Investigation of the Transition-Metal- and Acid-Catalyzed Reactions of β-(*N*-Tosyl)amino Diazo Carbonyl Compounds

Nan Jiang, Zhihua Ma, Zhaohui Qu, Xiaoyu Xing, Linfeng Xie,[†] and Jianbo Wang*

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

wangjb@pku.edu.cn

Received May 28, 2002

A series of β-(*N*-tosyl)amino diazo carbonyl compounds have been prepared by nucleophilic condensation of *N*-tosylimines with acyldiazomethanes. The diazo decomposition of these diazo carbonyl compounds under various catalytic conditions, including Rh(II) carboxylates, Cu(I) and Cu(II) complexes, $PhCO_2Ag/Et_3N$, TsOH, and $SnCl_2$•$2H_2O$, has been investigated. It was found that, in most cases, the diazo decomposition gave preferentially 1,2-aryl migration product, but 1,2-hydride migration predominated when $PhCO_2Ag/Et_3N$ was the catalytic system. Hammett correlation has been applied in the analysis of the electronic effects of 1,2-aryl migration. The factors that govern the migratory preference and the mechanistic aspects of the reaction are discussed.

Introduction

1,2-Hydride, 1,2-alkyl, and 1,2-aryl migrations are frequently encountered in the transition-metal-complex-catalyzed decomposition of α-diazo carbonyl compounds.[1,2] In some cases, these migration reactions can compete with the typical reactions of α-diazo carbonyl compounds, such as X−H insertions and cyclopropanations. On the other hand, these reactions may be of synthetic utility in organic chemistry. For example, 1,2-hydride migration promoted by $Rh_2(O_2CCF_3)_4$ provides an efficient route to (*Z*)-α,β-unsaturated carbonyl compounds,[3] and $SnCl_2$-promoted 1,2-hydride migration of α-diazo-β-hydroxy esters, known as Roskamp homologation, leads to the formation of β-keto esters.[4]

- d

β-Substitution of α-diazo carbonyl compounds has been found to have marked influence on the reaction pathway of diazo decomposition. For example, $Rh_2(OAc)_4$-catalyzed decomposition of diazo compound **1** (Scheme 1) gives, after tautomerization, β-keto ester **2** as a result of 1,2-hydride migration,[2a,b] while acetoxy migration of **3** yields **4** 1,223TJ/F2 1 Tf7.2728 0,TD0 Tc312-

lamino group on its β-position.[5] The study reveals that, contrary to the α-diazo-β-hydroxy carbonyl compound **1** (X = OH) in which the diazo decomposition gives preferentially 1,2-hydride migration product, the corresponding reaction with **5** results in predominantly 1,2-aryl migration in most cases. It is also found that the migratory aptitude is affected by substituents on the aryl group, the catalytic conditions employed, and the structure of the diazo substrates.

Results

N-Tosyl diazoketamines **5a**−**p** were prepared by nucleophilic condensation of acyldiazomethane with *N*-sulfonylimines, as shown in Scheme 2. Deprotonation of acyldiazomethanes is usually achieved with lithium diisopropylamide (LDA).[6] We found that sodium hydride was a better base in our case because of its ease of handling and clean reaction. Thus, **6** was treated with NaH in anhydrous THF at 50 °C, followed by the addition of *N*-sulfonylimine **7** (Scheme 2). *N*-tosyl diazoketamines **5a**−**p** were obtained in good yields, as shown in Table 1. Although nucleophilic addition to *N*-sulfonylimines has been widely applied to organic synthesis,[7] to our best knowledge, there has been no systematic study on the nucleophilic addition of α-diazocarbonyl anion to *N*-sulfonylimines.[8]

During the course of this investigation, we discovered a much milder reaction condition for this condensation.[5c] We found that a catalytic amount of DBU (10−20% mol) was enough to promote the condensation efficiently in MeCN at room temperature. Moderate to good yields of **5a**−**p** were obtained, as shown in Table 1 (condition B). Since DBU is a much weaker base than LDA or NaH, the fact that the nucleophilic condensation can be efficiently promoted by this base suggests that the acidity of the proton attached to the diazo carbon of **6** is much greater than generally believed.[9] A similar reaction condition has also been employed to condense acyldiazomethanes **6** with aromatic or aliphatic aldehydes **7**, thus constituting a mild route to diazoketols **9**, which are useful precursors for the preparation of β-keto esters.[2,4]

