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Unexpected Stereoselective Synthesis of (*Z*)-β-Alkenyl Substituted β-Amino Phosphonates through β,γ-Dihydrogen Shift Reaction Catalyzed by a Copper(I) Complex and Iodine $[Cu(MeCN)_4]PF_6/I_2$

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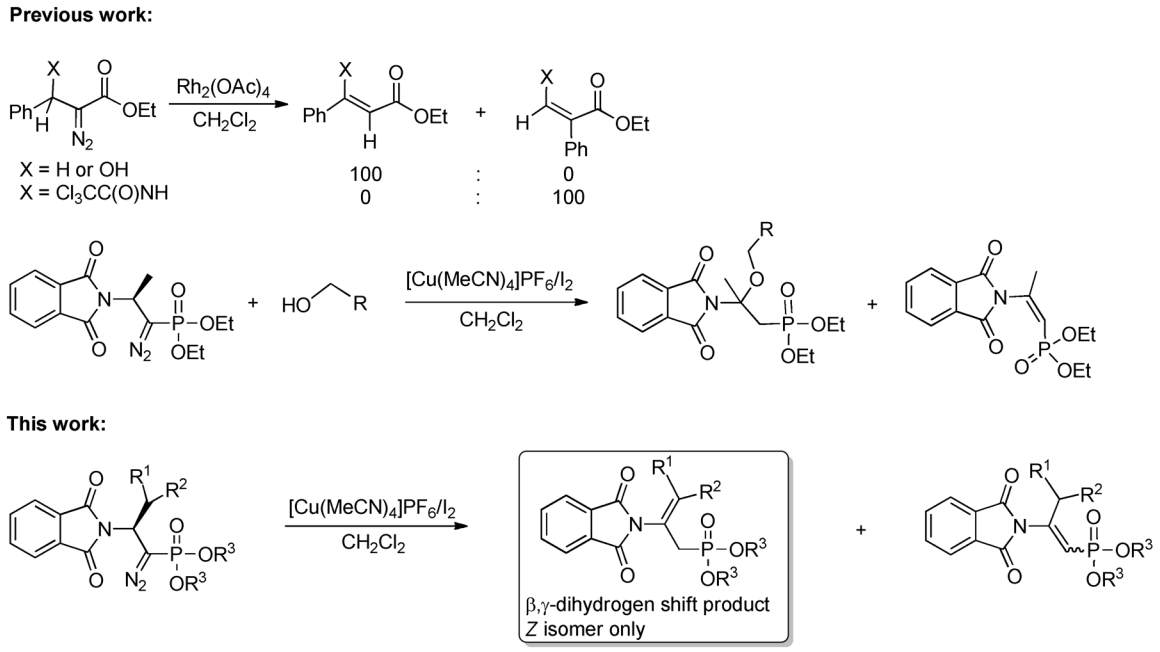
Abstract: A series of dialkyl α-diazophosphonates has been prepared from natural amino acids. The diazo decomposition of these diazophosphonate compounds with tetrakis(acetonitrile)copper(I) hexafluorophosphate/iodine, $[Cu(MeCN)_4]PF_6/I_2$, as catalyst has been investigated. It was found that the diazo decomposition of dialkyl α-diazophosphonates gave a mixture of β,γ-dihydrogen shift and 1,2-hydride migration products and afforded β-alkenyl-substituted β-amino phosphonates with the *Z* configuration. The mechanism of this novel diazo decomposition process was discussed.

Keywords: copper(I); $[Cu(MeCN)_4]PF_6$; diazo compounds; α-diazophosphonates; β,γ-dihydrogen shift; 1,2-hydride migration; iodine; tetrakis(acetonitrile)-copper(I) hexafluorophosphate

