Carbenoids

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Selective Functionalization of Aromatic C(sp^2)–H Bonds in the Presence of Benzylic C(sp^3)–H Bonds by Electron-Deficient Carbenoids Generated from 4-Acyl-1-Sulfonyl-1,2,3-Triazoles

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Abstract: *A rhodium(II)-catalyzed reaction of newly prepared 4-acyl-1-sulfonyl-1,2,3-triazoles with benzene, and its derivatives, is investigated. Acceptor/acceptor carbenoids generated from 4-acyltriazoles undergo selective insertion at aromatic C(sp^2)–H bonds in the presence of benzylic C(sp^3)–H bonds to produce N-sulfonylenaminones.*

The 4-aryl-1-sulfonyl-1,2,3-triazole scaffolds have emerged as precursors to α-imino metal carbene complexes.[1] Their ring-chain tautomerization generates α-imino diazo compounds, although the equilibrium lies towards the triazole form. Transition-metal catalysts, especially rhodium(II) carboxylate dimers, promptly trap the transient α-imino diazo compounds to give α-imino metal carbene complexes. These metal carbene complexes are regarded as donor/acceptor carbenoids. A number of synthetically useful transformations involving these donor/acceptor carbenoids as the key intermediates have been developed.[2] In contrast, the chemistry of acceptor/acceptor carbenoids, which are generated from triazoles and have two electron-withdrawing substituents, has been underdeveloped.[3,4] We now report a rhodium(II)-catalyzed reaction of newly prepared 4-acyl-1-sulfonyl-1,2,3-triazoles with benzene and its derivatives (Figure 1).[5–8] Acceptor/acceptor carbenoids generated from 4-acyltriazoles undergo selective insertion at the aromatic C(sp^2)–H bonds in the presence of the benzylic C(sp^3)–H bonds to produce *N*-sulfonylenaminones.[9]

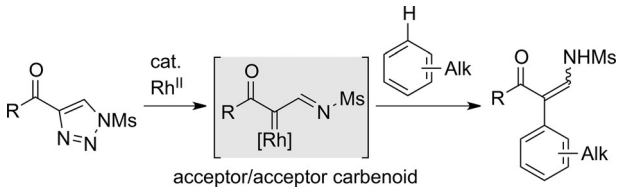
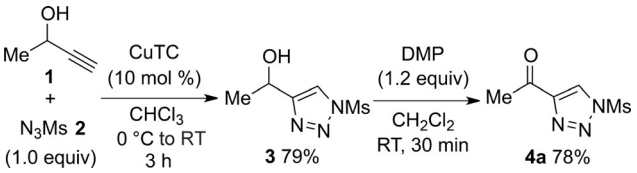


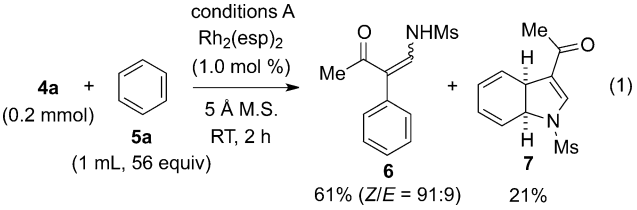
Figure 1. Aromatic C(sp^2)–H insertion of acceptor/acceptor carbenoids generated from 4-acyltriazoles. Ms = methanesulfonyl (mesyl).

Initially, 4-acetyl-1-mesyl-1,2,3-triazole (**4a**; 4-acetyltriazole) was prepared from but-3-yn-2-ol (**1**) and mesyl azide (**2**) by a copper(I)-catalyzed 1,3-dipolar cycloaddition reaction[10] and subsequent Dess–Martin oxidation of the hydroxy group of the resulting triazole **3** (Scheme 1). The isolated **4a** was a white solid and could be kept at −30 °C.



Scheme 1. Preparation of 4-acetyltriazole (**4a**). CuTC = copper(I) thiophene-2-carboxylate, DMP = Dess–Martin periodinane.

