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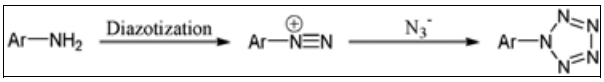

p-Nitrophenyl-, *p*-methoxyphenyl-, *p*-hydroxyphenyl-, *p*-t-butylphenyl-, *p*-$HOSO_2$-phenyl-, ^{15}N-*p*-*N,N*-dimethylaminophenyl-, $^{15}N_2$-*p*-*N,N*-dimethylaminophenyl-, and dicyanoimidazopentazole were obtained *via* different synthetic routes. Cesium, barium, potassium, and sodium salts of the arylpentazoles bearing acidic hydrogens were prepared. NMR spectra (^1H, ^{13}C) are reported for the arylpentazoles, their corresponding arylazides, and their salts.

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INTRODUCTION

In recent years, there has been an increased interest in polynitrogen compounds, mainly due to their use of them as candidates for high-energy density materials (HEDM), whose crucial characteristic from an energetic point of view is the ratio between the energy released in a fragmentation reaction and the specific weight. In such a reaction, only dinitrogen forms. This renders nitrogen clusters prime candidates as environmentally benign HEDMs. Some years ago, the novel v-shaped N_5^+ ion was synthesized [1], and since then, several N_5^+ salts have been reported [2,3]. This breakthrough in polynitrogen chemistry prompted much effort in isolating N_5^- from arylpentazoles. Calculations have shown that the *cyclo*-N_5^- is stable toward fragmentation to N_3^- and N_2 [4,5]. Beside the interest as an HEDM, pentazole is the last constituent of the azole series still remaining to be synthesized. Hitherto, the only way of constructing the N_5^- ring moiety is in the form of arylpentazoles. Arylpentazoles [6–8] were first synthesized and studied by Huisgen and Ugi in the late 1950s and early 1960s [9–13].

Some years ago, the pentazolate ion was detected experimentally by two groups independently [14,15]. Later on, Butler *et al.* [16] claimed the synthesis of the novel pentazole ring by oxidative cleavage of *p*-methoxyphenylpentazole. However, Schroer *et al.* [17] indicated that the synthesis and the conclusions were defective. Butler *et al.* [18] later published a thorough reinvestigation of the reaction of the dearylation of a multitude of heterocycles. However, only indirect proofs for the presence of pentazole or the pentazolate ion were obtained. These first two contradictory papers and the latter with indirect proofs show that more research is required in the area of pentazoles. To enable such research, arylpentazoles must be synthesized. Despite the need of good procedures to prepare different arylpentazoles, no general collection of synthetic procedures to yield solid arylpentazoles is available. The scope of this article is to describe the synthetic procedure of some arylpentazoles together with the isolation of solid arylpentazoles.

RESULTS AND DISCUSSION

The only available route to arylpentazoles is a two-step reaction starting from an aryl amine **1**, which is diazotized to give a diazocompound **2**, followed by addition of an azide ion yielding both the arylpentazole **4** and the arylazide **5** (Scheme 1). The only available route to arylpentazoles is a two-step reaction starting from an aryl amine **1**, which is diazotized to give a diazocompound **2**, followed by addition of an azide ion yielding both the arylpentazole **4** and the arylazide **5** (Scheme 1). According to Butler *et al.* [19], the mechanism of the pentazole formation does not proceed *via* a concerted [3+4] cycloaddition but through a stepwise formation *via* the pentazenes **3**, as shown in Scheme 1. If the azide adds in a *cis* fashion, in relation to the aryl ring, ring-closure to the pentazole cannot occur. The pentazene must first isomerize into a *trans*-configuration around the N-N double bond originating from the diazonium salt. The *trans,s-trans*-pentazene must also isomerize into the *trans,s-cis*-pentazene to allow cyclization, which could occur *via* rotation around the N—N single bond. Scheme 1 shows all possible configurations. The relative energies and the theoretical distribution between the different structures are currently being quantum mechanically calculated. Despite Butler's conclusions [19], a concerted cycloaddition will be evaluated in these calculations. The possibility of *cis-trans* isomerizations is uncertain and depends among other things on the conjugation in the pentazene system. However, this has little bearing on the results of the syntheses presented in this publication. N_2 can be expelled from all pentazenes to provide the arylazide. The prevalent problem encountered in the synthesis of

Table 1

Reaction conditions and yields of arylpentazole syntheses.

	R	Diazotization conditions	NaN_3 mixture	Yield (%)
a	OH	$NaNO_2$/HCl (conc)	H_2O	58
b	OCs	n.a.	n.a.	56[a]
c	OMe	Isoamyl nitrite/MeOH/HCl (conc)	MeOH-H_2O/*n*-heptane	10
d	*t*-Bu[b]	$NaNO_2$/HCl (conc)	MeOH-H_2O	8
e	NO_2	Isoamyl nitrite/MeOH/HCl (conc)	H_2O, $Zn(NO_3)_2$	

[a]Yield from **4a**.
[b]The diazonium salt was added to an azide solution.

arylpentazoles is the formation of the arylazide, which can be cumbersome to remove from the pentazole.

Different approaches to the synthesis of *p*-hydroxyphenylpentazole, **4a**, were evaluated. The method described by Benin *et al*. [20] turned out to be troublesome. The *p*-hydroxypentazole **4a** appeared to be very soluble in the reaction solvent, which led to low yields. In our hands, this procedure also gave irreproducible results. On the contrary, the procedure described by Vij *et al*. [14] worked well and was used with minor modifications (*i.e.*, diazotization in an acidic aqueous solution at 0°C followed by addition of the azide).

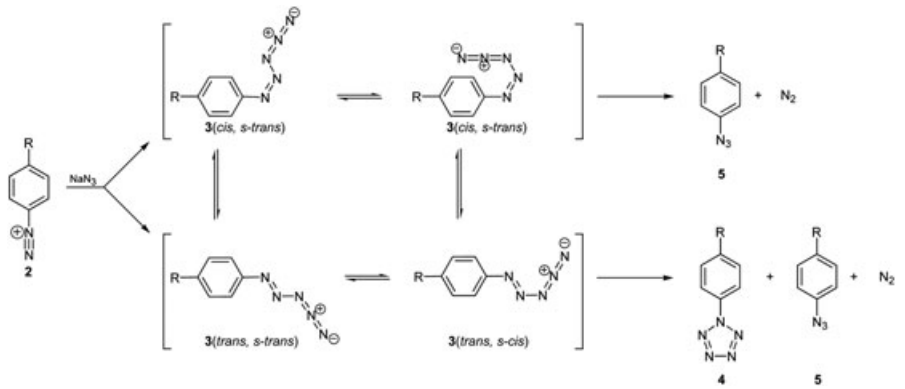
This yielded a greenish solid. ^{1}H-NMR in CD_3CN and CD_3OD at −10°C of this product showed that it was pure *p*-hydroxyphenylpentazole **4a** at 58% yield. Heating of the NMR sample to ambient temperature resulted in expulsion of nitrogen gas and formation of *p*-hydroxyphenylazide **5a**. Comparison of the UV-spectra of the *p*-hydroxypehenylpentazole **4a** and the *p*-hydroxyphenylazide **5a** revealed some differences, where the pentazole **4a** had a symmetrical peak with maximum at 275 nm. The UV max of azide **5a** was shifted to a lower wavelength at 225 nm together with a small shoulder on the red side of the main peak.

Benin *et al*. [20] discussed temperature dependence in the ratio between the formed arylazide and arylpentazole. The ratio of arylpentazole **4a** to arylazide **5a** changed from 1:2.0 at −30°C to 1:1.2 at 0°C. This behavior could be explained by pentazene formation. If the temperature is very low, the *trans,s-trans*-pentazene cannot isomerize into the *trans,s-cis*-pentazene, which is required for the ring-closure to the arylpentazole, comparing Scheme 1. Thus, raising the reaction temperature when the azide ion is introduced into the reaction mixture should favor the formation of *trans,s-cis*-pentazene. However, a higher temperature will increase the thermal decomposition of the arylpentazole and arylpentazenes into the arylazide. These contradicting trends ought to be valid for all arylpentazole syntheses. The reaction temperature must thus be carefully chosen to obtain a maximum yield of the desired product.