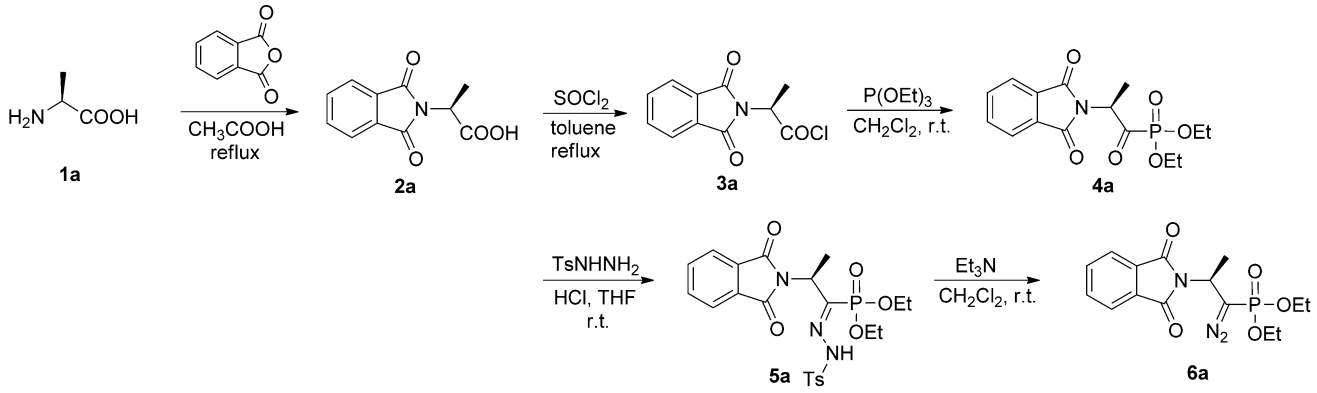
Diazo compounds are remarkably versatile metal carbene precursors which participate in metal-catalyzed rearrangements,[1] cycloadditions,[2] X–H (X = C, N, O, Si, S, etc.) bond insertions,[3] and 1,2-migration reactions.[4] Among the 1,2-migration reactions, the 1,2-hydride migration is generally predominant.[5] This migratory preference has also been known to be affected by steric and conformational factors.[6] Because of their unique properties and extensive applications, the interest in the chemistry of diazo compounds has been long standing. β-Substitution of α-diazo carbonyl compounds has been found to have a marked influence on the reaction pathway of diazo decomposition.[7] Exposure of β-substituted diazo compounds to $Rh_2(OAc)_4$ led to formation of β-keto esters as a result of 1,2-hydride migration presumably *via* tautomerization.[8] Furthermore, 1,2-hydride migration promoted by $Rh_2(O_2CCF_3)_4$ provides an efficient route to (*Z*)-α,β-unsaturated carbonyl compounds[9] (Scheme 1).

In contrast to that found in α-diazo carbonyl compounds, α-diazophosphonyl compounds have not been studied systematically in metal carbene reactions.[10] Recently, we reported that tertiary β-alkoxy-substituted β-amino phosphonate derivatives could be synthesized by treatment of α-diazo phosphonyl compounds, which are derived from natural amino acids, with alcohols catalyzed by tetrakis(acetonitrile)copper(I) hexafluorophosphate/iodine, $[Cu(MeCN)_4]PF_6/I_2$, at room temperature (Scheme 1).[11] The 1,2-hydride migration product – (*Z*)-diethyl [2-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl]-phosphonate – was obtained as a side product. As a natural extension of the 1,2-hydride migration reaction of diazo compounds, we conceived that α-diazo phosphonyl compounds may undergo a similar migration. However, when running a control experiment in the absence of alcohol, we unexpectedly observed the β,γ-dihydrogen shift product – a (*Z*)-β-alkenyl-substituted β-amino phosphonate. As a continuation of this investigation, we report our detailed study on this unprecedented reaction.

To systematically study the possible 1,2-hydride migration and β,γ-dihydrogen shift reaction, (*S*)-diethyl [1-diazo-2-(1,3-dioxoisoindolin-2-yl)propyl]phosphonate **6a** was synthesized through the condensation of L-alanine **1** and phathalic anhydride. Upon successful chlorination with $SOCl_2$ in toluene, **2a** afforded acyl chloride **3a**. After an Arbuzov reaction of **3a**, α-keto phosphonate **4a** was converted to tosylhydrazone phosphonate **5a** and the desired α-diazo phosphonate **6a** could be readily obtained by elimination from **5a** with Et_3N in CH_2Cl_2 (Scheme 2).[11]



Scheme 1. 1,2-Hydride migration and β,γ-dihydrogen shift.

