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α-Phosphono-δ-lactones from γ-lactones via a rhodium(II)-catalysed Wolff rearrangement

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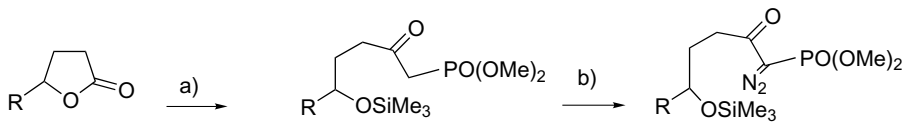
Abstract—ε-Trimethylsilyloxy-α-diazo-β-ketophosphonates were prepared in two steps from γ-lactones. After exposure to catalytic rhodium(II) in refluxing toluene and further aqueous treatment, they gave rise to α-phosphono-δ-lactones in moderate to good yields.

Over recent decades, intramolecular insertion reactions of metallocarbenes generated from α-diazo-β-ketocompounds into carbon–hydrogen or heteroatom–hydrogen bonds, have developed into an important method for the preparation of various carbocycles or heterocycles.[1] A Wolff rearrangement leading to a ketene can compete with the above processes. In the case of α-diazo-β-ketophosphonates this was first observed by Corbel et al.[2] and in the last few years we have reported that the rhodium(II) assisted decomposition of some γ,δ-unsaturated-α-diazo-β-ketophosphonates, led to the corresponding intermediate phosphono conjugated vinyl or aryl ketenes, giving rise to various compounds.[3] Recently we have decided to examine the behaviour of trialkylsilyloxy substituted α-diazo-β-ketophosphonates under rhodium-catalysed thermolysis and we report here our preliminary results.

The ε-trimethylsilyloxy diazo compounds **3** were prepared in two steps (Scheme 1). According to the procedure of Hoffmann et al.,[4] γ-lactones **1** were first converted into silyloxy ketophosphonates **2** which were submitted to the usual diazo transfer conditions.[3a]

When a solution of **3a** in dry toluene was slowly added to a refluxing suspension of 0.5 mol% of rhodium(II) acetate in the same solvent, we observed an instantaneous evolution of nitrogen and rapid disappearance of the starting material. After aqueous treatment and column chromatography, we obtained a hardly separable mixture of α-phosphono-δ-lactone **4a** (17%) and 2-phosphono-cyclopentenone **5** (37%)[5] (Scheme 2).[6]

The lactone **4a** results from a Wolff rearrangement of the intermediate metallocarbene **6** to the ketene **7** fol-



1 **2** **3**

a R = H **c** R = CH_3-CH_2
b R = CH_3 **d** R = CH_3-$(CH_2)_4$-CH_2

Scheme 1. (a) i. $LiCH_2PO(OMe)_2$ 1 equiv.; ii. LDA 1 equiv.; iii. $ClSiMe_3$ 2 equiv.; iv. NH_4Cl aq.: **2a** (69%), **2b** (84%), **2c** (90%), **2d** (39%). (b) TsN_3 1.1 equiv., K_2CO_3 1.1 equiv., CH_3CN: **3a** (63%), **3b** (81%), **3c** (71%), **3d** (82%).

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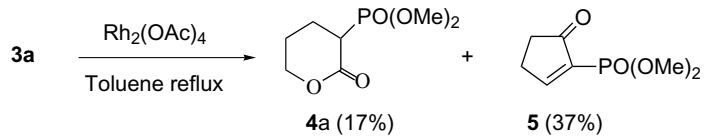


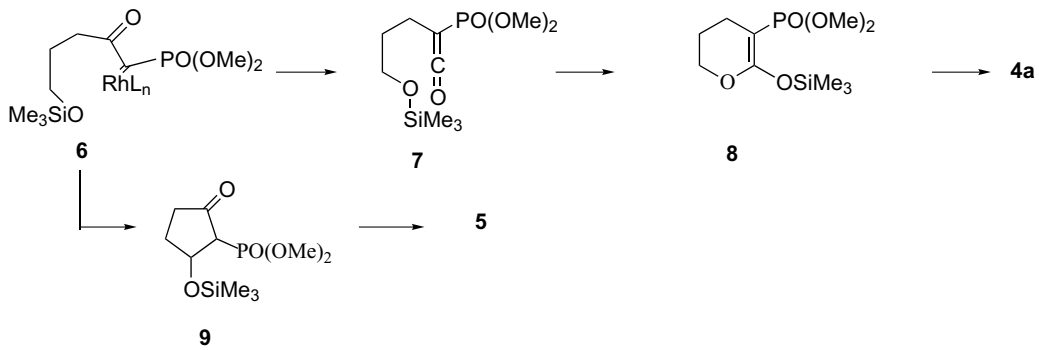
Scheme 2.