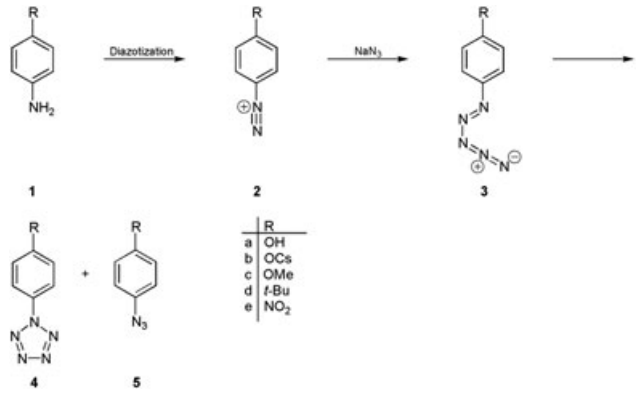
The cesium salt of *p*-hydroxyphenylpentazole **4b** was prepared by treatment of the *p*-hydroxyphenylentazole **4a** with a cold methanolic solution of cesium hydroxide (see Scheme 2). A mixture of the *p*-hydroxyphenylpentazole **4a** and the *p*-hydroxyphenylazide **5a** could easily be separated in this manner, as the cesium *p*-hydroxyphenylazide **5b** was removed by washing with cold acetone. The proton NMR showed no OH signal and all other signals were shifted compared to the *p*-hydroxyphenylpentazole **4a**.

It was also of interest to prepare arylpentazoles with electron-rich aryl moieties, since electrondonating groups on the aryl ring increase the stability of the arylpentazoles [21]. When the procedure described for the synthesis of *p*-hydroxyphenylpentazole **4a** in aqueous solution was applied

Scheme 1. Synthesis of arylpentazoles *via* arylpentazenes.



Scheme 2. Synthesis of arylpentazoles. Conditions and yields are given in Table 1.



to *p*-anisidine **1c**, a 1:0.95 mixture of *p*-methoxyphenylpentazole **4c** and *p*-methoxyphenylazide **5c** was collected. The ratio improved to 1:0.11, when the conditions described by Butler *et al*. [18,22] (*i.e.*, diazotization of *p*-anisidine with *iso*-amylnitrite in methanol) were used. To the resulting *p*-methoxyphenyldiazonium chloride **2c**, *n*-heptane was added to create a two-phase system, which subsequently was treated with sodium azide in a solution of methanol and water at –40°C to yield the corresponding arylpentazole **4c** in 10% yield. Although *p*-methoxyphenylpentazole **4c** has been prepared earlier, little analytical data were available [22]. Our investigations showed that this compound had its UV absorption maximum at 270 nm in acetonitrile. Also the UV-spectrum of *p*-methoxyphenylazide **5c** exhibit a shoulder (280 and 300 nm) on the red side of the main peak. The total maximum was at 256 nm. The Raman spectrum of the *p*-methoxyphenylpentazole **4c** and the *p*-methoxyphenylazide 5**c** yielded spectrum of similar kind. The main difference was a big peak at 1374 cm^{-1} for the pentazole **4c** but in the same region the azide **5c** had a big peak at 1303 cm^{-1}.

p-t-Butylphenylpentazole **4d** was obtained from *p-t*-butylphenylamine **1d** by diazotization with sodium nitrite, followed by treatment with sodium azide. Only small amounts of the pentazole **4d** was collected and the azide **5d** was the major product. The stability of *p-t*-butylphenylpentazole **4d** was significantly lower than the ones of *p*-methoxy- or *p*-hydroxyphenylpentazoles. The reprodubility of the yield of *p-t*-butylphenylpentazole **4d** was low, due to the high solubility of the product.

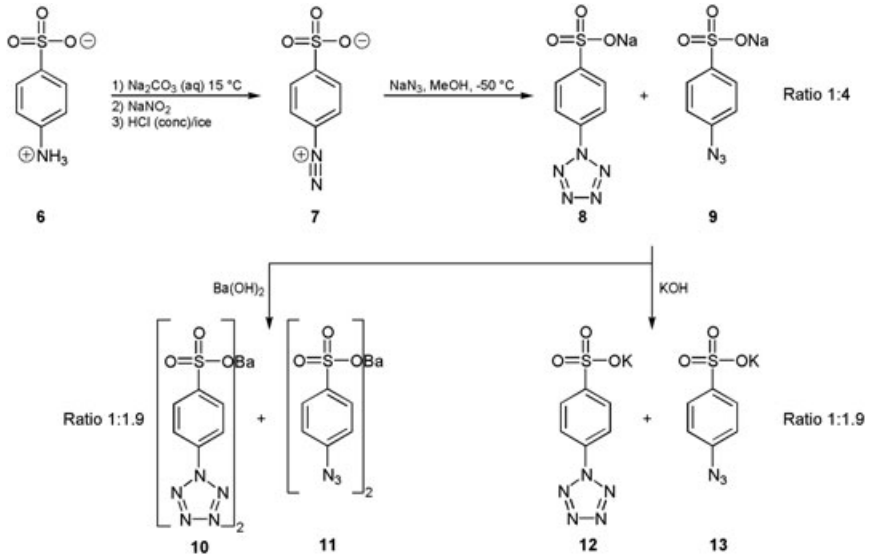
As electron-donating substituents stabilize the pentazole ring, the contrary is true to electron-withdrawing substituents [21]. An attempt was made to synthesize *p*-nitrophenylpentazole **4e** by the same procedure, as described above for *p*-methoxyphenylpentazole **4c**. Only a very pure, light yellowish powder of *p*-nitrophenylazide **5e**, without any trace of corresponding arylpentazole, was obtained. The next attempt was made with the same reaction conditions, but the addition of NaN_3 to the mixture was followed by addition of $Zn(NO_3)_2$ to stabilize the product. This yielded a solid product which according to ^{1}HNMR contained 7% of the desired *p*-nitrophenylpentazole **4e**, although the main product was still the *p*-nitrophenylazide **5e**. *p*-Nitrophenylpentazole **4e** was extremely unstable. When the NMR sample was allowed to reach room temperature, the peaks corresponding to the pentazole **4e** disappeared quickly and the only signals present belonged to the azide **5e**.

The first attempt to synthesize the salts of *p*-pentazolephenylsulfonic acid **8** (M = H) only yielded the zwitter-ionic diazonium salt of sulfanilic acid **7**, which is remarkably stable and did not react with the azide. One sample was dissolved and heated in DMSO-d_6 to approximately 45–50°C.

^{1}H-NMR at 25°C of this sample showed a mixture of the internal salt, the corresponding azide and a small amount of sulfanilic acid, although the internal diazonium salt was still the major component.

To obtain the *p*-pentazolephenylsulfonic acid **8**, the reaction conditions had to be modified (Scheme 3). The zwitter-ionic diazonium salt of sulfanilic acid **7** was isolated and purified. It was then subjected to a solution of sodium azide in anhydrous methanol. This protocol produced a solution of the desired sodium salt of *p*-pentazolephenylsulfonic acid **8** together with the corresponding azide **9**. NMR samples, taken from reaction mixture and analyzed in CD_3OD at −20°C, showed no signals that correspond to the diazonium salt **7**. There were two sets of signals, belonging to $Na^+(OSO_2PhN_5)$ and $Na^+(OSO_2PhN_3)$ in a 1:4 ratio. Pentazole **8** and azide **9** were not isolated. Treatment of the cold methanolic solution with $Ba(OH)_2$ resulted in a precipitate, which was filtered off and analyzed. ^{1}H-NMR (in CD_3OD at −20°C) showed two sets of signals that corresponded to $Ba^{2+}(OSO_2PhN_5)_2$ **10** and $Ba^{2+}(OSO_2PhN_3)_2$ **11** in a 1:1.9 ratio. When KOH was added to the methanolic solution of pentazole **8** and azide **9**, the corresponding potassium salts **12** and **13** were observed with same ratio as in the case with barium. The choice of counter ion did not influence the NMR spectra. Different solvents led to some shifts of NMR signals. Biesemeier *et al.* [23]

Scheme 3. Synthesis of the salts of *p*-pentazolephenylsulfonic acid.

