ORGANOMETALLICS

Addition of Oxime Derivatives to Alkynyl Fischer Carbene Complexes

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Supporting Information

ABSTRACT: The addition of oxime derivatives to alkynyl Fischer carbene complexes has been explored through a combined experimental and computational approach. Up to four different heterocycles with diverse regiochemistry and ring size were found, depending on the starting ketone. The reaction mechanism was studied by DFT methods.

INTRODUCTION

In the last few decades Fischer carbene complexes have become a powerful synthetic tool for organic chemists.¹⁻⁴ In particular, these compounds have proven to be extremely useful for the synthesis of carbocycles of different sizes through [3 + 2 + 1](Dötz benzannulation),⁵ [2 + 1] (cyclopropanation),⁶ [2 + 2],⁷ [3+2],⁸ [3+3],⁹ [4+2],¹⁰ and [4+3]^{11,12} cyclizations. These organometallic species have also been used in the construction of an increasing number of heterocycles.^{13–15} Due to the extremely versatile behavior of Fischer carbene complexes, they have been labeled as "chemical multitalents".^{16–18} Different reactivity levels are found when Fischer carbene complexes are used in combination with unsaturated nitrogen compounds. The most important work was carried out by Hegedus, who developed a useful photochemical synthesis of β -lactams from carbene complexes and imines.¹⁹ Other reports include the 1,2⁻²⁰ and 1,4-addition²¹ of imines to α_{β} -unsaturated carbene complexes and the cycloaddition of azadienes to unsaturated Fischer carbene complexes.^{11,22–24} We recently described²⁵ the use of acyloximes in the photochemical synthesis of isoquinoline derivatives through a two-step, one-pot reaction sequence. First, the iminyl radical is easily generated by a nitrogenoxygen bond cleavage. The subsequent addition of the newly formed radical to unsaturated systems yields the heterocyclic compounds with ease and in good yields. This reaction mechanism has been further explored by means of theoretical calculations²⁶ and EPR studies.²⁷ Both aryl and alkynyl groups can be used in either inter- or intramolecular reactions. We extended the scope of this photochemical behavior of acyloximes when confronted with Fischer alkynyl carbene complexes (Scheme 1).14 We showed how nitrogen-centered radicals generated by the action of UV light are capable of reacting with alkynyl Fischer carbene complexes in two ways, i.e. 1,2- and 1,4-addition, and our results constitute the first reported example of a photochemically driven reaction of this kind.





After a comprehensive mechanistic exploration, it was demonstrated that **3** and **4** were formed through two different pathways (Schemes 2 and 3).

The photochemical nature of the reaction was explored by performing a test at room temperature in the dark. After the





Received: June 21, 2012 Published: September 6, 2012 Scheme 3. Proposed Mechanism for the Formation of 4



reaction mixture was stirred for 3 h, only traces of 3a were obtained, together with a large amount of unreacted starting compounds 1a and 2a.¹⁴ However, this incipient result—together with experimental difficulties associated with the photochemical reactivity of oxime derivatives with alkynyl Fischer carbene complexes—prompted us to explore the thermal version of this reaction.

RESULTS AND DISCUSSION

The thermal reaction was carried out under several sets of reaction conditions by varying solvents, temperature, and reaction time. The most relevant results were obtained on heating a mixture of 1a and 2a (1.2 equiv) in toluene at 90 °C for 18 h. Three different products were isolated (Scheme 4).

As can be seen, compound **6a** was the main product. We have previously described the formation of this compound through a thermal pathway.¹⁴ Two minor compounds were isolated by HPLC along with the main product. Compound **7a** (related to **4** in Scheme 3 and in previous work¹⁴) has a sevenmembered ring (in contrast to **6a**), while **8a** also has a fivemembered ring with a different regiochemistry relative to **6a**.

The general applicability of the reaction was assessed. With this aim in mind, several ketones were employed to generate the acetyloximes and these were subsequently reacted with alkynyl carbene **2a**. The results are summarized in Table 1.

