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ZnI_2 Catalysed [2+2] versus [3+2] Cycloaddition of an Allyltrimethylsilane with 3-butyn-2-one : Confirmation of a Cyclobutene By-product Formation.

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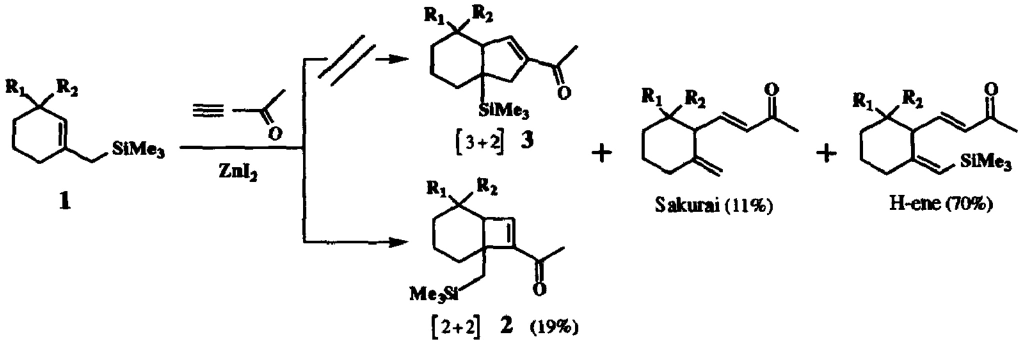
Abstract: NMR experiments unequivocally show that the by-product obtained from the ZnI_2-promoted reaction of an allyltrimethylsilane with 3-butyn-2-one is a [2+2] cycloaddition compound. This fact corroborates our previously described assignment. In the experimental conditions used, the reaction occurs without 1,2-silyl shift.

Recently, we have described the ZnI_2 catalysed H-ene reaction of allylsilanes with 3-butyn-2-one[1]. In the case of the unsubstituted allyl derivative 1 ($R_1 = R_2 = H$), we have reported the formation of a [2+2] cycloadduct 2 in 19% yield (Scheme 1).



Scheme 1

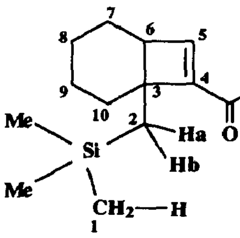
In 1990, Knölker et al.[2] described the formation of trimethylsilylcyclopentanes as by-products in the course of the titanium-tetrachloride-promoted addition of allyltrimethylsilane to α, β-unsaturated ketones (the Sakurai reaction). Since then, these authors[3] have mentioned several reports that erroneously[4-11] described the formation of trimethylsilylmethylcyclobutanes as by-products of the Sakurai reaction and they strongly suggest that the [2+2] cycloadduct reported even more recently by us[1] has to be reassigned and is in fact a [3+2] cycloadduct[12,13]. We wish to report here spectroscopic evidence showing that our first [2+2] cycloadduct assignment **2** was correct: in the experimental conditions used, the by-product (19% yield) of the H-ene reaction previously described is the bicyclo [4.2.0] octene **2** and not the bicyclo [4.3.0] nonene **3**.

In the ^1H NMR spectral data of **2**, which are summarized in Table 1, the presence of an AB spin system signal at high field (δ 0.80 and 1.18, J= -14.8 Hz) showed that the CH_2-2 cannot be an allylic endocyclic one (see $C\underline{H}_2SiMe_3$ chemical shift of **4**, Table 2). On the contrary, in a cyclopentenic structure like **3** these protons would have a chemical shift of ~ 2-3 ppm (δ 2.22-2.60 in the case of **5**, Table 2).

The ^{13}C NMR, DEPT and XHCORR experiments defined the chemical shift of this same CH_2 at δ 27.08 ppm. This chemical shift is not surprising, the one of a $\underline{C}H_2$-$SiMe_3$ exo to a cyclobutene (Table 2) or a cyclohexane[14] ring being at 20.02 and 25.36 ppm respectively. This shows the dramatic effect of the molecular skeleton on the ^{13}C chemical shift of these CH_2[15]. Moreover, Knolker's results[13] show that the chemical shifts of the two endocyclic CH_2 α to the double bond of a cyclopentenic structure are at 33.71 and 37.22 ppm, *e.g.* shifted to a lower field.

In order to complete the structural assignment for **2**, a heteronuclear multiple bond correlation experiment[16] was conducted (Fig. and Table 1). Three bond cross-peaks from the H-1 to C-2 and, reversely from the H-2a and H-2b to C-1 are observed, whereas no three bond cross-peak is observed between H-1 and the quaternary C-3 (δ 48.02). *A contrario*, a three bond cross-peak from H-1 to the quaternary carbon should be the characteristic[16] of a structure like **3**. These facts obviously and unambiguously confirmed that **2** contains a bicyclo [4.2.0] octene.

Table 1. ^1H (200 MHz) & ^{13}C (50 MHz) NMR Data for **2**$^{a,\ b}$



2

^1H δ
$SiMe_3$ -0.05 (s,9H)
CH_2-2 0.80 and 1.18 (AB, 2H, J = - 14.8)
CH_2 cycle 1.25 - 1.88 (m, 8H)
CH_3-12 2.14 (s, 3H)
CH-6 2.45 (td, 1H, J = 3.8, 3.8, 1.0)
CH-5 6.73 (d, 1H, J = 1.0)

^{13}C δ
0.39 ($SiMe_3$); 17.92, 18.31 and 23.53 (3 CH_2 cycle); 25.78 (CH_3-12); 27.08 (CH_2-2); 31.75 (CH_2-10 cycle); 46.45 (CH-6); 48.02 (C-3); 146.87 (CH-5); 154.61 (C-4); 194.20 (CO-11)

a- Recorded in $CDCl_3$, Coupling Constant in Hz.
b- Assignments are Based on DEPT, XHCORR and COLOC Data.