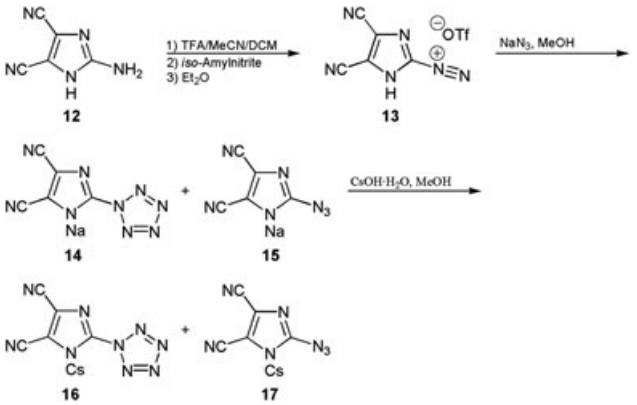


synthesized the sodium and potassium salts of **8** in a similar manner, but did not discuss the high stability/low reactivity of **7**.

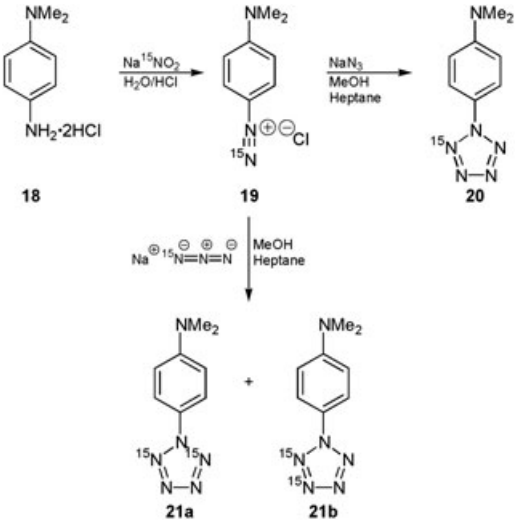
Arylpentazoles with electron-withdrawing substituents, such as *p*-nitrophenylpenbtazole **4e**, are very unstable. Nonetheless, arylpentazoles with such properties and, furthermore, pentazoles soluble in water were prepared. The synthesis was performed, starting from the commercial available 2-amino-4,5-imidazoledicarbonitrile **12** (Scheme 4). Anhydrous diazotization [24] yielded the isolable, diazonium trifluoroacetate **13**. Addition of sodium azide yielded sodium 2-pentazolylimidazole-4,5-dicarbonitril **14** together with the sodium 2-azidoimidazole-4,5-dicarbonitrile **15**. The corresponding cesium 2-pentazolylimidazole-4,5-dicarbonitrile **16** was obtained by treating the solution with CsOH. The identification of the arylpentazole and azide was possible by analysis of the changes in the UV absorption pattern and ^{13}C-NMR in cold solutions and at ambient temperature. None of the compounds **14**, **15**, and **16** in Scheme 4 had any signals in ^{1}H-NMR, as there are no protons in the products.

For the synthesis of the labeled compounds, diazotization was performed with $Na^{15}NO_2$ to yield the labeled diazonium salt **19**, which in turned was used to synthesize either the mono-labeled pentazole **20** or the di-labeled pentazole **21** (Scheme 5). The mono-labeled pentazole **19** contained 28% of the azide, according to ^{1}H-NMR. The di-labeled *p-N,N*-dimethylaminophenylpentazole was synthesized by the use of labeled sodium azide in the cyclization step. The second labeled nitrogen was incorporated either in the third position (**21b**) or in the fifth position (**21a**) of the pentazole ring.

Scheme 4. Synthesis of salts of 3,4-dicyanoimidazopentazole and 3,4-dicyano-2-azidoimidazole.



Scheme 5. Synthesis of mono- and di-labeled *p-N,N*-dimethylaminophenylpentazole. Formation of the corresponding arylazides is omitted for clarity.



CONCLUSIONS

We have prepared, isolated, and characterized eight arylpentazoles in their solid state. The choice of synthetic procedure depended on the desired product. The factors varied to obtain higher yields were the solvent, diazotization procedure, and reaction temperature during the cyclization into the desired arylpentazole. Furthermore, the preparation of ^{15}N mono- and di-labeled *p-N,N*-dimethylaminophenylpentazole was accomplished.

EXPERIMENTAL

General. The prepared pentazoles were stored under liquid N_2 to prevent any thermal decomposition. The samples were at all times handled at low temperatures. The samples were for instance weighed into precooled bottles and NMR and UV/vis samples were prepared by dissolution of the substances in cooled solvents. NMR and UV/vis experiments of arylpentazole samples were run at –20°C, unless otherwise stated. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. UV/vis spectra were recorded on a PerkinElmer Lambda 40. IR Raman spectra were recorded on a Bruker IFS 50/FRA106. Melting points were determined on a Mettler DSC. The low thermal stability of the arylpentazoles prevented any elemental analysis.

***p*-Hydroxyphenylpentazole (4a).** This compound was prepared according to the published procedure [14] with minor modifications. *p*-Hydroxyphenylamine hydrochloride (2.62 g, 18 mmol) was dissolved in water (45 mL), cooled in an ice-salt bath to –3°C, slightly acidified with conc. HCl (3.07 mL, 36 mmol). Sodium nitrite (1.35 g, 19.5 mmol) was added to the solution over 7–8 min, and the solution was stirred for another 7–8 min. An ice-cold aqueous (7 mL) solution of NaN_3 (1.22 g, 18.75 mmol) was added to the produced *p*-hydroxyphenyldiazonium chloride. The formed suspension was stirred at 0–2°C for another 10–12 min before it was quickly filtered, washed with ice-cold water (2 × 5 mL), and dried in vacuum at –10 to 0°C to produce a green–grey solid (1.70 g, 58%).

***p*-Hydroxyphenylpentazole (4a).** T_{dec} 53–58°C, ^{1}H-NMR (CD_3OD): 7.99 (2H, d, J = 8.0), 7.03 (2H, d, J = 8.0); ^{1}H-NMR (D_2O): 7.69 (2H, d, J = 8.9), 6.77 (2H, d, J = 8.9); ^{1}H-NMR (CD_3CN) 9.11 (1H, s, OH), 7.96 (2H, d, J = 8.1); 7.08 (2H, d, J = 8.1); ^{13}C-NMR (CD_3CN) 160.77 (q), 123.86 (d), 119.97 (q), 117.25 (d).

***p*-Hydroxyphenylazide (5a).** ^{1}H-NMR (CD_3OD, +25°C) 6.88 (2H, d, J = 6.7), 6.80 (2H, d, J = 6.7). ^{1}H-NMR (D_2O, +25°C) 6.66 (2H, d, J = 8.8), 6.55 (2H, d, J = 8.8); ^{1}H-NMR (DMSO-d_6, +25°C) 9.50 (1H, s, OH), 6.93 (2H, d, J = 8.0), 6.80 (2H, d, J = 8.0); ^{13}C-NMR (CD_3OD, +25°C) 146.45 (s), 122.87 (s), 111.47 (d), 108.07 (d).

Cesium salt of *p*-hydroxyphenylpentazole (4b). This compound was prepared according to the published procedure [14] with minor modifications. A crude 1:1 mixture of *p*-hydroxyphenylpentazole (1.364 g, 8.4 mmol) and the corresponding azide (1.129g, 8.4 mmol) (*i.e.*, 2.493 g total) was added to dry methanol (15 mL, –45°C). To this suspension, $CsOH{\cdot}H_2O$ (20 mmol) in dry methanol (15 mL –45°C), was added slowly *via* syringe. The temperature was raised to –20°C over 2 h. The obtained brown solution was concentrated *in vacuo* at –20°C. The remaining brown solid was collected and washed on a filter with cooling (–30°C) with cold, dry acetone (3 × 10 mL, –40°C). The acetone solution contained $CsOPhN_3$ (2.24 g, 100%). The creamy residue was nearly pure $CsOPhN_5$ (1.41 g, 56%). ^{1}H-NMR (CD_3OD, –10°C): 7.77 (2H, d, J = 7.1), 6.73 (2H, d, J = 7.1); ^{13}C-NMR (CD_3OD, –10°C): 153.40 (s), 142.64 (s), 123.30 (d), 120.60 (d).); ms: *m/z*: 161.9 $[OPhN_5]^-$ (100), 133.9 $[M\text{-}N2]^-$ (35, 106.0 $[M\text{-}2N_2]^-$ (40).

Cesium salt of *p*-hydroxyphenylazide (5b). ^{1}H-NMR (CD_3OD, –10°C): 6.70 (2H, d, J = 6.7), 6.61 (2H, d, J = 6.7); ^{13}C-NMR (CD_3OD, +25°C): 165.04 (s), 126.62 (s) 120.60 (d), 120.42 (d).