It can be seen from the results that this reaction is extremely sensitive to the oxime derivative employed. As explained above, the compound with the five-membered ring (6a) was the main product for the benzophenone acetyloxime. However, when the fluorenone acetyloxime was tested, the five-membered ring with the opposite regiochemistry (8b) was the only isolated product. In the case of indanone acetyloxime, a new structure with a sixmembered ring, 9c, was formed (Scheme 5). Finally, compound 6d was isolated in the case of the acetophenone acetyloxime. In all four cases shown in Table 1 products from the addition of the oxime derivative and the carbene complex were obtained, but these results are, at first glance, far from being easily optimized. In the three first entries the main Article

Table 1. Addition of Acetyloximes to 2a

		product (yield, %)			
entry	ketone				
1	benzophenone	6a (31)	7a (5)	8a (4)	
2	fluorenone			8b (24)	
3	indanone				9c (15)
4	acetophenone	6d (19)			

Scheme 5. Thermal Addition of Indanone Oxime Derivatives to Alkynyl Fischer Carbene Complexes



product structure differs in the regiochemistry or the size of the cycle (products 6-9). Only on using benzophenone (entry 1) and acetophenone (entry 4) was the reaction outcome similar. The absence of the minor products is presumably due to the lower reaction yields obtained.

The structures of **6a**, **7a**, **8a**,**b**, and $9c^{28}$ were confirmed by Xray diffraction studies (Figure 1), whereas the formation of 6d was determined by comparison of its spectroscopic data with those of 6a. In each case, the acetyl moiety is lost during the course of the reaction and we therefore checked the effect of changing this unit on the reaction outcome. The equivalent reaction was carried out under the same conditions but with the acetyloximes replaced by oximes. In every case, the change to oximes did not lead to substantial changes in either the product ratio or yield. For instance, replacement of benzophenone acetyloxime 1a by the equivalent oxime gave a similar crude product. The main product was 6a, and this was obtained in 40% yield (in comparison with 31% using the acetyloxime; Table 1, entry 1). In the case of acetophenone derivatives, the yield of **6d** changed from 19% (acetyloxime; Table 1, entry 4) to 13% (oxime). Similarly, the use of chromium carbene complexes did not alter the reactivity, but in any case slightly lower yields were found. This difference is believed to be caused by the lower stability of the chromium analogues.

Due to the very different reaction outcome, even when slight modifications were introduced, we decided to perform a theoretical study of the thermal reaction in order to fully understand the reaction mechanism. This step is a prerequisite before the reaction can be turned into a synthetically useful process.

Computational Details. All calculations were carried out using the Gaussian 03 program package.²⁹ Since DFT methods combine the importance of including electron correlation effects and the possibility of dealing with large systems, ground

Scheme 4. Thermal Addition of Benzophenone Oxime Derivatives to Alkynyl Fischer Carbene Complexes





Figure 1. X-ray diffraction structures for 6a, 7a, 8a,b, and 9c.

state molecular geometries were optimized within the nonlocal density approximation (NLDA), including Becke's³⁰ nonlocal exchange corrections as well as Perdew's³¹ inhomogeneous gradient corrections for correlation (BP86). For C, O, N, and H, the standard split-valence 6-31G* basis set³² was employed. For the tungsten atom, the Hay-Wadt effective core potential³³ was used with the minimal basis set split to [441/ 2111/21] (LanL2DZ). The geometry was fully optimized without any symmetry constraint for all model compounds. Optimized structures were characterized as minima or saddle points by frequency calculations, which also allowed the ZPE and thermal corrections to be obtained. The Fischer carbene complex was calculated without any simplification. Although both chromium and tungsten carbene complexes have proven utility in these reactions, we used the tungsten complex despite the greater computational cost, as better experimental results were obtained. Oximes were used in the calculation, as they yield the same experimental compounds as acetyloximes, but at a smaller computational cost.

Theoretical Calculations. We started the theoretical study by modeling the reaction between the benzophenone oxime and alkynyl carbene complex 2a. As explained above, this reaction led to the formation of 6a-8a. According to the literature,¹ two different reactive pathways could emerge when confronting a nucleophile with alkynyl carbene complexes. These two possibilities are due to the presence of two reactive points: i.e., the carbene carbon atom and the β alkyne carbon atom. Thus, we computed these two paths and the results are shown in Figure 2.

In the first route, transition structure **B-TS** is formed through nucleophilic attack of the nitrogen oxime atom at the β alkyne carbon atom. The geometry of the carbene complex is modified accordingly by decreasing the alkyne C–C–C angle and lengthening the C–C triple-bond distance (1.240 Å in **A**, 1.277 Å in **B-TS**). Modifications in the W–C bond length and C_{carbene}–C_{akyne} distance also respond to this attack. The second route involves the attack on the carbene carbon atom, and this leads to an increase in the W–C bond length (2.170 Å in **A**, 2.322 Å in **C-TS**) while the alkyne moiety is barely altered. A



Figure 2. Nucleophilic attack. Distances are given in angstroms and free energies in kcal/mol relative to A.





comparison of the two transition structures reveals only minor differences in the C=N distances, a finding consistent with the nucleophilic attack by the nitrogen atom lone pair, but large differences in the N–C bond distances that are being formed.

