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Article

Rhodium(II)-Catalysed Intramolecular O-H Insertion of α-Diazo-γ-Azido-δ-Hydroxy-β-Ketoesters. Evidence for a Novel Sigmatropic Rearrangement of an Allylic Azide Intermediate

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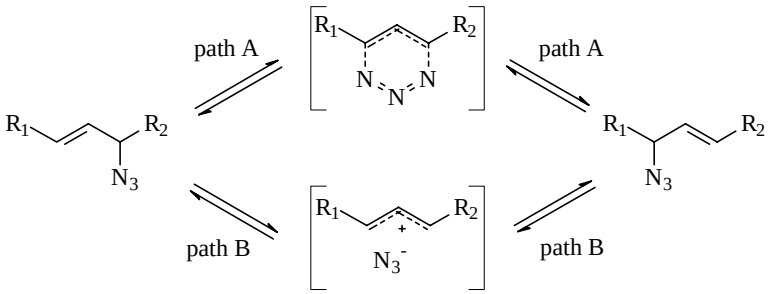
3(2H)-Furanona-2-carboxilatos têm sido preparadas em bons rendimentos e seletividade moderada (d.e. *ca* 60%), a partir da reação de inserção de O-H intramolecular de δ-hidroxi-α-diazoésteres catalisada por $Rh_2(OAc)_4$. Observou-se que as furanonas 2,5-*cis* substituídas são formadas inicialmente na reação, sofrendo epimerização quando submetidas à cromatografia em sílica gel, fornecendo os isômeros 2,5-*trans* correspondentes. A decomposição de γ-azido-δ-hidroxi-α-diazoestéres catalisada por $Rh_2(OAc)_4$ também forneceu 3(2H)-furanona-2-carboxilatos. Estes compostos são formados a partir de transformações sequenciais, envolvendo primeiramente uma reação de inserção de O-H intramolecular, seguido de um rearranjo sigmatrópico concertado [3,3] do intermediário alil azida.

The $Rh_2(OAc)_4$ catalyzed intramolecular O-H insertion reaction of δ-hydroxy-α-diazoesters affords 3(2H)-furanone-2-carboxylates in good yield but with moderate selectivity (d.e. *ca* 60%). The initially formed 2,5-substituted *cis*-furanones were found to epimerize to the corresponding 2,5-*trans* isomers when subjected to silica gel chromatography. The $Rh_2(OAc)_4$ catalyzed decomposition of γ-azido-δ-hydroxy-α-diazoesters also furnished 3(2H)-furanone-2-carboxylates. These compounds are derived by a sequential O-H insertion reaction followed by a concerted [3,3]-sigmatropic shift of the allylic azide intermediate.

Keywords: *diazoesters; intramolecular OH insertion; 3(2H)-furanone; rhodium (II)*

Introduction

Allylic azides are described as species co-existing in equilibrium between regioisomers[1-3]. In 1960, Gagneux, Winstein and Young reported that α- and γ- substituted allyl azides rapidly form an equilibrium mixture of the two isomers and the rate and equilibrium constants of this rearrangement were measured[1]. Two mechanisms can be postulated to rationalize this transformation: (1) a concerted, [3,3]-sigmatropic rearrangement (path A), in which the stereochemical integrity of the molecule is preserved and (2) a dissociative process involving ion-pair formation (path B), whereby the initial stereochemistry can be lost (Scheme 1). It was noted that the rearrangement was remarkably insensitive to changes in solvent as well as to



Scheme 1.

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alkyl substitution[1-3]. These observations are indicative of very little charge separation in the transition state, and it is generally assumed that the equilibration occurs *via* a cyclic transition state (*i.e.*, path A). Other examples of allylic azide isomerizations have been documented and support these concepts[4,5]. However, a definitive proof which unequivocally distinguishes between the above two mechanistic possibilities is still under investigation.

During the course of our studies dealing with the O-H insertion reaction of α-diazo-γ-azido-δ-hydroxy-β-ketoesters, we encountered a novel reaction which bears significantly on the mechanism of the allylic azide rearrangement[6]. The detailed results of these investigations are reported herein.