The triazole **4a** was compared with 4-phenyl-1-mesyl-1,2,3-triazole (4-phenyltriazole) in reactions with benzene (**5a**) and its derivatives. No reaction occurred when 4-phenyltriazole (0.20 mmol) was treated with $Rh_2(esp)_2$ (1.0 mol %; esp = α,α,α′,α′-tetramethyl-1,3-benzene-dipropionate) and 5 Å molecular sieves (5 Å M.S.) in a benzene solution (**5a**; 1 mL, 56 equiv) at room temperature (conditions A). In contrast, **4a** (0.20 mmol) did react with **5a** under the same reaction conditions, and after 2 hours, furnished the C(sp^2)–H insertion product **6** in 61 % yield along with the [3+2] cycloadduct **7** (21 %) [Eq. (1)].[11] The *N*-sulfonylenaminone **6** consisted of *E*- and *Z*-isomers, and the *Z*-isomer, having an intramolecular hydrogen bond (N-H···O=C), was predominant.[12] Thus, the carbenoid generated from **4a** was considerably more reactive toward **5a** than that generated from 4-phenyltriazole.



4-Phenyltriazole (0.20 mmol) failed to react with fluorobenzene (**5b**, 1 mL, 53 equiv) at room temperature, and even at an elevated temperature of 70 °C. In contrast, **4a** (0.20 mmol) reacted with **5b** at the *para* position at room temperature to afford the C(sp^2)–H insertion product **8** in 50 % yield [Eq. (2)].[13] No *ortho*-substituted product was identified by ^{1}H NMR (400 MHz) spectroscopy.

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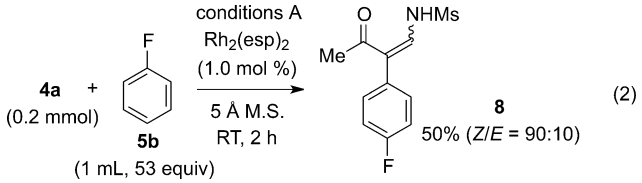
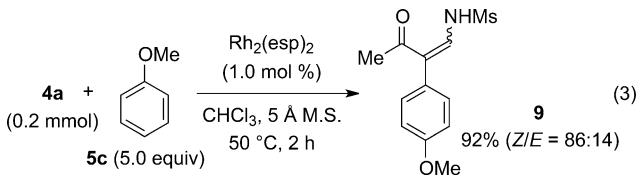
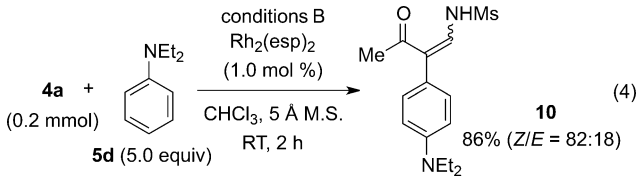


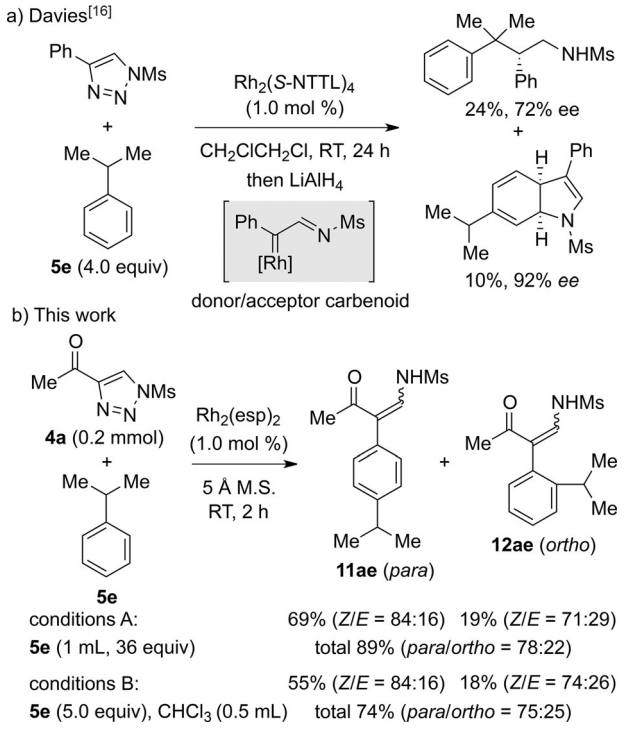
It was reported that 4-phenyltriazole reacted with anisole (**5c**)[14] and *N*,*N*-diethylaniline (**5d**)[15] at 100 °C to afford the corresponding insertion products resulting from reactions at the *para* C(sp^2)–H bonds. **4a** also gave the *para*-substituted products **9** and **10** when 5.0 equivalents of **5c** and **5d**, respectively, was used in 0.5 mL of chloroform at lower temperatures (conditions B) [Eqs. (3) and (4)]. No *ortho*-substituted product was identified by ^{1}H NMR (400 MHz) spectroscopy.