Having prepared **5a**−**p**, we then proceeded to examine the diazo decomposition of these compounds under various reaction conditions, as depicted in Scheme 3. α-Diazoketamine **5a** (Ar = C_6H_5, R = H) was the first substrate

TABLE 1. NaH- or DBU-Promoted Condensation of Acyldiazomethanes with *N*-Tosylimines

		N-tosylimine **7**			yield (%)[a]	
entry	acyldiazomethane **6** R^1	Ar	R	product	condition A[b]	condition B[c]
1	OEt	C_6H_5-	H	**5a**	74	72
2	OEt	*p*-$MeOC_6H_4$-	H	**5b**	85	77
3	OEt	*m*-BrC_6H_4-	H	**5c**	83	70
4	OEt	*m*-$CF_3C_6H_4$-	H	**5d**	*d*	82
5	OEt	*m*-CNC_6H_4-	H	**5e**	*d*	49
6	OEt	*p*-PhC_6H_4-	H	**5f**	79	78
7	OEt	*p*-FC_6H_4-	H	**5g**	*d*	63
8	OEt	*p*-ClC_6H_4-	H	**5h**	68	70
8	OEt	*o*-MeC_6H_5-	H	**5i**	87	66
9	OEt	*o*-AllyloxyC_6H_4-	H	**5j**	*d*	73
10	OEt	2,4-$Cl_2C_6H_3$-	H	**5k**	32	69
11	OEt	2,6-$Cl_2C_6H_3$-	H	**5l**	26	77
12	OEt	3,5-$(MeO)_2C_6H_3$-	H	**5m**	70	75
13	OEt	C_6H_5-	Me	**5n**	81	<20
14	C_6H_5	C_6H_5-	H	**5o**	*d*	76
15	CH_3	C_6H_5-	H	**5p**	*d*	57

[a] Yields after column chromatographic purification with silica gel. [b] Condition A: NaH/THF, 50 °C. [c] Condition B: 10 mol % DBU/MeCN, room temperature. [d] Not tried.

TABLE 2. Effects of Catalyst on 1,2-Phenyl vs 1,2-Hydride Migratory Selectivity

entry	catalyst	reaction conditions	product ratio[a] **10a:11a:12a**	overall yield[b] (%)
1	$Rh_2(OAc)_4$	CH_2Cl_2, 0 °C	85:3:12	98
2	$Rh_2(acam)_4$	CH_2Cl_2, 0 °C	85:6:9	95
3	$Rh_2(O_2CCF_3)_4$	CH_2Cl_2, 0 °C	57:4:39	97
4	$Cu(acac)_4$	CH_2Cl_2, 25 °C	56:32:12	91
5	$Cu(hfacac)_4$	CH_2Cl_2, 25 °C	38:44:18	94
6	$Cu(MeCN)_4PF_6$	CH_2Cl_2, 25 °C	64:7:29	89
7	$PhCO_2Ag$	Et_3N, THF, reflux	27:16:57	81
8	$SnCl_2{\cdot}2H_2O$	CH_2Cl_2, 0 °C	17:62:21	87
9	TsOH	CH_2Cl_2, 0 °C	29:71:0	89

[a] The product ratio was determined by ^1H NMR (400 MHz) of the crude product. [b] Combined yields of **10a**, **11a**, and **12a** after column chromatography.

ligands in $Cu(hfacac)_2$ and $Cu(MeCN)_4PF_6$ reduced the selectivity, especially in the case of $Cu(MeCN)_4PF_6$.

We also examined the diazo decomposition of **5a** in refluxing THF with $PhCO_2Ag/Et_3N$, a typical Wolff rearrangement catalyst.[11] We were astonished to find that the 1,2-hydride migration product **12a** was favored (57%) in this case. No products due to Wolff rearrangement were observed. For comparison, the diazo decomposition was also carried out under photolysis conditions ($h\nu > 300$ nm) in benzene at room temperature. The photolysis gave 1,2 migration products **10a**, **11a**, and **12a** in 94% yield and with a ratio of 42:40:18. Again, no Wolff rearrangement products were detected.

Since diazo decomposition could also be promoted with catalytic Lewis acid and protonic acid, we next proceeded to treat diazoketamine **5a** with $SnCl_2{\cdot}2H_2O$ and TsOH, respectively. In both cases 1,2-phenyl migration products are predominant, as shown in Table 2 (entries 8 and 9).