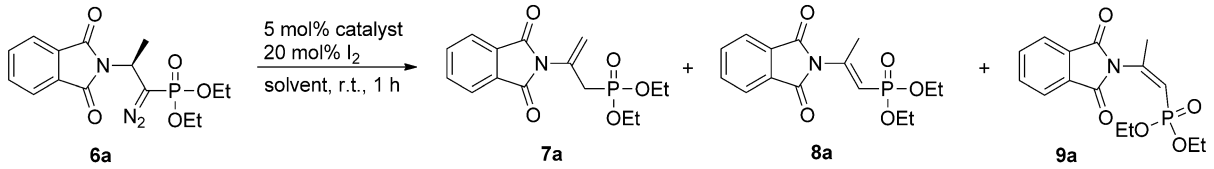


Scheme 2. Synthesis of α-diazo phosphonate **6a**.

With the diazo phosphonyl compounds **6** in hand, we then proceeded to study their reaction with different kind of the catalysts. α-Diazophosphonyl compound **6a** was the first substrate studied to examine the effect of the catalysts on the reaction, and the results are summarized in Table 1. The results revealed that with iodine (20 mol%) as co-catalyst $Cu(MeCN)_4BF_4$, CuOTf, $CuOTf{\cdot}1/2\,C_6H_6$, $Cu(OTf)_2$, CuI, TCCu, AgOTf and $Rh_2(OAc)_4$ were able to promote this reaction. Three products have been isolated or identified in the ^1H NMR spectra, the β,γ-dihydrogen shift product diethyl 2-(1,3-dioxoisoindolin-2-yl)allylphosphonate **7a**, the 1,2-hydride migration product (*E*)-diethyl [2-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl]phosphonate **8a**, and its *Z*-isomer **9a** (Scheme 1).

From Table 1, it is clear that the diazo decomposition could be effected under various reaction conditions and that the ratio of the three products depends on the catalysts employed (Table 1, entries 1–8). In the presence of TfOH (20 mol%) or $BF{\cdot}Et_2O$ (20 mol%), the diethyl α-diazo phosphonate **6a** can participate in this reaction in good yield (Table 1, entries 9 and 10). It is worthwhile noting that the combined yields, after column chromatography, of the three products range from 28 to 65%. The ratio of **7a**/(**8a**+**9a**) reflects the migratory aptitude of the β,γ-dihydrogen shift *vs.* the 1,2-hydride migration, and shows a noticeable dependence on the kind of catalysts. With $Rh_2(OAc)_4$ as the catalyst, β,γ-dihydrogen shift was predominant (50:50, Table 1, entry 8). Stronger electron-withdrawing ligands in $[Cu(MeCN)_4]PF_6$ resulted in better selectivity between β,γ-dihydrogen

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalysts	Solvent	Product ratio (**7a**:**8a**:**9a**)[b]	Overall yield [%][c]
1	$Cu(MeCN)_4BF_4$	CH_2Cl_2	50:35:15	51
2	CuOTf	CH_2Cl_2	28:44:28	30
3	$CuOTf{\cdot}1/2\,C_6H_6$	CH_2Cl_2	50:30:20	50
4	$Cu(OTf)_2$	CH_2Cl_2	25:50:25	28
5	CuI	CH_2Cl_2	28:50:22	28
6	TCCu[d]	CH_2Cl_2	29:29:42	33
7	AgOTf	CH_2Cl_2	29:43:28	30
8	$Rh_2(OAc)_4$	CH_2Cl_2	50:33:17	50
9[e]	TfOH	CH_2Cl_2	46:27:27	65
10[e]	$BF_3{\cdot}Et_2O$	CH_2Cl_2	32:37:31	53
11	$Cu(MeCN)_4PF_6$	CH_2Cl_2	55:33:12	55
12	$Cu(MeCN)_4PF_6$	$PhCH_3$	–	–
13	$Cu(MeCN)_4PF_6$	THF	–	–
14	$Cu(MeCN)_4PF_6$	Et_2O	–	–
15	$Cu(MeCN)_4PF_6$	$ClCH_2CH_2Cl$	40:44:16	40
16[f]	$Cu(MeCN)_4PF_6$	CH_2Cl_2	0:93:7	38