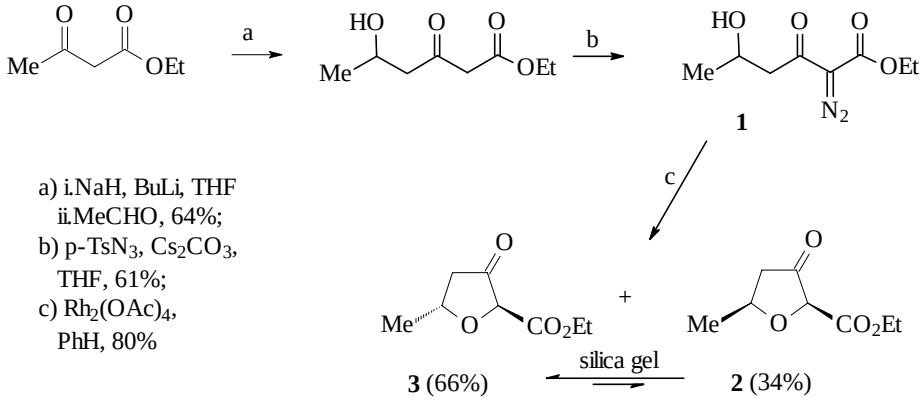
Results and Discussion

The use of diazo carbonyl compounds in transition metal-mediated insertion reactions has been extensively studied, particularly for the synthesis of theoretically interesting compounds as well as natural products[7-9]. However, only a few examples dealing with the preparation of oxygenated heterocycles *via* an O-H insertion reaction have been reported[9-13]. Over the past years, we have been studying several aspects of the Rh(II)-catalyzed O-H insertion reaction in order to increase its synthetic utility, especially toward the synthesis of 3(2H)-furanones[6,10]. While carrying out these studies, we observed that various δ-hydroxy-diazoketoesters[14] underwent a smooth Rh(II)-catalyzed cyclization to afford 2-carboethoxy substituted 3(2H)-furanones.

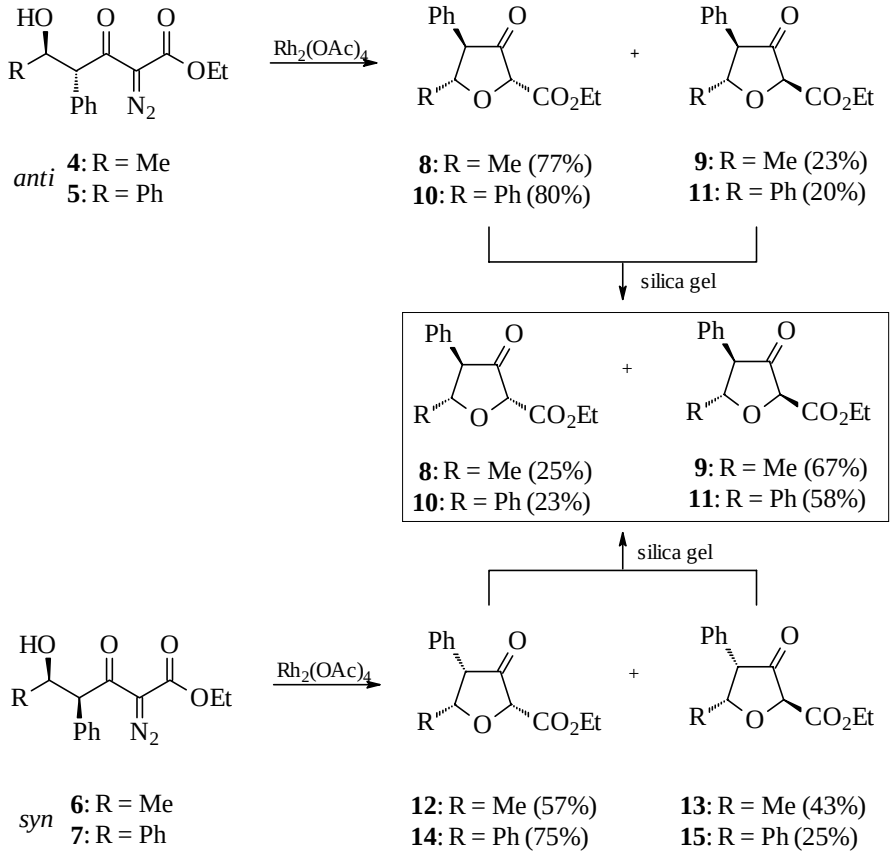
Diazoester **1** was selected as a model compound for the initial studies and was readily prepared in two steps by the reaction of the dianion of ethyl acetoacetate[15] with acetaldehyde followed by a diazo transfer reaction[16,17] (overall yield of 40%, Scheme 2). The $Rh_2(OAc)_4$ catalyzed reaction of diazoester **1** was carried out in refluxing benzene and cleanly afforded the expected O-H insertion products **2**/**3** as a 2:1-mixture of diastereoisomers. The ratio of isomers was determined by examination of the ^{1}H-NMR spectrum of the crude reaction mixture[18]. Silica gel chromatography furnished pure samples of both the *cis* and *trans* substituted 3(2H)-furanones **2** and **3** in 80% yield. The product ratio observed after chromatography (**2**:**3** = 1:2) suggested that a partial epimerization of the *cis* to the *trans* furanone **3** occurred under the chromatographic conditions.