On the basis of these results, it is clear that the 1,2-phenyl migration pathway dominates in most cases during the diazo decomposition of **5a,** except in the case promoted by $PhCO_2Ag$ where 1,2-hydride migration is favored. To assess the effect of substrates on product selectivity, we set out to study reactions of a series of *N*-tosyl diazoketamines under three different catalytic conditions, $Rh_2(OAc)_4$, TsOH, and $PhCO_2Ag/Et_3N$. The corresponding results are summarized in Tables 3−5, respectively.

TABLE 3. Diazo Decomposition Catalyzed by $Rh_2(OAc)_4$

			isolated yield (%)	
entry	*N*-tosyl α-diazo-ketamine	product ratio[a] **10:11:12**	**10**	**12**
1	**5a**	85:3:12	71[b]	*c*
2	**5b**	84:9:7	79[b]	*c*
3	**5c**	73:5:22	53[d]	18[b]
4	**5d**	62:5:33	59[d]	24[b]
5	**5e**	51:6:47	48[d]	20[b]
6	**5f**	92:4:4	86[d]	*c*
7	**5g**	93:3:4	87[d]	*c*
8	**5h**	75:12:13	68[b]	*c*
9	**5i**	*e*	81[d]	*c*
10	**5j**	*e*	76[d]	*c*
11	**5k**	*e*	84[b]	*c*
12	**5l**	*e*		90[d,f]
13	**5m**	71:6:23	68[d]	*c*
14	**5n**	*e*	90[d]	*c*

[a] The product ratio was determined by ^1H NMR (400 MHz). [b] Yields after column chromatography. [c] 1,2-Hydride migration products **12** and the *cis* isomer of the phenyl migration products **11** could not be isolated due to their minute amount. [d] Yields after single recrystallization of the crude product. [e] Ratio not determined. [f] The yield refers to the *trans* isomer (*E*)-ethyl 3-(2,6-dichlorophenyl)-3-(*N*-tosyl)amino-2-propenoate.

For most reactions catalyzed by $Rh_2(OAc)_4$, the *trans* isomer **10** from 1,2-aryl migration was the only product

---

[11] Newman, M. S.; Beal, P. F., III. *J. Am. Chem. Soc.* **1950**, *72*, 5163.

TABLE 4. Diazo Decomposition Catalyzed by $PhCO_2Ag$

entry	*N*-tosyl α-diazo-

isolated from the reaction mixture. Although both **11** and **12** were detectable on TLC and in ^1H NMR of the crude products, they were not isolated due to their minute quantity. In cases where a significant amount of **12** was formed (entries 3−5), it was isolated and the yields were determined after column chromatographic purification. It is interesting to note that electron-withdrawing substituents on the phenyl ring (*m*-Br, *m*-CF_3, and *m*-CN, entries 3−5) seem to reduce the migratory aptitude of the aryl group relative to the hydrogen. Remarkably, 1,2-hydride migration dominates completely (entry 12) over 2,6-dichlorophenyl group migration, and the major product **12l** was isolated in excellent yield. Obviously, the migratory aptitude of the aryl group is influenced to some degree by the electronic effect imposed by the ring substituents.

For $PhCO_2Ag/Et_3N$-catalyzed reactions, the predominant formation of 1,2-hydride migration product appears to be general. As shown in Table 4, for substrates with either electron-withdrawing groups (entries 3−5 and 7) or an electron-donating group (entry 2), the main product is *β*-aryl-*β*-(*N*-tosyl)enamino ester **12**. Interestingly, the product ratio of 1,2-aryl vs 1,2-hydride migration catalyzed by silver benzoate is rather independent of the electronic nature of the aryl substituents.