***p*-Methoxyphenylpentazole (4c).** This compound was prepared according to Butler *et al.* [18]. ^{1}H-NMR (CD_3CN): 8.03 (2H, d, J = 6.9), 7.17 (2H, d, J = 6.9), 3.87 (3H, s); ^{13}C-NMR (CD_3CN): 162.46 (s), 133.61 (s), 123.60 (d), 115.64 (d), 55.80 (q).

***p*-Methoxyphenylazide (5c).** T_m 34–37°C; ^{1}H-NMR (CD_3CN, +25°C): 6.97 (2H, d, J = 6.8), 6.91 (2H, d, J = 6.8), 3.72 (3H, s); ^{13}C-NMR (CD_3CN, +25°C): 158.18 (s), 133.19 (s), 121.04 (d), 116.20 (d).

***p-t*-Butylphenylpentazole (4d).** *p-t*-Butylphenylamine (3.73 g, 25 mmol) was suspended in water (18 mL), cooled to 0°C and treated with conc. HCl (5.18 mL, 62.5 mmol). Sodium nitrite (1.90 g, 27.5 mmol) was added over 15 min. The reaction mixture was kept for 40 min at –3 to –5°C until everything had dissolved. A solution of sodium azide (1.79 g, 27.5 mmol) in methanol (22 mL) and water (4 mL) was cooled to –45°C and the prepared diazonium salt (*vide supra*) was added carefully over 15 min. During the addition, the temperature of reaction mixture was kept between –40 and –50°C. After completion of the addition, the reaction was stirred for another 10 min and then filtered through a precooled (–30°C) filter. The obtained white precipitate was not washed to avoid loss of material. Drying on the filter yielded 0.92 g of a crude product as a 1:1.3 mixture of *p-t*-butylphenylpentazole 0.43 g (8%) and *p-t*-butylphenylazide (0.49 g, 11%). One extraction of the mother liquor with ether yielded additionally 2.12 g (48%) *p-t*-butylphenylazide as a pale yellow oil.

***p-t*-Bu-phenylpentazole (4d).** ^{1}H-NMR (CD_2Cl_2): 8.08 (2H, d, J = 8.2), 7.67 (2H, d, J = 8.2), 1.38 (9H, s); ^{1}H-NMR (CD_3CN); 8.05 (2H, d, J = 8.2), 7.72 (2H, d, J = 8.2), 1.34 (9H, s); ^{13}C-NMR (CD_2Cl_2): 120.55 (d), 118.55 (d), 30.99 (q); ^{13}C-NMR (CD_3CN): 169.82 (s), 139.80 (s), 128.00 (d), 121.39 (d), 35.80 (s), 30.92 (q).

***p-t*-Bu-phenylazide (5d).** ^{1}H-NMR (CD_2Cl_2, +25°C): 7.41 (2H, d), 6.99 (2H, d), 1.33 (9H, s); ^{1}H-NMR (CD_3CN, +25°C): 7.40 (2H, d, J = 8.0), 6.98 (2H, d, J = 8.0), 1.25 (9H, s); ^{13}C-NMR (CD_2Cl_2, +25°C): 148.75 (s), 137.64 (s), 127.29 (d), 119.08 (d), 34.68 (s), 31.62 (q); ^{13}C-NMR (CD_3CN, +25°C): 149.15 (s), 138.14 (s), 127.75 (d), 119.59 (d), 35.08 (s), 31.56 (q).

***p*-Nitrophenylpentazole (4e).** The diazotization was performed as described above for *p*-anisidine, *vide supra*, starting from 15 mmol *p*-nitroaniline. The addition of NaN_3 (1 equiv.) to the mixture was followed by addition of 3 equiv. of $Zn(NO_3)_2$ in a minimum amount of water. After 30 min of stirring, a solid was filtered off, washed with methanol:water 1:1 mixture (2 × 5 mL), and dried (work up at –32°C) gave 1.82 g of a solid product. According to ^{1}H-NMR, the product was a 1:0.07 mixture of *p*-nitrophenylazide and *p*-nitrophenylpentazole.

***p*-Nitrophenylpentazole (4e).** ^{1}H-NMR (CD_3CN): 8.51 (2H, d, J = 7.8), 8.39 (2H, d, J = 7.8).

***p*-Nitrophenylazide (5e).** ^{1}H-NMR: (CD_3CN, +25°C) 8.22 (2H, d, J = 7.2), 7.22 (2H, d, J = 7.2); ^{13}C-NMR (CD_3CN, +25°C: 148.14 (s), 142.15 (s), 126.50 (d), 120.71 (d).

***p*-Nitrophenyldiazonium salt (2e).** ^{1}H-NMR (CD_3CN, +25°C): 8.28 (2H, d, J = 8.8), 7.65 (2H, d, J = 8.8).

***p*-Pentazolphenylsulfonates (8, 10, 12).** To a suspension of sulfanilic acid (2.60 g, 15.0 mmol) in water (15 mL), aqueous solution of Na_2CO_3 (8 mL H_2O, 0.88 g $NaHCO_3$, 8.3 mmol) was added dropwise. After 10 min, when everything had dissolved, the solution was cooled down to 15°C and $NaNO_2$ (1.14 g, 16.5 mmol) was added over 10 min. After 10 min of stirring at the same temperature, the reaction mixture was poured onto crushed ice (17.0 g), containing conc. hydrochloric acid (3.6 mL, 43.5 mmol). The product precipitated and formed a suspension. After 15 min of stirring the resulting cold (0°C), thick, white suspension of *p*-sulfobenzenediazonium betaine **7** was quickly filtered, washed with ice-cold water (2 × 5 mL), and dried on a cold filter by letting air pass through it for 10 min. The betaine **7** was then suspended in precooled (−20°C) dry methanol (35 mL). The suspension was cooled to −50°C before dropwise addition of a saturated solution of NaN_3 (975 mg, 15 mmol) in dry methanol (30 mL, −50°C) over 30 min. Stirring continued for 4.5 h at maintained temperature, before a light solution formed. A suspension of $Ba(OH)_2{\cdot}H_2O$ (789 mg, 2.5 mmol) in methanol (20 mL, −50°C) was added to the solution over 5 min. After 2.5 hours of stirring at −50°C, the formed suspension was filtered through a filter with cooling jacket (−30°C) and washed with cold (−50°C) dry methanol (2 × 5 mL) and dried on the same filter at the same temperature (−30°C) to obtain 1.24 g product as a white solid (30% pentazole and 59% azide with respect to the $Ba(OH)_2$). The use of KOH (0.35 equiv.) provided identical results with almost exactly the same ratio of $K^+(^-OSO_2PhN_5)$ to $K^+(^-OSO_2PhN_3)$.

***p*-Sulfobenzenediazonium betaine (7).** ^{1}H-NMR (CD_3CN) 8.65 (2H, d, J = 8.9), 8.10 (2H, d, J = 8.9); ^{1}H-NMR (DMSO-d_6) 8.66 (2H, d, J = 8.9), 8.10 (2H, d, J = 8.9); ^{13}C-NMR (DMSO-d_6) 144,10 (s), 142.30 (s), 133.32 (d), 127.95 (d). ^{1}H-NMR (D_2O) 8.73 (2H, d, J = 8.9), 8.31 (2H, d, J = 8.9). ^{1}H-NMR (CD_3OD) 8.69 (2H, d, J = 8.0), 8.29 (2H, d, J = 8.0).

Sodium (8), barium (10), and potassium (12) *p*-pentazolephenylsulfonates. ^{1}H-NMR (CD_3OD) 8.35 (2H, d, J = 8.8), 8.15 (2H, d, J = 8.8); ^{13}C-NMR (CD_3OD) 148.8 (s), 136.2 (s), 129.2 (d), 122.4 (d).

Sodium (9), barium (11) and potassium (13) salts of *p*-azidophenylsulfonate. ^{1}H-NMR (D_2O) 7.78 (2H, d, J = 7.5), 7.19 (2H, J = 7.5); ^{13}C-NMR (D_2O) 143.48 (s), 138.90 (s), 127.55 (d), 119.61 (d); ^{1}H-NMR (CD_3CN) 7.61 (2H, d), 7.06 (2H, d); ^{13}C-NMR (CD_3CN) 145.44 (s), 139.24 (s), 127.35 (d), 118.27 (d); ^{1}H-NMR (CD_3OD) 7.84 (2H, d, J = 7.8), 7.17 (2H, J = 7.8).