Strikingly contrasting results were obtained when 4-phenyltriazole and **4a** were reacted with isopropylbenzene (**5e**). Almost no reaction occurred when the 4-phenyltriazole (0.20 mmol) was treated with $Rh_2(esp)_2$ (1.0 mol %) and 5 Å M.S. in an isopropylbenzene solution (**5e**, 1 mL, 36 equiv) (conditions A). Davies et al. reported that the reaction of 4-phenyltriazole with **5e**, using $Rh_2(S\text{-NTTL})_4$ as the catalyst, (1.0 mol %) gave the C(sp^3)–H insertion product (24 %, 72 % *ee*) and a [3+2] cycloadduct (10 %, 92 % *ee*; Scheme 2 a).[16] In contrast, when the reaction conditions A were applied to **4a**, the *N*-sulfonylenaminones **11ae** and **12ae** were obtained in 69 and 19 % yields, respectively (Scheme 2 b). The *para*/*ortho* ratio (**11ae**/**12ae**) was 78:22. No C(sp^3)–H insertion product was formed.[17] When **4a** was reacted with 5.0 equivalents of **5e** in 0.5 mL of chloroform (conditions B), **11ae** and **12ae** were obtained in slightly lower yields (55 %/18 %) with a similar *para*/*ortho* ratio (75:25). The acceptor/acceptor carbenoid generated from **4a** is so electrophilic that it is attacked by the π electrons of the benzene ring. In contrst, the donor/acceptor carbenoid generated from 4-phenyltriazole is not electrophilic enough to be attacked by the π electrons, and instead acts upon the secondary benzylic C(sp^3)–H σ bond,[7d,8] the bond dissociation energy of which is about 90 kcal mol^{-1},[5b] through a three-centered transition state.[5a]

Thus, a significant difference was observed between **4a** and 4-phenyltriazole in the sites of the reaction with **5e**. We



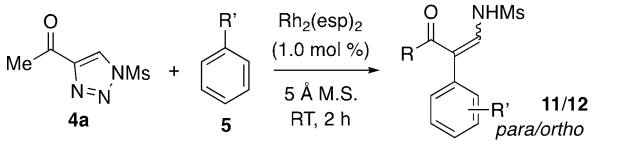
Scheme 2. Contrasting results of the reaction with isopropylbenzene (**5e**).

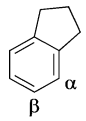
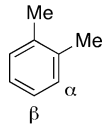
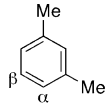
next studied the reaction of **4a** with benzene derivatives, having alkyl substituents, in more detail under the reaction conditions A and B (Table 1). Monosubstituted alkylbenzenes (**5f–h**) gave the corresponding *N*-sulfonylenaminones in total yields ranging from 75 to 92 % (entries 1–3). The *para*/*ortho* ratios were around 3:1 ≈ 4:1. Even *tert*-butylbenzene (**5i**) showed a similar ratio (entry 4). Thus, the steric bulkiness of the alkyl substituent hardly influenced the *para*/*ortho* selectivity, as it depends upon the electronic effects. Dialkyl-substituted benzenes (**5j–l**) also participated in the aromatic C(sp^2)–H insertion reaction (entries 5–7). *p*-Xylene and mesitylene failed to give any products, probably because of steric reasons. Thus, the C–H insertion reaction took place at aromatic C(sp^2)–H bonds whereas benzylic C(sp^3)–H bonds remained intact.

