1,2-Vinyl and 1,2-Acetylenyl Migration in Rh(II) Carbene Reaction: Remarkable Bystander Effect

Weifeng Shi, Fengping Xiao, and Jianbo Wang*

Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

wangjb@pku.edu.cn

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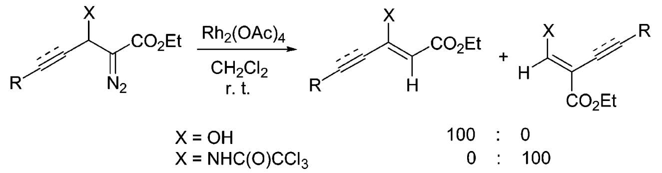

A series of β-(trichloroacetyl)amino α-diazo carbonyl compounds have been synthesized, and their Rh(II)-catalyzed reaction was investigated. 1,2-Migration was the predominant reaction pathway, and the migratory aptitude was found to be dramatically affected by the β-substituents. The 1,2-vinyl and 1,2-acetylenyl group migration occurs preferentially in the presence of β-hydrogen in $Rh_2(OAc)_4$-catalyzed reaction of β-(trichloroacetyl)amino α-diazo carbonyl compounds. A possible reaction mechanism is discussed.

Introduction

1,2-Migration is one of the fundamental reactions of free carbenes and metal carbenes.[1] The migratory aptitude of these reactions has been an intriguing problem over the past decades. In both metal carbene and free carbene reactions, 1,2-hydrogen migration is usually predominant. Nonmigrating substituents, so-called bystanders, are found to be influential over the migratory aptitude in free carbene reactions.[2,3] In the catalytic reaction of α-diazo carbonyl compounds with Rh(II) or Cu(I) carbene as reactive intermediates, 1,2-hydrogen migration is also a frequently encountered reaction, which can compete with the typical reactions of α-diazo carbonyl compounds such as X−H insertions and cyclopropanations. The 1,2-hydrogen migration may be useful in organic synthesis. For example, 1,2-hydrogen migration promoted by $Rh_2(O_2CCF_3)_4$ is an efficient route to (Z)-α,β-unsaturated carbonyl compounds.[4]

In contrast to that found in free carbene reactions, the effects of a bystander group on the 1,2-migration have not been studied systematically in Rh(II) carbene reactions. Recently, we have observed that the bystander group has a dramatic effect on the 1,2-migratory aptitude (1,2-H vs 1,2-Ar). For example, for diazo compound **1**, it has been known that in $Rh_2(OAc)_4$-catalyzed reactions when X is H or OH, 1,2-hydrogen migration products **2** (X = H or OH) are given exclusively.[4,5] However, when X is (N-tosyl)amino group, 1,2-phenyl migration occurs predominantly to give **3** as the major product (Scheme 1). When X is (trichloroacetyl)amino group, only 1,2-phenyl migration product **3** was observed.[6] The intriguing effect of the substituent promotes us to further study the effect of a bystander over the 1,2-migratory aptitude. In this paper, we report that 1,2-double- and 1,2-triple-bond migrations completely suppress the 1,2-hydrogen migration when there is a (trichloroacetyl)amino group presenting as a bystander group.

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[2] For reviews, see: (a) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84. (b) Liu, M. T. H. *Acc. Chem. Res.* **1994**, *27*, 287.

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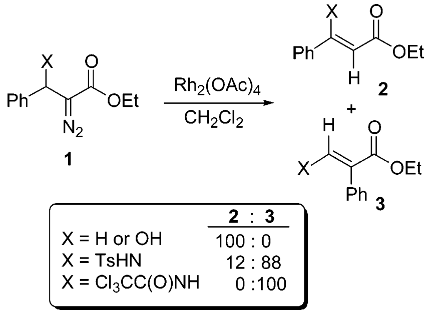
[4] (a) Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436. (b) Taber, D. F.; Herr, R. J.; Pack, S. K.; Geremia, J. M. *J. Org. Chem.* **1996**, *61*, 2908.

