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Titanium-mediated addition of diallylsilanes to oxalyl chloride: formation of a diquinane

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Abstract

The titanium tetrachloride mediated reaction of the *cis*,*cis*-2,6-dimethyl-1,8-bis(trimethylsilyl)-2,6-octadiene with oxalyl chloride yielded 1-hydroxy-4-methyl-8-(1-propen-2-yl)bicyclo[3.3.0]oct-3-en-2-one of which the structure was confirmed by X-ray crystallographic analysis.

Keywords: Acylation; Oxalyl chloride; Diallylsilane; Titanium tetrachloride

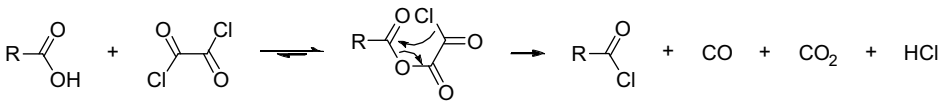
Oxalyl chloride is a versatile reagent giving rise to carboxylic derivatives and a building block for the formation of heterocyclic products. It is known as acyl halide reagent since hemi-oxalyl chloride decomposes to CO, HCl and CO_2, and the equilibrium is thus driven to the side of the new acyl halide (Scheme 1).[1]

Generally, Friedel–Crafts acylation reactions of aromatic compounds with oxalyl chloride occur with decarbonylation[2] but the formation of glyoxyl chloride derivatives has been observed.[3] Organometallic reagents react with oxalyl chloride to give α-diketones,[4] whereas diorganometallic reagents led to cyclic ketones with decarbonylation.[5] Finally, oxalyl chloride represents a versatile C2 building block in the heterocyclization reactions occurring with bis-nucleophiles.[6] Interestingly, oxalyl chloride reacts with certain olefinic derivatives to give α,β-unsaturated acyl chlorides.[7]

Some years ago, we demonstrated that the acylation of 1,8-bis(trimethylsilyl)-2,6-octadiene with oxalyl chloride occurred with decarbonylation to give 2,5-diethylidenecyclopentanone,[8] and more recently, we have observed that the (*E*,*E*)-2,3,6,7-tetramethyl-1,8-bis(trimethylsilyl)-2,6-octadiene leads to the (*meso*)-2,5-di(isopropenyl)-2,5-dimethylcyclopentanone (Scheme 2).[9]

In both the cases, the phosgene does not react with these diallylsilanes even with prolonged reaction time.

As these reactions with oxalyl chloride are a straightforward way to the preparation of α,α′-substituted cyclopentanones, we have studied its condensation with the *cis*,*cis*-2,6-dimethyl-1,8-bis(trimethylsilyl)-2,6-octadiene **1** coming



Scheme 1. Formation of acyl halides from oxalyl chloride and acids.

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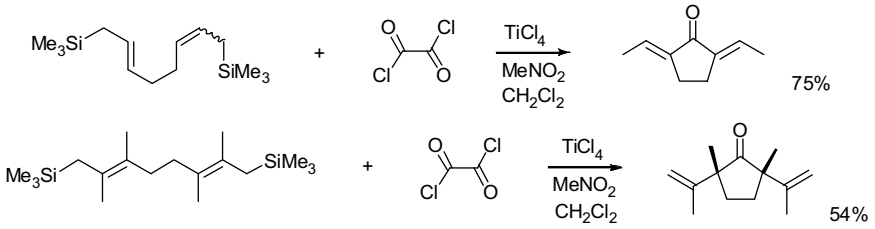
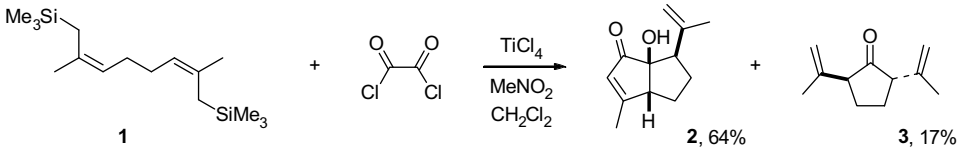


Scheme 2. Reaction of oxalyl chloride and 1,8-bis(trimethylsilyl)-2,6-octadienes.



Scheme 3. Formation of diquinane **2** by the reaction of *cis*,*cis*-2,6-dimethyl-1,8-bis(trimethylsilyl)-2,6-octadiene **1** and oxalyl chloride.

from the reductive dimerization of isoprene by lithium metal in the presence of trimethylchlorosilane.[10] Surprisingly, a diquinane **2** was obtained in fair yield and the expected cyclopentanone **3** appeared as a by-product after 2 h at −90 °C and 20 h at −60 °C[11] (Scheme 3).

