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Synthesis of 1,2,4-Triazoles from Tosylmethyl Isocyanide and Aryldiazonium Compounds[1]

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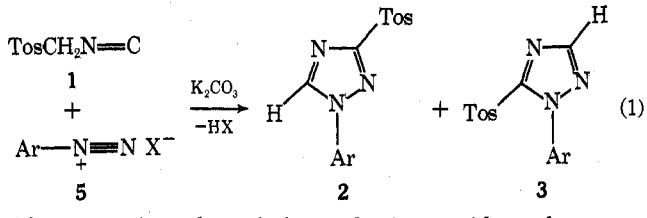
Received September 18, 1975

The coupling of diazonium salts and compounds XCH_2Y with an activated methylene group leads to formation of hydrazones. These reactions occur either without[3] or with loss (i.e. the Japp–Klingemann reaction)[4] of one of the activating functionalities X or Y. Ring-closed products are not usually formed in these processes.[3,4]

As a continuation of our work on synthetic applications of tosylmethyl isocyanide[5] (TosMIC, 1), we wish to report the synthesis of 1,2,4-triazoles from TosMIC and diazonium salts, according to eq 1. TosMIC accommodates, be-

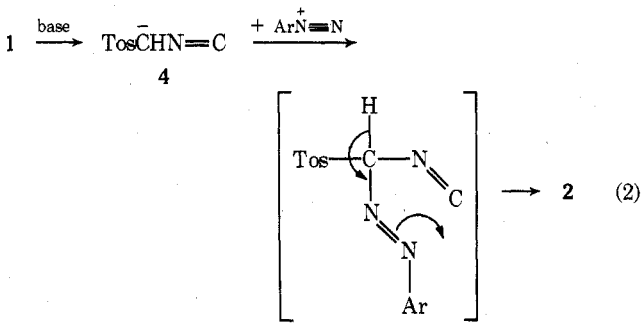


(1)

sides an activated methylene, the isocyanide carbon as a second reactive site. This offers the opportunity to form cyclic products. Thus, a number of azoles (oxazoles,[5a] imidazoles,[5b] thiazoles,[5c] and pyrroles[5d]) has been synthesized previously from TosMIC and C=O, C=N, C=S, and C=C containing substrates.[6]

It now appears that the N≡N triple bond of diazonium salts also is capable of undergoing cycloadditions with TosMIC[2,3] to give 1-aryl-3-tosyl-1,2,4-triazoles (**2**), together with minor amounts of the isomeric 1-aryl-5-tosyl-1,2,4-triazoles (**3**). The construction of the 1,2,4-triazole nucleus by this method, i.e., by formation of the N_1–C_5 and N_2–C_3 bonds, has a precedent in the Einhorn–Brunner reaction of diacylamines and hydrazines.[7]

The formation of the main product **2** is explained by eq 2, in close analogy with mechanisms proposed for previous

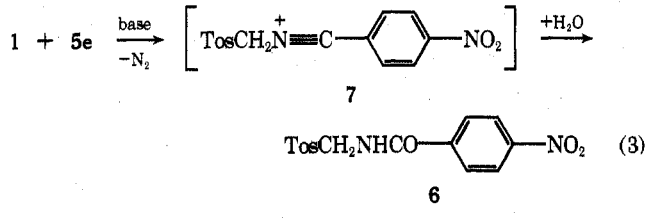


(2)

TosMIC reactions.[8] TosMIC anion **4** is assumed to attack the electrophilic β nitrogen of the diazonium ion, followed by ring closure and a proton shift to give **2**.