[5] (a) Pellicciari, R.; Fringuelli, R.; Ceccherelli, P.; Sisani, E. *J. Chem. Soc., Chem. Commun.* **1979**, 959. (b) Ikota, N.; Takamura, N.; Young, S. D.; Ganem, B. *Tetrahedron Lett.* **1981**, *22*, 4163. (c) Hoffmann, K.-L.; Regitz, M. *Tetrahedron Lett.* **1983**, *24*, 5355. (d) Hudlicky, T.; Olivo, H. F.; Natchus, M. G.; Umpierrez, E. F.; Pandolfi, E.; Volonterio, C. *J. Org. Chem.* **1990**, *55*, 4767. (e) Taber, D. F.; Hoerrner, R. S. *J. Org. Chem.* **1992**, *57*, 441. (f) Ohno, M.; Itoh, M.; Umeda, M.; Furuta, R.; Kondo, K.; Eguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 7075.

[6] (a) Jiang, N.; Qu, Z.; Wang, J. *Org. Lett.* **2001**, *3*, 2989. (b) Jiang, N.; Ma, Z.; Qu, Z.; Xing, X.; Xie, L.; Wang, J. *J. Org Chem.* **2003**, *68*, 893. (c) Shi, W.; Jiang, N.; Zhang, S.; Wu, W.; Du, D.; Wang, J. *Org. Lett.* **2003**, *5*, 2243.

10.1021/jo050173c CCC: $30.25

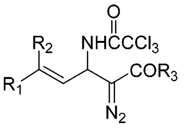
SCHEME 1. Effect of β-Substituent on the 1,2-Hydride vs 1,2-Phenyl Migration



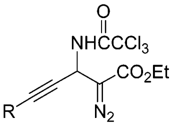
	2 : 3
X = H or OH	100 : 0
X = TsHN	12 : 88
X = Cl$_3$CC(O)NH	0 :100

Results and Discussion

To systematically study the possible 1,2-double- and 1,2-triple-bond migration, the β-(trichloroacetyl)amino α-diazo carbonyl compounds **4a**−**e** and **5a**,**b** were synthesized through the nucleophilic addition of acyldiazomethane with aldehyde to give β-hydroxy α-diazo compounds, which were followed by the reaction with Cl$_3$CCN/DBU.[6c]



4a, R$_1$ = Ph, R$_2$ = H, R$_3$ = OEt
4b, R$_1$ = H, R$_2$ = H, R$_3$ = OEt
4c, R$_1$ = CH$_3$, R$_2$ = H, R$_3$ = OEt
4d, R$_1$ = H, R$_2$ = Ph, R$_3$ = OEt
4e, R$_1$ = CH$_3$, R$_2$ = H, R$_3$ = CH$_3$

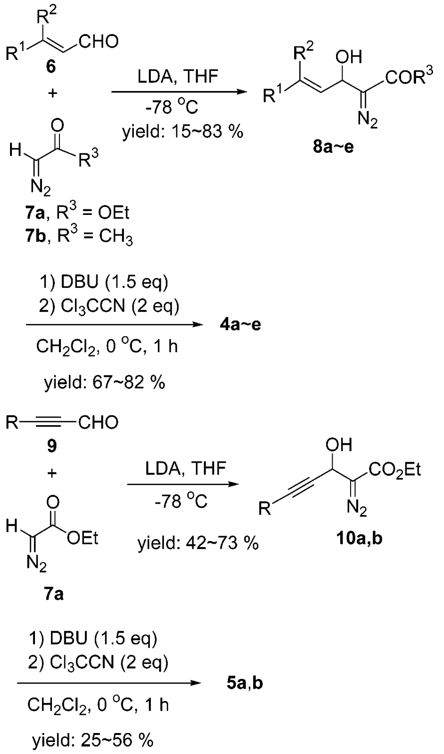


5a, R = C$_5$H$_{11}$
5b, R = Ph

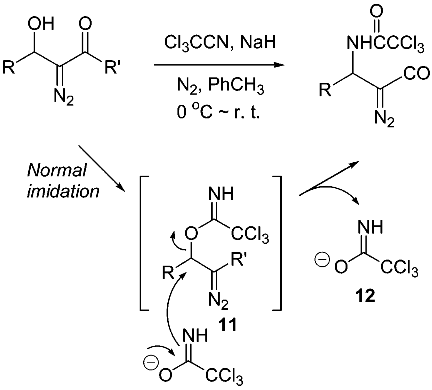
We have previously observed that the β-position of α-diazo carbonyl compounds is liable to nucleophilic substitution, which allows us to prepare a series of diazo compounds with various substituents in the adjacent position of the diazo group.[7] Thus, the nucleophilic addition of acyldiazomethane **7** with aldehyde **6** or **9** gave β-hydroxy α-diazo compounds **8a**−**e** or **10a**,**b**,[5c,8] which were followed by the reaction with Cl$_3$CCN/DBU. The β-(trichloroacetyl)amino-substituted diazo compounds **4a**−**e** and **5a**,**b** were obtained in reasonable yields (Scheme 2). **4a**−**e** and **5a**,**b** are generally more stable than the corresponding β-hydroxy α-diazo compounds. They can be stored in a refrigerator for weeks without decomposition. The structures of the β-(trichloroacetyl)-amino-substituted diazo compounds were confirmed by spectral data. For compound **4a**, the structure was further determined by X-ray crystallographic analysis.

