## HEXAMETHYLDISILANE AS A SOURCE OF BOTH TRIMETHYLSILYL AND PENTAMETHYLDISILYL ANIONS, FORMATION OF A SUBSTITUTED PENTAMETHYLDISILYL STABLE ENOL

Ella B. Nadler and Zvi Rappoport\*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

<u>Summary</u>: The reaction of dimesitylketene with MeLi/Me<sub>3</sub>SiSiMe<sub>3</sub> gives in addition to the expected 2,2-dimesityl-1-trimethylsilylethenol, also the unexpected stable simple enol 2,2-dimesityl-1-pentamethyldisilylethenol.

We recently reported the isolation of the first stable silicon-substituted simple enol <u>1</u> from the reaction of dimesitylketene <u>2</u> and trimethylsilyl lithium, prepared in situ from hexamethyldisilane (<u>3</u>) and MeLi, in HMPA.<sup>1</sup> In addition to this, enol <u>4</u>,<sup>2</sup> (from addition of MeLi to <u>2</u>) and a product derived from the reaction of <u>1</u> with the solvent, <sup>3</sup> were isolated.

During a repeated preparation of  $\underline{1}$  we noted that although the product showed only a single spot on TLC using 98% petroleum ether : 2% ether eluent and gave a 1 : 4 : 18 ratio of the OH, Mes-H and Mes-Me signals in the <sup>1</sup>H NMR spectrum, three <u>Me-Si</u> signals were observed. Suspecting that a compound structurally related to  $\underline{1}$  is also formed in a small amount, different TLC eluents were tried. Indeed, two spots were observed using petroleum ether : CH<sub>2</sub>Cl<sub>2</sub>. Separation gave both  $\underline{1}$  and a new compound with an almost identical <sup>1</sup>H NMR spectrum except at the <u>Me-Si</u> region. This was identified as a new stable simple enol containing two silicon atoms, i.e., 2,2-dimesity1-1-pentamethyldisilylethenol 5 <sup>4</sup> (eq. 1). The pure compound decomposed partially on standing for 2 Me<sub>3</sub>SiSiMe<sub>3</sub> (<u>3</u>)/MeLi Mes<sub>2</sub>C=CC(0)  $\xrightarrow{\text{Mes}_2\text{C=C}(\text{OH})\text{SiMe}_3 + \text{Mes}_2\text{C=C}(\text{OH})\text{Me } + \frac{2}{1}$  (1) + Mes<sub>2</sub>C=C(OH)SiMe<sub>2</sub>SiMe<sub>3</sub> + solvent-derived product Mes = Mesity1

days at 55<sup>0</sup>C or on evaporation of the solvent from its solution. The C,H analysis results were approximate and erratic, presumably due to decomposition or to incomplete combustion. Although attempts to get crystals for X ray diffraction failed, unequivocal evidence for the presence of two silicon atoms in 5 is given by (i) the silicon analysis,

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(ii) the appearance of two Me-Si signals at -0.12 and 0.10 ppm in a 2:3 ratio and
 (iii) the high resolution mass spectrum.

The relative ratios of the three stable enols <u>1</u>, <u>4</u> and <u>5</u> and the solvent-derived product depend on the contact time of <u>3</u> with the MeLi before the addition of <u>2</u>, on the reaction temperature and probably on the stirring rate. Minor variations in these parameters change the distribution of products profoundly. Control experiments showed that at least one minute of contact is required in order to cleave <u>3</u> by the MeLi. For shorter reaction times unreacted MeLi adds to <u>2</u> and increases the yield of <u>4</u>, whereas for contact times longer than 2 minutes the reaction with HMPA becomes significant. The reaction is apparently independent of the grade of the MeLi since both old and new samples gave <u>5</u>. Bearing the above in mind the procedures below demonstrate cases in which either <u>1</u> and <u>4</u>, <sup>5</sup> or <u>1</u> and <u>5</u> were formed in the absence of a solvent-derived product.