Decomposition of the *anti* (**4**/**5**) and *syn* (**6**/**7**) γ-hydroxy-α-diazoesters[14] was carried out in a similar fashion, producing the expected 3(2H)-furanones in high yield but as a mixture of diastereomers (Scheme 3). In all four cases, the major product corresponded to the 2,5-substituted *cis*-isomer (1.3-4.0:1) as determined from the ^{1}H-NMR spectrum of the crude reaction mixture[18]. It should be noted that the stereochemical relationship between the 4- and 5-substituents present in the starting material is retained in the final products, as the O-H insertion reaction does not affect the relative disposition of these two stereocenters. As was previously observed with the 3(2H)-furanone system (*i.e.*, **2**/**3**), extensive epimerization occurred when each pair of diastereoisomers (**8**/**9**, **10**/**11**, **12**/**13**, **14**/**15**) was subjected to silica gel chromatography. The 3(2H)-furanones **8**/**9** (R = Me) and **10**/**11** (R = Ph) were obtained in good yield and with similar ratios (**9**:**8** = **11**:**10** = 2.5:1). In each case, the major product obtained was the 2,5-substituted *trans*-isomer (**9** and **11**, Scheme 3). Careful analysis of the remaining fractions isolated from the chromatographic column indicated that no other epimer was present. Other rhodium catalysts were also utilized to promote this reaction ($Rh_2(cap)_4$, $Rh_2(pfb)_4$) and they showed similar selectivity, but afforded the various insertion products in lower yields.

The detailed mechanism of the Rh(II)-catalyzed intramolecular insertion reaction which fully explains the observed preference for the formation of the 2,5-substituted *cis*-furanones remains unknown and this is under current investigation. From the results obtained, it is clear that the substituents on the furan ring and the transient bulky rhodium carbenoid moiety play a key role in controlling the newly formed stereogenic center. The silica gel-promoted



Scheme 2.



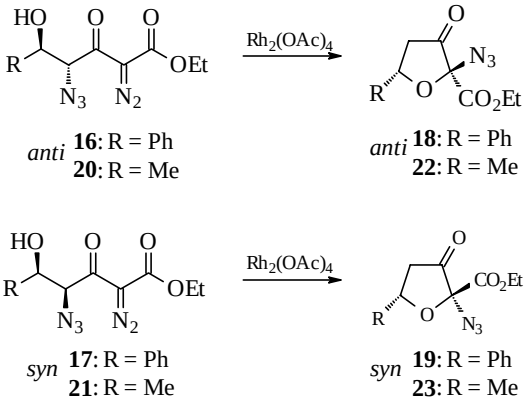
Scheme 3.

epimerization of the 2,5-*cis*-substituted furanone to the respective *trans*-isomer suggests that the former is the kinetic product while the latter is the thermodynamic one. These results are supported by semi-empirical (AM1-SPARTAN) and molecular mechanics (MM2-SPARTAN) calculations[19], which indicate that the 2,5-*trans* isomers are thermodynamically favored in all cases, with a ΔH_f of 0.5-2.5 kcal/mol less than the corresponding 2,5-*cis* isomers.