The direct conversion of β-hydroxy α-diazo compounds to the corresponding β-(trichloroacetyl)amino compounds in the normal imidation reaction is due to the liability of the β-position to nucleophilic substitution. The initially formed normal imidation product **11** was converted to trichloroacetamides through S$_N$2 substitution by nucleophile **12**, thus forming the relatively strong C−N bond (Scheme 3). Similarly, the β-acetoxy group of α-diazo compounds has been found to be substituted with various nucleophiles such as RS$^-$ and p-TolSO$_2$$^-$.[7]

SCHEME 2. Preparation of β-(Trichloroacetyl)amino α-Diazo Carbonyl Compounds



SCHEME 3. Mechanism of the Formation of β-(Trichloroacetyl)amino α-Diazo Compounds



With the diazo compounds **4a**−**e** and **5a**,**b** in hand, we then proceeded to study their reaction with the catalysis of Rh$_2$(OAc)$_4$. As shown in Table 1, the Rh$_2$(OAc)$_4$-catalyzed reaction of **4a**−**e** gave 1,2-vinyl migration products in moderate to high yields. ^{1}H NMR inspection of the crude product shows that there are no trace 1,2-hydrogen migration products in each case. In the cases when R^1 = alkyl and R^2 = H, the bicyclo[1.1.0]butane derivatives **14b**,**c**,**e** were also formed in moderate yields.[9,10]

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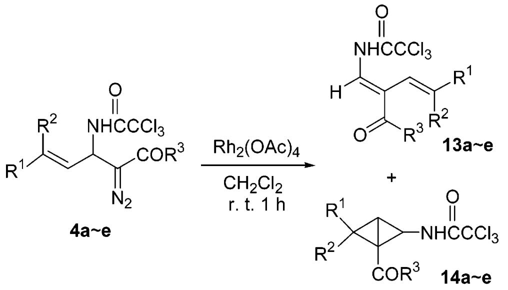
[7] (a) Shi, W.; Zhang, B.; Liu, B.; Xu, F.; Xiao, F.; Zhang, J.; Zhang, S.; Wang, J. *Tetrahedron Lett.* **2004**, *45*, 4563. (b) Xu, F.; Shi, W.; Wang, J. *J. Org. Chem.* **2005**, *70*, 4191.

[8] Pellicciari, R.; Natalini, B.; Sadeghpour, B. M.; Marinozzi, M.; Synder, J. P.; Williamson, B. J.; Kuethe, J. T.; Padwa, A. *J. Am. Chem. Soc.* **1996**, *118*, 1.

[9] For early reports on the synthesis of bicyclo[1.1.0]butane derivatives, see: (a) Wiberg, K. B.; Ciula, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 5261. (b) Blanchard, E. P., Jr.; Cairncross, A. *J. Am. Chem. Soc.* **1966**, *88*, 487 and references therein.

[10] Bicyclo[1.1.0]butane formation in Rh(II)-catalyzed reaction of diazo compound has also been reported by Ganem et al.; see ref 5b.

TABLE 1. $Rh_2(OAc)_4$-Catalyzed Reaction of 4a−e



entry	diazo compound	yield (%) (**13** + **14**)[a]	ratio of **13**:**14**[b]
1	**4a**	84	100:0
2	**4b**	97	52:48
3	**4c**	100	56:44
4	**4d**	98	100:0
5	**4e**	85	60:40

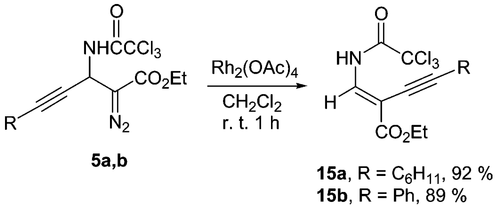
[a] Isolated yield for **13** and **14** combined. [b] Product ratio was determined by ^{1}H NMR of the crude product.

