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ONE-POT-CONVERSION OF 1-SILOXY-CYCLOALKENES TO 4-SILOXY SPIRO[n,2]ALKANES BY DIETHYLZINC-METHYLENE IODIDE[1]

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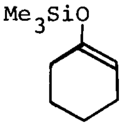
We have already reported that cyclopropanation of **1** with the Simmons-Smith reagent(CH_2I_2-Zn(Cu)) gave **2**.[2] It has also been reported that the unusual product **3** was obtained when a smaller amount of the solvent(Et_2O) was used for this reaction.[3] The exomethylene compound **3** has been ascertained to be formed through the isomerization of **2** by zinc iodide which is generated during the course of the Simmons-Smith reaction. Notably, under the reaction conditions to give **3**, no trace of a spiro-ether **4** which could arise by further cyclopropanation of the C=C bond of **3** has been obtained. Several attempts for the selective synthesis of spiro-ethers of the type **4** directly from **1** using Simmons-Smith reaction have never met with satisfactory results.[3]



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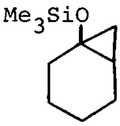

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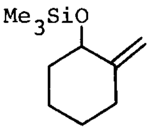

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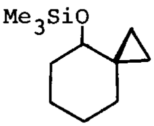

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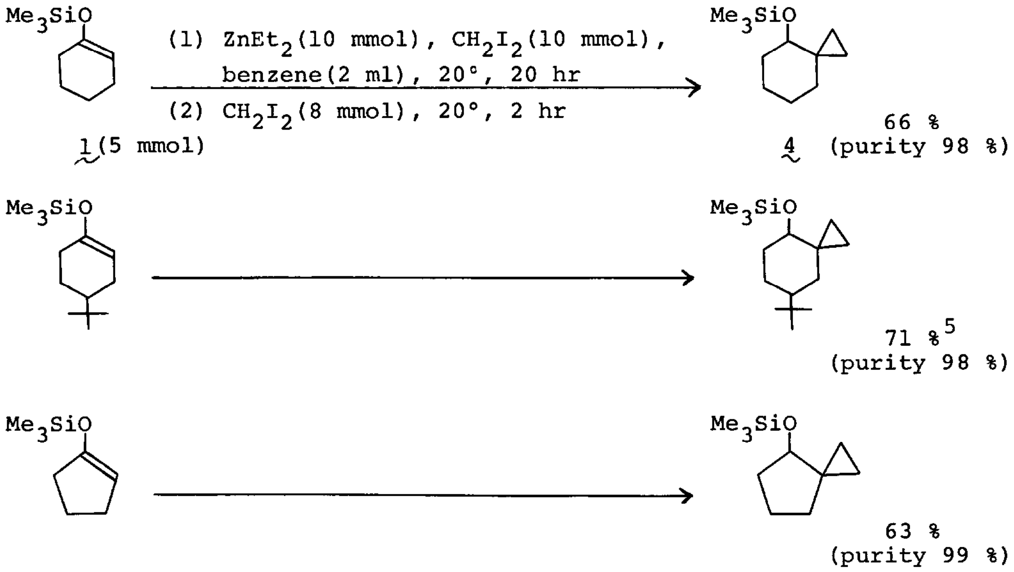
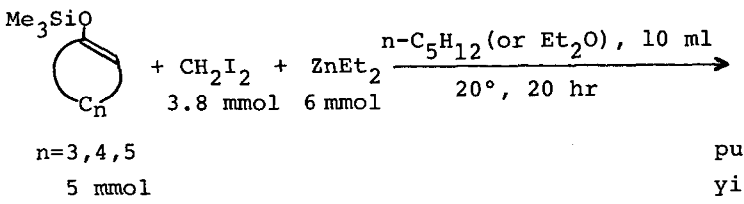
We now wish to report the one-pot-synthesis of spiro-ethers of the type **4** by the reaction of enol silyl ethers **1** with diethylzinc-methylene iodide.[4] Results are shown in Scheme I. The present spiro-ether synthesis is remarkable in the sense that the three sequential reactions(**1**→**2**, **2**→**3**, and **3**→**4**) take place in the same reaction vessel to give the desired spiro-ethers **4** exclusively.

For the selective synthesis of spiro-ethers, it is important to use an aromatic solvent(benzene or anisole) in a smaller amount relative to the substrates as in the ratio shown in Scheme I. When the reaction was carried out using a relatively large amount of benzene, a mixture of three products were obtained because of slower and incomplete conversion of 2 to 3. For example, the reaction of 1 (3.3 mmol) with $ZnEt_2$ (2.5 mmol) and CH_2I_2 (3.7 mmol) in benzene (10 ml, a larger amount) at 20° for 24 hr gave a mixture of 2 (20 %), 3 (74 %), and 4 (6 %).

Scheme I. One-Pot-Synthesis of 4-Siloxyspiro[n,2]alkanes by the Reaction of Enol Silyl Ethers with Diethylzinc and Methylene Iodide.



