Reaction of N-Sulfonyl-1,2,3-Triazole with β -Diketone

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Imino carbenoids I derived from N-sulfonyl-1,2,3-triazoles 1 can undergo useful tandem reactions, because they have a nucleophilic imino group in addition to an electrophilic carbenoid moiety.^{1,2} In present study, we investigated that Rh(II)-catalyzed reaction of Nsulfonyl-1,2,3-triazoles 1 with various β -diketones 2. Enaminone 3aa and 2,3-fused pyrrole 4aa were formed by any Rh(II)-catalyzed reaction of N-tosyl-1,2,3-triazole 1a with cyclic diketone 2a (Table 1, Entries 1-3). It was revealed that 3aa was produced predominantly by more sterically hindered Rh₂(piv)₄ catalyst (Table 1, Entry 3). However, less sterically hindered Rh₂(OAc)₄-catalysed reaction gave preferentially 4aa (Table 1, Entry 1). In addition, triazole skeleton-remained 5aa and 5'aa were obtained as major product by Rh(OAc)4-catalyzed reaction and non-Rh(II) catalyzed reaction (Table 1, Entry 1 and 4). On the other hand, 5aa and 5'aa were not isolated by Rh₂(piv)₄-catalyzed or Rh₂(hex)₄-catalyzed reaction.



Table 1. Reaction of triazole 1a with dimedone 2a under various conditions^a

Entry	Rh cat.	Yield ^b (%)				Ratio	Ratio
		3aa	4aa	5aa	5'aa	3aa : 4aa	5aa : 5'aa
1	Rh ₂ (OAc) ₄	9	19	29	10	32 : 68	74 : 26
2	Rh ₂ (hex) ₄	39	8	-	-	83 : 17	-
3	Rh ₂ (piv) ₄	47	4	-	-	92:8	-
4	None	-	-	32	29	-	52 : 48

^aConditions: 1 (1.0 mmol), 2 (3.0 mmol), 4 Å MS (400 mg), and Rh(II) catalyst (2 mol%) were combined in toluene (5 ml) and stirred at 100 °C under an argon atmosphere. ^bIsolated yield.

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