When diazoketamines **5a**, **5b**, **5d**, **5f**, and **5g** were treated with 1 mol % TsOH at 0 °C in anhydrous CH_2Cl_2, the diazo compounds disappeared within 30 min to give a mixture of 1,2-aryl migration products **10** and **11**. In contrast to the reactions catalyzed by $Rh_2(OAc)_4$, 1,2-hydride migration product **12** could not be detected in the ^1H NMR of the crude reaction mixture in this case. Moreover, *cis*-α-aryl-*β*-enamino ester **11** was formed as the major product. The *cis* isomer is obviously more stable than the corresponding *trans* isomer because of the intramolecular hydrogen bonding in the former case. Since *cis*/*trans* isomerization of α-aryl-*β*-enamino esters was observed during the silica gel column chromatographic separation, it is likely that the predominant formation of the *cis* isomer in TsOH-catalyzed reactions could also result from such isomerization promoted by TsOH. This was indeed confirmed by carrying out the reaction of **5a** in the presence of a 10-fold amount of TsOH (10% mol) at room temperature. As expected, the ratio of *cis* to *trans* changed from 71:29 to 95:5. At this point it is unclear as to what relative percentage of the product selectivity results from the intrinsic *cis*/*trans* migratory selectivity vs *cis*/*trans* isomerization.

Discussion

Our results clearly indicate that 1,2-migratory selectivity in the decomposition of **5** varies drastically with the ligands and the type of metal contained in the catalysts. It is generally accepted that in transition-metal-catalyzed diazo decomposition, a metal carbene instead of a free carbene is involved as an intermediate. The metal carbene is a resonance hybrid of a formal metal carbene (**13**) and a metal-stabilized carbocation (**14**), which together describe the reactivity of the intermediate.[12] It seems reasonable then that the reactivity of such an intermediate may be influenced by factors such as the ligands, metal, and R group on the phenyl ring.

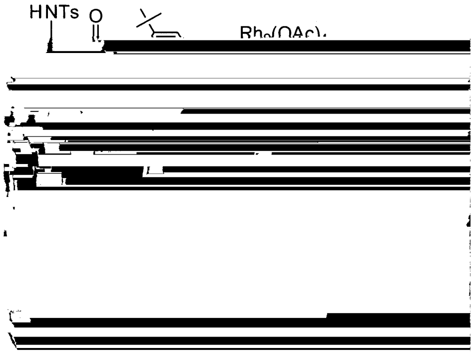
First, different ligands on Rh or Cu catalysts exert a profound effect on the competitive 1,2-aryl vs 1,2-hydride migratory selectivity, as shown in Table 1. There seems to be a general trend that electron-withdrawing ligands enhance 1,2-hydride migration for both Rh- and Cu-catalyzed decompositions. This trend can be rationalized in terms of the increase in electrophilicity (more contribution from carbocation-like structure **14**) of the intermediate metal carbene, which results in a more reactive carbene center and its reduced ability to discriminate migrating substituents. Such observations are consistent with the selectivity trends previously reported for C−H insertion regioselectivity and cyclopropanation diastereoselectivity, in which electron-withdrawing ligands on Rh and Cu catalysts were found to decrease the selectivity.[10]

To understand the steric effect around the metal carbene center, we prepared diazo ester **15** (Scheme 4) and subjected it to the usual decomposition condition with $Rh_2(OAc)_4$. Interestingly, **15** failed to decompose with $Rh_2(OAc)_4$, even in refluxing $ClCH_2CH_2Cl$ (83 °C). We believe this is due to the bulky 2,6-di-*tert*-butyl-4-methylphenyl group, which prevents the approach of the negatively polarized diazo carbon to the axial position of the hindered Rh(II) catalyst. Circumstantial evidence for this explanation is given by the fact that **15** was rapidly decomposed to give 1,2-phenyl migration products **16** and **17** (Scheme 4) with a catalytic amount of TsOH at 0 °C in CH_2Cl_2.

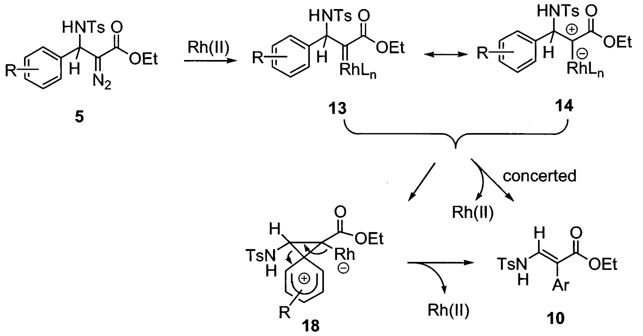
---

[12] For a recent mechanistic investigation on Rh(II)-mediated diazo decomposition, see: (a) Qu, Z.; Shi, W.; Wang, J. *J. Org. Chem.* **2001**, *66*, 8139. (b) Pirrung, M. C.; Liu, H.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 1014.

