

# Bis(trimethylsilyl)ketene acetals as 1,3-dinucleophiles. Formation of an anhydride from (pentacarbonyl)(phenylethoxy)tungstacarbene

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## Abstract

The carbene complex  $(\text{CO})_5\text{W}=\text{C}(\text{Ph})\text{OEt}$  (**1**) reacts with the ketene acetal  $\text{Me}_2\text{C}=\text{C}(\text{OSiMe}_3)_2$  (**2**) in the presence of *t*-BuOK to give the anhydride  $\text{C}_{12}\text{H}_{12}\text{O}_3$  (**3**) characterized by an X-ray analysis, upon cleavage of both oxygen–silicon bonds, elimination of the ethoxy group, insertion of CO, and elimination of  $\text{W}(\text{CO})_4$ .

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Silyl enolethers as well as silyl ketene acetals are now classical partners of aldehydes and ketones in the Mukaiyama aldolization reaction. In that respect, bis(trimethylsilyl)ketene acetals are especially valuable [1–3]. Moreover, they can be used, first in conjunction with epoxides, according to route A (Scheme 1) for the preparation of  $\gamma$ -butanolides as the result of an intramolecular reaction [4,5]. In that instance, the bis (TMS) ketene acetals behave, on a formal point of view, as a 1,2-dipole, interacting with the epoxide first as a C-nucleophile then as a C-electrophile, the overall transformation being a 2 + 3 cycloaddition.

Second, we described recently their behaviour as easy to use precursors of 1,3-C,O dinucleophiles formed upon successive cleavage of the two oxygen–silicon bonds according to route B (Scheme 1) [6,7]. This special reactivity allowed us to synthesize inter alia  $\gamma$  lactones upon a 2 + 3 cycloaddition of these dinucleophiles to suitably metal-activated carbon–carbon double bonds

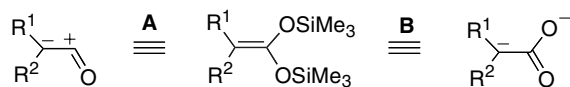
of arene chromium tricarbonyl complexes [6], of 1/4-allyl complexes of palladium [7], and more recently of piperazines even without any metal [8].

Herein, we describe a further example of the unique behaviour of this type of ketene acetals: their addition to a Fischer carbene complex of tungsten which led to the formation of an anhydride.

Thus, addition of a molar solution of *t*-BuOK in THF (1 eq) to a THF solution of the ketene acetal **2** (1 eq) at  $-40^\circ\text{C}$  led to the corresponding enolate [6,7]. This solution was then added, at the same temperature to complex **1** (0.8 eq) in THF. After stirring at that temperature for 1 h, warming to room temperature and stirring for a further 2 h, work up as usual followed by flash silicagel chromatography led to a white, crystalline solid, mp  $85^\circ\text{C}$  in 30% yield [9].

According to the physical data, no metal was present in this compound. The  $^1\text{H}$  NMR spectrum was very simple: a first observation was the disappearance of the signals for the ethoxy group of the starting complex. It displayed only three types of signals, two singlets at respectively  $\delta$  0.98 and 1.49 ppm, attributable to the methyl groups of the starting ketene acetal, five aromatic

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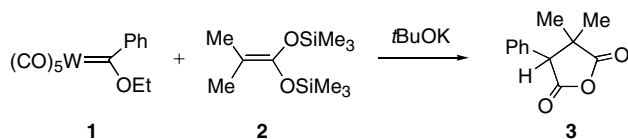


Scheme 1.

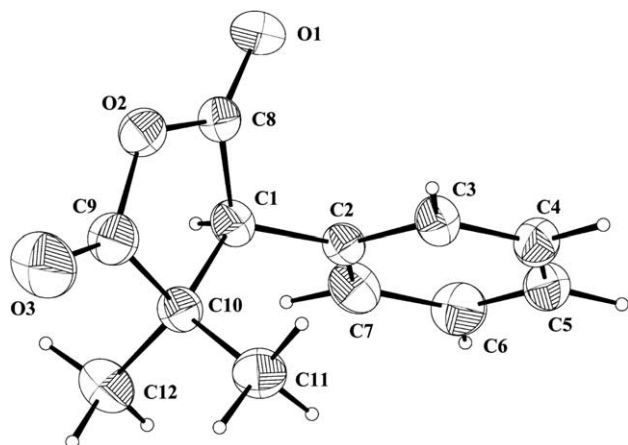
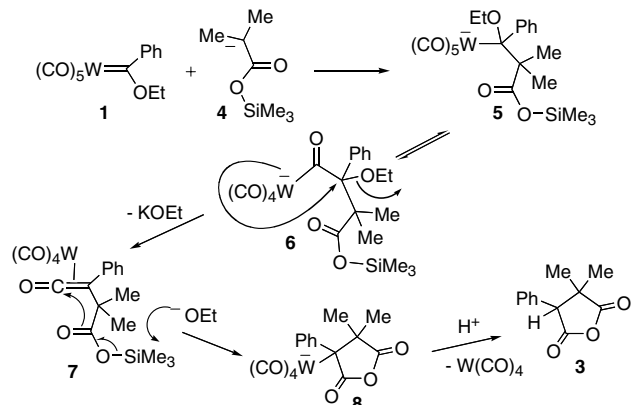
protons between  $\delta$  7.13 and 7.37 ppm originating from the carbene complex, and a singlet corresponding to one proton at  $\delta$  4.10 ppm. The  $^{13}\text{C}$  NMR spectrum confirmed the presence, besides the aromatic carbons, of the two methyl groups at  $\delta$  22.40 and 24.44 ppm, of a quaternary carbon at  $\delta$  46.72 ppm and of a methine group at  $\delta$  58.25 ppm. Most important was however the presence of signals for two carbonyl groups at  $\delta$  170.62 and 176.00 ppm. Taken together with the mass spectrum, these data agreed only with a structure such as **3**, thus an anhydride (Scheme 2).