Several pathways are conceivable for the formation of the isomeric side-product **3**. These include, as an initial step, attack of TosMIC anion **4** at N_α rather than N_β of the diazonium ion, or, alternatively, attack at N_β by **4** through its isocyano carbon. Reaction through a diazotate anion, which also is present in the basic medium,[9] seems less likely since no **2c** (or **3c**) was formed from benzenediazonium tetrafluoroborate at pH > 13.[10] In fact, the formation of the triazoles **3** is the first illustration of a reversed addition of TosMIC to an unsaturated substrate.[8]

The reactions of TosMIC were carried out with a series of para-substituted benzenediazonium compounds, as well as with 3-pyridinediazonium chloride and α-naphthalenediazonium tetrafluoroborate (eq 1). As appears from Table I, that the highest yields of **2** were obtained from benzenediazonium salts with electron-donating substituents. A completely different reaction was observed with *p*-nitrobenzenediazonium tetrafluoroborate (**5e**). Instead of triazoles, the only product isolated was *N*-tosylmethyl-*p*-nitrobenzamide (**6**, 39%), apparently formed by nucleophilic displacement of nitrogen and hydration of the nitrilium ion[11] **7** (eq 3). For structural proof, **6** was prepared inde-



(3)

pendently (62% yield) by a Mannich condensation of *p*-toluenesulfinic acid, formaldehyde, and *p*-nitrobenzamide.

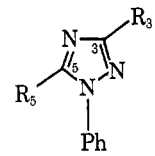
Structural Assignment of 2 and 3. The ^1H NMR, ir, and mass spectra of the isomers **2** and **3**, which were separable by preparative TLC, are consistent with the assigned structures (see Experimental Section). To differentiate between the substitution patterns in the isomeric triazoles,

Table I

		Compd 2		Compd 3	
Ar	X^-	% yield	Mp, °C	% yield	Mp, °C
a *p*-Dimethylaminophenyl	BF_4	94	177–178.5		
b *p*-Methoxyphenyl	Cl	80	144–145.5	12	141–142.5
c Phenyl	BF_4	40	120.5–122.5	18	112–114.5
d *p*-Acetylphenyl	BF_4	28	169–171.5	9	133.5–135.5
e *p*-Nitrophenyl[a]	BF_4				
f 3-Pyridyl	Cl	15	168.5–174[b]	3	127–128
g α-Naphthyl	BF_4	38	147.5–149.5		

[a] No triazole formed; see text and eq 3. [b] Dimorphous.

Table II
^{13}C NMR Data[a] of Triazoles 2c, 3c, and 8



Compd	R_3	R_5	C_3 δ	C_3 $^1J_{C-H}$[b]	C_3 $^3J_{C-H}$	C_5 δ	C_5 $^1J_{C-H}$[b]	C_5 $^3J_{C-H}$
8	H	H	151.8	208 (d)	12.5 (d)	140.3	212 (d)	7.5 (d)
2c	Tos	H	162.8		12.0 (d)	142.5	216 (d)	
3c	H	Tos	150.0	211 (d)		152.7		8.0 (d)

[a] Chemical shifts δ in parts per million downfield from Me_4Si; coupling constants J in hertz, multiplicity in parentheses. [b] For all other aromatic carbons $^1J_{C-H}$ is 165 ± 5 Hz.

the ^{13}C NMR spectra of **2c** and **3c** are compared with those of 1-phenyl-1,2,4-triazole (**8**, Table II). The ^{13}C NMR spectrum of **8**[12a] has not been reported previously; however, the signals at δ 151.8 and 140.3 can be assigned unambiguously to the heterocyclic ring carbons C_3 and C_5, respectively. This is based on (1) a large $^1J_{C-H}$ (>200 Hz);[13] (2) comparison with other 1-substituted 1,2,4-triazoles where C_3 is found at lower field than C_5.[13] By necessity, the structures of **2c** and **3c** are then as indicated. The tosyl substituent causes a considerable downfield shift (11–13 Hz) of the carbon to which it is attached directly, but it hardly affects the chemical shift of the other ring carbon.