SCHEME 4



SCHEME 5



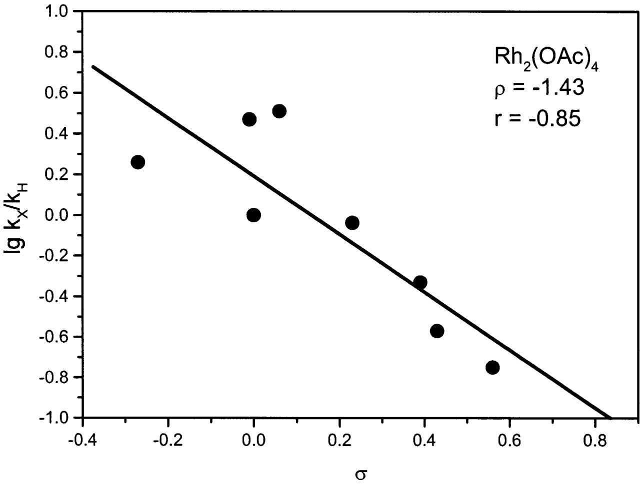
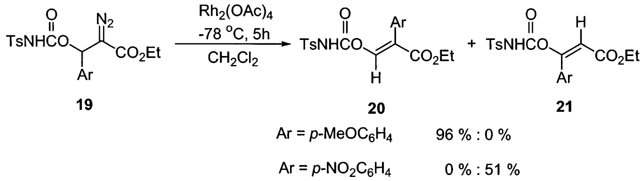


FIGURE 1. Hammett correlation of the relative migratory aptitude of the $Rh_2(OAc)_4$-catalyzed reaction.

SCHEME 6



On the basis of these results and those reported in the literature,[2,3] a possible reaction mechanism can be proposed for $Rh_2(OAc)_4$-catalyzed reactions, as depicted in Scheme 5. The first step involves the formation of rhodium(II) carbene intermediate **13** or **14**, as generally believed for Rh(II)-mediated diazo reactions.[12] The subsequent aryl migration may proceed through a bridged phenonium ion, **18**, or through a process in which the substituent migrates simultaneously with the dissociation of the rhodium(II) catalyst. The former pathway is similar to the well-known 1,2-shift in carbonium ions.[13]

If the bridged ion intermediate **18** is involved in the reaction pathway, the orbital system of the aryl group is expected to assist the stabilization of the carbonium ion or partial carbonium ion through delocalization. In this case, a significant substituent electronic effect is expected, as in the case of 1,2-aryl shift in carbonium ions. To substantiate this mechanism, the relative migratory aptitude of the aryl group, k_X/k_H, was calculated from the product distribution data in Table 3, by taking 1,2-hydride migration as the internal reference for each reaction.[14,15] The relative migratory aptitude was further analyzed with Hammett substituent constants.[16] As shown in Figure 1, although the data do not fit well to the Hammett equation ($\rho = -1.43$ with σ, $r = -0.85$), the obvious trend is that an aryl group with electron-donating substituents has a higher migratory aptitude. This trend suggests that the aryl group is migrating to an electron-deficient carbon, in agreement with the fact that rhodium(II) carbene is electrophilic. However, the relatively small magnitude of the reaction constant seems to disfavor a bridged ion pathway. If a bridged ion were involved, a stronger substituent electronic effect should have been observed, especially for the *p*-methoxy group because it would have direct interaction with the developing positive or partial positive charge.[13,17] Thus, the moderate effect imposed by the substituents on the migratory aptitude of an aryl group lends its support to a concerted migration pathway, although a composite of the two pathways cannot be ruled out.

It is useful to compare these electronic effects to those of similar reactions involving α-diazo-β-hydroxy carbonyl compounds and their derivatives. For α-diazo-β-hydroxy carbonyl compounds **1** (X = OH), literature information and our study indicate that 1,2-hydride migration dominates in all cases,[2a,b] even when the β-substituent is a *p*-methoxyphenyl group (**1**, X = OH, R = *p*-$MeOC_6H_4$). However, when the β-hydroxyl group is derivatized, 1,2-aryl migration may dominate in some cases. For example, Kanemasa has demonstrated that 1,2-migratory selectivity of competing aryl vs hydride shift could be reversed by modifying the electronic property of the migrating aryl group in diazo compound **19**, as depicted in Scheme 6.[18] Thus, 1,2-hydride shift in **19** is preferred over *p*-nitrophenyl migration to give **21**, while changing *p*-NO_2 to

---

(13) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper Collins Publishers: New York, 1987; p 434.

