Pergamon

Tetrahedron Letters 43 (2002) 4131–4132

TETRAHEDRON LETTERS

2-Phosphonocyclopenten-2-ones from ε-*tert*-butyldimethylsilyloxy-α-diazo-β-ketophosphonates via a rhodium(II)-catalysed C–H insertion reaction

Wissam Dayoub,[a] Youssef Diab[b] and Alain Doutheau[a,*]

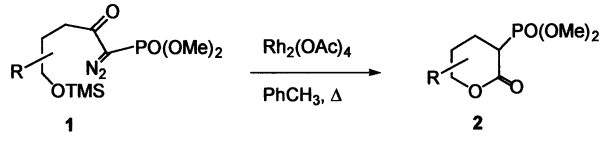
[a]*Laboratoire de Chimie Organique, Département de Biochimie, Institut National des Sciences Appliquées, 20 avenue A. Einstein, 69621 Villeurbanne, France*

[b]*Université Libanaise, Faculté des Sciences-2, Fanar, Jdaidet el-Matn, Lebanon*

Received 16 April 2002; accepted 19 April 2002

Abstract—The exposure of certain primary ε-*tert*-butyldimethylsilyloxy-α-diazo-β-ketophosphonates to the action of catalytic rhodium(II) in refluxing toluene leads to a C–H insertion followed by elimination of the silyloxy group to give 2-phosphonocyclopenten-2-ones in fairly good yields.

In the recent years, the Rh(II)-catalysed C–H insertion reaction of α-diazocarbonyl compounds has been widely used for the construction of various five-membered carbocycles.[1] For instance, it has been shown by Yakura et al. that the treatment by rhodium acetate of ε-*tert*-butyldimethylsilyloxy-α-diazo-β-ketosulfones[2] or α-diazo-β-ketoesters[3] gave rise to 2-methoxycarbonyl- or 2-phenylsulfonyl-cyclopenten-2-ones resulting from an insertion reaction followed by elimination of the silyloxy group.



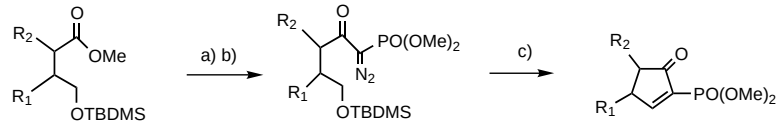
1 2

Scheme 1.

By contrast, we recently reported[4] that, after exposure to catalytic rhodium(II) in refluxing toluene and further hydrolysis, the trimethylsilyloxy ethers of type **1**, in which the vicinity of C_5–H bond was sterically hindered, gave mainly α-phosphono-δ-lactone **2** resulting from a Wolff rearrangement[5] of the intermediate metallocarbene (Scheme 1).

We report in this note that, when the same reaction conditions were applied to certain primary *tert*-butyldimethylsilyloxy ether analogues of compounds **1**, the insertion reaction did occur and gave rise to cyclopentenones.

The new starting diazo compounds **4a–d** were easily prepared, in two steps, from known (*S*)-methyl-3,4-*tert*-butyldimethylsilyloxy butanoate **3a**[3] or readily available[6] esters **3b–d** (Scheme 2). When submitted to



3a R_1 = TBDMSO, R_2 = H
3b R_1 = CH_3, R_2 = H
3c R_1 = $TBDMSOCH_2$, R_2 = H
3d R_1 = R_2 = CH_3

4a (50%)
4b (58%)
4c (50%)
4d (64%)

5a (74%)
5b (70%)
5c (67%)
5d (71%)

Scheme 2. *Reagents*: (a) $LiCH_2PO(OMe)_2$ (2.1 equiv.). (b) TsN_3, K_2CO_3, CH_3CN. (c) $Rh_2(OAc)_4$, $PhCH_3$, reflux.

* Corresponding author. Fax: 33 04 72 43 88 96; e-mail: lco@insa-lyon.fr

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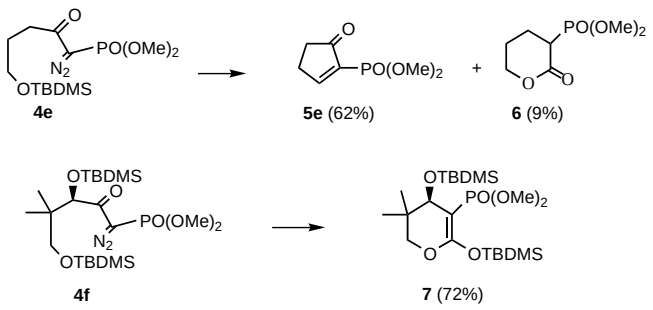
PII: S0040-4039(02)00761-X



Scheme 3.

the action of catalytic rhodium acetate in refluxing toluene, compounds **4** gave rise to the corresponding cyclopentenones **5** as the sole detectable product in the indicated yields.[7]

Under the same conditions, diazo **4e** gave the cyclopentenone **5e** in 62% yield besides a small amount of the lactone **6** (9%) (Scheme 3). Since we have previously observed[4] that the trimethylsilyloxy analogue of **4e** gave the same compounds, in 37 and 17% yields, respectively, these results demonstrated that beside the known site-directed effect of the silyloxy group,[8] which promotes insertions of metallocarbenes into the adjacent C–H bond, the course of the reaction is significantly influenced by the nature of the alkyl substituents on the silicon atom. Finally, we found that diazo **4f**[9] led to the sole ketene silyl acetal **7** resulting from a Wolff rearrangement. Thus, in this case, the replacement of the trimethylsilyloxy group by the *tert*-butyldimetylsilyloxy one did not modify the result of the reaction,[4] probably because the vicinity of the C_5–H bond was too hindered to allow the insertion reaction to take place.