An analytically pure sample of 4,5-diphenylfuran-3-one-2-carboxylate (**11**) could be isolated by crystallization (ether-petroleum ether) and was fully characterized as the 2,5-*trans*-4,5-*trans* isomer. On the basis of this observation, a simple method to prepare gram quantities of the diastereomerically pure 3(2H)-furanone **11** which avoids chromatographic separation of both the starting diazoesters **5**/**7** and the product **11** was developed. A crude mixture of anti-**5** and syn-**7** hydroxydiazoesters was treated with $Rh_2(OAc)_4$, and this was followed by filtration through a *plug* of silica gel and crystallization of the resulting oil to give 3(2H)-furanone **11** in 51% yield. Further studies exploring the reactivity of furanone **11** and its use as a *synthon* for synthetic transformations are in progress.

Extension of the carbenoid insertion method to the *anti*- and *syn*-isomers of α-diazo-γ-azido-δ-hydroxy-β-ketoesters **16** and **17** was next investigated (Scheme 4). Interestingly, the $Rh_2(OAc)_4$ catalyzed decomposition of these diazoesters gave rise to the unexpected 3(2H)-furanones **18** and **19** in *ca* 80% yield. In both cases, only a single diastereoisomer was obtained. A related set of results was encountered using the *anti*- and *syn*-diastereomers of ethyl 4-azido-2-diazo-5-hydroxy-3-oxo-hexanoates **20** and **21**, furnishing the 2-azido-3(2H)-furanones **22** and **23**.

This unexpected transformation can be rationalized by an initial insertion of the rhodium carbenoid into the adjacent O-H bond to first produce the 4-azido substituted 3(2H)-furanone **24**. This intermediate **24** rapidly equili-



Scheme 4.

brates with its enol form **25** which then undergoes a subsequent [3,3]-sigmatropic shift with complete stereospecificity in a suprafacial manner[1-5]. The rearranged allylic azide intermediate **26** thus formed furnishes the observed 3(2H)-furanones *via* a keto-enol equilibration (Scheme 5).

Experimental

Melting points are uncorrected. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded in $CDCl_3$ solution, using TMS as internal standard. Infrared spectra of liquids were acquired using neat samples, and KBr pellets were used for solids. Mass spectra were determined at an ionizing voltage of 70 eV. All chemicals were of reagent grade and were used as received.

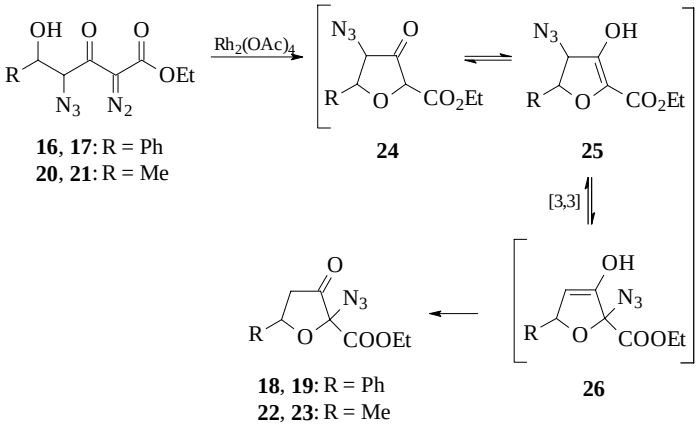
General procedure for the preparation of the Furan-3-one-2-carboxylates

METHOD A: A solution of 1.1 mmol of the appropriate hydroxydiazoester in 10 mL of anhydrous benzene under argon at rt was treated with a catalytic amount of rhodium(II) acetate (1-2 mol%). The resulting mixture was immediately immersed in a preheated oil bath (80-90 °C) and refluxed until all starting material was consumed (followed by IR). After cooling, the reaction mixture was concentrated under reduced pressure and filtered through a plug of silica gel using a 1:1 mixture of ethyl ether/hexane as the eluent. The resulting residue was subjected to flash silica gel chromatography (ethyl ether/hexane 1:1) to give the respective furan-3-one-2-carboxylate.

METHOD B: A solution of 0.9 mmol of the appropriate hydroxy diazo ester in 12 mL of anhydrous CH_2Cl_2 under argon at rt was treated with a catalytic amount of rhodium(II) acetate (1-2 mol%). The resulting mixture was stirred at rt for 3 h, concentrated under reduced pressure and filtered through a plug of silica gel using a 1:1 mixture of ethyl ether/hexane as the eluent to give the furan-3-one-2-carboxylate.

