化 学 学 报
ACTA CHIMICA SINICA

研究论文
Article

DOI: 10.6023/A12060337

硫叶立德[2,3]-σ 重排反应迁移基团活性研究

李玉叶 ,　黄重行　许鹏飞　张艳　王剑波*,

(א у б б א א 100871)

(˝Ω ╗ у ˝Ω 730000)

у у Ю, б а [2,3]-σ ⩚ .
^{1}H NMR , б а ⩚ ⩚ , ҿ
[2,3]-σ ⩚ , а у ⩚ . й ⩚
.

˝Ω ; [2,3]-σ ; ; ; у ⩚

Studies on the Reactivity of Migrating Group in [2,3]-Sigmatropic Rearrangement of Sulfur Ylides

Li, Yuye ,　Huang, Zhongxing　Xu, Peng-Fei　Zhang, Yan　Wang, Jianbo*,

(( )
, , , ,)
(, ,)

Abstract The [2,3]-sigmatropic rearrangement of sulfur ylides is unique and useful reaction in organic synthesis. In this study, the reactivity of sulfides containing three different migrating groups (propargyl, allyl, and allenyl) in [2,3]-sigmatropic rearrangement of sulfur ylides has been compared. The competition reactions of phenylethyldiazoacetate with sulfides through sulfonium ylide [2,3]-sigmatropic rearrangement are designed under Rh(II)- or Cu(I)-catalyzed reaction conditions. Both intra- and intermolecular competitions of sulfides bearing two different migrating groups have been carried out. The ratio of products has been determined by ^{1}H NMR in order to compare the reactivity of different sulfides bearing allyl, propargyl or allenyl groups. Obvious disparity of the reactivity of these sulfides in [2,3]-sigmatropic rearrangement has been observed. Experimental data indicate that the tendency of preferential [2,3]-sigmatropic rearrangement has the following order: propargyl sulfide allyl sulfide allenyl sulfide. Catalysts such as $Rh_2(OAc)_4$, $Rh_2(O_2CCF_3)_4$, and $Cu(CH_3CN)_4PF_6$ ligated with a series of diimine ligands have been investigated for these reactions. Rh(II) complexes are found more efficient than Cu(I) complexes, and $Rh_2(O_2CCF_3)_4$ is more efficient than $Rh_2(OAc)_4$. The efficiency of different catalytic system has been explained based on the proposed reaction mechanism. The reaction catalyzed by Rh(II) complexes is suggested to be different from that catalyzed by Cu(I) complexes. In the case of Cu(I)-catalyzed reaction, Cu(I)-bonded sulfur ylide is considered as the predominant intermediate, while the [2,3]-sigmatropic rearrangement is suggested to proceed through free ylide. Both steric hindrance and electronic properties of ligands influence the ratio and selectivity in Cu(I)-catalyzed reactions. This study provides useful information for further investigation of [2,3]-sigmatropic rearrangement of sulfur ylides.

Keywords sulfur ylide; [2,3]-sigmatropic rearrangement; metal carbene; migratory group; catalytic reaction

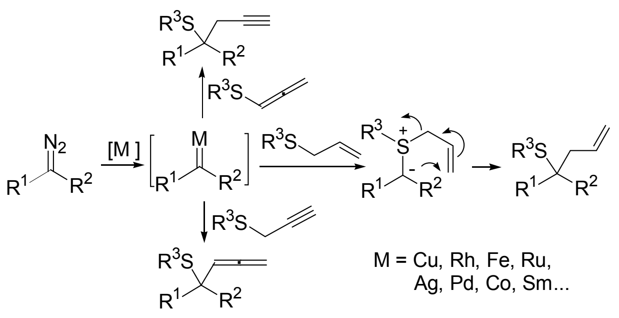
1 引言

у , [2,3]-σ ⩚
⩚ .
, й Æ у
. [2,3]-σ ⩚ ,
й . ÿ 1968 ⩚
[1], [2,3]-σ ⩚ у

у , ⩚
˝Ω [2,3]. ⩚ ,
˝l , [4]. а
˝l , 1 equiv.
, й . ˝l ╗
у [5], б ⩚ .
, ⩚ æ,

* E-mail: wangjb@pku.edu.cn; Tel.: 0086-010-6275-7248; Fax: 0086-010-6275-7248.
Received June 24, 2012; published September 3, 2012.
Supporting information for this article is available free of charge via the Internet at http://sioc-journal.cn.
Project supported by the National Natural Science Foundation of China (Nos. 21072009, 21172005), National Basic Research Program of China (973 Program, No. 2009CB825300), The Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.
⩚ (Nos. 21072009, 21172005) (973 Program, No. 2009CB825300) ╠
╠.