The structural assignment of **2c** and **3c** is further supported by uv. The λ_{max} of **3c** shows a blue shift as compared with **2c**, since the N_1 phenyl (in **3c**) is twisted out of the plane of the triazole ring[14] because of the vicinal tosyl substituent. Also, the ^{1}H NMR signal of the N_1 phenyl in **3c** is almost a perfect singlet.[15]

Finally, the spectral evidence was corroborated by the following chemical conversions: (1) heating **2c** with a solid mixture of NaOH and KOH gave 3-hydroxy-1-phenyl-1,2,4-triazole (**9**, 37% yield), which was identical with an authentic sample; (2) similarly, **3c** gave in 40% yield the known 1-phenyl-Δ^2-1,2,4-triazolin-5-one (**10**); (3) compound **2c** was prepared recently in our laboratory by an independent route from N^1-phenyl-C-tosylformamidrazone and triethyl orthoformate.[16]

Experimental Section

The diazonium salts were prepared in the usual way.[17] Tosylmethyl isocyanide (TosMIC, **1**) was prepared by dehydration of N-tosylmethylformamide.[18] All compounds **2** and **3** showed the usual ^{1}H NMR signals for the tosyl protons at δ 2.4 (s, 3) and an AB q (4) at δ 7.3–8.2.

1-*p*-Dimethylaminophenyl-3-tosyl-1,2,4-triazole (2a). A solution of TosMIC (9.75 g, 50.0 mmol) and *p*-dimethylaminobenzenediazonium tetrafluoroborate (23.5 g, 100 mmol) in a mixture of Me_2SO (200 ml), MeOH (160 ml), and H_2O (80 ml) was cooled in ice–salt. To the stirred solution was added in 45 min a solution of K_2CO_3 (10.5 g, 76 mmol) in 100 ml of cold water. After stirring for another 10 min the reaction mixture was poured in 4 l. of ice–water, almost saturated with NaCl. The precipitate was collected, washed with water, and dried. Column chromatography (alumina, CH_2Cl_2–THF, 3:2) gave 16.0 g (94%) of **2a**, mp 172–175°. An analytically pure sample was obtained by preparative TLC (alumina, CH_2Cl_2), followed by crystallization from hot ethanol: mp 177–178.5°; ir (Nujol) 1335 and 1150 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.44 (s, 1, H_5), 7.56, 7.41, 6.80, 6.66 (q, 4, J = 9 Hz), 3.00 (s, 6); mass spectrum M$^+$ *m/e* 342. Anal. Calcd for $C_{17}H_{18}N_4O_2S$: C, 59.63; H, 5.30; N, 16.35; S, 9.37. Found: C, 59.5; H, 5.3; N, 16.5; S, 9.5.

1-*p*-Methoxyphenyl-3-tosyl-1,2,4-triazole (2b) and 1-*p*-Methoxyphenyl-5-tosyl-1,2,4-triazole (3b). To a solution of TosMIC (683 mg, 3.50 mmol) in Me_2SO (11 ml), MeOH (16 ml), and H_2O (2 ml), cooled in ice–salt, was added K_2CO_3 (1.40 g, 10.1 mmol). After stirring for 15 min a diazonium chloride solution, obtained from *p*-methoxyaniline (0.51 g, 4.1 mmol) in 10.6 ml of 1 *N* HCl and $NaNO_2$ (0.31 g, 4.5 mmol) in 10 ml of water, was added in 30 min. The work-up, analogous to **2a**, resulted in the separation of **2b** and **3b** by preparative TLC on alumina, eluting successively with CH_2Cl_2–Et_2O–pentane (2:2:1) and CH_2Cl_2–Et_2O–MeOH (2:2:0.01 and 1:1:0.01). Compound **2b** was obtained as a pale yellow solid, 920 mg (80%), mp 142–145°. Crystallization from benzene gave an analytically pure sample: mp 144–145.5°; ir (Nujol) 1330 and 1140 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1, H_5), 7.68, 7.53, 7.09, 6.93 (q, 4, J = 9 Hz), 3.88 (s, 3); mass spectrum M$^+$ *m/e* 329. Anal. Calcd for $C_{16}H_{15}N_3O_3S$: C, 58.34; H, 4.59; N, 12.76; S, 9.74. Found: C, 58.3; H, 4.5; N, 12.7; S, 9.8. Furthermore, 140 mg (12%) of white **3b** was obtained after one crystallization from benzene–pentane, mp 138–140.5°. Another crystallization from benzene–pentane provided an analytically pure sample: mp 141–142.5°; ir (Nujol) 1330, 1160, and 1145 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.04 (s, 1, H_3), 7.58, 7.42, 7.11, 6.95 (q, 4, J = 9 Hz), 3.91 (s, 3); mass spectrum M$^+$ *m/e* 329. Anal. Calcd for $C_{16}H_{15}N_3O_3S$: see **2b.** Found: C, 58.4; H, 4.6; N, 12.7; S, 9.8.