Ethyl 5-methyl-3-oxo-tetrahydrofuran-2-carboxylate (2/3). To a mixture containing 2.2 g (55.0 mmol) of NaH (60% dispersion in mineral oil, previously washed with anhydrous benzene) in 35 mL of dry THF under argon at -15 °C was added dropwise 6.4 mL (50.2 mmol) of ethyl acetoacetate in 35 mL of dry THF. The reaction was then warmed to -5 °C and stirred for 45 min, followed by addition of 33.2 mL (53.1 mmol) of a 1.6 M solution of n-butyllithium. After stirring for 30 min, a solution of 4.5 mL (80.5 mmol) of acetaldehyde in 4 mL of dry THF was added, the reaction was warmed to 0-5 °C and stirred for an additional 2 h. The mixture was then quenched with brine, acidified with 10% HCl, diluted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$ and filtered. Concentration under reduced pressure followed by flash chromatography afforded 5.6 g (64%) of ethyl 5-hydroxy-3-oxo-hexanoate as a yellow oil; IR (neat) 3460, 1740 and 1714 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.13 (d, 3H, J = 6.5 Hz), 1.20 (t, 3H, J = 7.5 Hz), 2.31 (m, 2H), 3.0-3.1 (br, 1H), 3.40 (s, 2H), 4.11 (q, 2H, J = 7.5 Hz) and 4.19 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0, 22.5, 49.8, 51.1, 61.4, 63.7, 167.0 and 203.4.

To a mixture containing 5.60 g (17.2 mmol) of cesium carbonate in 100 mL of dry THF under argon at rt was added 2.99 g (17.2 mmol) of the hydroxy ester prepared above. After stirring at rt for 1 h, a solution of 3.40 g (17.2 mmol) of p-toluenesulfonyl-azide in 50 mL of dry THF was added dropwise. The reaction was stirred for an additional 1 h and then poured into 100 mL of water. The organic layer was separated, the H_2O-phase was extracted twice with ether and the combined organic extracts were washed with H_2O and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography furnished 2.1 g (61%) of ethyl 2-diazo-5-hydroxy-3-oxo-hexanoate **1** as a yellow oil; IR (neat) 3460, 2138, 1716 and 1652 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, 3H, J = 6.5 Hz), 1.24 (t, 3H, J = 7.0 Hz), 2.81 (dd, 1H, J = 17.5 and 9.0 Hz), 3.00 (m, 1H), 3.1-3.2 (br, 1H), 4.17 (m, 1H) and 4.21 (q,



16, **17**: R = Ph
20, **21**: R = Me

24 **25**

18, **19**: R = Ph
22, **23**: R = Me

26

Scheme 5.

2H, J = 7.0 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.2, 22.5, 48.3, 61.5, 64.2, 161.1 and 192.7.

Ethyl 5-methyl-3-oxo-tetrahydrofuran-2-carboxylates (**2**/**3**) were obtained from **1** as a colorless oil (80%; **3**/**2** = 2:1) using Method A; **2**: IR (neat) 1770 and 1745 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, 3H, J = 7.0 Hz), 1.46 (d, 3H, J = 6.0 Hz), 2.21 (dd, 1H, J = 18.0 and 10.0 Hz), 2.62 (m, 1H), 4.20 (m, 2H), 4.36 (s, 1H) and 4.37 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 21.1, 43.7, 62.0, 73.3, 80.8, 165.9 and 207.8; HRMS Calcd. for $C_8H_{12}O_4$ (M^+): 172.0736. Found: 172.0726. **3**: IR (neat) 1770 and 1745 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, 3H, J = 7.0 Hz), 1.41 (d, 3H, J = 6.0 Hz), 2.17 (dd, 1H, J = 18.0 and 10.0 Hz), 2.60 (dd, 1H, J = 18.0 and 6.0 Hz), 4.20 (m, 2H), 4.52 (s, 1H) and 4.69 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 21.0, 43.6, 62.0, 74.2, 80.2, 166.6 and 208.3; HRMS Calcd. for $C_8H_{12}O_4$ (M^+): 172.0736. Found: 172.0727.