In **B-TS** the N–C_{alkyne} distance is 1.919 Å, whereas in **C-TS** the N–C_{carbene} distance is 1.795 Å. This situation should be reflected in the relative stabilities of the two structures, as in **B-TS** the negative charge is mainly located on the metal fragment.



Figure 4. Cyclization step in the formation of 6a.

These two transition structures lead to two different products, for which the addition of the oxime has taken place on the alkyne triple bond (**B**) or the W=C bond (**C**). In the case of **B** the structure of the Fischer carbene complex is maintained, with a W=C bond of 2.275 Å, and the relative energy reflects this fact. In the case of **C**, the addition to the W=C bond leads to a longer W-C distance (2.379 Å) and a less stable structure. **B** is clearly more stable than **C**, and it is formed through a pathway of lower energy (**B-TS** vs **C-TS**). Thus, at this point there will be a clear preference for the formation of **B**.

The next step in the reaction mechanism consists of a [1,2]-W(CO)₅ migration (Figure 3). In **D-TS** the metal fragment moves from the carbenic carbon to the adjacent atom with W–C distances of 2.540 and 2.754 Å. This geometrical change is associated with a considerable increase in energy, and this causes intermediate **D** to be quite unstable. Thus, **D** will rapidly progress along the reaction path or will return to the previous, more stable minimum **B**. This migration was initially proposed by Dötz et al.³⁴ to explain cyclodimerization of Fischer alkynyl carbene complexes, and the intermediate is stable enough to be identified spectroscopically.³⁵ In addition, this migration was also found in related reactions of Fischer carbene complexes.¹¹ In these examples, [1,2]-migration promotes the subsequent cyclization to yield the reaction products, as happens in the case described here.

Once **D** is formed, it will quickly progress through a cyclization step. The electron-rich carbon atom located next to the metal fragment can attack the iminic carbon to yield a fivemembered cycle (Figure 4). As can be seen, in **E-TS** this cyclization step takes place, as the C–C distance is already 2.626 Å. Accordingly, the C==N distance lengthens from 1.355 Å in **D** to 1.370 Å in **E-TS** and the C–C bond distance changes from 1.269 Å in **D** to 1.314 Å in **E-TS**. Cyclization is completed in **E** to yield a precursor of **6a**. Due to the high energy of **D**, the cyclization step has to surmount an energy barrier of only 8.6 kcal/mol. Formation of **6a** from **E** involves the loss of the metal fragment and the removal of the OH of the oxime functionality. This kind of transformation has already been found in related reactions of alkynyl Fischer carbene complexes and 1-hydroxy-1-azabutadiene derivatives.²²





Figure 5. Energetic profile for the formation of 6a.

the initial attack of the oxime nitrogen atom at the β alkyne carbon atom to yield intermediate **B** (18.2 kcal/mol) together with the formation of **D** (also 18.2 kcal/mol), although the formation of **E-TS** corresponds with the maximum in energy along the reaction path. On the other hand, a global minimum in the reaction path is reached with the formation of **E**, which is 3.4 kcal/mol more stable than the reactants.

Experimentally **6a** was found to be the main reaction product, but another two products were also isolated from the reaction mixture, **7a** and **8a**. Thus, we also explored by computational means the fate of **C**, which is formed after nucleophilic attack at the carbenic atom. The next step in the reaction mechanism for **C** is shown in Figure 6. The new, more stable minimum **F** was found through a [1,3]-W(CO)₅ migration. The driving force for this step is the generation of **F**, a more stable structure. In the transition structure **F-TS**, the metal fragment migrates through a cyclic structure. The new intermediate **F** has extended conjugation, and this accounts for its higher stability. This step has been suggested previously²²



Figure 6. Metal fragment migration step in the formation of 7a.



Figure 7. Cyclization step in the formation of 7a.

and was later found¹² in cyclization reactions of Fischer carbene complexes—in the latter case charge stabilization was invoked to justify the formation of analogues of F.