(14) 1,2-Hydride migration may also be affected by the substitution on the phenyl ring; therefore, a question remains when taking the 1,2-hydride migration as internal reference. For a theoretical investigation of the influence of bystander substituents on the 1,2-H and 1,2-Ph migration in free carbene, see: Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. *J. Phys. Chem. A* **1998**, *102*, 8467.

(15) The relative migratory aptitude data as well as the Hammett correlation with σ^+ and σ^- have been submitted as Supporting Information.

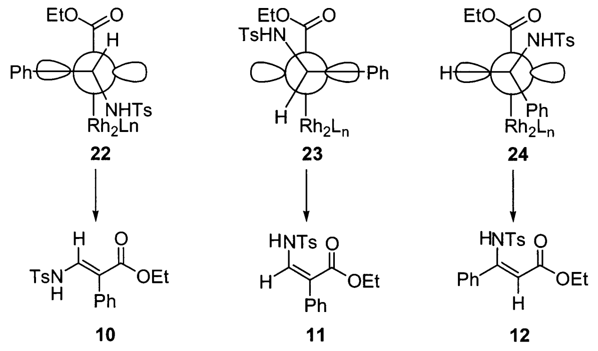
(16) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(17) Brown, H. C.; Kim, C. J. *J. Am. Chem. Soc.* **1971**, *93*, 5765.

(18) Kanemasa, S.; Araki, T.; Kanai, T.; Wada, E. *Tetrahedron Lett.* **1999**, *40*, 5059.

p-MeO reverses the aptitude and leads to the main product **20**. For diazo decomposition of α-diazo-*β*-acetoxy carbonyl compound **3** (Scheme 1), the acetoxy migration is predominant, probably through a five-membered ring intermediate in which the acetoxy carbonyl oxygen interacts with the positively polarized rhodium carbene.[2b,j,k]

To further understand the migratory preference of aryl vs hydrogen, we need to consider a conformational requirement involved in the migration process. We envision the migrating group to be perpendicular to the plane of the sp^2-hybridized carbene carbon, such that it can best overlap with the empty p orbital on the carbene carbon. Three representative conformations are depicted by **22**−**24** that would lead to each migration product, respectively.



The results summarized in Tables 2 and 3 show that, for the Rh(II)-catalyzed reaction, in all cases the thermodynamically less stable *trans* isomer **10** from 1,2-aryl migration is the major product. The product ratios were determined by ^{1}H NMR of the crude products before column chromatography, and we have confirmed that the *trans*/*cis* isomerization does not occur under the Rh(II)-mediated reaction condition. Therefore, the product distributions obtained in this case originate from the diazo decomposition reaction itself but not isomerization. The predominate formation of *trans* 1,2-aryl migration products implies that the conformational factors may play a role in determining the migratory preference.[19,20] In other words, the rhodium(II) carbene intermediate may preferentially take the formation of **22** that is in favor of aryl migration to give the *trans* product.

To assess the relative stability of the three conformations **22**−**24** shown above, we undertook computational calculations on the rhodium-complexed carbenoid (represented by resonance structures **13** and **14** in Scheme 5) using augmented MM2 parameters in the CAChe package.[21] We first built the model catalyst $Rh_2(OAc)_4$ and optimized its structure using MM2. All O−Rh bond lengths after optimization were equal, and the Rh−Rh bond length was in good agreement with that previously reported.[22] We then continued to build the remainder of the carbenoid complex and carried out an optimized conformational search using various geometry labels for dihedral angles. The energy of each conformation was optimized by the augmented MM2 parameters provided in the CAChe package. The conformations represented by **22**−**24** were optimized by locking the migrating H or Ph group parallel to the empty p orbital (on the assumption that this allows for the maximum overlap during the migration) on the carbene center. The results show that conformation **23** is the most stable conformation, in which case Ph migration appears to be favored over H migration; however, this would lead to the *cis* isomer **11**. The conformation required for the phenyl migration (**22**) to give the *trans* isomer product **10** would put NHTs on the side of Rh and its ligands, an apparently sterically hindered situation. We felt that this approach was oversimplified because the C−Rh bond in the carbenoid intermediate might have departed to some extent during the actual reaction, thus reducing the steric interaction between NHTs and the ligands on the rhodium. Nevertheless, the same argument could presumably apply to **24**.