Ethyl 5-Methyl-3-oxo-4-phenyl-tetrahydrofuran-2-carboxylates 8 and **9** were obtained from **4** as a pale yellow oil (92%; **9**/**8** = 2.5:1) using Method A; IR (neat) 1772 and 1740 cm^{-1}; **8**: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, J = 7.0 Hz), 1.51 (d, 3H, J = 6.0 Hz), 3.34 (d, 1H, J = 10.5 Hz), 4.28 (m, 3H), 4.59 (s, 1H) and 7.10-7,40 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 19.4, 60.9, 62.2, 79.8, 81.2, 127.9, 128.5, 128.85, 133.5, 165.4 and 207.1. **9**: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.31 (t, 3H, J = 7.0 Hz), 1.46 (d, 3H, J = 6.0 Hz), 3.26 (d, 1H, J = 10.5 Hz), 4.28 (m, 2H), 4.73 (m, 1H), 4.80 (s, 1H) and 7.10-7-40 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.2, 19.6, 61.2, 62.1, 80.7, 81.3, 127.85, 128.9, 129.0, 133.8, 166.9 and 208.4; HRMS Calcd. for $C_{14}H_{17}O_4$ (MH^+): 249.1125. Found: 249.1127.

Ethyl 5-Methyl-3-oxo-4-phenyl-tetrahydrofuran-2-carboxylates 12 and **13** were obtained from **6** as a pale yellow oil (**12**/**13** = 1.3:1), before the filtration through silica gel, using Method A; IR (neat) 1770 and 1738 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, 1.35H, J = 6.5 Hz), 1.13 (d, 1.65H, J = 6.5 Hz), 1.29 (t, 1.35H, J = 7.0 Hz), 1.30 (t, 1.65H, J = 7.0 Hz), 3.66 (d, 0.55H, J = 7.0 Hz), 3.72 (d, 0.45H, J = 7.0 Hz), 4.28 (m, 2H), 4.60 (s, 0.55H), 4.63 (m, 0.55H), 4.73 (s, 0.45H), 4.98 (m, 0.45H) and 7.05-7.35 (m, 5H); **12**: ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 16.8, 57.0, 62.1, 77.3, 80.7, 127.6, 128.8, 129.1, 133.9, 165.3 and 207.9. **13**: ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 16.6, 56.9, 62.2, 77.9, 79.7, 127.7, 128.9, 129.6, 133.7, 166.4 and 208.1. Filtration through silica gel promoted epimerization to the 3(2H)-furanones **9**/**8** (92%; **9**/**8** = 2.5:1).

Ethyl 4,5-Diphenyl-3-oxo-tetrahydrofuran-2-carboxylates 10 and **11** were obtained from **5** as a pale yellow oil (81%; **11**/**10** = 2.5:1) using Method B; IR (neat) 1772 and 1742 cm^{-1}; **10**: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.36 (t, 3H, J = 7.0 Hz), 3.71 (d, 1H, J = 10.5 Hz), 4.33 (m, 2H), 4.79 (s, 1H), 5.19 (d, 1H, J = 10.5 Hz) and 7.00-7,40 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 61.8, 62.4, 81.3, 85.1, 126.4, 128.0, 128.7, 128.8, 129.0, 129.1, 132.8, 138.4, 165.6 and 206.5. 3(2H)-Furanone **11** could be separated by crystallization from ethyl ether, furnishing colorless needles; mp 97-98°C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.35 (t, 3H, J = 7.0 Hz), 3.62 (d, 1H, J = 10.5 Hz), 4.33 (m, 2H), 5.01 (s, 1H), 5.69 (d, 1H, J = 10.5 Hz) and 7.00-7,45 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.2, 61.7, 62.3, 80.8, 86.2, 126.0, 127.9, 128.6, 128.65, 129.0, 129.1, 133.5, 138.5, 166.8 and 207.7; Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85; Found: C, 73.46; H, 5.83.

Ethyl 4,5-Diphenyl-3-oxo-tetrahydrofuran-2-carboxylates 14 and **15** were obtained from **7** as a pale yellow oil (**14**/**15** = 3:1), before the filtration through silica gel, using Method B; IR (neat) 1772 and 1745 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.36 (t, 2.25H, J = 7.0 Hz), 1.38 (t, 0.75H, J = 7.0 Hz), 3.96 (d, 0.75H, J = 7.5 Hz), 4.08 (d, 0.25H, J = 7.5 Hz), 4.35 (m, 2H), 4.79 (s, 0.75H), 5.02 (s, 0.25H), 5.63 (d, 0.75H, J = 7.5 Hz), 6.05 (d, 0.25H, J = 7.5 Hz) and 7.00-7.40 (m, 10H). Filtration through silica gel afforded the epimerized products, 3(2H)-furanones **11**/**10** (81%; **11**/**10** = 2.5:1).