***p*-Hydroxyphenylsulfonic acid.** ^{1}H-NMR (D_2O) 7.65 (2H, d, J = 7.9), 6.93 (2H, d, J = 7.9); ^{1}H-NMR (CD_3OD) 7.66 (2H, d, J = 8.6), 6.80 (2H, d, J = 8.6).

Sodium (14) and cesium salts (16) of 3,4-dicyanoimidazopentazole. 2-Amino-4,5-imidazoledicarbonitrile 12 (2.74 g, 20.0 mmol) was dissolved in dry CH_2Cl_2 (15 mL) and CH_3CN (8 mL). The solution was cooled to 0°C and TFA (3.21 mL, 42 mmol) was added dropwise. The solution was further cooled to −30°C before the dropwise addition of *iso*-amylnitrite (3.22 mL, 24 mmol). The clear, yellow solution was stirred for 1 h at the same temperature to produce a light suspension. The reaction mixture was additionally cooled to −70°C before the addition of cold (−70°C) dry ether (30 mL). The suspension was filtered on a filter with a cooling jacket (−28°C). The solid diazonium trifluoroacetate **13** was washed with cold dry ether (5 mL), slightly dried, and immediately transferred into a three-neck flask with cold dry methanol (20 mL). *WARNING*: This must be done with utmost care, as the diazonium salt was very sensitive to mechanical stimuli and released much energy, when investigated by DSC. Its melting point was 148°C.

The suspension was cooled to −70°C. Then a suspension (maintained below −40°C) of NaN_3 (1.43 g, 22 mmol) in methanol (10 mL) was added slowly, and the reaction mixture was stirred for 1.5 h. Temperature was increased to −45°C. Samples were taken from the reaction mixture for UV and NMR analysis at low temperatures. The solution was reduced to half its volume *in vacuo* at low temperature to produce the sodium salt as a solid.

Sodium 3,4-dicyanoimidazopentazolate (14). ^{13}C-NMR (CD_3OD): 152.02 (s), 118.43 (s), 115.06 (s).

Cesium salt of 3,4-dicyano-2-azidoimidazole (15). ^{13}C-NMR (CD_3OD, +25°C): 152.50 (s), 118.82 (s), 115.49 (s).

The remaining methanolic solution, containing about 10 mmol, was treated at −40°C with 4 mL of a methanolic solution of $CsOH{\cdot}H_2O$. Forty minutes of stirring produced a suspension, which was filtered, washed with cold methanol (1 mL), and dried under vacuum at −30°C to produce the cesium salt of 3,4-dicyanoimidazopentazole.

Cesium 3,4-dicyanoimidazopentazolate (16). ^{13}C-NMR (CD_3OD): 152.24 (s), 118.65 (s), 115.25 (s).

Cesium salt of 3,4-dicyano-2-azidoimidazole (17). ^{13}C-NMR (CD_3OD, +25°C): 152.52 (s), 118.85 (s), 115.56 (s).

^{15}N-*p*-*N,N*-Dimethylaminophenylpentazole (20). The diazotization was performed as described below for **21**, *vide infra*. A cold (0°C) solution of *p*-*N,N*-dimethylaminophenyldiazonium dihydrochloride (15 mmol) in water (8 mL) was added in small portions to a cold (−40°C) solution of sodium azide (1.04 g, 16 mmol) in water (3 mL) and methanol (14 mL) over 12 min. This produced a thick green–grey suspension, which was stirred for another 20 min at the same (−40°C) temperature, before it was filtered off on a filter with a cooling jacket (−30°C). The mother liquor was stirred for 15 min at −30°C, before being filtered again in the same manner. The combined precipitates were washed with a cold (−40 to −50°C, 2 × 7 mL) 1:1 mixture of water and methanol and then two times with acetone (3 mL): water (4 mL) mixture, and dried to get ^{15}N-*p*-*N,N*-dimethylaminophenylpentazole as a grey powder that contained about 15% *p*-*N,N*-dimethylaminophenylazide.

The methanol from the mother liquor was evaporated and the remaining *p*-*N,N*-dimethylaminophenylazide was extracted with ethylacetate. The crude product was purified by sublimation at 100°C to produce bright yellow needles.

$^{15}N_2$-*p*-*N,N*-Dimethylaminophenylpentazole (21). To a solution of *p*-*N,N*-dimethylphenylenediamine dihydrochloride (1248 mg, 5.97 mmol) in water (8 mL), precooled to 0°C. HCl (0.10 mL, 1.19 mmol) and solid $Na^{15}NO_2$ (460 mg, 6.57 mmol) were added over 15 min, keeping the temperature of between −2 and 0°C. After the addition was completed, the reaction mixture was stirred at the same temperature for 30 min. During the last 3 min of the reaction, air was bubbled through the solution to remove any free nitrogen oxides. A mixture of MeOH (8 mL) and *n*-heptane (1 mL) was cooled to −35°C, and the reaction mixture was transferred by syringe under N_2 flow to the solvent mixture, keeping the temperature of the

solution stable. A saturated solution of $Na^{15}NNN$ (434 mg, 6.57 mmol) in aqueous MeOH (8 mL, 50%) was added under intensive stirring in such a rate the temperature remained between −30 and −40°C. After 1 h of stirring, the reaction mixture was filtered (p4), and the filter cake washed with cold MeOH (3 mL), acetone (2 mL), and *n*-heptane (1 mL). Then a small amount of crude product (40 mg, mixture of $^{15}N_2$-*p*-*N,N*-dimethylaminophenylpentazole and *p*-*N,N*-dimethylaminophenylazide 1:0.5 according to ^{1}H-NMR) was obtained. The cold filtrate was stirred for another 15 min at −30°C and then filtered again. The obtained filter cake was washed and dried as described above to get the product (65 mg, mixture 1:0.18 $^{15}N_2$-*p*-*N,N*-dimethylaminophenylpentazole and *p*-*N,N*-dimethylaminophenylazide) as a grey solid. Then the filtrate was left stirring for 2.5 h at −20 to −25°C. Additional product precipitated and was filtered off. The same washing and drying procedure as above yielded another 120 mg of a grey solid as a 1:0.15 mixture of $^{15}N_2$-*p*-*N,N*-dimethylaminophenylpentazole and *p*-*N,N*-dimethylaminophenylazide.

$^{15}N_2$-*p*-*N,N*-Dimethylaminophenylpentazole. ^{1}H-NMR (CD_2Cl_2) 7.96 (2H, d, J = 9.1 Hz), 6.83 (2H, d, J = 9.1 Hz), 3.10 (6H, s, Me); ^{13}C-NMR (CD_2Cl_2) 151.98 (s), 141.18 (s), 122.06 (d), 111.77 (d), 40.47 (q).

***p*-*N,N*-Dimethylaminophenylazide.** ^{1}H-NMR (CD_2Cl_2) 6.92 (2H, d, J = 9.0 Hz), 6.77 (2H, d, J = 9.0 Hz), 2.91 (6H, s, Me); ^{1}H-NMR (CD_3CN) 6.94 (2H, d, J = 9.0 Hz), 6.76 (2H, d, J = 9.0 Hz), 2.96 (6H, s, Me); ^{13}C-NMR (CD_3CN) 149.76 (s), 128.87 (s), 120.71 (d), 114.83 (d), 41.04 (q); ^{13}C-NMR (CD2Cl2) 149.00 (s), 128.54 (s), 120.20 (d), 114.19 (d), 41.13 (q).