A variety of 4-acyltriazoles (**4b–f**; R = Et, *n*Bu, *i*Pr, Ph, and 4-ClC_6H_4) were also readily prepared from the corresponding propargylic alcohols through the 1,3-dioplar cycloaddition/Dess–Martin oxidation procedure, and they were reacted with **5f** under the reaction conditions A (Table 2). The corresponding *N*-sulfonylenaminones were obtained in total yields ranging from 73 to 98 % and the *para*/*ortho* ratios were around 5:1.[18]

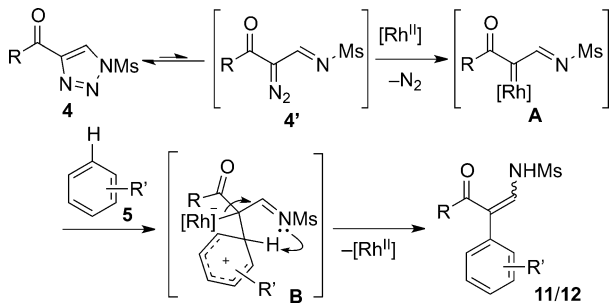
We assume an electrophilic aromatic substitution pathway for the production of the *N*-sulfonylenaminones **11** and **12** (Scheme 3). Ring-chain tautomerization of **4** gives the diazo compound **4′**, which promptly reacts with rhodium(II) to generate the acceptor/acceptor carbenoid **A** with extrusion of molecular nitrogen. π-Electrons of a substituted benzene attack the electrophilic carbenoid carbon center to form the Wheland-type intermediate **B**. An attack at a more electron-rich sp^2-hybridized carbon center would be favored. Next, the

Table 1: Rhodium(II)-catalyzed reaction of **4a** with various alkyl-substituted benzenes (**5**).[a]



Entry	R′ (**5**)	**11**/**12**	conditions A[b,c] **11** [%] (*Z*/*E*) **12** [%] (*Z*/*E*) **11**+**12** [%] (*para*/*ortho*)	conditions B[b,c] **11** [%] (*Z*/*E*) **12** [%] (*Z*/*E*) **11**+**12** [%] (*para*/*ortho*)
1	Me (**5f**)	**11af**/**12af**	75 (88:12) 14 (77:23) 89 (*p*/*o* = 84:16)	63 (87:13) 16 (75:25) 79 (*p*/*o* = 80:20)
2	Et (**5g**)	**11ag**/**12ag**	75 (87:13) 17 (76:24) 92 (*p*/*o* = 81:19)	54 (86:14) 22 (72:28) 77 (*p*/*o* = 71:29)
3	*i*Bu (**5h**)	**11ah**/**12ah**	66 (88:12) 22 (79:21) 88 (*p*/*o* = 75:25)	54 (89:11) 21 (79:21) 75 (*p*/*o* = 72:28)
4	*t*Bu (**5i**)	**11ai**/**12ai**	67 (82:18) 21 (58:42) 88 (*p*/*o* = 77:23)	60 (84:16) 21 (50:50) 81 (*p*/*o* = 75:25)
5	 **5j**	**11aj**/**12aj**	54 (86:14) 41 (79:21) 95 (*β*/*α* = 57:43)	35 (86:14) 28 (80:20) 63 (*β*/*α* = 56:44)
6	 **5k**	**11ak**/**12ak**	35 (87:13) 62 (75:25) 97 (*β*/*α* = 35:65)	31 (86:14) 49 (75:25) 80 (*β*/*α* = 39:61)
7	 **5l**	**11al**	60 (74:26) (*α* only)	34 (76:24) (*α* only)

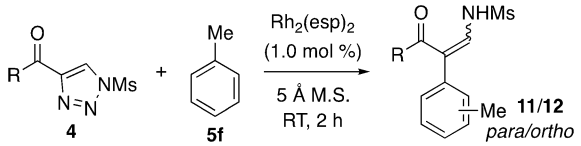
[a] Reaction conditions A: **4a** (0.20 mmol), **5** (1 mL), $Rh_2(esp)_2$ (2 μmol), and 5 Å M.S. (42 mg); Reaction conditions B: **4a** (0.20 mmol), **5** (1.0 mmol), $Rh_2(esp)_2$ (2 μmol), and 5 Å M.S. (42 mg) in $CHCl_3$ (0.5 mL). [b] Yield of product after chromatographic purification. [c] *Z*/*E* ratios of **11** and **12** determined by ^{1}H NMR spectroscopy.