Ethyl *anti*-2-Azido-3-oxo-5-phenyl-tetrahydrofuran-2-carboxylate (**18**) was obtained from **16** as a pale yellow oil (78%) using Method A; IR (neat) 2115, 1762 and 1740 cm^{-1}; ^{1}H-NMR ($CDCl_3$,, 300 MHz) δ 1.35 (t, 3H, J = 7.0 Hz), 2.75 (dd, 1H, J = 18.0 and 10.0 Hz), 3.04 (dd, 1H, J = 18.0 and 6.0 Hz), 4.37 (q, 2H, J = 7.0 Hz), 5.46 (dd, 1H, J = 10.0 and 6.0 Hz) and 7.30-7.50 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0, 43.2, 63.5, 78.5, 91.2, 126.3, 128.9, 129.1, 138.2, 164.7 and 202.5.

Ethyl *syn*-2-Azido-3-oxo-5-phenyl-tetrahydrofuran-2-carboxylate (**19**) was obtained from **17** as a pale yellow oil (79%) using Method A; IR (neat) 2112, 1760 and 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.37 (t, 3H, J = 7.0 Hz), 2.77 (dd, 1H, J = 18.0 and 8.5 Hz), 3.14 (dd, 1H, J = 18.0 and 7.0 Hz), 4.33 (q, 2H, J = 7.0 Hz), 5.59 (dd, 1H, J = 8.5 and 7.0 Hz) and 7.35-7.45 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 43.7, 63.1, 78.2, 90.6, 126.5, 128.8, 129.4, 139.0, 165.2 and 203.5; HRMS Calcd. for $C_{13}H_{13}NO_4$ (M^+-N_2): 247.0845. Found: 247.0852.

Ethyl *anti*-2-Azido-5-methyl-3-oxo-tetrahydrofuran-2-carboxylate (**22**) was obtained from **20** as a pale yellow oil (81%) using Method A; IR (neat) 2124, 1778 and 1745 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.29 (t, 3H, J = 7.0 Hz), 1.46 (d, 3H, J = 6.5 Hz), 2.35 (dd, 1H, J = 18.5 and 7.0 Hz), 2.87 (dd, 1H, J = 18.5 and 7.0 Hz), 4.29 (m, 2H) and 4.72 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0, 21.9, 41.6, 63.2, 73.9, 90.3, 165.3 and 204.1.

Ethyl *syn*-2-Azido-5-methyl-3-oxo-tetrahydrofuran-2-carboxylate (**23**) was obtained from **21** as a pale yellow oil (77%) using Method A; IR (neat) 2120, 1775 and 1745 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, J = 7.0 Hz), 1.48

(d, 3H, J = 6.5 Hz), 2.34 (dd, 1H, J = 18.0 and 10.0 Hz), 2.74 (dd, 1H, J = 18.0 and 5.5 Hz), 4.28 (m, 2H) and 4.57 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.9, 20.6, 42.3, 63.3, 73.7, 91.1, 164.8 and 203.2; HRMS Calcd. for $C_8H_{11}O_4$ (M^+-N_3): 171.0657. Found: 171.0651.

Conclusion

Functionalized 3(2H)-furanones were prepared in good yield and with moderate diastereoselectivity from the rhodium-catalyzed intramolecular O-H insertion reaction of α-diazo-δ-hydroxy-β-ketoesters. When α-diazo-γ-azido-δ-hydroxy-β-ketoesters were employed in this reaction, stereospecific transfer of the azido group to the migration terminus of the rearranged 3(2H)-furanone occurred. This result is consistent with a concerted [3,3]-shift as the mechanism for the interconversion of allylic azides.

It is important to note that there are only a few examples in the literature describing the synthesis of furan-3-one-2-carboxylates[11-13,20]. Some 3(2H)-furanones have been isolated from natural sources[20a,21], and have also been used as substrates for the synthesis of biologically active compounds[22]. Thus, the rhodium(II) catalyzed insertion reaction of δ-hydroxy-α-diazoesters represents a highly efficient method to prepare various 3(2H)-furanones.

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