[a] Unless otherwise noted, all reactions were carried out using α-diazo phosphonate **6a** (0.28 mmol, 1 equiv.) in 2 mL solvent with 5 mol% of $[Cu(MeCN)_4]PF_6$ and 20 mol% of I_2 at 25 °C for 4 h (before addition 1 h, after addition 3 h).
[b] The product ratio was determined by ^1H NMR of the crude product.
[c] Overall yield of the mixture of **7a**, **8a** and **9a** after silica gel chromatograph.
[d] TCCu = copper(I) thiophene-2-carboxylate.
[e] 20 mol% catalyst was used.
[f] No I_2 was added as the co-catalyst.

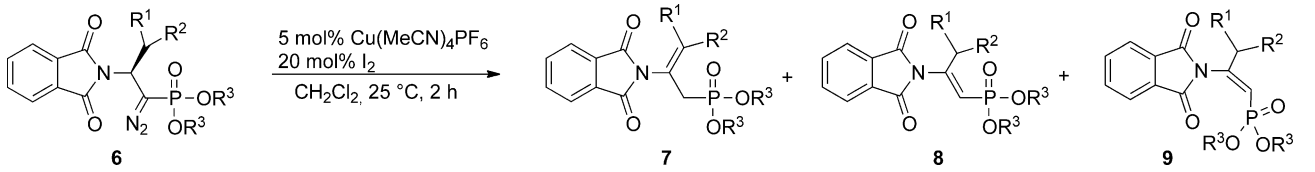
shift and 1,2-hydride migration (55:45, Table 1, entry 11).

With the best catalyst $[Cu(MeCN)_4]PF_6$ being identified, we next carried out the β,γ-dihydrogen shift reaction in different solvents to determine the best solvent for this reaction. Among the various solvent tested, toluene, tetrahydrofuran, and diethyl ether could not afford the expected products (Table 1, entries 12–14). The reaction only gave a complex mixture in these solvents. On the other hand, the Cu(I)-catalyzed reaction of **6a** occurred efficiently in 1,2-dichloroethane with 40% combined yield (Table 1, entry 15). The most suitable solvent was found to be dichloromethane. With further optimization of the reaction conditions, we found that in the absence of iodine the 1,2-hydride migration products **8a** and **9a** were formed in significant amounts (Table 1, entry 16). Thus, the optimal reaction conditions for this transformation were determined to be 0.28 mmol α-diazo phosphonate **6a**, 5 mol% of $[Cu(MeCN)_4]PF_6$ as catalyst and 20 mol% of I_2 as co-catalyst in 2 mL CH_2Cl_2 as solvent at room temperature.

Based on the above optimization efforts, the substrate scope of this reaction was investigated (Table 2). The impact of substituent groups at the β-position of dialkyl α-diazophosphonates **6** which are derived from different natural amino acids was evaluated. The tested α-diazophosphonates **6a** and **6b** with different substituents on the β-position, such as methyl and isobutyl groups afforded good yields of β,γ-dihydrogen shift products **7a** and **7b**, the 1,2-hydride migration products **8a** and **8b** and *Z* isomers **9a** and **9b** (Table 2, entries 1 and 2). In cases where the substituent groups on the β-position of dialkyl α-diazophosphonates **6** are changed to benzyl and *p*-tolyl acetate groups, a significant amount of **7c** and **7d** was formed, this was isolated and the yields were determined after column chromatographic purification (Table 2, entries 3 and 4). It is astonishing to note that diethyl α-diazophosphonates **6e–6g** which are derived from valine, isoleucine, and methionine could not undergo this reaction to give the desired products. The starting materials **6e–6g** were decomposed under the reaction conditions (Table 2, entries 5–7).