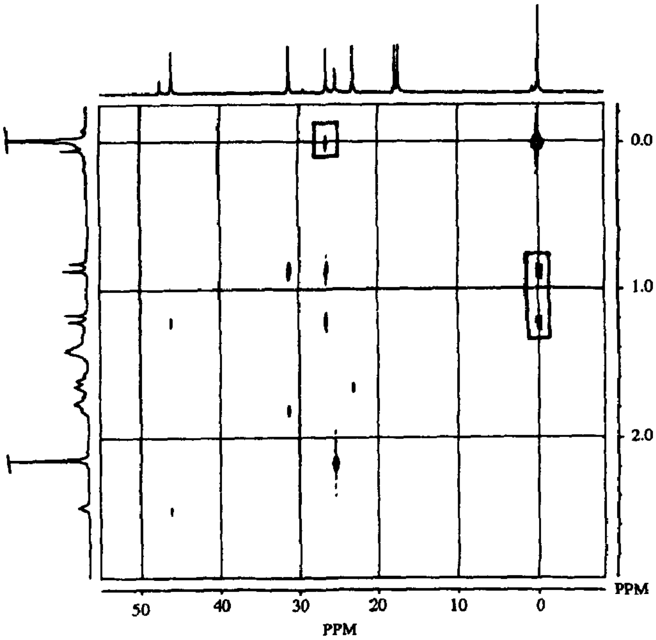
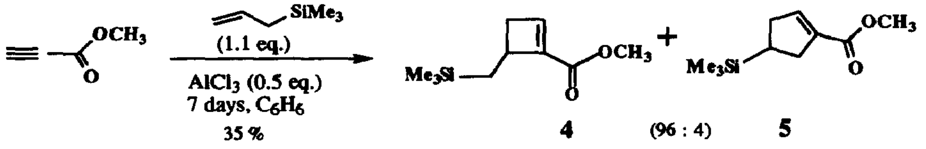


Fig. COLOC Experiment (300 MHz) for **2**. Typical ^1H signal ...^{13}C Correlations are Displayed by Bold Rectangles.

In order to avoid any ambiguity, we have leant on the chemical results of Snider[17] who, in 1979, has showed that methyl propiolate undergoes a $AlCl_3$-catalysed reaction with allyltrimethylsilane to give the corresponding cyclobutene **4**. The ^1H NMR spectrum described by this author squared perfectly with the proposed structure and enhances our assignment (δ exocyclic $C\underline{H}_2SiMe_3$ 0.53 and 1.24 ppm).

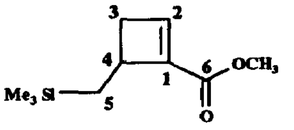
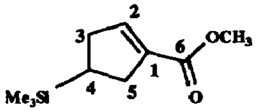
However, in order to compensate for the unpublished ^{13}C NMR spectrum, we have reinvestigated the reaction (Scheme 2).



Scheme 2

During the recording of these spectra, and having the cyclopentenyl structure in the mind, we have taken an interest in an apparently negligible (~ 4 % yield) impurity present in the "pure" cyclobutene **4**: in fact, we have identified this "impurity" as the [3+2] cyclopentene annulation product **5** (Scheme 2 and Table 2).

Table 2. ^1H (200 MHz) & ^{13}C (50 MHz) NMR Data for **4** and **5**

 **4**	 **5**
^1H δ $SiMe_3$ -0.03 (s,9H) CH_2-5 0.53 and 1.24 (AMX, 2H, J = -14.6, 12.4, 3.1) CH_2-3 1.94 (dt, 1H, J = -15.3, 1.4) and 2.62 (ddd, 1H, J = -15.3, 3.8, 1.1) CH-4 3.01 (dddd, 1H, J = 12.4, 3.8, 3.1, 1.4) OCH_3 3.65 (s, 3H) CH-2 6.65 (td, 1H, J = 1.4, 1.1)	^1H δ $SiMe_3$ -0.06 (s,9H) CH-4 1.44 (quin, 1H, J = 9.3) CH_2-3 and 5 2.22-2.60 (m, 4H) OCH_3 3.67 (s, 3H) CH-2 6.75 (broad t, 1H, J = 2.2)
^{13}C δ -1.37 ($SiMe_3$); 20.02 (CH_2-5); 35.89 (CH_2-3); 38.82 (CH-4); 50.46 (OCH_3); 143.35 (CH-2); 144.25 (C-1); 161.98 (CO-6)	^{13}C δ -3.43 ($SiMe_3$); 23.03 (CH-4); 33.28* and 35.18* (CH_2-3 and 5); 51.24 (OCH_3); 144.21 (CH-2); 146.04 (C-1); 164.95 (CO-6)

* These assignments may be interchanged

In summary, the Lewis acid utilized seems to play a dramatic effect on the mechanism and, therefore, on the course of the reaction. In the conditions of our experiments[1] the allyltrimethylsilane moiety reacts without sila-Wagner-Meerwein rearrangement[18] (1,2-silyl shift). Our previously described assignment is correct: the by-product of our reaction is the bicyclo [4.2.0] octene **2**.

Further studies are under investigation in our laboratory to explain these facts.

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