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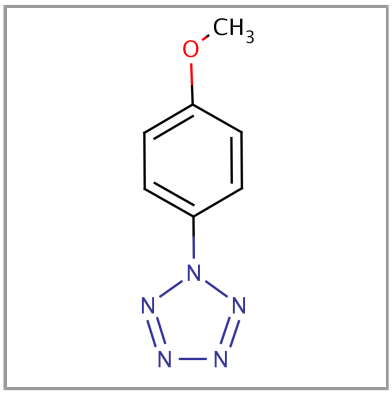
4c



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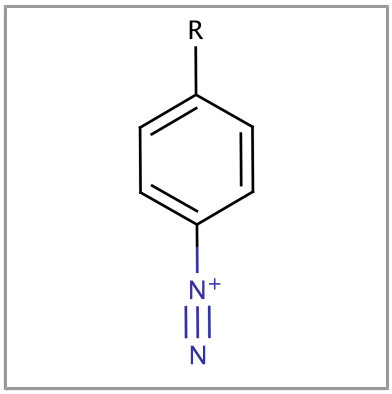

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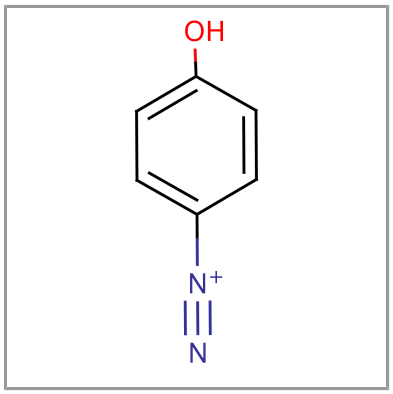

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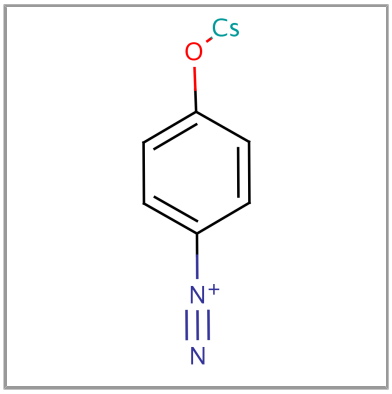

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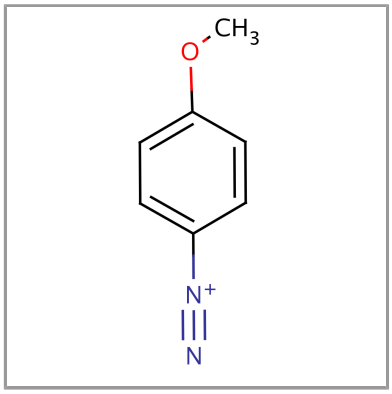

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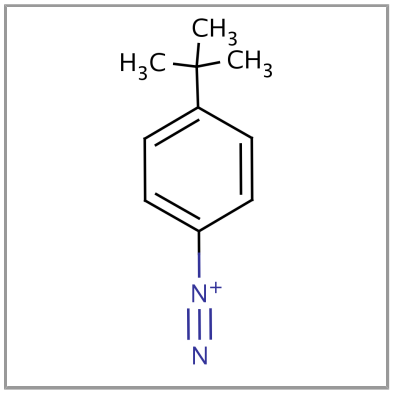

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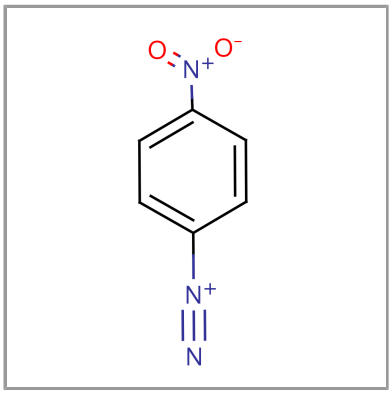

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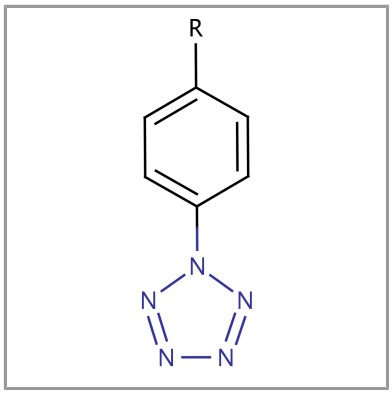

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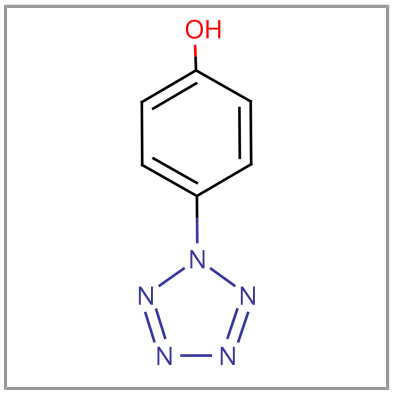

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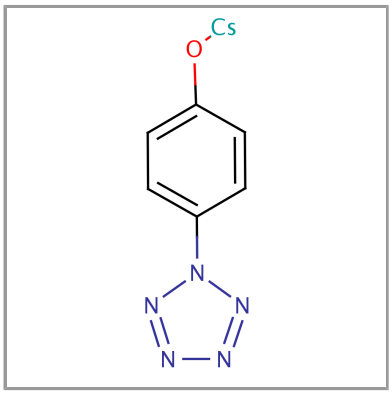

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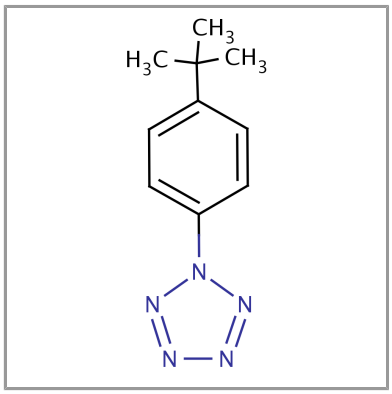

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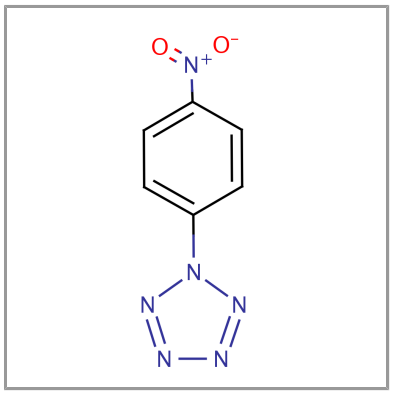

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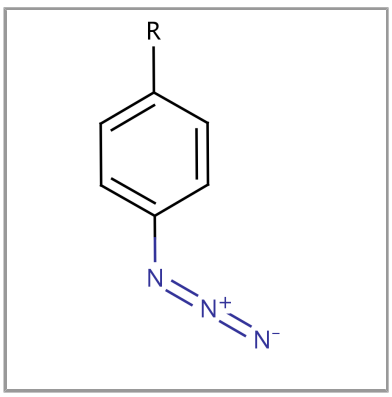

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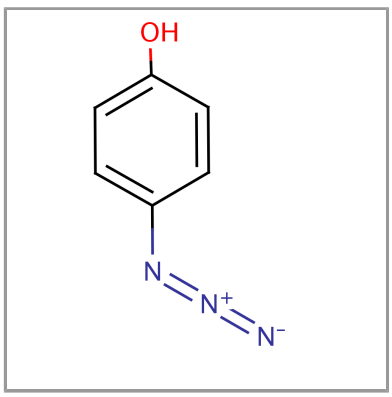

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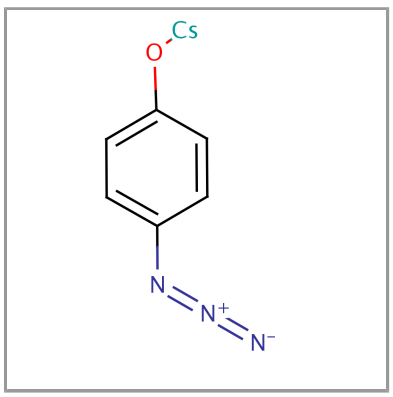

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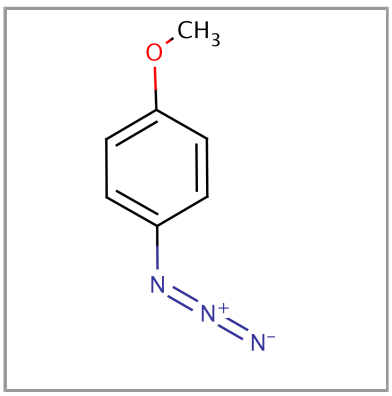

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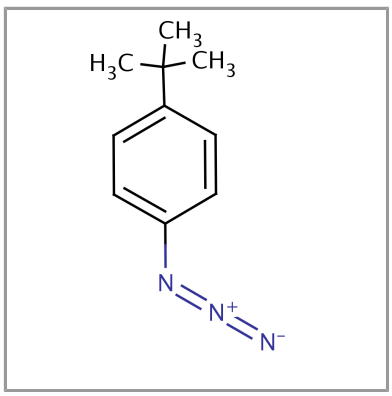