Scheme 3. Plausible mechanism for the formation of **11**/**12** from **4** and **5**.

anionic rhodium releases an electron pair, which induces the nitrogen to abstract a proton completing an electrophilic aromatic substitution.

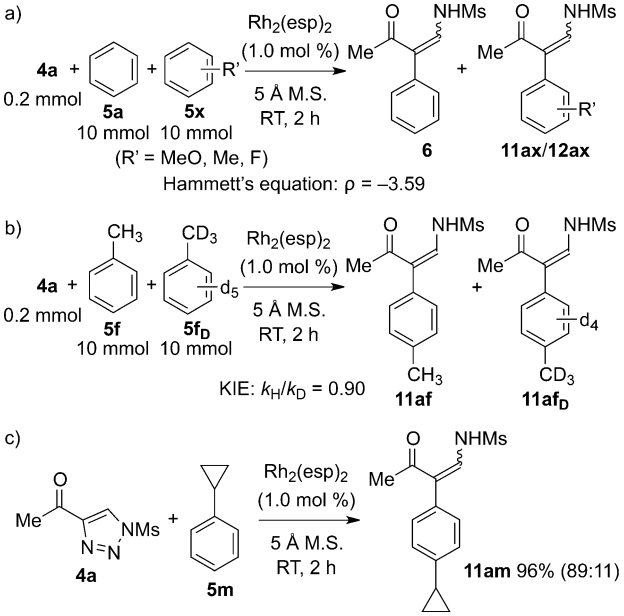
Table 2: Rhodium(II)-catalyzed reaction of various 4-acyltriazoles (**4**) with **5f**.[a]



Entry	R (**4**)	**11**/**12**	conditions A[b,c] **11** [%] (*Z*/*E*), **12** [%] (*Z*/*E*) **11**+**12** [%] (*para*/*ortho*)
1	Et (**4b**)	**11bf**/**12bf**	83 (87:13), 15 (80:20) 98 (*p*/*o* = 85:15)
2	*n*Bu (**4c**)	**11cf**/**12cf**	66 (86:14), 9 (72:28) 75 (*p*/*o* = 87:13)
3	*i*Pr (**4d**)	**11df**/**12df**[d]	60 (87:13), 18 (83:17) 78 (*p*/*o* = 77:23)
4	Ph (**4e**)	**11ef**/**12ef**	62 (78:22), 11 (59:41) 73 (*p*/*o* = 85:15)
5	4-ClC_6H_4 (**4f**)	**11ff**/**12ff**	68 (80:20), 13 (65:35) 80 (*p*/*o* = 84:16)

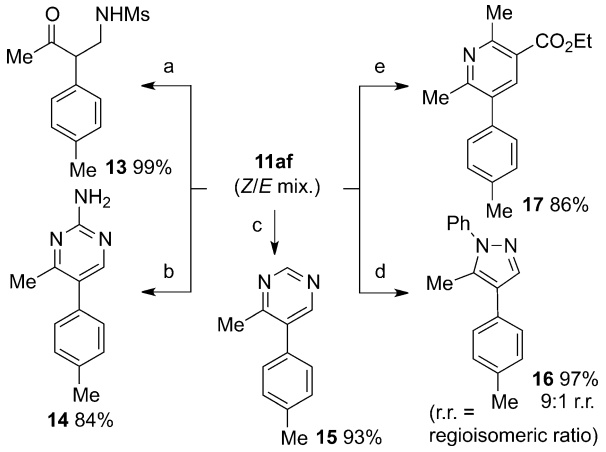
[a] Reaction conditions A: **4** (0.20 mmol), **5f** (1 mL), $Rh_2(esp)_2$ (2 μmol), and 5 Å M.S. (42 mg). [b] Yield of product after chromatographic purification. [c] *Z*/*E* ratios of **11** and **12** determined by ^{1}H NMR spectroscopy. [d] 70 °C.