The next step in the reaction mechanism corresponds to a cyclization step (Figure 7). The molecule is now in the right disposition to allow the interaction between its two extremes. Electron density located on the metal fragment can promote a nucleophilic attack on the closest aromatic ring. At the same time, the metal fragment moves to the neighboring carbon atom in a complex geometrical change that finally leads to the transition structure **G-TS**. Although both changes have an influence on the geometry, the biggest deformation comes from the movement of the metal fragment and the nucleophilic attack on the aromatic ring is less influential. Due to the complex atomic movement involved, we performed IRC calculations to connect the three stationary points in order to ensure that **G-TS** is really the transition structure that connects these two minima (Figure 8).



Figure 8. IRC connecting F, G-TS, and G.

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1.520

Figure 9. Hydrogen atom migration step in the formation of 7a.



Figure 10. Energetic profile for the formation of 7a.





Once cyclization has taken place, the final structure that is similar to 7a is formed through a hydrogen migration (Figure

9). The driving force for this step comes from the high stabilization of H with respect to G due to the recovery of aromaticity in the phenyl ring. Thus, **H** is 0.3 kcal/mol more stable than the reactants and 15.3 kcal/mol more stable than **G**. In the transition structure **H-TS** the hydrogen atom is located between the initial and final positions (C–H distances of 1.355 and 1.445 Å) and the imaginary frequency is 1083.0i, a characteristic value for a hydrogen migration.

The final step corresponds to a reductive elimination with loss of the metal fragment to yield 7a. This step has been previously found in related transformations.²² The energetic profile for this reaction is shown in Figure 10. For the formation of G-TS and H-TS it is necessary to surmount energetic barriers of considerable height. In addition, the final computed product is only slightly more stable than the reactants. These facts help to explain the low yield observed for the formation of 7a.

As shown in Scheme 4, another product was detected in the reaction of alkynyl carbene complex 2a with benzophenone acetyl oxime 1a. A product with a five-membered ring was found in low yield. Compound 8a has a regiochemistry different from that of 6a. The formation of 8a can be explained by starting from intermediate C, which is obtained by nucleophilic attack of the oxime derivative nitrogen atom at the carbenic carbon. Once C is formed, a direct cyclization step leads to I—the precursor of 8a (Figure 11). The formation of the final product 8a involves reductive elimination as described above.

The energetic profile for this process is shown in Figure 12. As can be seen, the first step is common in the two routes



Figure 12. Energetic profile for the formation of 8a.

leading to the formation of 7a and 8a. Furthermore, the ratedetermining step in both cases has a similar energy barrier (G-TS and I-TS). Thus, 7a and 8a should be formed in similar yields—a situation that was confirmed experimentally.

As explained above, a very different reaction outcome was found when diverse oxime derivatives were used. The formation of 6a-8a was detected on using benzophenone acetyloxime 1a. However, only 8b was isolated in the case of the reaction with fluorenone acetyloxime and only 9c was obtained for the indanone derivative. Given that the oxime derivatives share some common features, it seems reasonable to expect a general reaction mechanism as outlined for 1a. The variation in product ratios is probably due to small differences in the energy for the relevant transition structures for the path leading to each type of product. Thus, in order to explain the different reactivity, we carried out selected calculations on the key structures for the oxime derivatives. As shown in Figure 2, two reaction paths are available for the reaction of oxime derivatives with alkynyl Fischer carbene complexes: i.e., nucleophilic attack on the carbenic C atom or on the β alkyne C atom. In the case of **2a**, attack at the β alkyne C atom leads to B-TS and subsequently to the formation of 6a, the main product, while attack onat the carbenic C atom leads to C-TS

and the formation of 7a and 8a. B-TS is ca. 5 kcal/mol more stable than C-TS, a finding that is consistent with experimental results. Similar calculations were carried out on a fluorenone oxime (Figure 13).



Figure 13. Energetic profile for the reaction of alkynyl carbene complex 2a with fluorenone oxime.

It can be seen that the formation of K-TS (equivalent to B-TS, attack at the β alkyne C atom) has to surmount the same energy barrier (18.2 kcal/mol), whereas L-TS (equivalent to C-TS, attack at the carbenic C atom) is more stable (15.0 kcal/mol). This situation is due to the planar disposition of the fluorenone moiety compared to the benzophenone, which eliminates the steric hindrance with the pentacarbonylmetal fragment. In this case, L-TS will be preferred and the formation of **8b** will eventually be achieved, as confirmed by experimental data.