Zinc iodide may play an important role for cyclopropyl-allylic isomerization in the present system as well as in the case of Simmons-Smith reaction. The isomerization of 2 to 3 has been found to be slower in diethyl ether or n-pentane than in benzene. These facts in turn provide a reliable method for the cyclopropanation of enol silyl ethers. The optimized conditions for the exclusive formation of 1-trimethylsiloxybicyclo[n.1.0]alkanes of the type 2 are shown in the following equation.

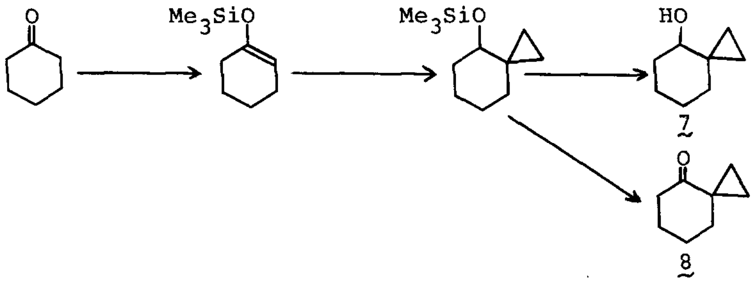


purity 98-100 %

yield in n-C_5H_{12} (or Et_2O)

n=3	81 (70) %
n=4	82 (78) %
n=5	75 (79) %

Spiro-ethers thus obtained directly from enol silyl ethers can be easily converted to corresponding spiroalkanols or spiroalkanones. For example, treatment of the spiro-ether **4** with 0.1N-NaOH/MeOH gave spiro[5,2]octan-4-ol(**7**) in 94 % yield, whereas pyridinium chlorochromate/CH_2Cl_2[6] gave spiro[5,2]octan-4-one(**8**) in 76 % yield. Since the enol silyl ether **1** can be prepared in high yield from cyclohexanone, the present reaction provides an efficient method for the conversion of the cyclohexanone to **7** or **8**. Multistep and low overall yield syntheses of **7**[7] or **8**[8] have been reported. For example, Crandall and Seidewand prepared spiroalkanone **8** via three steps from 2-carboethoxycyclohexanone(9 % overall yield).[8a]



*One-pot-procedure for 4-trimethylsiloxyspiro[5,2]octane (**4**). A typical procedure:* Under a dry nitrogen atomosphere, to a stirred solution of 1-trimethylsiloxycyclohexene (**1**) (0.85 g, 5 mmol), diethylzinc (1.0 ml, 10 mmol), and dry benzene (2 ml) was added methylene iodide (2.68 g, 10 mmol) during 20 min at 20°C. After stirring for 20 hr, an additional methylene iodide(2.14g, 8 mmol) was added in one portion(slightly exothermic, temperature reached to 40°) for the completion of the reaction. Then the mixture was stirred for an additional 2 hr, diluted with diethyl ether(20 ml) and poured into cold saturated aq NH_4Cl(50 ml). The aqueous layer was extracted twice with diethyl ether(2×10 ml). The combined ether extract was washed with aq $NaHCO_3$ and water and dried over $MgSO_4$. After removal of the solvent, the residue was distilled to give 0.65 g(66 %)of 4-trimethylsiloxyspiro[5,2]octane, bp 83-85°(20 mm); NMR(CCl_4)δ 0.05(s, 9H), 0.0-0.5 (m, 4H), 1.0-2.0(m, 8H), 3.14-3.36(c, 1H); MS, m/e 198, 183, 170, 155, 75, 73. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.49; H, 11.62.

Spiro[5,2]octan-4-ol(**7**):

To a solution of 0.1N-NaOH and 10 ml of MeOH was added **4**(0.597g, 3 mmol) at room temperature. After stirring for 30 min at 25°C MeOH was evaporated in vacuo. Then, to the resulting oil was added 20 ml of ether and the solution was washed with 20 ml of water. The aqueous layer was extracted four times with 5 ml portions of ether and the combined extract was dried over $MgSO_4$. After removal of ether, the vacuum distillation gave 0.355 g(94 %) of spiro[5,2]-octan-4-ol(**7**), bp 90-94°(23 mm), whose spectral data(IR, NMR, MS) were identical with those of an authentic sample.[7a]

Spiro[5,2]octan-4-one(**8**):

To a stirred suspension of pyridinium chrolochlomate(1.62 g, 7.5 mmol) in CH_2Cl_2 (10 ml),[6] 4-trimethylsiloxyspiro[5,2]octane(**4**) (0.99 g, 5 mmol) in 1 ml of CH_2Cl_2 was added in one portion. After 1.5 hr, 10 ml of dry ether was added and the supernatant decanted from the black gum. The residue was washed four times with 3 ml portions of dry ether. The combined solution was passed through a short pad of Kieselgel 60. After removal of the solvent, the vacuum distillation gave 0.471 g(76 %) of spiro[5,2]octan-4-one, bp 80-81°(28 mm); ir(neat) 1693 cm^{-1}; NMR(CCl_4) δ 0.59(d-d, 2H), 1.22(d-d, 2H), 1.40-2.64(m, 8H); MS, m/e 124, 96.

References and Notes

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