137.6 (C), 138.8 ($2\times\text{C}$), 143.6 ($2\times\text{C}$) 156.8 (C).

Anal for $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}$: C, 71.23; H, 6.29; N, 17.49. Found: C, 71.23; H, 6.32; N, 17.53.

1-[5-(tert-butyl)-1H-tetrazol-1-yl]-2,2-dimethylpropan-1-one (1c)

White solid; yield: 70% (0.032 g); mp: 104–106°C.

IR (KBr): 1732, 1264, 1218, 1045, 703.

^1H NMR (400 MHz, MeOD- d_4): δ = 1.42 (s, 18H).

^{13}C NMR (100 MHz, MeOD- d_4): δ = 29.5 ($3\times\text{CH}_3$), 31.8 ($3\times\text{CH}_3$), 165.7 (C), 214.1 (CO).

Anal for $\text{C}_{10}\text{H}_{18}\text{N}_4\text{O}$: C, 57.12; H, 8.63; N, 26.64. Found: C, 57.12; H, 8.62; N, 26.66.

3,3-dimethyl-1-(1-pivaloyl-1H-tetrazol-5-yl)butan-2-one (1d)

Brown solid; yield: 80% (1.18 g).

^1H NMR (400 MHz, MeOD- d_4): δ = 2.74 (s, 18H), 2.80 (s, 2H).

^{13}C NMR (100 MHz, MeOD- d_4): δ = 26.4, 26.8, 27.5 ($3\times\text{CH}_3$), 27.6, 27.7, 27.9 ($3\times\text{CH}_3$), 31.7 (CH_2), 39.3 (C), 45.5 (C), 152.5 (C), 182.5 (C=O), 210.1 (C=O).

Anal for $\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_2$: C, 57.12; H, 7.99; N, 22.21. Found: C, 57.10; H, 8.01; N, 22.24.

2,2-dimethyl-1-(5-methyl-1H-tetrazol-1-yl)propan-1-one (1e)

White solid; yield: 85% (1.43 g); mp: 152–157°C.

^1H NMR (400 MHz, MeOD- d_4): δ = 0.92 (s, 9H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, MeOD- d_4): δ = 8.4 (CH_3), 26.8 (CH_3), 27.6 ($2\times\text{CH}_3$), 39.3 (C), 154.1 (C), 182.5 (CO).

Anal for $\text{C}_7\text{H}_{12}\text{N}_4\text{O}$: C, 49.99; H, 7.19; N, 33.31. Found: C, 49.96; H, 7.14; N, 33.33.

1-(5-benzhydryl-1H-tetrazol-1-yl)-2,2-dimethylpropan-1-one (1f)

White solid; yield: 90% (1.58 g); mp: 154–158°C.

^1H NMR (400 MHz, MeOD- d_4): δ = 1.07 (s, 9H), 5.80 (s, 1H), 7.23–7.38 (m, 10H).

^{13}C NMR (100 MHz, MeOD- d_4): δ = 26.8, 27.5, 27.6 ($3\times\text{CH}_3$), 39.3 (C), 47.8 (CH), 128.6 ($2\times\text{CH}$), 129.6 ($4\times\text{CH}$), 129.9 ($4\times\text{CH}$), 140.8 ($2\times\text{C}$), 159.9 (C), 182.5 (C=O).

Anal for $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}$: C, 71.23; H, 6.29; N, 17.49. found: C, 71.24; H, 6.26; N, 17.445.

Naphthalene-Catalysed Lithiation of Compounds 1. Preparation of Products 2. General Procedure

A solution of the protected tetrazoles **1** (0.5 mmol) in THF (2 mL) was dropwise added to a green suspension of lithium powder (70 mg, 10 mmol) and naphthalene (26 mg, 0.2 mmol) in THF (5 mL), under Ar, at 0 °C. After stirring at the same temperature for the time indicated in Table 1, methanol (5 mL) was carefully added, the cooling bath was removed and the reaction was stirred till it reached room temperature. The free tetrazoles **2** were obtained in pure form after extraction with EtOAc, in the yields indicated in Table 1. The obtained tetrazoles **2** were characterised by comparison of their physical and spectroscopic data with the ones of the tetrazoles that we had previously synthesized.

Acknowledgements

This work was financially supported by The A.N.D.R.S (Agence Nationale pour le Développement de la - Recherche en Santé) (Algérie) and the Department of Organic Chemistry of the University of Alicante (Spain). We are very grateful to the Spanish Ministerio de Asuntos Exteriores y de Cooperación for a cooperation grant (AP/039112/11). We are very grateful to Dr. Rosa Ortiz for her valuable help.

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