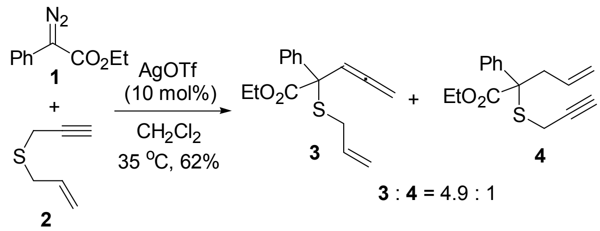
ป . , ง
Æ , б ป
[2,3,4b]. ป ,
, ป
.
ง Æ a ,
ง ป [6];
ง , Fischer ,
[7a]; [7b]
. ง ป ,
ง a ῼ
. ง Ю,
ป б ง
[2,3]-σ ป (б ป й
Doyle-Kirmse ป [8]). ป ง ʺI
, Æ б ป
,
[2,3]-σ — (Scheme 1)[2,3]. a
ง Э ,
ง й ง
, Æ ง . ง
,
ง ป [9],
[2,3]-σ ป [10].



Scheme 1

ง ง б [2,3]-σ ป
ง ง [2,3a,3d,3f h,11] ง [2,3e,12],
[13] [3c,14] [15] [16] [17]
[18] [19] ง , ง
[2,3]-σ ป . ป ,
ง , a
ง [2,3]-σ ป [2,3].
, ง ,
ป [2,3]-σ ป ,
, й ,
[3d,14a,20]. a
[2,3]-σ ป б ,
ὰ [21,22].
[2,3]-σ ป ,

Э ҿ ,
Ў a . й , ῼ
ป
. Davies [22] 2009 ,
Ag(I) ง [2,3]-σ ป
, **1**
2 й ,
3 **4**, ^{1}H NMR
й 4.9 1. ,
,
[2,3]-σ ป ,
(Scheme 2).
[2,3]-σ ป
ป , ง
ป .



Scheme 2

2 结果与讨论

Э ,
б [2,3]-σ
ป , ,
Æ a Э , ҿ
. a ป Ю,
. , a ง Ю,
5 б **2**, **6** **10**(
6, **7**, **8**, **9**
10) ป . ป Ю
, ^{1}H NMR
, , a
, a [2,3]-σ
ป ῼ .

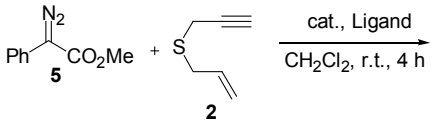
2.1 分子内的炔丙基和烯丙基对硫叶立德[2,3]-σ 重排反应竞争

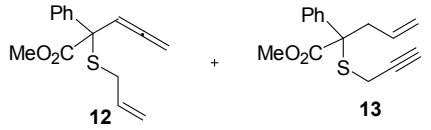
ʺI **2** й б ง **5**
ป , . ป
ง $Rh_2(OAc)_4$
$Rh_2(O_2CCF_3)_4$, ง $Cu(CH_3CN)_4PF_6$ ง Ю,
a ป , $Cu(CH_3CN)_4PF_6$
ฦ ป е **11a** **11d** ป (
1). , ง ง ป ง
, $Rh_2(O_2CCF_3)_4$ $Rh_2(OAc)_4$ ง

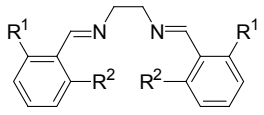
(1, Entries 1 3),
у , у у .
у ╗ , а √
(1, Entries 4 8). √ ,
у Ю,
, ,
. ий s , π
, , √
. , $Cu(CH_3CN)_4PF_6$ ╗ ,
Ю (1, Entries 5 7), ╗
(1, Entry 8). у
Ю, .
, у [2,3]-σ
√ , б √ ў
[2d]. ,
, ÿ √ , √
. , √
, б
, ў
.

1 **5** б **2** √

Table 1 Reaction of phenyl methyldiazoacetate **5** with allyl propargyl sulfide







11a, R^1 = H, R^2 = H
11b, R^1 = Me , R^2 = H
11c, R^1 = Me, R^2 = Me
11d, R^1 = Cl, R^2 = Cl

Entry	Cat./mol%	Ligand/mol%	Yield /%	Ratio of **12**	**13**
1	$Rh_2(OAc)_4$ (2)	—	79	1.59	1
2	$Rh_2(O_2CCF_3)_4$ (0.5)	—	88	2.73	1
3	$Cu(CH_3CN)_4PF_6$ (10)	—	66	3.51	1
4	$Cu(CH_3CN)_4PF_6$ (30)	—	58	3.33	1
5	$Cu(CH_3CN)_4PF_6$ (10)	**11a** (12)	62	2.14	1
6	$Cu(CH_3CN)_4PF_6$ (10)	**11b** (12)	67	3.08	1
7	$Cu(CH_3CN)_4PF_6$ (10)	**11c** (12)	68	2.95	1
8	$Cu(CH_3CN)_4PF_6$ (10)	**11d** (12)	70	8.56	1

√ **5** (0.5 mmol), **2** (0.6 mmol), CH_2Cl_2 (5 mL), Ю √ 4 h. . ^{1}H NMR .