Encl <u>1</u> is formed by addition of  $Me_3Si^-$  to <u>2</u>. The anion is presumably formed by nucleophilic displacement on the silicon atom of <u>3</u> by MeLi (eq. 2).<sup>6</sup> The driving force is the formation of the Si-Me bond at the expense of the weaker Si-Si bond,<sup>7</sup> coupled

 $\text{Li}^{+}\text{Me}^{-}$   $\text{Si}\text{Me}_{3}^{-}$   $\text{Si}\text{Me}_{3}^{-}$   $\text{Me}_{3}\text{Si}^{-}\text{Li}^{+}$  (2) with the higher stability of the Me<sub>3</sub>Si<sup>-</sup> anion compared with the methyl anion.<sup>8</sup>

The formation of 5 requires a parallel reaction of 2 with the  $Me_3SiMe_2Si^-$  anion. The latter is probably displaced in the reaction of either MeLi or  $Me_3SiLi$  on a methyl group of 3 (eq. 3).<sup>9</sup> The bond dissociation energies of Me-Me and Me-SiMe<sub>3</sub> are 90.4 and 89.4 kcal mol<sup>-1</sup>, respectively,<sup>7</sup> so that the driving force for this methyl transfer reaction is the stabilization of the  $Si_2Me_5^-$  ion by the  $\alpha$ -SiMe<sub>3</sub> group. The occurrence Li<sup>+</sup>  $Me_3Si^- \longrightarrow Me_-SiMe_3Si-Me_+ - SiMe_2SiMe_3 Li^+$  (3) of reaction 3 was mentioned hitherto only rarely<sup>4,10</sup> probably due to the favorable competition by reaction 2. However, considering the formation of only a few percent of 5, reaction 2 is not overwhelmingly faster than reaction 3. Consequently, Si<sub>2</sub>Me<sub>5</sub><sup>-</sup> derived products may be formed in other reactions involving formation of Me<sub>3</sub>Si<sup>-</sup> from 3.<sup>4</sup>

It is not surprising that the  ${}^{1}$ H and IR spectra of <u>1</u> and <u>5</u> are similar. The absence of significant mass spectral loss of Si<sub>2</sub>-containing fragments from <u>5</u> contrasts the loss of several Si-containing fragments in the mass spectrum of <u>1</u>.

The isomeric ketones of  $\underline{1}$  and  $\underline{5}$  were not detected in the reaction mixtures. This was rationalized for  $\underline{1}$  on theoretical grounds,<sup>1</sup>,<sup>11</sup> but the second silicon in  $\underline{5}$  may change the situation. This question is under investigation.

<u>2,2-Dimesity1-1-trimethy1sily1ethenol (1).</u> To a stirred solution of hexamethy1disilane (2.21 ml, 10.8 mmol) in hexamethy1phosphoramide (HMPA, 8.9 ml) under dry argon at  $-1^{\circ}$ C, MeLi (7.7 ml, 1.4 M in cyclohexane, 10.8 mmol) was injected. The resulting redbrown solution was stirred for 2 minutes and dimesity1ketene (2 g, 7.2 mmol) in dry ether (20 ml) was added. Stirring in an ice-bath continued for an additional hr at  $-1^{\circ}$ C. The mixture was then decomposed with 5% HCl solution (100 ml), extracted with ether (3x 50 ml) and the organic phase was washed successively with a saturated aqueous NaHCO<sub>3</sub> solution (2x30 ml) and water (30 ml), dried (MgSO<sub>4</sub>) and evaporated, leaving a crude white product (2.35 g). The TLC showed several spots. Chromatography on a Si60 (230-400 mesh) nitrogen pressure column using 2 : 98 ether - petroleum ether (40-60°C) eluent, gave 1.25 g (49%) of enol <u>1</u>. Recrystallization from ethanol gave white crystals, mp 123°C. A second fraction (0.12 g, 4%) was identified as enol <u>4</u>.

