115-11-7; phenyltribromomethylmercury(II), 3294-60-8; C_6H_5HgBr, 1192-89-8.

References and Notes

(1) (a) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6161 (1954); (b) W. von E. Doering and P. M. LaFlamme, *ibid.*, **78**, 5447 (1956).

(2) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4149 (1962).

(3) L. Skattebol and S. Solomon, *Chem. Scand.*, **17**, 1683 (1963).

(4) (a) J. Hine, E. L. Pollitzer, and H. Wagner, *J. Amer. Chem. Soc.*, **75**, 5607 (1953); (b) J. Hine, A. D. Ketley, and K. Tanabe, *ibid.*, **82**, 1398 (1960).

(5) (a) P. Skell and A. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956); (b) P. Skell and A. Garner, *ibid.*, **78**, 5430 (1956); (c) P. Skell and I. Starr, *ibid.*, **81**, 4117 (1959).

(6) D. Seyferth, *Accounts Chem. Res.*, **5**, 65 (1972).

(7) See, for example, the phase transfer modification described by L. Skattebol, G. A. Abskharoun, and T. Greibrokk, *Tetrahedron Lett.*, 1367 (1973).

(8) We thank Professor James A. Moore for calling to our attention the portion of the Ph.D. thesis of Thomas Newton (University of Delaware, 1973) wherein it is reported that *carbon monoxide* could be identified mass spectrometrically as a side product from the reaction of KO-*t*-Bu with bromoform. This finding was rationalized by a scheme similar to reaction sequence 3–6 (*vide infra*) followed by decomposition of the formyl bromide to CO and HBr.

(9) With the exception of one terse mention of its preparation by hydroboration [G. Zweifel, A. Horng, and J. T. Snow, *J. Amer. Chem. Soc.*, **92**, 1427 (1970)], we have found no reports of the synthesis or properties of **1**.

(10) Even at −50°, evolution occurred at a rate of 7 ml/min.

(11) D. Seyferth and R. L. Lambert, *J. Organometal. Chem.*, **16**, 24 (1969).

(12) LAOCOON III (S. Castellano and A. A. Bothner-By, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind., Program No. 111) simulation was required to extract the exact chemical shifts and coupling constants of the A_2B allenic proton resonances.

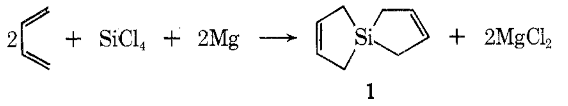
A Facile One-Step Synthesis of 5-Silaspiro[4.4]nona-2,7-diene

Robert G. Salomon

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

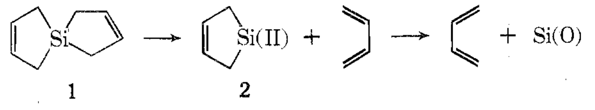
Received July 25, 1974

We wish to report a facile one step multiple annelation synthesis of the novel unsaturated heterocycle, 5-silaspiro-[4.4]nona-2,7-diene (1) from silicon tetrachloride and 1,3-butadiene. We find that a mildly exothermic reaction ensues upon stirring a suspension of "active magnesium"[1] in tetrahydrofuran under an atmosphere of butadiene. The resulting mixture reacts vigorously with silicon tetrachloride to give the title compound in preparatively useful yield.[2] The assignment of the structure is based on elemental analysis: nmr (CCl_4) δ 1.46 (8 H) and 5.86 (4 H), ir (neat) 839, 942, 1100, 1170, 1205, 1395, 1600, 2900, and 3040 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 53 (52), 54 (49), 55 (61), 67 (49), 81 (56), 82 (99), 83 (47), 108 (44), 136 (100), 137 (46).



1

The major fragmentation involves extrusion of a silylene 2 (*m/e* 82). Related thermal reductive cycloeliminations of dimethylsilylene from 1,1-dimethyl-1-silacyclo-3-pentene derivatives are well known.[3] Interestingly, in the case of **2**, atomic silicon would result from a second extrusion.



1 2

One feature of the present synthesis is especially noteworthy. This is the great reactivity of "active magnesium" toward 1,3-butadiene which allows the reductive silylation to be performed under unprecedentedly mild conditions. The reaction of butadiene, dichlorodimethylsilane, and ordinary magnesium powder in hexamethylphosphoric triamide requires several days at elevated temperatures.[4] The reaction must be conducted in an autoclave, and the yield for this single annelation giving 1,1-dimethyl-1-silacyclo-3-pentene is about the same as we obtain in our *double annelation.*

Experimental Section

5-Silaspiro[4.4]nona-2,7-diene. The reaction is conducted in a 2-l. three-neck flask equipped with a Dry Ice–acetone condenser which is topped by a head of nitrogen. One neck is stoppered and another is fitted with a rubber serum cap. Butadiene is introduced through the serum cap with a hypodermic needle and the reaction is stirred magnetically.

A suspension of "active magnesium" (0.25 mol) in tetrahydrofuran (500 ml) is stirred under an atmosphere of butadiene (32 g) until the exothermicity subsides. Then $SiCl_4$ (0.09 mol) is added dropwise with a hypodermic syringe. After stirring overnight at room temperature, cold 10% HCl (250 ml) is cautiously added (vigorous evolution of excess butadiene) followed by water (250 ml) and pentane (150 ml). The aqueous phase is extracted with pentane (200 ml) and the combined pentane extracts are washed with water (200 ml), saturated aqueous Na_2CO_3 (200 ml), and saturated aqueous NaCl (200 ml), and dried (Na_2SO_4). If greater quantities of aqueous washes are employed, voluminous sticky precipitates and emulsions result. Distillation gives **1**, bp 65–68° (13 mm), 21% based on $SiCl_4$. *Anal.* Calcd for $C_8H_{12}Si$: C, 70.51; H, 8.88. Found: C, 69.97; H, 8.86.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—1, 52856-32-3; 1,3-butadiene, 106-99-0; magnesium, 7439-95-4; silicon tetrachloride, 10026-04-7.

References and Notes

(1) R. D. Rieke and P. M. Hudnall, *J. Amer. Chem. Soc.*, **94**, 7178 (1972).

(2) Many "diene–magnesium compounds" have been reported previously. Experimental details are generally lacking. (a) H. E. Ramsden, J. E. Engelhart, and W. Naegele, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967 Abstract No. 9-41; (b) M. Yang, K. Yamamoto, N. Otake, M. Ando, and K. Takase, *Tetrahedron Lett.*, 3843 (1970); (c) M. Yang, M. Ando, and K. Takase, *Tetrahedron Lett.*, 3529 (1971).

(3) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

(4) J. Dunogues, R. Calas, J. Dedier, and F. Pisciotti, *J. Organometal. Chem.*, **25**, 51 (1970).

Reaction of *tert*-Butyl Hydroperoxide and α-Cumyl Hydroperoxide with Acetic Acid[1]

W. E. Cass* and Arun K. Bahl

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Received July 1, 1974

Following the chance observation that the hydroperoxide titer of a dilute solution of *tert*-butyl hydroperoxide in acetic acid decreased significantly on standing for several hours at room temperature, we investigated the system and found that direct esterification of the hydroperoxide occurred.[2,3] The reaction was strongly catalyzed by sulfuric acid. Equilibrium and kinetic data were obtained.

An investigation of the system, α-cumyl hydroperoxide–acetic acid, indicated that esterification probably occurred, but that the peroxy ester decomposed, as formed, *via* a