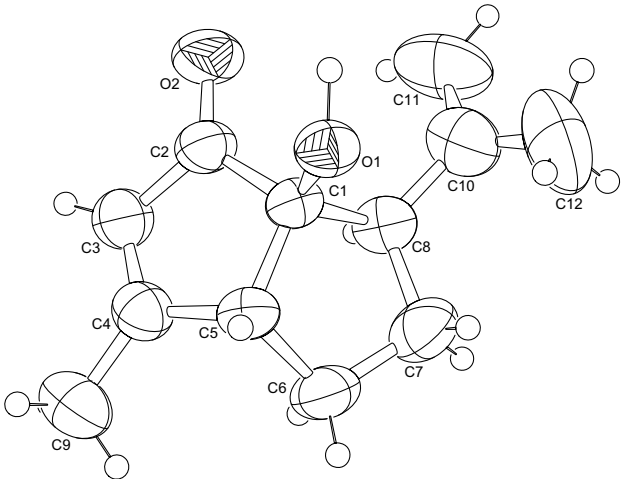


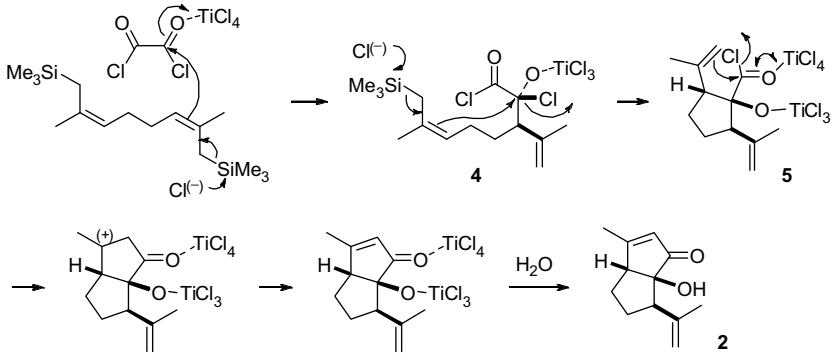
Fig. 1. ORTEP drawing for **2**. Non-hydrogen atoms are drawn with 50% probability thermal ellipsoids.[13]

The structure of **2** was determined according to spectral data and has been achieved by an X-ray diffraction analysis (Fig. 1).[12]

The formation of diquinane[14] **2** may result from an acylation step giving rise to **4** followed by the addition of the second allylsilane moiety to the tetrahedral intermediate (or the corresponding ketone) leading to **5** and then by an intramolecular acylation of the ethylenic bond (Scheme 4).

The isolated case of intramolecular acylation came from the trans structure of **5** which allowed the isopropenyl and the chloroformyl groups to be close (contrary to the previous cases (Scheme 2)).

In the hope to trap the intermediate coming from **5**, the reaction mixture was hydrolyzed after 2 h at −90 °C with an ice-cold ammonium chloride solution. The alone product was cyclopentanone **3** (60% yield).[15] Consequently, cyclopentanone **3** results from the hydrolysis of intermediate **5**. By a spontaneous reaction, the α-hydroxylated acyl chloride decomposes to CO and HCl.[16] A striking step was the cyclization of **4** by the attack of the second allylsilane moiety on the tetrahedral intermediate (or the corresponding ketone) and not on the carbon atom of the acyl chloride.



Scheme 4. Mechanism of the formation of diquinane **2**.

In conclusion, we have described a C2 homologation of **1**, which led to a new functionalized diquinane. To the best of our knowledge, it is the first example of the formation of two carbon–carbon bonds from oxalyl chloride leading to a bicyclic compound.[6]

