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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

XCIV. PREPARATIONS OF 8-SILATRICYCLO[3.2.1.0^{2,4}]OCT-6-ENES, NEW PHOTOCHEMICAL SILYLENE GENERATORS

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Summary

The reaction of siloles with cyclopropene afforded products representative of a new organosilicon ring system, 8-silatricyclo[3.2.1.0^{2,4}]oct-6-ene, which proved to be photolytic silylene generators.

Organosilylenes may be generated from various compounds either by thermolysis or by photolysis [1]. We have reported in a previous paper that 1,2,3-trisilacycloheptane derivatives are convenient precursors of the silylenes [2]. In this paper we report a new organosilicon ring system which generates organosilylenes by photolysis.

Four 8-silatricyclo[3.2.1.0^{2,4}]oct-6-enes (I) were prepared by the reaction of a silole with cyclopropene in methylene chloride or chloroform at 0 - 40°C. As a typical example, an excess of cyclopropene, generated from allyl chloride and sodium amide [3], was led into a methylene chloride solution of 1,1-dimethyl-2,5-diphenylsilole (IIa; R=H, $R^1=R^2$=Me) [4] at 0°C. After 3hr, the greenish-yellow color due to the silole disappeared. After evaporation of the solvent, the residual solid was recrystallized from ethanol to yield 1,5-diphenyl-8,8-dimethyl-8-silatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (Ia; R=H, $R^1=R^2$=Me) in 71% yield, mp 121-122°C; nmr δ (CCl_4) -0.38(3H, s, $SiCH_3$). 0.40(3H, s, Si-CH_3), 0.86(1H, dt, J=7.6Hz, 5.4Hz, C_3-H_{exo}), 1.27(1H, dt, J=5.4Hz, 3.7Hz, C_3-H_{endo}), 2.06(2H, dd, J=3.7Hz, 7.6Hz, 2H, $C_{2,4}$-H), 5.96(2H, s, $C_{6,7}$-H), 7.01 - 7.39(10H, m, aromatic protons); mass M^+ m/e 302(35), 72(100).*

The structure of (Ia) is compatible with its spectral data and the stereochemistry of the cyclopropane ring was assigned to be endo on the basis of Alder's rule [5]. In the same way, other 8-silatricyclo[3.2.1.$0^{2,4}$]oct-6-enes (Ib, Ic and Id) have been prepared. (Ib; R=Ph, $R^1=R^2$=Me): mp 159°C; nmr δ (CCl_4), 0.48(3H, s, $SiCH_3$), 0.88(3H, s, $SiCH_3$), 1.34(2H, m, C_3-H); 2.27(2H, dd, J=7.0Hz, 3.5Hz, $C_{2,4}$-H), 6.64-7.26(20H, m, aromatic protones); mass M^+ m/e 454. (Ic; R=R^1=Ph, R^2=Me): mp 199°C; nmr δ (CCl_4), 0.61(3H, s, $SiCH_3$), 1.31(2H, m, C_3-H), 2.23(2H, dd, J=7.0Hz, 4.0Hz, $C_{2,4}$-H), 6.60-8.30(25H, m, aromatic protons); mass M^+ m/e 516. (Id; R=$R^1=R^2$=Ph): mp 242°C; nmr δ (CCl_4), 1.35(2H, m, C_3-H), 2.18(2H, dd, J=7.5Hz, 2.5Hz, $C_{2,4}$-H), 6.75- 8.01(30H, m, aromatic protons); mass M^+ m/e 578.

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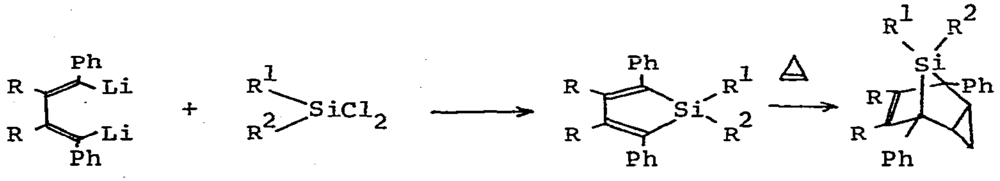
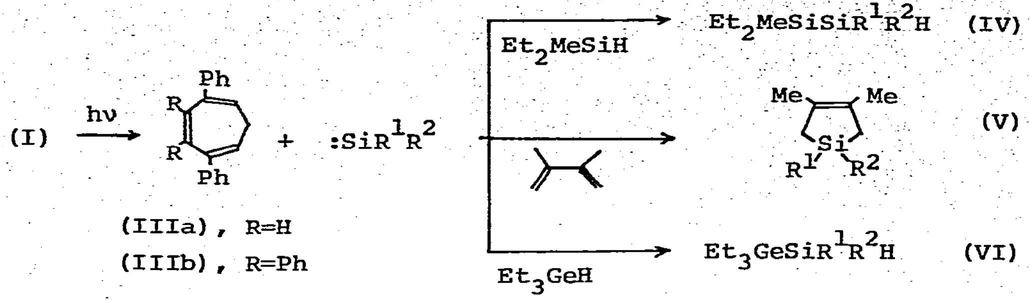
* Satisfactory elemental analyses were obtained for all new compounds reported in this paper.