UV  $\lambda_{max}$  (hexane): 211 sh nm ( $\epsilon$  16,400), 259 nm (6700) ; IR  $\nu_{max}$  (nujol): 3480 (s,OH), 1605 (s, C=C) cm<sup>-1</sup> ; <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>, using the CHCl<sub>3</sub> signal at 7.25 ppm as an internal standard): -0.07 (9H,s,SiMe<sub>3</sub>), 2.13, 2.16, 2.22, 2.23 (18H,4s,Mes-Me , broad due to a dynamic process at room temperature), 4.80 (1H,s,OH), 6.75, 6.85 (4H,2s,2 Mes-H, broad); <sup>13</sup>C NMR  $\delta$  (CDCl<sub>3</sub>, CHCl<sub>3</sub> signal at -77 ppm): -1.68 (si-Me), 20.99, 21.46 ( $\beta$ - and  $\beta$ '- $\alpha$ -Me), 20.78, 20.85 ( $\beta$ - and  $\beta$ '-p-Me), 123.40 (C<sub> $\beta$ </sub>), 131.58 , 135.30, 135.82, 136.64 (Mes-C<sub>ipso</sub>), 128.74, 129.90 , 138.86, 138.94 (Mes-C), 157.49 (C<sub> $\alpha$ </sub>); Mass spectrum (EI, 68 eV, room temperature ; m/e , relative abundance, assignment): 352 (91,M), 262 (21,M-SiMe<sub>3</sub>OH), 247 (26, M-SiMe<sub>3</sub>OH-Me), 232 (15, M-SiMe<sub>3</sub>OH-2Me) , 73 (100, SiMe<sub>3</sub>).

Anal. C, 78.22 ; H, 8.95. Calcd. for C<sub>23</sub>H<sub>32</sub>OSi: C, 78.35 ; H, 9.15%.

<u>2,2-Dimesity1-1-pentamethyldisilylethenol (5)</u>. When the crude solid (2.35 g) obtained from a similar reaction after filtering the solvent-derived product was chromatographed on the same column using 10%  $CH_2CI_2$  - 90% petroleum ether (40-60°C) eluent, enol <u>1</u> was again the main product (0.67 g , 23%). Another fraction of a white solid (60 mg , 2%) was recrystallized from ethanol, giving <u>5</u>, mp 103°C.

<sup>1</sup>H NMR δ(CDC1<sub>z</sub>): -0.12 (6H,s,SiMe<sub>2</sub>), 0.10 (9H,s,SiMe<sub>3</sub>), 2.15, 2.17, 2.22, 2.25 (18H,

4s,Mes-Me), 4.81 (1H,s,OH), 6.75, 6.84 (4H,2s,Mes-H); IR  $v_{max}$ (nujol): 3470-3480 (m,OH), 1600 (m) cm<sup>-1</sup>. Mass spectrum (70 eV,90°C; m/e, relative abundance,assignment): 410 (9,M), 338 (22,MH-SiMe<sub>3</sub>), 322 (2,M-SiMe<sub>3</sub>-Me), 305 (9, M-SiMe<sub>3</sub>-Me-OH), 263 (5, MH-SiMe<sub>3</sub>SiMe<sub>2</sub>OH), 251 (2,Mes<sub>2</sub>CH), 161 (12, MH-Mes<sub>2</sub>C), 147 (6,MesCO), 133 (12,MesCH<sub>2</sub>),119 (3,Mes), 77 (9,Ph), 75 (100,SiMe<sub>2</sub>OH), 73 (32,SiMe<sub>3</sub>). High resolution mass spectrum (70 eV, 100°C): 410.24291 (calcd. for M,  $C_{25}H_{32}OSi_2$  410.24612), 337.19836 (calcd. for M-SiMe<sub>3</sub>,  $C_{22}H_{29}OSi$  337.19877), 75.02636 (calcd. for Me<sub>2</sub>SiOH,  $C_{2}H_{7}OSi$  75.026614).