Acknowledgements

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References and notes

1. (a) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; Vol. 6, pp 3814–3818; (b) Wood, T. R.; Jackson, F. L.; Baldwin, A. R.; Longenecker, H. E. *J. Am. Chem. Soc.* **1944**, *66*, 287–289; (c) Speziale, A. J.; Smith, L. R. *J. Org. Chem.* **1962**, *27*, 3742–3743; (d) Speziale, A. J.; Smith, L. R.; Fedder, J. E. *J. Org. Chem.* **1965**, *30*, 4306–4307; (e) Zhang, A.; Nie, J. *J. Agric. Food Chem.* **2005**, *53*, 2451–2455.
2. (a) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1976**, 601–602; (b) Alexandrou, N. E. *J. Chem. Soc. C* **1969**, 536–537; (c) Sokol, P. E. *Org. Synth.* **1964**, *44*, 69–71.
3. Psiorz, M.; Schmid, R. *Chem. Ber.* **1987**, *120*, 1825–1828.
4. Faust, R.; Weber, C. *J. Org. Chem.* **1999**, *64*, 2571–2573.
5. Chen, C.; Xi, C.; Jiang, Y.; Hong, X. *J. Am. Chem. Soc.* **2005**, *127*, 8024–8025.
6. Langer, P. *Synlett* **2006**, 3369–3381.
7. (a) Kharasch, M. S.; Kane, S. S.; Brown, H. C. *J. Am. Chem. Soc.* **1942**, *64*, 333–334; (b) Bergmann, F.; Weizmann, M.; Dimant, E.; Patai, J.; Szmuskowicz, J. *J. Am. Chem. Soc.* **1948**, *70*, 1612–1617.
8. Tubul, A.; Santelli, M. *Tetrahedron* **1988**, *44*, 3975–3982.
9. Aouf, C.; El Abed, D.; Ibrahim-Ouali, M.; Giorgi, M.; Santelli, M. *Eur. J. Org. Chem.* **2007**, 3115–3121.
10. The same procedure giving rise to 1,8-bis(trimethylsilyl)-2,6-octadiene from 1,3-butadiene (Ref. 8) was used with isoprene. Compound **1**, 31% yield, colourless oil, bp 85–90 °C, 0.2 Torr; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.02$ (s, 18H), 1.50 (s, 4H), 1.65 (s, 6H), 1.91–1.93 (m, 2H), 1.97 (br d, $J = 7.0$ Hz, 2H), 5.00 (br s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -0.85$ (q), 23.4 (t), 26.4 (q), 29.1 (t), 122.4 (d), 133.1 (s) ppm.
11. A 50 mL two-necked flask equipped with a thermometer, a stopcock to a rubber balloon filled with argon and a magnetic stirring bar was charged with anhydrous CH_2Cl_2 (15 mL) and anhydrous nitromethane (1.3 mL, 23.4 mmol). The solution was cooled to −60 °C and $TiCl_4$ was introduced (1.14 g, 0.7 mL, 6 mmol) followed by the slow addition of oxalyl chloride (0.76 g, 510 μL, 6 mmol) in anhydrous CH_2Cl_2 (1 mL). After 15 min. the solution was cooled to −90 °C and a solution of **1** (2 g, 6 mmol) in CH_2Cl_2 (5 mL) was slowly added. After 2 h of stirring, the solution was allowed to warm to −60 °C for 20 h. The reaction mixture was poured onto ice and NH_4Cl. After the common work-up procedure, the crude product was flash chromatographed on silica gel eluting with petroleum ether/ether (85:15) to give **2** (740 mg, 3.85 mmol, 64%) and **3** (167 mg, 1.0 mmol, 17%).
12. 1-Hydroxy-4-methyl-8-(1-propen-2-yl)bicyclo[3.3.0]oct-3-en-2-one (**2**). White crystals, mp 103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.36$ (q, $J = 6.0$ Hz, 1H), 1.80 (s, 3H), 1.89 (q, $J = 5.7$ Hz, 1H), 2.03 (s, 3H), 2.08–2.13 (m, 2H), 2.32 (dd, $J = 5.7$, 11.4 Hz, 1H), 2.58 (s, 1H), 3.07 (t, $J = 8.5$ Hz, 1H), 4.86 (s, 1H), 5.06 (s, 1H), 5.70 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.7$ (q), 24.6 (q), 26.8 (t), 33.1 (t), 51.7 (d), 57.8 (d), 85.5 (s), 114.6 (t), 125.9 (d), 142.7 (s), 178.3 (s), 207.9 (s) ppm.
13. For a review concerning the synthesis of polyquinane natural products, see: Mehta, G.; Srikrishna, A. *Chem. Rev.* **1997**, *97*, 671–719.
14. Crystal data and structure refinement. CCDC-679420 contains the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk].
Formula: $C_{12}H_{16}O_2$; M_w: 192.25; crystal colour: colorless; crystal size/mm^3: 0.3 × 0.25 × 0.1; crystal system: orthorhombic; space group: $P2_12_12_1$; a/Å: 6.8975(2); b/Å: 8.1786(3); c/Å: 19.8019(7); V/Å^3: 1117.06(7); Z: 4; D_c/g cm^{-3}: 0.928; μ(Mo-Kα)/cm^{-1}: 1.143; No. of unique data: 1500; No. parameters refined: 127; No. refl. in refinement: (1500; $F^2 > 4\sigma F^2$: 1085); R: 0.0575 [$F^2 > 4\sigma F^2$]; wR: 0.1541 [$F^2 > 4\sigma F^2$] ($w = 1/[\sigma^2(F_o^2) + (0.0926P)^2 + 0.1991P]$ where $P = (F_o^2 + 2F_c^2)/3$); goodness of fit: 1.107; residual fourier/e Å^{-3}: −0.166; 0.145.
15. 2,5-bis(Propen-2-yl)cyclopentanone (**3**): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.70$ (s, 3H), 1.78–1.85 (m, 2H), 2.77 (t, $J = 8.6$ Hz, 1H), 4.78 (s, 1H), 4.89 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$ (q), 26.7 (t), 57.7 (d), 113.7 (t), 141.9 (s), 216.0 (s) ppm.
16. Pyruvyl chloride undergoes a fragmentation reaction to yield acetyl chloride, see: Tanner, D. D.; Das, N. C. *J. Org. Chem.* **1970**, *35*, 3972–3974.