It appears that the conformational analysis could not provide conclusive explanation for the preferential Ph migration in the reaction of **5**. Considering the fact that for the similar α-diazo-*β*-hydroxy carbonyl compound **1** ($X = OH$) the diazo decomposition almost exclusively gave H migration products,[2a] the nature of the *β*-substitution is obviously the crucial factor in determining which group migrates preferentially. In free carbene chemistry, it has long been recognized that the ease of migration is affected by nonmigrating substituents (i.e., bystanders);[14,19,23] however, the similar bystander effect in the transition-metal-complex-catalyzed diazo reaction has rarely been documented previously. Further systematic investigation is required to elucidate the mechanism of this effect.

To further elucidate factors that may affect the migratory aptitude, $Rh_2(OAc)_4$-catalyzed reaction of diazoketones **5o** and **5p** and diazoamides **25** and **26** was investigated (Scheme 7). The reaction of diazoketones **5o** and **5p** gave predominately 1,2-phenyl migration products **27** and **28**, just as the corresponding reaction of diazo ester **5a**. The reaction with diazoamides **25** and **26**, however, resulted in 1,2-hydride migration products **29** and **30** as the only isolated products. This result indicates that other structural factors exist that may override the effect of the *β*-NHTs group in dictating the preferential 1,2-aryl migration.

For the $PhCO_2Ag/Et_3N$-catalyzed reaction, similar electronic effect analysis has been performed using the product distribution data collected in Table 4. A smaller magnitude of the reaction constant was obtained (Figure 2, $\rho = -0.20$, $r = -0.82$). The Hammett linear correlation for this catalytic system is not so good, but the general trend of the electronic effects is the same as in the Rh(II)-mediated reaction. The $PhCO_2Ag$ and Et_3N combination has been widely applied in the Wolff rearrangement of α-diazo carbonyl compounds; however, the exact mechanism of how this catalytic system decomposes diazo

---

(19) A recent study of the 1,2-migration in singlet free carbene concludes that the molecular geometry of the carbene intermediate is responsible for the higher 1,2-alkyl migration. See: Farlow, R. A.; Thamattoor, D. M.; Sunoj, R. B.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 3257.

(20) Aggarwal, V. K.; Sheldon, C. G.; Macdonald, G. J.; Martin, W. P. *J. Am. Chem. Soc.* **2002**, *124*, 10300.

(21) Structure optimization was conducted by an augmented version of Allinger's MM2 force field provided in the CAChe system, version 3.1. The optimized structures have been submitted as Supporting Information.

(22) Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8991.

(23) For a review, see: Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84.

compounds is still not clear.[11,24] It is worthwhile to compare this catalytic system with $Rh_2(O_2CCF_3)_4$. In the $Rh_2(O_2CCF_3)_4$-catalyzed reaction of **5a**, the amount of 1,2-hydride migration products increased significantly compared to that in $Rh_2(OAc)$

carefully added. Usual workup gave a crude product, which was purified by column chromatography with silica gel.

With DBU as the Base (Condition B). To a solution of acyldiazomethane **6** (1.2 mmol) in anhydrous CH_3CN (5 mL) at room temperature under N_2 were added successively a solution of DBU (0.1 mmol) in anhydrous CH_3CN (1 mL) and *N*-tosylimine **7** (1 mmol) in anhydrous CH_3CN (4 mL) via syringes. After being stirred at room temperature for 8 h, the reaction was quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2 (20 mL). The solvent was removed by evaporation under reduced pressure, and the crude product was purified by flash chromatography to yield *N*-tosyl diazoketamines **5a**−**p**.[27]

Data for 2,6-di-*tert*-butyl-4-methylphenyl 2-diazo-3-(*N*-tosyl)amino-3-phenylpropanoate (15): yield 71% (condition B); mp 160 °C dec; IR 3422.5, 2092.6, 1637.5, 1335.0 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.22 (d, 18H), 2.29 (s, 3H), 2.41 (s, 3H), 5.35 (d, $J = 6.2$ Hz, 1H), 5.68 (d, $J = 6.2$ Hz, 1H), 7.07 (s, 2H), 7.25−7.28 (m, 7H), 7.75 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.40, 21.46, 31.37, 34.96, 35.04, 53.63, 61.81, 126.10, 126.87, 126.90, 128.43, 128.79, 129.74, 134.74, 136.42, 137.93, 142.19, 142.40, 143.80, 165.36; MS (FAB) *m/z* 554 $[(M + Li)^+$, 18], 528 (30), 397 (8), 157 (17), 115 (100). Anal. Calcd for $C_{31}H_{37}N_3O_4S$: C, 67.98; H, 6.81; N, 7.67. Found: C, 67.80; H, 7.04; N, 7.43.