These bicyclo[1.1.0]butane derivatives have considerable stability, thus allowing the collection of necessary spectral data for characterization, although a suitable crystal has not been obtained for X-ray diffraction. The formation of bicyclo[1.1.0]butane derivatives is obviously due to the intramolecular cyclopropanation of the Rh(II) carbene.

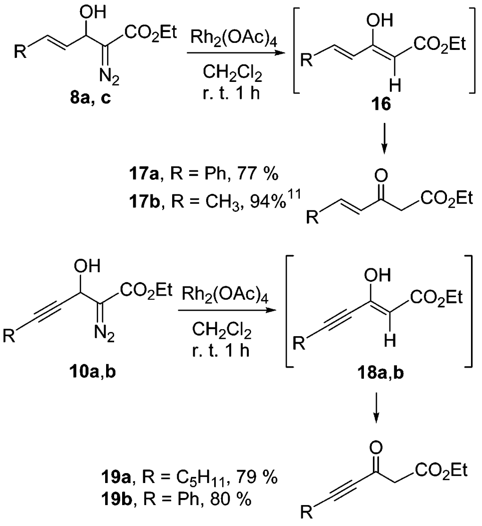
It is worthwhile to note that the 1,2-migration proceeds with retention of double-bond geometry, as shown by the reactions of **4a** and **4d** (Table 1, entries 1 and 4). The migrated olefin geometry can be established by the coupling constants of the olefinic protons ($J = 16.8$ Hz for **13a** and 12.3 Hz for **13d**, respectively). The stereospecificity of the reaction suggests that the 1,2-migration follows a concerted reaction mechanism. It is also found that the ratio of 1,2-migration versus intramolecular cyclopropanation (**13**:**14**) cannot be altered by varying the ligands of the Rh(II) catalysts, the solvent, and the reaction temperature as shown by the data summarized in Table 2.

For diazo compounds **5a** and **5b**, similar reaction with $Rh_2(OAc)_4$ gave 1,2-triple-bond migration in high isolated yields (Scheme 4). Again, there was no 1,2-hydrogen migration as judged by crude ^{1}H NMR.

SCHEME 4. $Rh_2(OAc)_4$-Catalyzed Reaction of 5a,b



SCHEME 5. $Rh_2(OAc)_4$-Catalyzed Reaction of β-Hydroxyl α-Diazo Carbonyl Compounds



For comparison, we have also studied the corresponding $Rh_2(OAc)_4$-catalyzed reaction of diazo compounds **8a**,**c**[11] and **10a**,**b** (Scheme 5). In all these cases, the reaction gave 1,2-hydrogen migration product in high yields. No 1,2-double- or 1,2-triple-bond migration could be detected from crude ^{1}H NMR spectra.

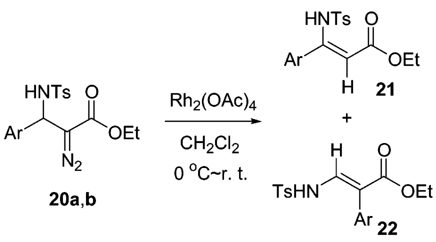
The above results demonstrate dramatic substituent effects on the 1,2-migratory aptitudes. One possible interpretation of this phenomenon can be arrived at by considering the electronic effects of the substituents. It has been suggested that Rh(II)−carbene intermediate is a resonance hybrid of a formal metal carbene and a metal-stabilized carbon cation.[12] As in the 1,2-migration of singlet carbene, the σ-bond of the migrating group overlaps with the empty p orbital of the carbene carbon, thus causing a charge transfer from the migration origin to the carbene carbon. A previous Hammett correlation analysis of the relative migratory aptitude gave a reaction constant of -1.43 with σ-constants, which suggests the partial positive charge development at the carbon to