The following results from mechanistic experiments are in agreement with the mechanism shown in Scheme 3. First, the Hammett constant was determined by carrying out competitive reactions of **4a** with **5a** and its derivatives (Scheme 4a; see the Supporting Information). The ρ value was −3.59, thus suggesting that a positively charged transition state is developed starting from **5**. Next, a kinetic isotopic effect was measured using equimolar amounts (10 equiv each) of **5f** and $\mathbf{5f_D}$ in the reaction of **4a** (Scheme 4b). An inverse isotopic effect ($k_H/k_D = 0.90$) was observed. This value is



Scheme 4. Mechanistic studies. a) Hammett's equation. b) Kinetic isotope effects. c) Cyclopropylbenzene as radical probe.

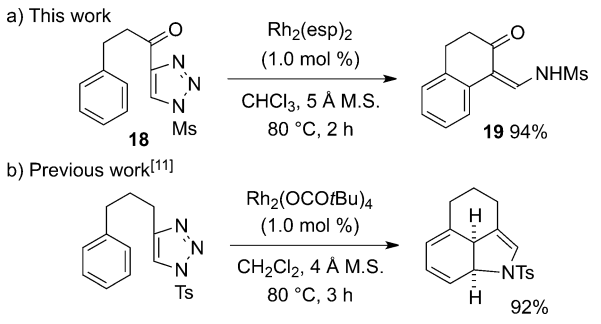
similar to that reported for the an iron(II)-catalyzed aromatic C(sp^2)–H insertion reaction with ethyl diazoacetate.[7f] Furthermore, a reaction was carried out using cyclopropylbenzene (**5m**) as the radical probe (Scheme 4c).[19] No cyclopropane-ring-opened product was formed, thus indicating it unlikely that long-lived radical intermediates were involved.



Scheme 5. Synthetic transformations of **11af**. a) H_2 (1 atm), 10 mol% Pd/C(en), MeOH; b) HN=C(NH_2)$_2$·HCl, NaOH, EtOH; c) HN=$CHNH_2$·HCl, pyridine; d) $PhNHNH_2$, EtOH; e) $MeCOCH_2CO_2Et$, NH_4OAc, AcOH.

The product **11af** was further transformed (Scheme 5).[20] The carbon–carbon double bond was reduced to give the β-amino ketone **13** in 99% yield when treated with H_2 (1 atm) and a Pd/C(en) catalyst. Various heterocycles were synthesized. Treatment of **11af** with guanidine, formamidine, phenylhydrazine, and ethyl acetate afforded the pyrimidines **14**/**15**, pyrazole **16**, and pyridine **17**, respectively.

An intramolecular reaction successfully occurred with the 4-(3-phenylpropanoyl)-1,2,3-triazole (**18**; Scheme 6a).[21] A six-membered-ring product (**19**) was formed in 94% yield through intramolecular insertion at the aromatic C(sp^2)–H bonds. We previously reported that a donor/acceptor carbenoid generated from 4-(3-phenylpropyl)-1,2,3-triazole gave a [3+2] cycloadduct (Scheme 6b).[11] It is interesting that the triazoles of similar skeletons follow contrasting mechanistic pathways depending on their electronic nature.



Scheme 6. Aromatic C(sp^2)–H insertion vs. [3+2] cycloaddition in intramolecular reaction with α-imino rhodium carbenes. Ts = *p*-toluenesulfonyl.

In summary, we have disclosed the interesting reactivity of acceptor/acceptor carbenoids generated from 4-acyltriazoles toward benzene (**5a**) and its derivatives. They insert selectively into aromatic C(sp^2)–H bonds in the presence of benzylic C(sp^3)–H bonds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arenes · C–H insertion · carbenoids · reaction mechanisms · rhodium

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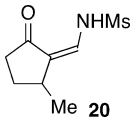

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