To assess the effect of substrates on product selectivity, we set out to study reactions of a series of dialkyl α-diazophosphonates **6h–6m** under $[Cu(MeCN)_4]PF_6/I_2$ catalytic conditions. The migratory product aptitude was dependent upon the size of the R^3 group. When the bulk of R^3 group was in-

Table 2. Scope of the reaction.[a]



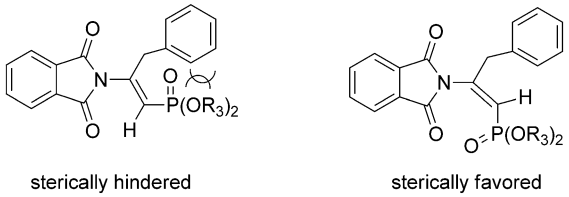
Entry	Product	R^1	R^2	R^3	Product ratio (**7**:**8**:**9**)[b]	Overall yield (%)[c]
1	**7a**	H	H	Et	55:33:12	55
2	**7b**	$CH(CH_3)_2$	H	Et	62:27:11	67
3	**7c**	Ph	H	Et	76:0:24	52
4	**7d**	*p*-$AcOC_6H_4$	H	Et	76:0:24	51
5	**7e**	CH_3	CH_3	Et	–	–
6	**7f**	CH_3	Et	Et	–	–
7	**7g**	CH_2SCH_3	H	Et	–	–
8	**7h**	H	H	Me	54:34:12	68
9	**7i**	H	H	*i*-Pr	70:26:4	72
10	**7j**	H	H	*n*-Bu	60:31:9	74
11	**7k**	Ph	H	Me	67:0:33	60
12	**7l**	Ph	H	*i*-Pr	84:0:16	70
13	**7m**	Ph	H	*n*-Bu	75:0:25	80
14	**7n**	$(CH_2)_3NPhth$	H	Et	trace:55:45	33

[a] Reaction conditions: α-diazo phosphonate **6** (0.28 mmol) in 2 mL of CH_2Cl_2 at 25 °C in the presence of 5 mol% of $[Cu(MeCN)_4]PF_6$ and 20 mol% of I_2 for 4 h (before addition 1 h, after addition 3 h).

[b] The product ratio was determined by ^1H NMR of the crude product and the configuration of **7** was assigned as *Z* from the ^1H-^1H NOESY spectrum.

[c] Overall yield of the mixture of **7**, **8** and **9** after silica gel chromatograph.

creased from methyl to butyl, the main products (*Z*)-β-alkenyl-substituted β-amino phosphonates **7** resulted (Table 2, entries 8–13). Interestingly, when dialkyl α-diazo phosphonates **6k–6m** which are derived from phenylalanine were treated with 5 mol% $[Cu(MeCN)_4]PF_6$ and 20 mol% iodine in CH_2Cl_2 at room temperature, the diazo compounds disappeared with 30 min to give a mixture of **7k–7m** and **9k–9m**. 1,2-Hydride migration *E* isomers **8k–8m** could not be detected in the ^1H NMR spectra of the crude reaction mixtures in these cases (Table 2, entries 11–13). We suspect that the increased steric congestion between benzyl and phosphonate groups reduces the ratio of **8** (Scheme 3). When (*S*)-diethyl [1-diazo-2,6-bis(1,3-dioxoisoindolin-2-yl)hexyl]phosphonate **6n** was employed in this reaction, only 1,2-hydride migration products **8n** and **9n** were observed (Table 2, entry 14). The structure of **9a** was confirmed by single crystal X-ray diffraction (Figure 1).[12]



Scheme 3. The steric congestion between benzyl and phosphonate groups.