Crystals of the new compound were grown from solutions of hexane and dichloromethane which allowed an X-ray analysis [10], confirming (Fig. 1) the suggested structure **3**. This compound results indeed from the addition of the ketene acetal to the carbene complex with loss of the two TMS and of the ethoxy groups, along with the insertion of a CO group (Scheme 3).

This result can be rationalized in view of previous observations from this Laboratory [11,12] and from others [13,14]. The addition of nucleophiles to Fischer carbene complexes to give useful functionalized tetrahedral intermediates is now well established: addition of the enolate **4** originating from the ketene acetal and potassium *t*-butoxide probably led to a potassium (1-alkoxy



Scheme 2.

Fig. 1. X-ray structure of compound **3**.

Scheme 3.

3-oxatrimethylsilylcarboxylate)pentacarbonyl tungstate (**5**). At this stage a CO insertion reaction, as observed in many instances for such intermediates [15,16], would take place. Metal-assisted elimination of the ethoxy group in **6** might then lead to a coordinated ketene complex **7**. Finally, an intramolecular interaction of the TMS ester group with the central carbon of the ketene function would furnish the observed anhydride **3** via **8**. The key point of this transformation is the loss of potassium ethoxide, which then triggers the cleavage of the second silicon–oxygen bond and allows the interaction of the oxygen nucleophilic terminus of the ketene acetal with the coordinated ketene [17,18].

Since the so formed anhydride is moisture sensitive, especially on silica gel, care must be taken during the purification step, to avoid erratic results due to decomposition reactions.

The result described herein confirms again the peculiar behaviour of bis(trimethylsilyl)ketene acetals as 1,3-carbon,oxygen dinucleophiles and the possible use of carbene complexes as precursors of ketenes. This result is in contrasting difference with the reaction of bis(dialkyl)ketene acetals with Fischer carbene complexes described by Wulff et al. [19] which led to lactones as the result of a nucleophilic addition, a C–H insertion but without any CO insertion. It displays a new example of the easy base-assisted cleavage of the silicon–oxygen bonds and of the intramolecular interaction of a nucleophile, here a trimethylsilyl ester, with the central carbon of a coordinated ketene.

## Supplementary material

Crystallographic data for the structural analysis of the anhydride **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 266338. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033,

e-mail: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>.

### Acknowledgement

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- [9] **3**: m.p. 85 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.98 (s, 3H), 1.50 (s, 3H), 4.10 (s, 1H), 7.14 (m, 2H), 7.37 (m, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 22.40 (CH<sub>3</sub>), 24.44 (CH<sub>3</sub>), 46.72 (Cq), 58.25 (CH<sub>2</sub>), 128.75, 129.10, 131.18 (C Ar), 170.62 (CO), 176.00 (CO); HRMS for C<sub>12</sub>H<sub>13</sub>O<sub>3</sub> (M + 1), 205.0865, observed, 205.0868.
- [10] X-ray data for **3**: C<sub>12</sub>H<sub>13</sub>O<sub>3</sub>, monoclinic, *P*2(1)/*n*, *a* = 8.660(3), *b* = 8.563(4), *c* = 14.614(6) Å, α = 90°, β = 99.77(2)°, γ = 90°, *V* = 1068.0(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.27 g/cm<sup>3</sup>, *F*(000) = 2394, *T* = 295 K, *S* = 1.14. The structure was solved by direct methods using an Enraf-Nonius MACH-3 automated diffractometer with Mo Kα radiation λ = 0.71069 Å. All non hydrogen atoms were refined using anisotropic thermal parameters. A total of 2394 independent reflections were collected, of which 1140 (*F*<sub>o</sub>)<sup>2</sup> > 3σ(*F*<sub>o</sub>)<sup>2</sup> were used for refinement. Final *R* = 0.0517 and *R*<sub>w</sub> = 0.0618.
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