1-Phenyl-3-tosyl-1,2,4-triazole (2c) and 1-phenyl-5-tosyl-1,2,4-triazole (3c) were prepared, analogously to **2a**, from TosMIC and benzenediazonium tetrafluoroborate. They were separated similarly to **2b** and **3b** by elution (twice) with CH_2Cl_2–Et_2O–pentane (1:2:2) to give the following. (1) **2c** (40%), mp 121–123° (from benzene–pentane). One more crystallization gave an analytically pure sample: mp 120.5–122.5°; ir (Nujol) 1330 and 1150 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.58 (s, 1, H_5), 8.11–~7.3 (m, 9); mass spectrum M$^+$ *m/e* 299; uv (96% EtOH) λ_{max} 249 nm (log ε 4.32). Anal. Calcd for $C_{15}H_{13}N_3O_2S$: C, 60.05; H, 4.38; N, 14.04; S, 10.71. Found: C, 60.1; H, 4.4; N, 14.2; S, 10.6. (2) **3c** (18%) (from MeOH–pentane), mp 119.5–121.5°. Further crystallization from MeOH–pentane and from Et_2O–pentane gave an analytically pure sample: mp 112–114.5°; ir (Nujol) 1325, 1165, and 1145 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.02 (s, 1, H_3), 7.56 (s, 5); mass spectrum M$^+$ *m/e* 299; uv (96% EtOH) λ_{max} 241 nm (log ε 4.24). Anal. Calcd for $C_{15}H_{13}N_3O_2S$: see **2c.** Found: C, 60.2; H, 4.4; N, 13.9; S, 10.6.

1-*p*-Acetylphenyl-3-tosyl-1,2,4-triazole (2d) and 1-*p*-acetylphenyl-5-tosyl-1,2,4-triazole (3d) were synthesized analogously to **2a**, from TosMIC and *p*-acetylbenzenediazonium tetrafluoroborate. The precipitate from the aqueous NaCl solution was washed with water, dried, and chromatographed over a column of alumina, containing 5% of activated carbon, using CH_2Cl_2–THF (10:1). The resulting solid was stirred with benzene–THF (2:1) to provide a first crop of near-white **2d**, mp 165–168° (22%). The concentrated mother liquor was chromatographed according to the procedure for **2b** and **3b**, using CH_2Cl_2–benzene (7:3). Obtained were the following. (1) A second crop of **2d**, mp 164–167° (6%, total yield 28%). Crystallization from EtOH and from THF provided an analytical sample: mp 169–171.5°; ir (Nujol) 1680 (C=O), 1335 and 1155 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.80 (s, 1, H_5), 8.22, 8.09, 7.92, 7.78 (q, 4, J = 8 Hz), 2.65 (s, 3); mass spectrum M$^+$ *m/e* 341. Anal. Calcd for $C_{17}H_{15}N_3O_3S$: C, 59.81; H, 4.43; N, 12.31; S, 9.39. Found: C, 59.8; H, 4.6; N, 12.1; S, 9.4. (2) **3d**, 9% of a brown-white solid, mp 128–132°. Crystallization from EtOH and from Et_2O–THF (2:1) provided an analytically pure sample: mp 133.5–135.5°; ir (Nujol) 1680 (C=O), 1320, 1165, 1140 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 8.25, 8.11, 7.85, 7.70 (q, 4, J = 8.5 Hz), 8.06 (s, 1, H_3), 2.68 (s, 3); mass spectrum M$^+$ *m/e* 341. Anal. Calcd for $C_{17}H_{15}N_3O_3S$: see **2d.** Found: C, 59.8; H, 4.5; N, 12.3; S, 9.4.