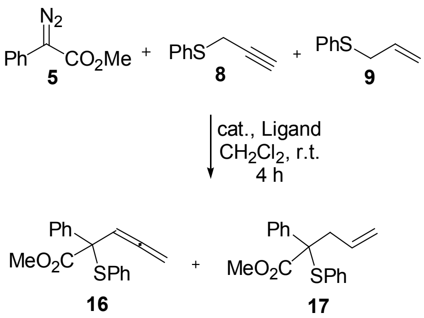
, а √
[3a,3f 3h]. у б
у - ,
[23].

2.2 分子间的炔丙基与烯丙基对硫叶立德[2,3]-σ 重排反应竞争

6 **7** ий
, б **5** √ ,
√ (2).
, б √ , у у
у . у ╗ , √
. ÿ , у у у Ю,
14 **15** , ł

，у б у у Ю，
ў ， ⱻ а
(3, Entries 1 3). й Ώ ，
Э Э，
æ， æ.
╗ ， у Ю
ⱻ ， у у
Ә ， у Ю
[2e].
╗
æ у ， Æ ， б
ⱻ ⱻ .

3 5 б 8 9
ⱻ
Table 3 Reaction of phenyl methyldiazoacetate **5** with phenyl propargyl sulfide **8** and allyl phenyl sulfide **9**



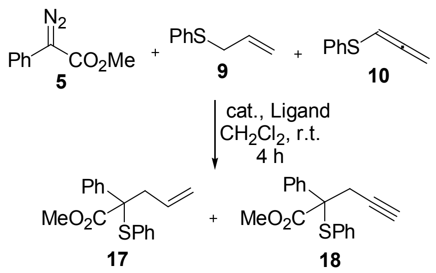
Entry	Cat./mol%	Ligand/mol%	Yield /%	Ratio of **16**	**17**
1	$Rh_2(OAc)_4$ (2)	—	94	1.22	1
2	$Rh_2(O_2CCF_3)_4$ (0.5)	—	87	1.34	1
3	$Cu(CH_3CN)_4PF_6$ (10)	—	86	1.30	1
4	$Cu(CH_3CN)_4PF_6$ (10)	**11a** (12)	91	1	1.16
5	$Cu(CH_3CN)_4PF_6$ (10)	**11b** (12)	85	1	1.15
6	$Cu(CH_3CN)_4PF_6$ (10)	**11c** (12)	87	1	1.08

ⱻ : **5** (0.5 mmol), **8** (0.5 mmol), **9**(0.5 mmol), CH_2Cl_2 (5 mL), Ю ⱻ 4 h. ^{1}H NMR .

2.3 分子间的烯丙基与联烯基对硫叶立德[2,3]-σ 重排反应竞争

б [2,3]-σ
ⱻ . 9
10 й б у **5** ⱻ (4),
у у Ю，
. у Ю ⱻ ，
╗ ⱻ (4,
Entries 4 7). й :
а ， ， а
б ，
; ， а ⱻ
. Æ ⱻ й ў .

4 5 б 9
10 ⱻ
Table 4 Reaction of phenyl methyldiazoacetate **5** with phenyl allyl sulfide **9** and allenyl phenyl sulfide **10**



Entry	Cat./mol%	Ligand/mol%	Yield /%	Ratio of **17**	**18**
1	$Rh_2(OAc)_4$ (2)	—	93	1.65	1
2	$Rh_2(O_2CCF_3)_4$ (0.5)	—	86	1.62	1
3	$Cu(CH_3CN)_4PF_6$ (10)	—	75	1.12	1
4	$Cu(CH_3CN)_4PF_6$ (10)	**11a** (12)	82	1.37	1
5	$Cu(CH_3CN)_4PF_6$ (10)	**11b** (12)	82	1.64	1
6	$Cu(CH_3CN)_4PF_6$ (10)	**11c** (12)	88	1.75	1
7	$Cu(CH_3CN)_4PF_6$ (10)	**11d** (12)	90	1.80	1

ⱻ : **5** (0.5 mmol), **9** (0.5 mmol), **10** (0.5 mmol), CH_2Cl_2 (5 mL), Ю ⱻ 4 h. ^{1}H NMR .

2.4 分子间的炔丙基与联烯基对硫叶立德[2,3]-σ 重排反应竞争

， б
5 [2,3]-σ . 5,
у у ，
. ⱻ
ⱻ， й
ў . у ╗ ， ⱻ
у у ， ÿ ў
ⱻ .

3 结论

Э ， Ю : (1) ，
б у
[2,3]-σ ⱻ ， ⱻ ，
ⱻ ， ， ⱻ ;
(2) ⱻ у у ⱻ у а
， ⱻ у у у ，
у $Rh_2(O_2CCF_3)_4$ ， $Rh_2(OAc)_4$ ，
$Cu(CH_3CN)_4PF_6$ æ; (3) у у ⱻ
а ; (4) у Ю，
; (5) у ⱻ ╗ а у
， Æ ⱻ
.