Tetrahedron Letters,Vol.24,No.33,pp 3521-3522,1983
Printed in Great Britain
0040-4039/83 $3.00 + .00

A CONVENIENT SYNTHESIS OF 1,1,3,4-TETRAMETHYLSILOLE : A STABLE IVB-METALLOLE

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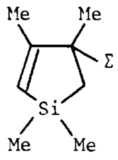
Summary

1,1,3,4-tetramethyl-3-phenylcarbamoyl-1-silacyclopent-4-ene is found to undergo quantitative decomposition in refluxing CCl_4 to regiospecifically afford 1,1,3,4-tetramethylsilole which is remarkably stable toward dimerisation, and is easily converted into its iron carbonyl-diene complex.

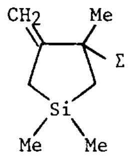
The first non C-substituted metalloles of group IVB were recently identified in monomeric form[1,2] and derivatized by cycloadditions and metal complexation[3]. These reactive metalloles dimerize (4 + 2) at room temperature. Indeed, only the dimerized form of 1-methylsilole could be observed[4].

Singlet oxygen reacts with 1,1,3,4-tetramethyl-1-silacyclopent-3-ene to afford a mixture of allylic alcohols (1,2) which were dehydrated over aluminium oxide (300°C) to produce dienes 5 and 6. Silole 5 (15%) could not be isolated[5].

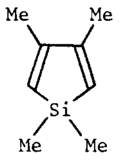
We now report that thermolysis of the phenylcarbamates[6] is a vastly superior method for conversion of these alcohols to silole 5. When a mixture of alcohols 1 and 2 (80/20) was refluxed in pentane (10 h) with phenylisocyanate, pure carbamate 3 was obtained in 85% yield [m.p. 155°-157°C ; ^{1}H-NMR ($CDCl_3$) δ 0.14 (3H,s,SiMe) 0.21 (3H,s,SiMe) 1.47 (3H,s,C(3)Me) 1.90 (3H,d,J∿1 Hz , C(4)Me) 5.63 (1H,m,C(5)H)]



Σ = OH (1), $\mathrm{O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHPh}$ (3)



Σ = OH (2), $\mathrm{O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHPh}$ (4)



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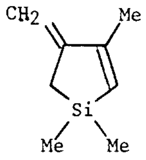

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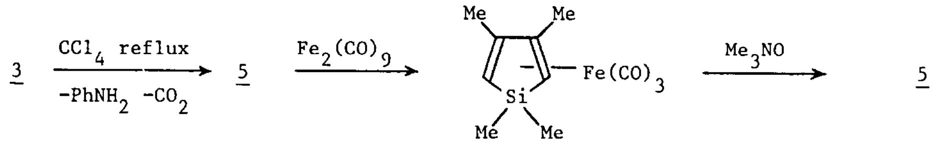
Alcohol 2 was less reactive to PhNCO than 1, however prolonged heating (ca. 1 day) did not allow isolation of the desired carbamate 4, as decomposition occurred to produce diene 6.

After heating a solution of 3 in CCl_4 for 10 h, distillation afforded pure silole 5 in 80% yield [b.p. 58°C/30 mm Hg ; ^{1}H-NMR (CCl_4) δ 0.10 (6H,s,SiMe) 1.96 (6H,s,CMe) 5.46 (2H,s, C(2)H,C(5)H)] . Isomeric diene 6 could not be detected in the distillate by NMR.



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Reaction of silole 5 with $Fe_2(CO)_9$ (refluxing C_6H_6) produced the expected diene complex 7 as a yellow liquid isolated by silica-gel chromatography (C_6H_{14}/C_6H_6 , 80/20) [^{1}H-NMR (C_6D_6) δ -0.23 (3H,s,exo-SiMe) 0.45 (3H,s,endo-SiMe) 1.90 (6H,s,CMe) 1.48 (2H,s,C(2)H, C(5)H) ; IR νCO 1945 (broad) 2040 cm^{-1} ; MS (70 eV) M^+ 278 (8), $[M-CO]^+$ 250 (25), $[M-(CO)_2]^+$ 222 (31), $[M-(CO)_3]^+$ 194 (100%), 178 (56), 123 (34), 84 (52)]. Treatment of 7 with Me_3NO (refluxing C_6H_6)[7] regenerates silole 5.

This attractive synthetic route to the silole 5 and its stability (almost certainly due to the two methyl group's inhibition of (4 + 2) cyclodimerisation[8]) permit to facilitate further investigations in the chemistry of this class of compounds.

Acknowledgment

We thank Pr. T.J. Barton (Iowa State Univ.) for his critical reading of the manuscript.

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(Received in France 29 May 1983)