TABLE 2. Effect of Reaction Conditions on Ratio of 13c to 14c

entry	catalyst	solvent	temp	time (h)	yield (%)[a] (**13c** + **14c**)	ratio of **13c**:**14c**[b]
1	$Rh_2(OAc)_4$	CH_2Cl_2	0 °C	10	99	56:44
2	$Rh_2(O_2CCF_3)_4$	CH_2Cl_2	0 °C−rt	48	c	50:50
3	$Rh_2(O_2CC_7H_{15})_4$	CH_2Cl_2	0 °C	0.2	95	56:44
4	$Rh_2(NHCOCH_3)_4$	CH_2Cl_2	0 °C−rt	8	94	66:34
5	$Rh_2(NHCOCH_3)_4$	CH_2Cl_2	40 °C	1	96	60:40
6	$Rh_2(OAc)_4$	benzene	80 °C	0.1	86	61:39
7	$Rh_2(NHCOCH_3)_4$	benzene	80 °C	1	92	61:39
8	$Rh_2(OAc)_4$	benzene	0 °C	1	97	60:40
9	$Rh_2(NHCOCH_3)_4$	benzene	0 °C−rt	8	92	64:36
10	$Rh_2(OAc)_4$	$ClCH_2CH_2Cl$	83 °C	0.1	92	68:32
11	$Rh_2(NHCOCH_3)_4$	$ClCH_2CH_2Cl$	83 °C	0.5	99	62:38
12	$Rh_2(O_2CCF_3)_4$	CH_2Cl_2	40 °C	0.5	c	d

[a] Isolated yields after chromatography. [b] Product ratio was determined by ^{1}H NMR (300 MHz). [c] Products were not isolated due to incompletion of the diazo decomposition. [d] Only migration product was detected by TLC.

SCHEME 6. $Rh_2(OAc)_4$-Catalyzed Reaction of β-Tosylamino α-Diazo Carbonyl Compounds 20a,b



		21	:	22
20a, Ar = *p*-NO_2	65 %	100	:	0
20b, Ar = *p*-OMe	79 %	7	:	93$^{6b)}$

which the migrating group is originally attached.[6b,13] The following experiments clearly indicate the importance of electronic effects in affecting the migratory aptitude (Scheme 6). The electron-withdrawing NO_2 substituent in the aromatic ring of **20a** completely interdicts aryl migration, while the electron-donating MeO group has the opposite effect.

Theoretical treatment of 1,2-hydrogen and 1,2-phenyl migrations in singlet carbene at the B3LYP/6-311G*// B3LYP16-31G* level indicates that in the transition state of 1,2-hydrogen migration **23a**, more positive charge developed in the migration origin than in the transition state of 1,2-phenyl migration **23b** (Figure 1).[14] It is thus concluded that the 1,2-hydrogen migration can be viewed as largely resembling a hydride shift with significant charge separation in the transition state. If one accepts that the 1,2-migration in Rh(II)−carbene is similar to that in singlet carbene, as shown in transition states **24a** and **24b**, then the bystander substituent effects observed in this study can be easily understood. Because hydroxyl group is a strong π-electron-donating functionality, which can stabilize the positive charge in the transition state of 1,2-hydrogen migration, it accelerates the 1,2-hydrogen migration. Alkoxy and alkyl groups have similar effects.[4a,15] Conversely, since electron-withdrawing $NHCOCCl_3$ has less ability to stabilize positive charge, it retards the 1,2-hydrogen migration. Because C−C bond migration was less affected by the substituent due to the relatively small extent of charge separation in the transition state, the 1,2-vinyl and 1,2-acetylenyl migrations become competitive, completely suppressing the 1,2-H migration.

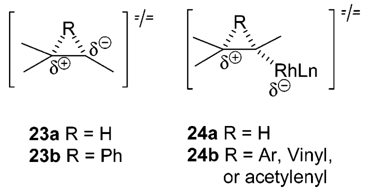


FIGURE 1. Transition states in singlet carbene and Rh(II) carbene reactions.

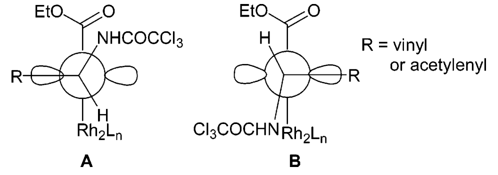


FIGURE 2. Conformations leading to 1,2-vinyl and 1,2-acetylenyl migrations.