lowed by the intramolecular nucleophilic attack of the ether–oxygen and migration of the silyl group to give the ketene silyl acetal **8**, which is further hydrolysed during aqueous treatment. The cyclopentenone **5** results from an intramolecular insertion reaction of **6** into the C_5–H bond, giving **9** and further elimination of trimethylsilanol (Scheme 3).[7,8]

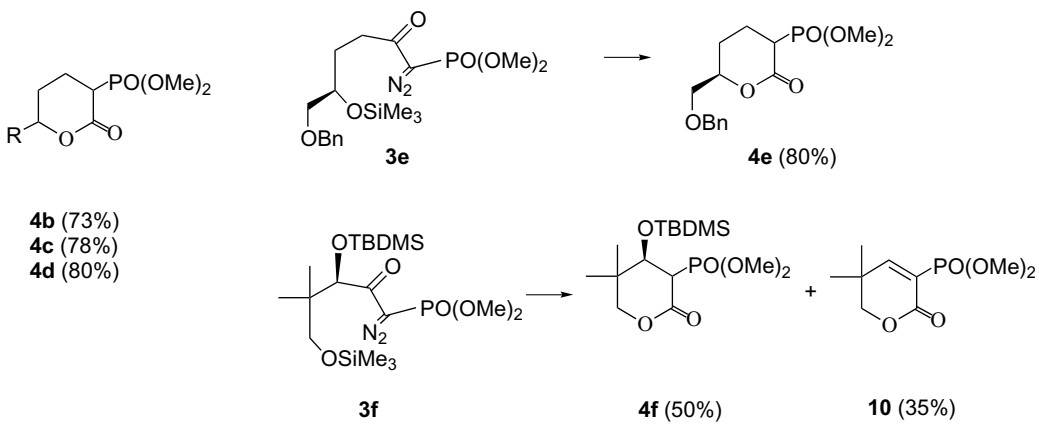
Under the same conditions, diazo compounds **3b–d** led to corresponding lactones **4b–d** (mixture of stereoisomers) in good yields as the sole detectable products.[9] The sequence can be carried out to prepare functionalised lactones. For instance, diazo ketophosphonates precursors **3e** and **3f** were prepared from (*R*)-4-benzyloxymethyl-4-butanolide[10] and (*R*)-2-(*tert*-butyldimethylsilyloxy)-3,3-dimethyl-4-butanolide[11] in 70 and 50%, respectively. The thermolysis of **3e** gave rise to lactone **4e** in 80%. In the case of **3f** we obtained a mixture of expected lactone **4f** and unsaturated lactone **10** resulting from elimination of the silyloxy group (Scheme 4).[12]

It is worth mentioning that when alcohol **11**[13] was submitted to the action of rhodium acetate in the same conditions as the parent compound **3b**, it did not lead to the lactone **4b**, but to the diketone **13** in 68% yield. This product results from a C_5–H insertion reaction leading to **12** followed by retroaldolisation (Scheme 5).

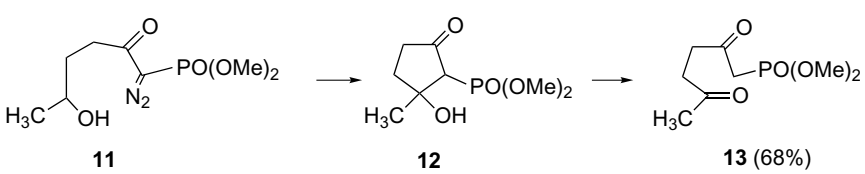
From the behaviour of **3a** and **11** during thermolysis, we can conclude that the insertion reaction of the



Scheme 3.



Scheme 4.



Scheme 5.

intermediate metallocarbene in the C_5–H bond is preferred to the Wolff rearrangement provided that the steric hindrance in the vicinity of C_5 is not too high. When the C_5–H bond is made less accessible due to the presence of a substituent on C_5 or of a *gem*-dimethyl group on C_4 combined with the trimethylsilyloxy group, only the Wolff rearrangement takes place, giving rise to lactones **4**.

In conclusion we report in this note that the rhodium(II)-catalysed thermolysis of ε-trimethylsilyloxy-α-diazo-β-ketophosphonates can give rise to α-phosphono-δ-lactones in moderate to good yields. We are currently exploring the behaviour of other trialkylsilyloxy β-keto-phosphonates and will report our results in due course.