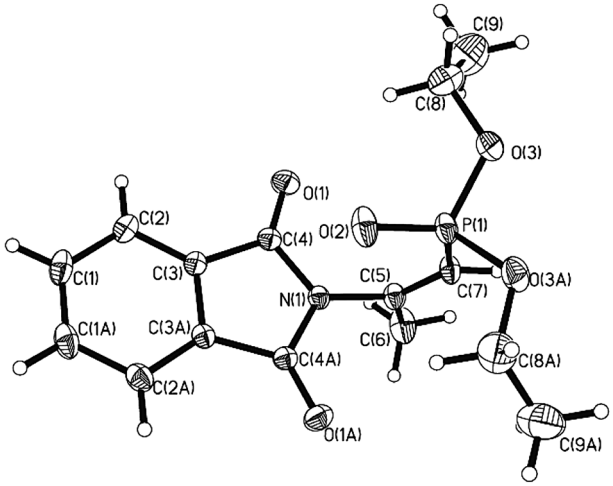
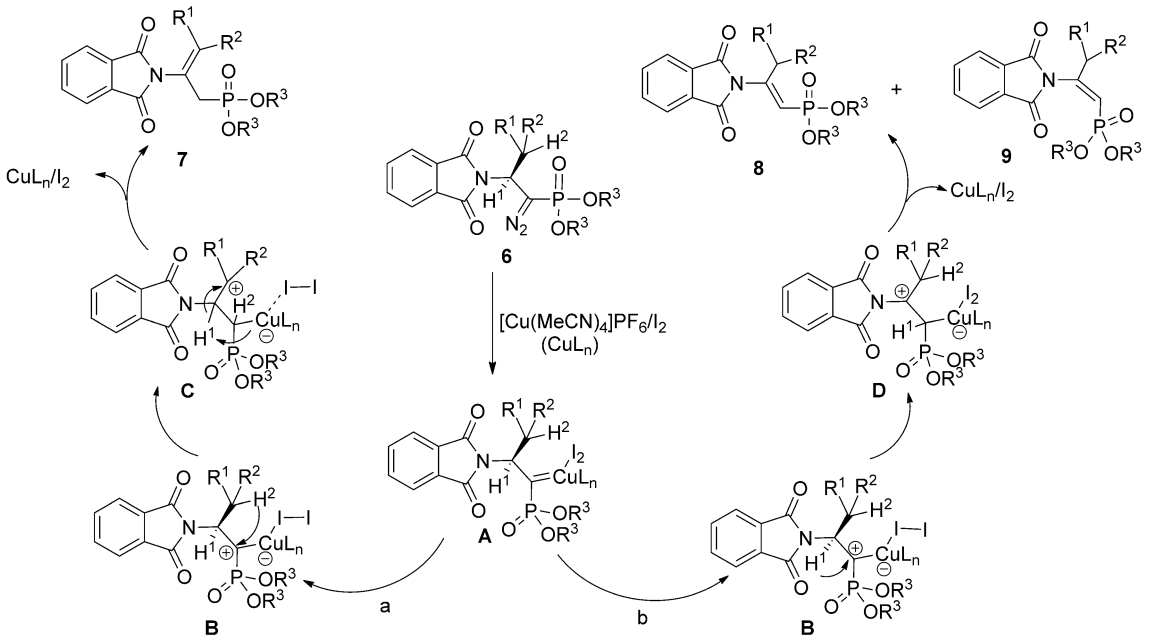


Figure 1. X-ray crystal structure of **9a**.

The possible mechanism for the reaction is shown in Scheme 4. The α-diazo phosphate **6** initially formed a metal carbene complex **A** with $[Cu(MeCN)_4]PF_6$ and iodine. It has been suggested that in the metal carbene intermediate **A**, the carbon attached to the metal has a partial positive charge (intermediate **B**).[13] The iodine may play a role in stabilizing the carbocation intermediates **A** and **B**.[11] Then the γ-hydrogen (H^2) on the phosphonate migrated to the carbene center through a resonance complex **B** to form

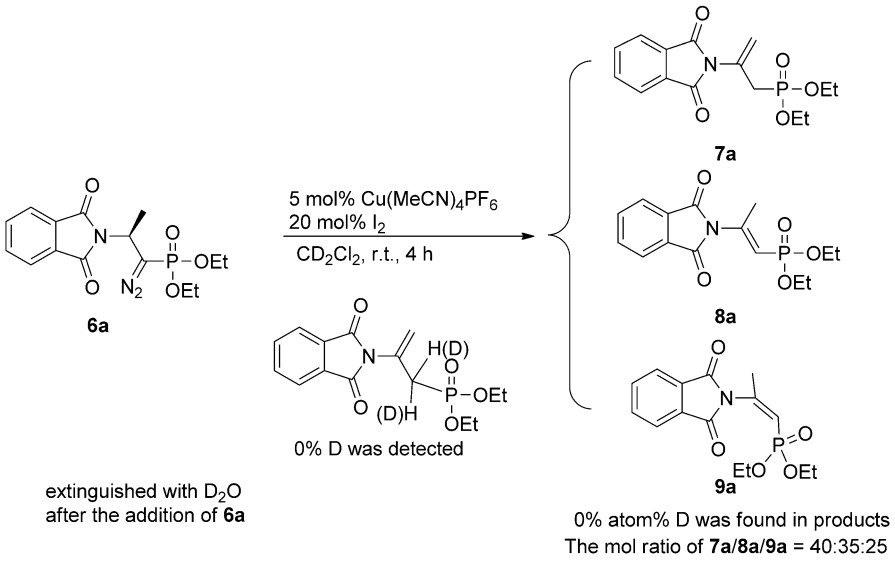


Scheme 4. Plausible reaction mechanism.