***N*,*N*-Dibenzyl 2-Diazo-3-(*N*-tosyl)amino-3-phenylpropanamide (25)**. Reaction condition B was followed, except 20 mol % DBU was used in this case: yield 54%; yellow solid; mp 113 °C dec; IR 3244.5, 2061.6, 1619.7, 1414.0 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.40 (s, 3H), 4.27 (d, 2H), 5.40 (d, $J = 8.2$ Hz, 1H), 5.55 (d, $J = 8.2$ Hz, 1H), 6.96−7.30 (m, 17H), 7.74 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.49, 49.78, 50.53, 126.24, 127.13, 127.26, 127.63, 127.99, 128.63, 128.64, 129.62, 135.74, 137.39, 138.38, 143.42, 165.94; MS (FAB) *m/z* 531 $[(M + Li)^+$, 22], 505 (57), 157 (14), 115(100), 91 (61). Anal. Calcd for $C_{30}H_{28}N_4O_3S$: C, 68.68; H, 5.38; N, 10.68. Found: C, 68.62; H, 5.37; N, 10.52.

3-[2′-Diazo-3′-(*N*-tosyl)amino-3′-phenylpropionyl]-2-oxazolidinone (26). Butyllithium (1 mL, 1.1 M in hexane, 1.1 mmol) was added dropwise to diisopropylamine (1.2 mmol) in anhydrous THF (6 mL) at −78 °C, under a nitrogen atmosphere. After the solution was stirred for about 15 min at the same temperature, 2-oxazolidinone diazoacetamide (155 mg, 1 mmol) in anhydrous THF (6 mL) was added dropwise. The solution was stirred for 30 min, and then a solution of *N*-tosyl benzaldimine **7a** (0.285 g, 1.1 mmol) in anhydrous THF (6 mL) was slowly added at −78 °C. The mixture was stirred until TLC indicated no starting diazoacetamide left (about 2 h). The reaction mixture was quenched with saturated aqueous NH_4Cl solution at the same temperature, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4. Purification by column chromatography with silica gel gave 0.332 g of a yellow solid (86%): mp 85 °C dec; IR 3451, 2104, 1776, 1642 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.74−3.90 (m, 2H), 4.27−4.36 (m, 2H), 5.50 (d, $J = 8.0$ Hz, 1H), 6.04 (d, $J = 7.6$ Hz, 1H), 7.25−7.28 (m, 7H), 7.25−7.28 (m, 7H), 7.74 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.43, 43.26, 54.86, 62.79, 126.34, 127.16, 128.27, 128.75, 129.58, 136.78, 137.01, 143.70, 152.64, 162.87; MS (FAB) *m/z* 421 $[(M + Li)^+$, 18], 395 (7), 157 (20), 115 (100), 49 (31). Anal. Calcd for $C_{19}H_{18}N_4O_5S$: C, 55.07; H, 4.38; N, 13.51. Found: C, 55.38; H, 4.72; N, 12.95.

General Procedure for $Rh_2(OAc)_4$-Catalyzed Diazo Decomposition of *N*-Tosyl Diazoketamines. A solution of *N*-tosyl diazoketamine (0.5 mmol) in CH_2Cl_2 (20 mL) was stirred at 0 °C under N_2, and then $Rh_2(OAc)_4$ (1 mg) was added. The reaction mixture was stirred at 0 °C for 10 min. The solvent was then removed under vacuum, and the residue purified by chromatography or recrystallization.[27]

General Procedure for Copper-Complex-Catalyzed Diazo Decomposition of *N*-Tosyl Diazoketamine. A solution of *N*-tosyl diazoketamine (30 mg, 0.08 mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature under N_2, followed by the addition of copper catalyst (10% mmol). The reaction