Anal. C, 72.55 ; H, 9.53 ( a repeated analysis of the same sample gave C, 71.75 ; H, 9.19) ; Si, 13.7%. Calcd. for  $C_{25}H_{38}OSi_2$  : C, 73.10 ; H, 9.33; Si, 13.68%.

## REFERENCES AND NOTES

- 1. Nadler, E.B.; Rappoport, Z.; Arad, D.; Apeloig, Y. J.Am. Chem. Soc., 1987, 109, 7837.
- 2. Nugiel, D.A.; Rappoport, Z. J.Am.Chem.Soc. , 1985 , 107 , 3669.
- The crystal structure of this compound will be reported elsewhere.
- 4. While this paper was in preparation we learnt that a similar reaction was recently reported: reaction of ethyl phenyl ketene with Me<sub>3</sub>SiLi (presumably prepared from <u>3</u>), followed by acylation gave the enol acetates of both the  $\alpha$ -SiMe<sub>3</sub> and the  $\alpha$ -Si<sub>2</sub>Me<sub>5</sub> derivatives in 54% and 20% yield, respectively (Leung-Toung, R.; Tidwell,T.T. <u>J.Org.</u> <u>Chem.</u>, submitted for publication, quoted by Tidwell,T.T., a paper submitted to <u>Acc.Chem.Res.</u>). We thank Prof. Tidwell for a preprint of the latter article.
- 5. Since the reaction was conducted before we realized that 5 can be formed, it is possible that 5 was formed in this reaction too. Three experiments following the procedure for formation of <u>1</u> gave also <u>5</u> in  $\leq 10$ % yield compared with that of <u>1</u>.
- For a recent paper discussing displacement on a silicon-substituted methyl group see: Kirmse, W.; Söllenböhmer, F.J. Chem. Soc., Chem. Commun., 1989, 774.
- 7. Corey, J.Y. in <u>The Chemistry of Organic Silicon Compounds</u> (Patai, S.; Rappoport,Z., Eds.), Wiley, Chichester, 1989, chap. 1, p. 6.
- Apeloig, Y. in <u>The Chemistry of Organic Silicon Compounds</u> (Patai, S.; Rappoport, Z., Eds.), Wiley, Chichester, 1989, chap. 2, p. 201.
- 9. A referee had commented that enol 5 may have been formed from cleavage of few percents of Me<sub>3</sub>Si(SiMe<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub>, n=1,2 impurities in 3. We exclude this possibility as the main route for formation of 5 since 400 MHz <sup>1</sup>H analysis of our sample of 3 (Aldrich, 98%, δ(CDCl<sub>3</sub>) = 0.027 ppm) showed only 0.5% of additional SiMe<sub>2</sub>- and SiMe<sub>3</sub>-containing signals at δ(CDCl<sub>3</sub>) = 0.052 and 0.076 ppm (δ(CCl<sub>4</sub>): 3 0.043 ppm; Me<sub>3</sub>SiSiMe<sub>2</sub>SiMe<sub>3</sub> 0.062 and 0.075 ppm : Fritz, G.; Grunert, B. Z. anorg. allg. Chem., 1981, 473, 59), whereas the 1/5 ratio obtained is 11.5. We thank Prof. Y. Apeloig for the NMR analysis.
- 10.Hudrlik, P.F.; Waugh, M.A.; Hudrlik, A.M. J.Organometal. Chem., 1984, 271, 69; Hudrlik, P.F.; Hudrlik, A.M.; Yimenu, T.; Waugh, M.A.; Nagendrappa, G. <u>Tetrahedron</u>, 1988, 44, 3791.
  11.Apeloig, Y.; Arad, D.; Rappoport, Z., submitted for publication.

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