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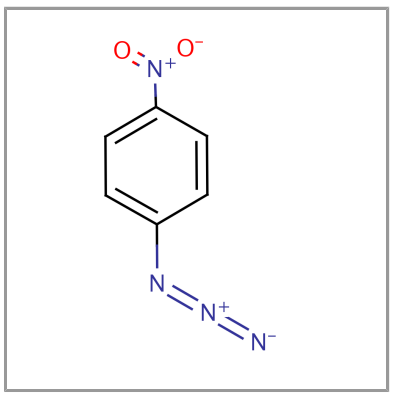

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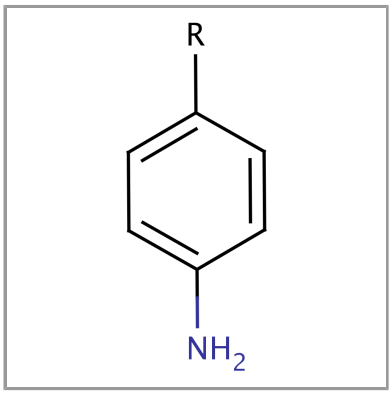

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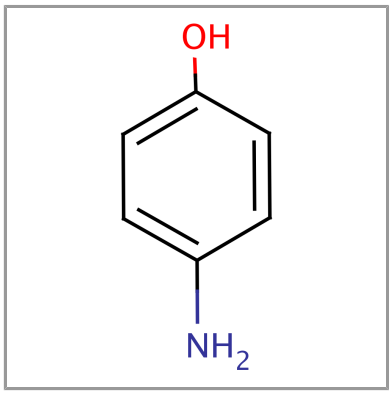

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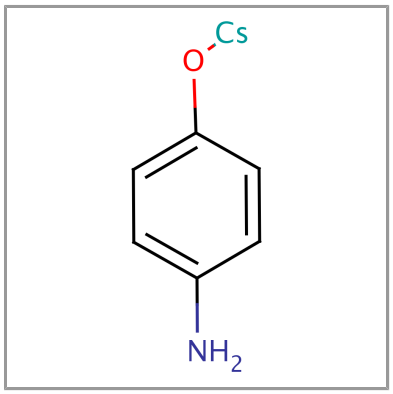

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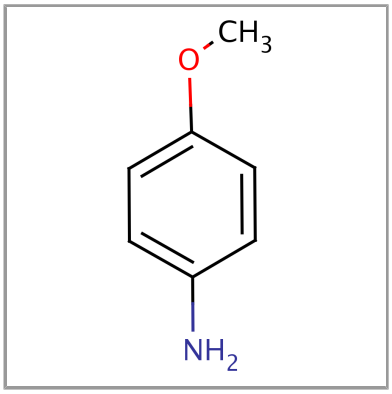

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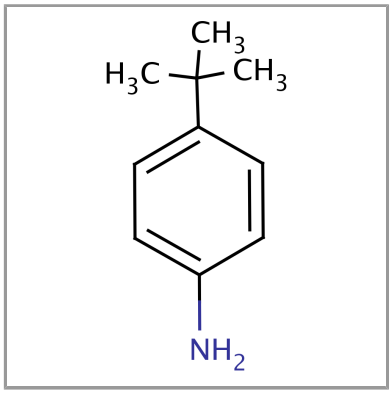

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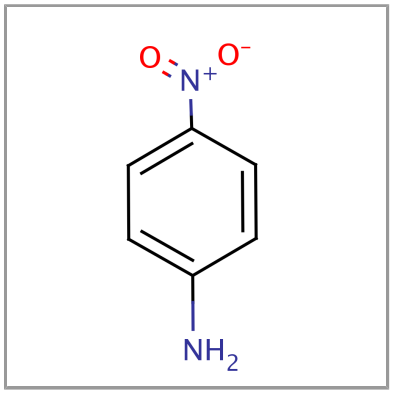

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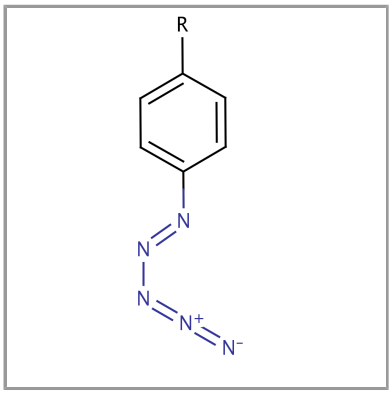

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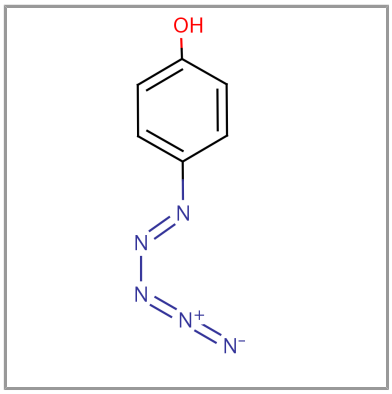

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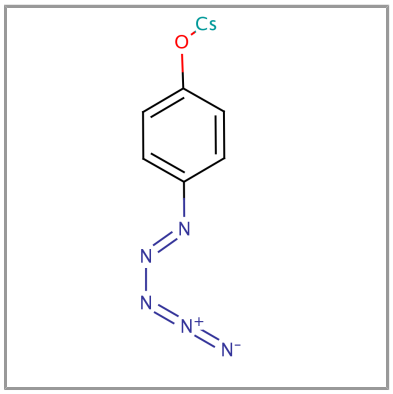

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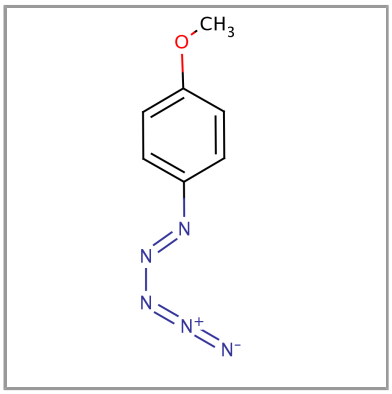

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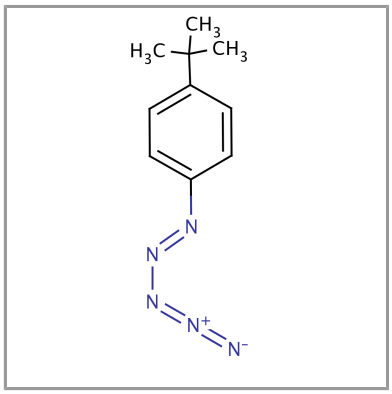

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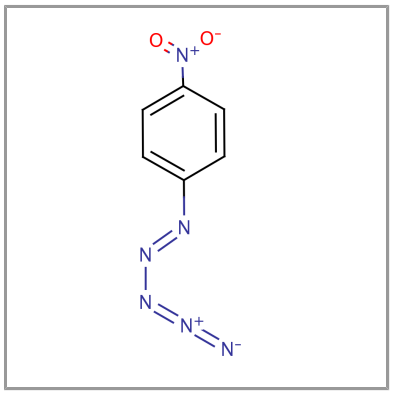

Compound Details Structure Search

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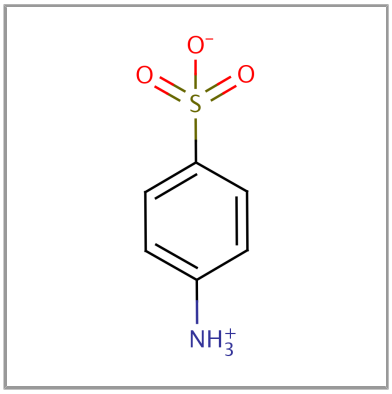

Compound Details Structure Search

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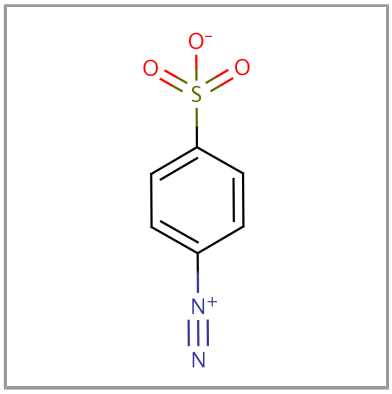