On the other hand, an interesting feature in the 1,2-vinyl and 1,2-acetylenyl bond migrations is that thermodynamically less stable products, that is to say, $NHCOCCl_3$ and ester groups with *E* configurations, are observed to be overwhelmingly predominant in all cases. All the reactions were analyzed with ^1H NMR of the crude products before column chromatography, and the (*Z*)-isomer could not be identified. However, the originally formed (*E*)-products could isomerize to their (*Z*)-counterparts on silica gel column. Moreover, we have confirmed that the *Z*/*E* isomerization does not occur under the Rh(II)-mediated reaction conditions, thus indicating that the predominant formation of (*E*)-products is due to the 1,2-migration reaction itself but not isomerization.

We have observed similar results in the previous study on 1,2-aryl migrations.[6b] The stereoselectivity implies that conformational factors may play a role in the migration process. For the migration to occur, it is necessary that the migrating σ-bond orient in parallel to the empty p orbital of the carbene carbon in the transition states (Figure 2). Considering conformations **A** and **B**, which will lead to (*Z*)- and (*E*)-1,2 vinyl or acetylenyl migration products, respectively, one may predict that (*Z*)-product would predominate because of the repulsion between $NHCOCCl_3$ and Rh(II)/ligands. However, one can argue that the migration concerts with dissociation of the Rh(II) catalyst. If this is the case, then in the transition state from the conformation **B** the C−Rh bond has departed to a considerable extent. As a result, the steric interaction between $NHCOCCl_3$ and Rh(II)/ ligands is reduced, and the *E* migration products formed preferentially. This argument is supported by the invariability of **13c** to **14c** with the change of Rh(II) catalyst ligands (Table 2).[16]

In summary, we have observed the 1,2-double-bond and 1,2-triple-bond migration in Rh(II) carbene reaction. The investigation demonstrates a remarkable substituent

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[11] Padwa et al. has reported the same reaction of diazo compound **8c**. Padwa, A.; Kulkarni, Y. S.; Zhang, Z. *J. Org. Chem.* **1990**, *55*, 4144.

[12] (a) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (c) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348. (d) Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686. (e) Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958. (f) Wang, P.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 3296. (g) Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8991. (h) Taber, D. F.; Song, Y. *J. Org. Chem.* **1996**, *61*, 6706. (i) Doyle, M. P.; Kalinin, A. V.; Ene, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 8837. (j) Taber, D. F.; You, K. K.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 547. (k) Wang, J.; Chen, B.; Bao, J. *J. Org. Chem.* **1998**, *63*, 1853.

[13] For comparison, in the 1,2-hydrogen migration of singlet arylchlorocarbene, Hammett analysis gave a reaction constant of −1.0 with σ-constants; see: Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1992**, *114*, 3604.

[14] According to the calculation by Keating et al., NPA partial charge in the carbon of 1,2-shift origin increases by +0.23 for 1,2-phenyl shift of benzylchlorocarbene ($PhCH_2CCl$), while for 1,2-H shift of methylchlorocarbene (MeCCl) the corresponding charge increase is +0.33. See ref 3c.

[15] Sarabia García, F.; Pedraza Cebrián, G. M.; Heras López, A.; López Herrera, F. J. *Tetrahedron* **1998**, *54*, 6867.

[16] Ligands of Rh(II) catalysts have been known to affect the chemoselectivity in competitive Rh(II) carbene transformations of diazo compounds. For a detailed study, see: Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669.

effect on the 1,2-migratory aptitude in Rh(II) carbene reaction. The results provide important information concerning the reaction mechanism of 1,2-migration of Rh(II) carbene.

Experimental Section

Caution: Diazo compounds are generally toxic and potentially explosive. They should be handled with care in a well-ventilated fume hood.

General Procedure for the Preparation of β-Vinyl and β-Acetylenyl β-(Trifluoroacetyl)amino α-Diazo Carbonyl Compounds 4a−e and 5a,b. β-Hydroxy α-diazo carbonyl compound (1.0 mmol), which was prepared following literature procedure,[5a,8] and DBU (1.5 mmol) were dissolved in anhydrous CH_2Cl_2 (10 mL). Trichloroacetonitrile (98%, 2.0 mmol) was added to the solution while it was stirring at 0 °C. The reaction was continued for 2−3 h at 0 °C. Solvent was removed under reduced pressure, and the crude residue was purified by column chromatography to give **4a**−**e** and **5a**,**b**.