In conclusion we report in this note a preparatively useful access to some 2-phosphonocyclopenten-2-ones which would be new valuable cyclopentanone building blocks.

References

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5. Corbel, B.; Hernot, D.; Haelters, J.-P.; Strutz, G. *Tetrahedron Lett.* **1987**, *28*, 6605–6608.
6. **4b** and **4c** were obtained quantitatively by catalytic hydrogenation of known corresponding conjugated esters. **4d** (mixture of stereomers, 85/15) was prepared in 96% yield by methylation of **4c**: McGarvey, G. J.; Williams, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1435–1437.
7. All new compounds gave spectral and analytical data in full agreement with proposed structures. **5a**. IR_{film} (cm^{-1}): 2980, 2970, 2862, 1730, 1602, 1265, 1060, 1030. ^1H NMR (200 MHz, $CDCl_3$): δ 8.04 (dd, 1H, $J_{H-P}=10.5$, $J=2.1$ Hz); 5.01 (ddd, 1H, $J=6.1$, $J=2.7$, $J=2.1$ Hz); 3.83 and 3.82 (2d, 6H, $J=11.3$ Hz); 2.85 (ABd, 1H, $J_{AB}=8.4$, $J=6.1$ Hz); 2.41 (ABd, 1H, $J=2.7$ Hz); 0.91 (s, 9H); 0.14 (s, 3H); 0.13 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.51 (d, $^2J_{CP}=10.2$ Hz); 174.54 (d, $^2J_{CP}=9.1$ Hz); 136.18 (d, $^1J_{CP}=189.4$ Hz); 69.95 (d, $^3J_{CP}=19.8$ Hz); 53.21 (d, $^2J_{CP}=5.8$ Hz); 45.98; 25.68; 18.06; –4.77; –4.81.
   HRMS (FAB): calcd for $C_{13}H_{25}O_5PSi$ [(M+H)$^+$]: 321.1287; found 321.1287.
   Selected spectroscopic data for **5b–d**. IR_{film} (cm^{-1}): **5b**: 1730, 1602. **5c**: 1725, 1600. **5d**: 1720, 1600. **5e**: 1720, 1600. ^1H NMR (200 MHz, $CDCl_3$). H-3. **5b**: 8.17 (dd, 1H, $^3J_{H-P}=10.4$, $J=2.4$ Hz). **5c**: 8.27 (dd, 1H, $^3J_{H-P}=10.5$, $J=2.4$ Hz). **5d**: 8.08 (dd, 1H, $^3J_{H-P}=10.6$, $J=2.1$ Hz). **5e**: 8.34 (td, 1H, $^3J_{H-P}=10.5$, $J=2.5$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$): C-3. **5b**: 181.30 (d, $^2J_{C-P}=11.3$ Hz). **5c**: 178.00 (d, $^2J_{C-P}=11.1$ Hz). **5d**: 178.99 (d, $^2J_{C-P}=10.7$ Hz). **5e**: 177.36 (d, $J=11.8$ Hz).
   IR_{film} (cm^{-1}): 2960, 2940, 2900, 2865, 1615, 1260, 1060, 1040, 840. ^1H NMR (200 MHz, $CDCl_3$): 4.21 (AB, 1H, $J=10.4$ Hz); 4.16 (AB, 1H); 3.65 and 3.60 (2d, 6H, $^2J_{H-P}=11.7$ Hz); 3.63 (m, 1H); 0.95 (s, 9H); 0.93 (s, 6H); 0.88 (s, 9H); 0.24 (s, 3H); 0.21 (s, 6H); 0.13 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.26 (d, $^2J_{C-P}=12.3$ Hz); 72.78; 74.92 (d, $^1J_{C-P}=206.5$ Hz); 71.54 (d, $^3J_{C-P}=6.7$ Hz); 51.55 (d, $^2J_{C-P}=6.1$ Hz); 51.39 (d, $^2J_{C-P}=5.3$ Hz); 33.83 (d, $^3J_{C-P}=8.8$ Hz); 26.37; 25.36; 22.66; 22.13; 18.47; 17.88; –3.53; –4.00; –4.12; –4.66.
   HRMS (FAB): calcd for $C_{21}H_{45}O_6P_1Si_2$ [(M+H)$^+$]: 481.2570; found 481.2568.
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