a tertiary carbocation intermediate **C**. For the migration to occur, the migrating bond needs to be parallel to the *p* orbital of the carbene carbon.[14] Furthermore, the proton H^1 was picked up by the copper catalyst and followed by the extrusion of Cu(I) catalyst to give the final product **7** (pathway a). The β-hydrogen on the phosphonate could also migrate to the carbene center to form a carbocation intermediate **D**. Following the 1,2-hydride migration and the losing of $[Cu(MeCN)_4]PF_6$ and iodine, the intermediate **D** transformed to by-products **8** and **9** through pathway b.

The substituent effect on migratory aptitude observed in this study can be simply rationalized by assuming that the 1,2-migration can stabilize the positive charge in the transition state. The migratory aptitude is largely governed by the stability of the products. The steric bulkier group in the β,γ-dihydrogen shift product **7** will obviously favor a large group, such as the benzyl group, because the steric hindrance can thus be relieved.

In order to explore the mechanism of this reaction, CD_2Cl_2 was used for the deuterium labelling experiment to investigate the proton-transfer process (Scheme 5). Compound **6a** was treated under the



Scheme 5. Deuterium labeling experiments processed with $CDCl_3$, determined by ^1H NMR.

standard reaction conditions with CD_2Cl_2 as solvent. After the reaction was complete, the mixture was extinguished with D_2O. The ^1H NMR results show that no deuterium was detected in the product. The results clearly indicate that the β,γ-dihydrogen shift was really an intramolecular process and ruled out the possibility that the hydrogen arouse from the work-up process after this reaction. Furthermore, with the use of aqueous dichloromethane solutions, the reaction proceeded efficiently and only afforded 1,2-hydride migration product **9a** with 52% yield.

In conclusion, we have reported an unexpected stereoselective synthesis of (*Z*)-β-alkenyl-substituted β-amino phosphonates through a β,γ-dihydrogen shift reaction of α-diazo phosphonates catalyzed by tetrakis(acetonitrile)copper(I) hexafluorophosphate/iodine, $[Cu(MeCN)_4]PF_6/I_2$. This investigation demonstrates that the diazo decomposition of α-diazo phosphonates which are derived from natural amino acid gives both 1,2-hydride migration and β,γ-dihydrogen shift products, depending on the substrate structures. The sterically bulkier group in substrate makes the β,γ-dihydrogen shift the major product in most cases. A plausible reaction mechanism has been proposed to explain the combined β,γ-dihydrogen shift and 1,2-hydride migration reaction. Further research for the extension of this reaction is currently underway in our laboratory.

Experimental Section

General Comments

The spectroscopic data of all compounds are given in the Supporting Information.

General Procedure for $[Cu(MeCN)_4]PF_6/I_2$-Catalyzed Reaction of Dialkyl α-Diazo Phosphonates 6

$[Cu(MeCN)_4]PF_6$ (0.014 mmol) and I_2 (0.056 mmol) in an oven-dried Schlenk tube were dissolved in 2 mL of freshly distilled CH_2Cl_2 under nitrogen. Dialkyl α-diazo phosphonate **6** (0.28 mmol) was diluted with 2 mL of CH_2Cl_2 and was drawn into a gastight syringe. It was then added to the reaction mixture dropwise over a period of 1 h with the help of a syringe pump. After the addition was complete, the reaction mixture was stirred for another 3 hour at 25 °C. The solvent was then removed under reduced pressure and the crude residue was purified by silica gel chromatography with the eluent [CH_2Cl_2/EtOAc, 15:1 (v:v)] to give the corresponding products **7**, **8** and **9**.

Acknowledgements

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