Acknowledgements

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References

1. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998.
2. Corbel, B.; Hernot, D.; Haelters, J.-P.; Strurtz, G. *Tetrahedron Lett*. **1987**, *28*, 6605–6608.
3. (a) Collomb, D.; Deshayes, C.; Doutheau, A. *Tetrahedron* **1996**, *52*, 6665–6684; (b) Collomb, D.; Doutheau, A. *Tetrahedron Lett*. **1997**, *38*, 1397–1398; (c) Léost, F.; Chantegrel, B.; Deshayes, C. *Tetrahedron* **1997**, *53*, 7557–7576; (d) Léost, F.; Deshayes, C.; Chantegrel, B. *Tetrahedron* **1998**, *54*, 6457–6474; (e) Léost, F.; Doutheau, A. *Tetrahedron Lett*. **1999**, *40*, 847–848.
4. Ditrich, K.; Hoffmann, R. W. *Tetrahedron Lett*. **1985**, *26*, 6325–6328.
5. For a similar result observed from ε-silyloxy-α-diazo-β-ketosulfones, see: Yakura, T.; Ueki, A.; Morioka, Y.; Kurata, T.; Tanaka, K.; Ikeda, M. *Chem. Pharm. Bull*. **1998**, *46*, 1182–1183.
6. All new compounds gave spectral and analytical data in full agreement with proposed structures.
7. For the formation of lactones by intramolecular nucleophilic attack of ketenes, see: (a) Boeckman, Jr., R. K.; Pruitt, J. R. *J. Am. Chem. Soc*. **1989**, *111*, 8286–8288; (b) Rahman, S. S.; Wakefield, B. J.; Roberts, S. M.; Dowle, M. D. *J. Chem. Soc., Chem. Commun*. **1989**, 303–304.
8. In the IR spectrum of the crude product resulting from thermolysis, before aqueous treatment, we observed besides the C=O band of the lactone **4a** at 1738 cm^{-1} a band at 1620 cm^{-1} attributed to the ketene silyl acetal group of **8a**.
9. For a different synthesis of 2-phosphono lactones, see: (a) Jackson, J. A.; Hammond, G. B.; Wiemer, D. F. *J. Org. Chem*. **1989**, *54*, 4750–4754; (b) Lee, K. J. A.; Jackson; Wiemer, D. F. *J. Org. Chem*. **1993**, *58*, 5967–5971.
10. Groth, P. E. U.; Huhn, T.; Richter, N.; Schmeck, C. *Tetrahedron* **1993**, *49*, 1619–1624.
11. Roy, R.; Rey, A. W. *Can. J. Chem*. **1991**, *69*, 62–69.
12. Typical procedure: to a suspension of rhodium(II) acetate (0.5 mol%) in refluxing dry toluene (20 mL), was added dropwise, over a 10 min period, a solution of **3e** (428 mg, 1 mmol) in dry toluene (10 mL). The mixture was stirred for an additional 10 min until the disappearance (TLC; pentane:AcOEt, 55:45) of the starting material. After evaporation of the solvent in vacuo, the mixture was diluted with ethyl acetate (100 mL) and the resulting solution stirred for 1 h at room temperature with a saturated aqueous solution of ammonium chloride (5 mL). The organic layer was then separated and dried ($MgSO_4$). After evaporation of the solvent the crude product was chromatographed on silica gel ($CHCl_3$:MeOH, 98:2) to give **4e** (262 mg, 80%) as a light-yellow oil. IR_{film} (cm^{-1}): 2985, 1738, 1260, 1060, 1030. ^1H NMR (200 MHz, $CDCl_3$): δ 7.31 (s, 5H), 4.54 (se, 2H), 4.47–4.63 (m, 1H), 3.85 and 3.75 (2d, 6H, $J=11$ Hz), 3.70–3.50 (m, 2H), 3.15 (dxm, 1H, $J=19.4$ Hz), 2.32–1.74 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): major isomer δ 166.00 (d, $^2J_{CP}=4.2$ Hz), 137.75, 128.48, 127.73, 79.53, 73.61, 71.56, 54.27–54.13–53.25 and 53.12 (2d, $^2J_{CP}=50.5$ Hz), 39.70 (d, $J_{CP}=138$ Hz), 24.37 (d, $^2J_{CP}=8.75$ Hz), 20.73 (d, $^3J_{CP}=4.2$ Hz). Minor isomer δ 166.35 (d, $^2J_{CP}=4.0$ Hz), 137.74, 128.48, 127.84, 79.68, 73.61, 71.56, 53.90 and 53.25 (2d, $^2J_{CP}=32.8$ Hz), 38.98 (d, $J_{CP}=139.6$ Hz), 22.80 (d, $^2J_{CP}=5.6$ Hz), 20.12 (d, $^3J_{CP}=4.4$ Hz). HRMS (FAB): calcd for $C_{15}H_{21}O_6P_1$ 329.11540; found, 329.11538.
13. This compound was obtained quantitatively by hydrolysis (AcOH aq.) of **3b**.