Reaction of N-Sulfonyl-1,2,3-Triazoles with β -Diketones

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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 the present study, we investigated that Rh(II)-catalyzed reaction of N-mesyl-1,2,3-triazoles (1a) with cyclic β -diketones 2.

Enaminones **3a** were formed as a major product by the 2 mol% Rh₂(piv)₄-catalyzed reactions of **1a** with 3 equiv. of **2a–c** (Table 1, Entries 1, 2, and 4). On the other hand, 2,3-fused pyrrole **4ac** were obtained in moderate yield by the 2 mol% Rh₂(hex)₄-catalyzed reaction of **1a** with 3 equiv. of dimedone (**2c**) (Table 1, Entry 3). The 2 mol% Rh₂(piv)₄-catalyzed reaction of **1a** with 3 equiv. 1,3-cyclopentanedione (**2e**), or 3 equiv. of 5-phenyl-1,3-cyclohexanedione (**2d**) gave triazole skeleton-remained products **5ae** and **5'ad**, respectively (Table 1, Entries 5, and 6). In addition, triazole skeleton-remained product was confirmed as a major product of the 2 mol% Rh₂(piv)₄-catalyzed reactions of **1a** with 1 equiv. of **2d**. However, triazole skeleton-remained product was not confirmed in the 5 mol% Rh₂(piv)₄-catalyzed reactions of **1a** with 1 equiv. of **2d**.

$$\begin{array}{c} Ph \\ N=N \end{array} \begin{array}{c} N-Ms \\ Rh \ cat. \\ -N_2 \\ solvent \end{array} \begin{array}{c} Ph \\ RR' \\ 3a \end{array} \begin{array}{c} Ph \\ RR' \\ RR' \\ RhL_n \\ I \end{array} \begin{array}{c} Ph \\ N-Ms \\ RR' \\ R$$

Table 1. Reaction of triazole 1a with cyclic β -diketones 2 under various conditions^a

Entry	2	R	R'	n	Rh cat.	Solvent	Temp.	Yield ^b (%)			
								3a	4a	5a	5'a
1	2a	Н	Н	1	Rh ₂ (piv) ₄	Toluene	100 °C	42	_	-	_
2	2b	CH ₃	н	1	Rh ₂ (piv) ₄	Toluene	100 °C	58	_	_	_
3	2c	CH ₃	CH ₃	1	Rh ₂ (hex) ₄	Toluene	100 °C	23	22	_	_
4	2c	CH ₃	CH ₃	1	Rh ₂ (piv) ₄	Toluene	100 °C	33	12	-	-
5	2d	Ph	н	1	Rh ₂ (piv) ₄	Toluene	100 °C	_	_	-	49
6	2e	н	н	0	Rh ₂ (piv) ₄	1,2-DCE	reflux	-	-	33	-

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

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