1-(3-Pyridyl)-3-tosyl-1,2,4-triazole (2f) and 1-(3-pyridyl)-

5-tosyl-1,2,4-triazole (3f) were prepared analogously to **2b** and **3b** from TosMIC and 3-pyridinediazonium chloride. No precipitate was formed by pouring the reaction mixture in the NaCl solution. Extraction with CH_2Cl_2 gave a black oil from which 20% of TosMIC was recovered by chromatography over a column of alumina with CH_2Cl_2. Continued chromatography with CH_2Cl_2 + 2% of MeOH gave a dark brown solid which was stirred with benzene to yield **2f**, mp 164–168° (11%). The mother liquor was concentrated and separated according to the procedure given for **2b** and **3b**, using CH_2Cl_2–Et_2O (1:1), giving the following. (1) A second crop of **2f**, mp 164–167° (4%, from benzene–pentane); the total yield of **2f** was 15% after correction for recovered TosMIC. Crystallization from EtOH gave an analytical sample: mp 168.5–174° (dimorphous); ir (Nujol) 1330 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 9.07–8.97 (m, 1), 8.88–8.75 (m, 1), 8.72 (s, 1, H_5), 8.30–8.10 (m, 1), 7.70–~7.4 (m, 1); mass spectrum M^+ *m/e* 300. Anal. Calcd for $C_{14}H_{12}N_4O_2S$: C, 55.99; H, 4.03; N, 18.65; S, 10.67. Found: C, 55.8; H, 4.1; N, 18.4; S, 10.9. (2) **3f** (3%, based on recovered TosMIC), mp 124–127° (from benzene–pentane). An analytically pure sample was obtained after crystallization from benzene–pentane: mp 127–128°; ir (Nujol) 1340 and 1150 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 8.99–8.72 (m, 2), 8.13–7.90 (m + s, 2, H_3), 7.66–~7.4 (m, 1); mass spectrum M^+ *m/e* 300. Anal. Calcd for $C_{14}H_{12}N_4O_2S$: see **2f**. Found: C, 55.8; H, 4.1; N, 18.7; S, 10.5.

1-(α-Naphthyl)-3-tosyl-1,2,4-triazole (2g) was prepared analogously to **2a** from TosMIC and α-naphthalenediazonium tetrafluoroborate. A readily solidifying black oil was obtained, which was chromatographed over a column of alumina (benzene). The resulting brown solid was crystallized from benzene–pentane to give **2g**, mp 144–146.5° (38%). Two more crystallizations from benzene–pentane gave an analytically pure sample: mp 147.5–149.5°; ir (Nujol) 1330 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 8.51 (s, 1, H_5), ca. 8.2–7.88 (m, 2), 7.77–~7.5 (m, 5); mass spectrum M^+ *m/e* 349. Anal. Calcd for $C_{19}H_{15}N_3O_2S$: C, 65.31; H, 4.33; N, 12.02; S, 9.18. Found: C, 65.0; H, 4.2; N, 12.2; S, 9.2.