Since cyclopropene is highly reactive, the cycloaddition occurs much more readily than that in the preparation of 7-silanorbornadines from 2,3,4,5-tetraphenylsilole (IId; R=Ph) with appropriate acetylens. Substitutents on the silicon atom are introduced through the silole by using corresponding chlorosilane as depicted in the following reactions.



(II) (I)

On irradiation with a low pressure mercury arc lamp, the silatricyclooctene (Ia) was found to give 2,5-diphenylcyclohepta-1,3,5-triene (IIIa) [6] quantitatively, which was transformed to an isomeric mixture of (IIIa) on prolonged irradiation. In the case of (Ib), (Ic) and (Id), 2,3,4,5-tetraphenylcycloheptatriene (IIIb) [7] was formed quantitatively on irradiation with a medium pressure mercury arc lamp. Thus the corresponding silylene should be generated on the photolysis of the silatricyclooctene (I). This was confirmed by trapping the silylenes evolved with diethylmethylsilane to give the corresponding insertion products in such a photolysis of (I) in the presence of an excess of the silane. 1,1-Diethyl-1,2,2-trimethyldisilane was thus obtained both from (Ia) in 10% yield and from (Ib) in 11% yield. 1,1-Diethyl-1,2-dimethyl-2-phenyldisilane (62% yield) and 1,1-dimethyl-1-methyl-2,2-diphenyldisilane (9% yield) were similarly isolated from the reaction mixtures of diethylmethylsilane with (Ic) and (Id), respectively.



Furthermore, photolysis of (Ic) in the presence of an excess of 2,3-dimethylbutadiene afforded 1,3,4-trimethyl-1-phenyl-1-silacyclopent-3-ene (V; R^1=Me, R^2=Ph)[8] in 11% yield as a sole addition product together with cycloheptadienes.

Insertion of an organosilylene into a Ge-H bond of triethylgermane was also investigated by employing (Ic) as the silylene generator. Photolysis of a benzene solution of (Ic) containing a large excess of triethylgermane under a nitrogen atomosphere gave the corresponding insertion product (VI; R^1=Me, R^2=Ph) in 32% yield together with tetraphenylcycloheptatrienes. This is the first example of insertion of an organosilylene into a Ge-H bond. In this case neither hexaethyldigermane nor methylphenylsilane was detected in the reaction mixture by means of GLC. Hydrogermanes are known to be better hydrogen donors than the corresponding hydrosilanes and a germyl radical tends to give a coupling product more efficiently in comparison with a silyl radical. Therefore, our results suggest that methylphenylsilylene generated from (Ic) has singlet character.

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References

1. (a) W.H.Atwell and D.R.Weyenberg, Angew.Chem., Internat. Ed., 8 (1969) 469;
   (b) A.Laporterie, J.Dubac, P.Mazerolles and M.Lesbre, Tetrahedron Lett., (1971) 4653;
   (c) M.Ishikawa and M.Kumada, Chem.Comm., (1971)612;
   (d) idem, J.Organometal.Chem., 42 (1972) 325;
   (e) M.Ishikawa, M.Ishiguro and M.Kumada, J.Organometal.Chem., 49 (1973) C71;
   (f) D.Seyferth and D.C.Annarelli, J.Amer.Chem.Soc., 97 (1975) 7162;
   (g) T.J.Barton, J.L.Witiak and C.L.McIntosh, J.Amer.Chem.Soc., 94 (1972) 6229;
2. (a) H.Sakurai, Y.Kobayashi and Y.Nakadaira, J.Amer.Chem.Soc., 93 (1971) 5272;
   (b) idem, ibid., 96 (1974) 2656.
3. G.L.Closs and K.D.Krantz, J.Org.Chem., 31 (1965) 638.
4. (a) W.H.Atwell and D.R.Weyenberg, J.Org.Chem., 32 (1967) 885;
   (b) H.Gilman, S.G.Cottis and W.H.Atwell, J.Amer.Chem.Soc., 86 (1964) 1595.
5. (a) K.N.Houk, Tetrahedron Lett., (1970) 2621;
   (b) T.Sasaki, S.Eguchi and F.Hibi, J.Org.Chem., 37 (1972) 2317;
   (c) R.A.Grieger and C.A.Eckert, J.Amer.Chem.Soc., 92 (1970) 2916, 7149.
6. T.Mukai, H.Kubota and T.Toda, Tetrahedron Lett., (1967) 3581.
7. T.J.Barton and M.A.Bartiste, Tetrahedron Lett., (1967) 2951.
8. M.Ishikawa, F.Ohi and M.Kumada, J.Organometal.Chem., 86 (1975) C21