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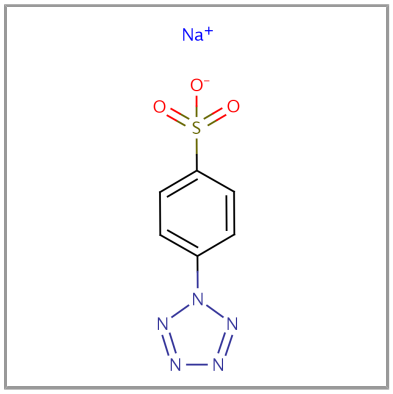

Compound Details Structure Search

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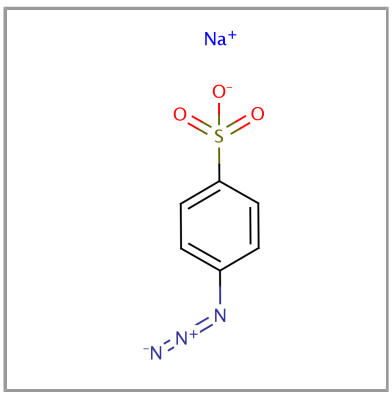

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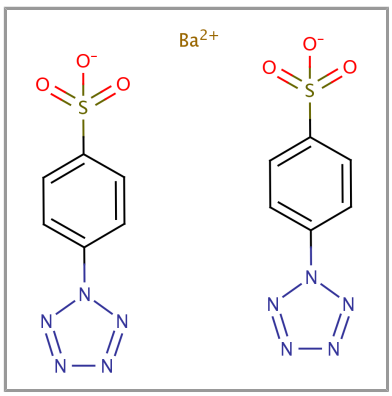

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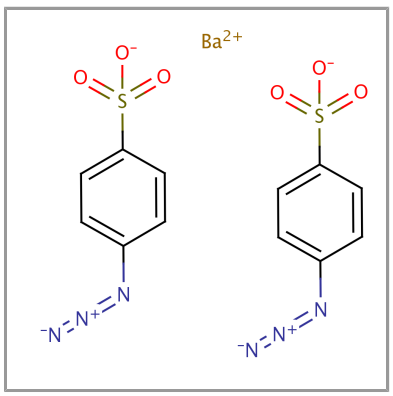

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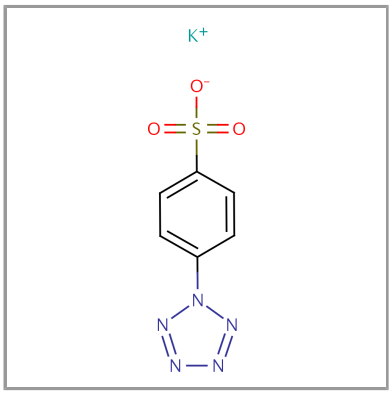

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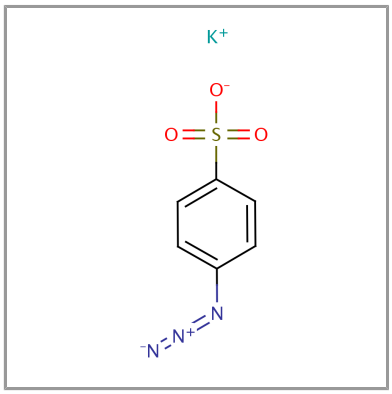

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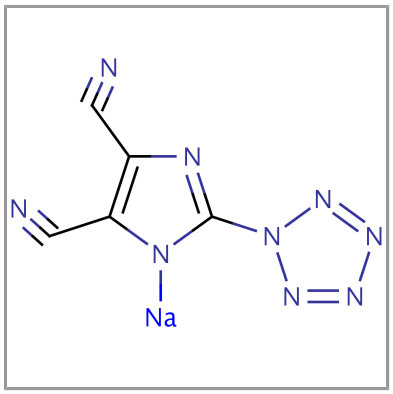

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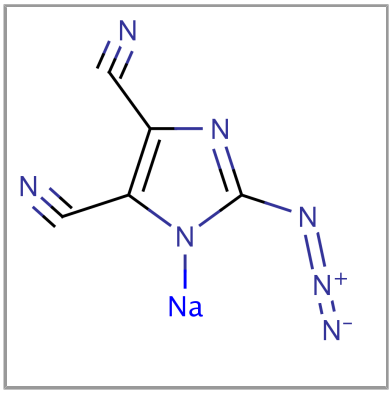

Compound Details Structure Search

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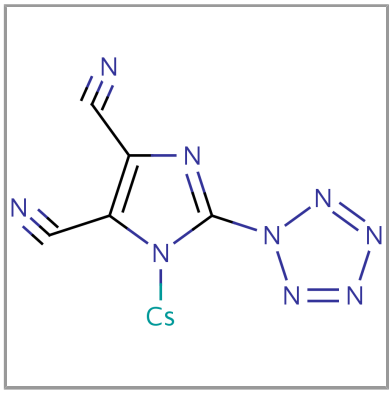

Compound Details Structure Search

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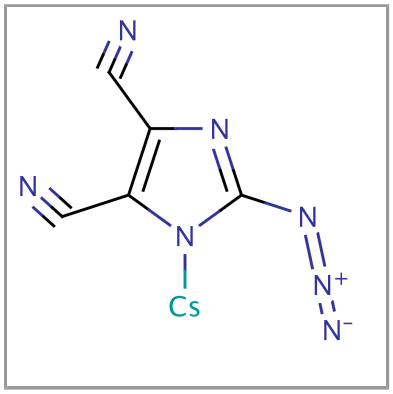

Compound Details Structure Search

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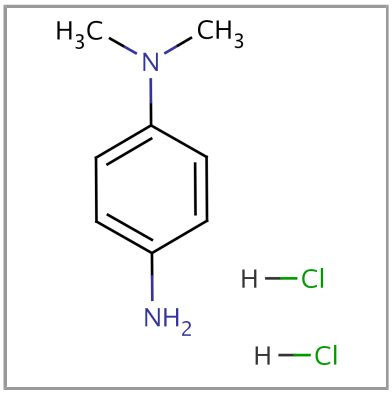

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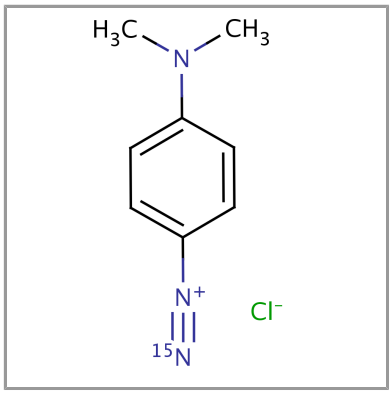

Compound Details Structure Search

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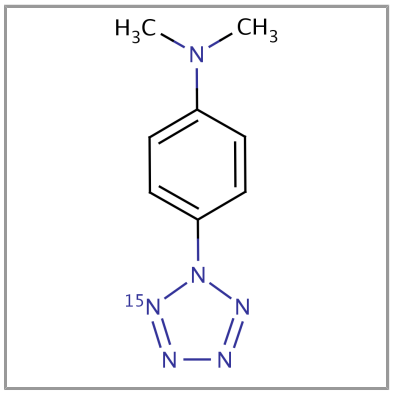

Compound Details Structure Search

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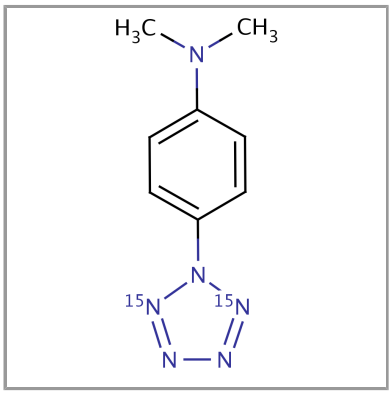

Compound Details Structure Search

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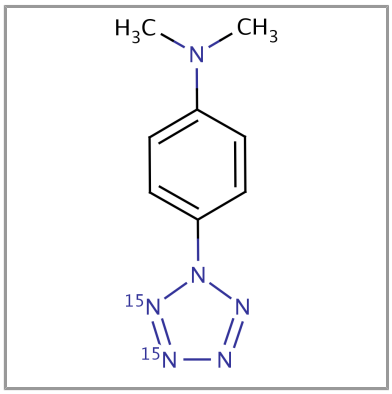

Compound Details Structure Search