***(E)*-Ethyl 2-Diazo-5-phenyl-3-(trichloroacetylamino)-pent-4-enoate (4a):** R_f (petroleum ether/acetone = 8:1) = 0.19; IR 3327, 2102, 1697, 1499, 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3H), 4.26 (q, J = 7.2 Hz, 2H), 5.41 (dd, J = 7.0, 6.6 Hz, 1H), 6.32 (dd, J = 15.8, 7.0 Hz, 1H), 6.65 (d, J = 15.8 Hz, 1H), 7.33 (m, 5H), 7.86 (br, d, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 50.7, 61.3, 92.2, 123.0, 126.7, 128.4, 128.6, 133.5, 135.3, 161.2, 165.8; MS *m/z* (EI) 361 [(M − 28)$^+$, 5], 289 (16), 216 (21) 200 (52), 198 (36), 155 (55), 115 (100). Anal. Calcd for $C_{15}H_{14}N_3O_3Cl_3$: C, 46.12; H, 3.61; N, 10.76. Found: C, 45.78; H, 3.66; N, 10.75.

$Rh_2(OAc)_4$-Catalyzed Reaction of 4a−e and 5a,b. To a stirring solution of anhydrous CH_2Cl_2 (25 mL) containing $Rh_2(OAc)_4$ (1 mol %) was added β-vinyl (or β-acetylenyl) β-(trichloroacetyl)amino α-diazo carbonyl compound (1.0 mmol). The reaction mixture was stirred for 1 h at room temperature. Solvent was removed under reduced pressure to give a crude residue, which was purified by silica gel column chromatography.

***(E)*-Ethyl 2-(*trans*-Styryl)-3-(trichloroacetyl)amino-2-propenoate (13a):** R_f (petroleum ether/acetone = 8:1) = 0.36; IR 3387, 2982, 1731, 1489, 1254, 1214, 786 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3H), 4.30 (q, J = 7.1 Hz, 2H), 6.80 (d, J = 16.8 Hz, 1H), 6.82 (d, J = 16.8 Hz, 1H), 7.26−7.47 (m, 5H), 7.96 (d, J = 11.6 Hz, 1H), 8.95 (d, J = 11.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 61.0, 91.5, 115.9, 119.8, 126.4, 128.6, 128.7, 130.4, 134.6, 135.9, 158.9, 165.6; MS *m/z* (EI) 361 (M$^+$, 20), 326 (5), 280 (6), 200 (100), 172 (35), 115 (56), 77 (13), 29 (33). Anal. Calcd for $C_{15}H_{14}NO_3Cl_3$: C, 49.68; H, 3.89; N, 3.86. Found: C, 49.39; H, 3.99; N, 3.68.

$Rh_2(OAc)_4$-Catalyzed Reaction of 8a,c and 10a,b. To a stirring solution of anhydrous CH_2Cl_2 (25 mL) containing $Rh_2(OAc)_4$ (1 mol %) was added the β-hydroxy α-diazo carbonyl compound (1.0 mmol). The reaction mixture was stirred for 1 h at room temperature. Solvent was removed under reduced pressure to give a crude residue, which was purified by silica gel column chromatography.

Ethyl 3-Oxo-4-octynoate (19a): R_f (petroleum ether/acetone = 8:1) = 0.79; IR 2934, 2214, 1743, 1679, 1647, 1613, 804 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3H), 1.21−1.66 (m, 6H), 1.33 (t, J = 7.2 Hz, 3H), 2.33−2.41 (m, 2H), 3.55 (s, 1.5H, keto form), 4.19 (q, J = 7.2 Hz, 3H), 5.28 (s, 0.25H, enol form), 11.89 (s, 0.25H, enol form); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 14.0, 18.9, 19.1, 22.0, 22.0, 27.1, 27.5, 30.9, 30.9, 51.4, 60.4, 61.4, 80.3, 96.1, 96.9, 155.0, 166.1, 178.9; MS *m/z* (EI) 210 (M$^+$, 8), 182 (11), 165 (9), 139 (18), 123 (100), 95 (25), 67 (49), 55 (50), 41 (41), 29 (90); HRMS (EI) *m/z* calcd for $C_{12}H_{18}O_3$ 210.1255, found 210.1247.

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Supporting Information Available: Spectral data for **4b**−**e**, **5a**,**b**, **13b**−**e**, **14a**,**b**,**e**, and **15a**,**b**, ^{1}H NMR or ^{13}C NMR spectra for compounds **13b**,**e** and **14e**, and ORTEP structure and X-ray crystallographic data of **4a** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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