***N*-Tosylmethyl-*p*-nitrobenzamide (6)** was prepared analogously to **2a** from TosMIC and *p*-nitrobenzenediazonium tetrafluoroborate. A dark brown solid was obtained, which was washed with CH_2Cl_2 and crystallized from acetone–pentane, yielding 39% of **6**, mp 211–213.5°. Further crystallization gave an analytical sample: mp 206.5–207° (slight dec); ir (Nujol) 1645 (C=O), 1545 and 1345 (NO_2), 1325 and 1130 cm^{-1} (SO_2); ^1H NMR (Me_2SO-d_6) δ ca. 10.0–9.7 (t, br, 1), 8.41, 8.26, 8.04, 7.90 (q, 4, J = 9 Hz), 4.94 (d, br, 2, J = 7 Hz); mass spectrum M^+ *m/e* 334. Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38; S, 9.59. Found: C, 53.8; H, 4.4; N, 8.4; S, 9.5. This compound was identical in all respects with a sample prepared independently by the procedure of Olijnsma et al.[19] for *N*-tosylmethylbenzamide; recrystallization of the crude product from acetone gave **6** in 62% yield, mp 203.5–204.5° (slight dec).

3-Hydroxy-1-phenyl-1,2,4-triazole (9). A powdered mixture of 1-phenyl-3-tosyl-1,2,4-triazole (**2c**, 450 mg, 1.51 mmol), NaOH (64 mg, 1.60 mmol), and KOH (136 mg, 2.43 mmol)[20] was heated for 10 min at 160°. The resulting brown solid was dissolved in 10 ml of an aqueous NaCl solution. After extraction with CH_2Cl_2 (10 ml), the solution was acidified to pH 1. The white precipitate was collected and stirred with CH_2Cl_2 (10 ml) to remove *p*-toluenesulfinic acid. The residual solid was collected, washed with water, and dried, yielding **9** (90 mg, 37%), mp 287° (subl). This compound was identical with an authentic sample, prepared by the method of Widman.[12a]

1-Phenyl-Δ²-1,2,4-triazolin-5-one (10) was prepared from **3c** analogously to the synthesis of **9**. The aqueous solution with the reaction product was neutralized with dilute sulfuric acid. Extraction with CH_2Cl_2 gave **10** as a white solid after removal of the solvent in 40% yield, after one recrystallization from Et_2O–pentane, mp 180.5–182.5°. Compound **10** has the same melting point (reported 182–184°,[21] 183–184° [22]) and the same characteristic ir and ^1H NMR data as reported previously.[22]

Registry No.—**1**, 39495-97-1; **2a**, 57428,35-0; **2b**, 57428-36-1; **2c**, 55860-44-1; **2d**, 57428-37-2; **2f**, 57428-38-3; **2g**, 57428-39-4; **3b**, 57428-40-7; **3c**, 57428-41-8; **3d**, 57428-42-9; **3f**, 57428-43-0; **5a**, 24564-52-1; **5b**, 4346-59-2; **5c**, 369-57-3; **5d**, 19262-73-8; **5e**, 456-27-9; **5f**, 35003-14-6; **5g**, 28912-93-8; **6**, 57428-44-1; **8**, 13423-60-4; **9**, 4231-68-9; **10**, 21434-16-2.

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Chemistry of Diaminomaleonitrile. I. Selective Preparations of Monoformyldiaminomaleonitrile and Imidazoles by Reaction with Formic Acid

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Received July 14, 1975

The reaction of diaminomaleonitrile (DAMN) and formic acid depends critically on the conditions under which the experiment is performed. Bredereck and Schmötzer[1] have reported the reaction of DAMN in anhydrous formic acid under mild conditions (<35°C, within 5 min) to give monoformyldiaminomaleonitrile in 50% yield. This reaction is accompanied by formation of tarry materials; an intractable black syrup is obtained after prolonged reaction times or at higher reaction temperatures. On the other hand, heating a heterogeneous mixture consisting of DAMN, formic acid, and xylene gives a fair yield (61%) of 4(5)-cyanoimidazole-5(4)-carboxamide (**4**)[2] with little tar formation.

We have examined the reaction in several solvents and found that monoformyldiaminomaleonitrile (**2**), 4,5-dicya-