The mechanism for the reaction should change when different oxime derivatives are used, as reflected by the data shown in Table 1. Specifically, in the case of indanone (entry 3) a different product was obtained (Scheme 5). The first steps in the reaction mechanism should be very similar to those discussed above. However, at a certain point, the acidic α protons could provide a competitive pathway. Fischer carbene complexes and related compounds are known to have acid/base reactivity.¹ A detailed mechanistic exploration of this step is currently underway using both computational and experimental tools, and the results will be published in due course.

As explained above, three different products (6a-8a) were obtained from the reaction of 1a and 2a (Scheme 4), with 6a obtained as the major product. However, as inferred from the computational data presented in Figures 6, 10, and 12, the formation of 7a and 8a should be preferred, as the points with highest energy along the path have values of 31-32 kcal/mol, while in the case of the formation of 6a the value is 38.2 kcal/ mol. These data are in clear disagreement with experimental results. It therefore seems clear that an alternative path must be operating. Considering that the formation of 6a requires the removal of the OH of the oxime functionality at some point, this could take place in any of the steps prior to surmounting the high energy barrier leading to **E** by any negatively charged metal fragment. Metal species with a certain electron density are ubiquitous in the chemistry of Fischer carbene complexes, but the exact nature of these structures and the more favorable step for the loss of OH are still unknown. However, indirect evidence for this alternative mechanism comes from the excess complex required in this and other examples^{14,22} for the reaction to reach completion. This step has also been invoked previously for similar reactions.²² Furthermore, bearing in mind that reaction of **3a** in refluxing acetonitrile leads to the formation of **6a** in 76% yield (Scheme 6),¹⁴ it seems reasonable to believe that the loss of the OH fragment could take place in the initial steps, before **D** is formed, through metal fragment cyclization.





Unfortunately, without further experimental information on the species involved in the process of OH loss, the computational study would be a complex task and is well beyond the scope of this paper. However, some evidence could be obtained from the formation reaction shown in Scheme 5 by computational means (Figure 14). As can be seen from the IRC calculation, the formation of **M** (equivalent to **6a**) takes place in only one step from **3a** after surmounting a barrier of 24.5 kcal/ mol. Furthermore, **M** is much more stable (34.3 kcal/mol) than **3a**. Thus, the formation of **M** could drive the reaction to completion. It should be noted that the data shown in Figure 14 cannot be compared with the energy values discussed previously, as the species computed have different numbers of atoms. To properly compare the different paths, the exact formation of 3a should be assessed. As stated above, this information is currently unavailable and a discussion of the formation of this compound is beyond the scope of this paper. However, as 3a constitutes a common intermediate for these and other relevant transformations, the mechanism leading to its formation is currently under investigation.

CONCLUSIONS

We have presented here a new type of reactivity that allows the generation of up to four different types of nitrogenated heterocycles by using oxime derivatives and alkynyl Fischer carbene complexes. Both the regiochemistry and the size of the cycle can be modified by changing the starting ketone used to synthesize the oxime derivative. Thus, the mechanism of ring formation was found to be very dependent on the ketone moiety. On the other hand, chromium and tungsten can be used in the carbene moiety and both oxime and acetyloximes yield similar products. Consequently, both the metal and the oxime derivative were found to affect the mechanism to minor extent. The mechanism of the reaction was explored in an effort to understand this transformation before any subsequent modification could be devised to improve the reaction outcome. However, with the data currently available, the formation of some products found in the crude reaction mixture cannot be completely explained and further studies will be needed. Although in the present form this reaction provides low yields, it represents a new type of reactivity that would allow the synthesis of complex heterocycles with ease and in very few steps. Further efforts are required to turn this reaction into a synthetically useful tool and to expand the synthetic scope.



Figure 14. IRC calculation for the formation of M from 3a.

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EXPERIMENTAL SECTION

General Procedure. To 1 equiv of oxime acetate dissolved in toluene was added 1.2 equiv of the corresponding alkynyl Fischer carbene, and the mixture was heated for ca. 18 h at 90 °C. The reaction was monitored by TLC. Once the reaction was complete, the solution was cooled to room temperature. The solvent was removed and the crude product was purified by silica gel column chromatography (hexane/EtOAc 90/10).

ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving experimental procedures, characterization data, X-ray diffraction data, and Cartesian coordinates for the geometries discussed in the text. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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