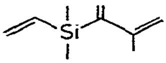
Journal of Organometallic Chemistry, 64 (1974) 343—349

SENSITIZED PHOTOCHEMICAL REACTIONS OF SOME SILYL-1,3-BUTADIENES: SYNTHESIS OF 2,2,4-TRIMETHYL-3-METHYLENE-2-SILABICYCLO[2.1.1]HEXANE

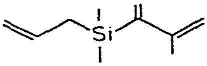
JOHN W. CONNOLLY
University of Missouri-Kansas City, Kansas City, Mo. 64110 (USA)
(Received May 1st, 1973)

Summary

The photolysis of 2,4,4-trimethyl-4-sila-3-methylene-1,5-hexadiene



yielded 2,2,4-trimethyl-3-methylene-2-silabicyclo[2.1.1]hexane as the only volatile photoproduct in high yield. However, 2,4,4-trimethyl-4-sila-3-methylene-1,6-heptadiene

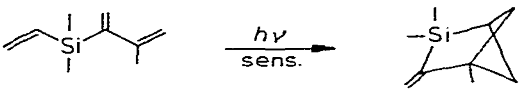


was found to be photochemically non-reactive under identical reaction conditions, and the 1-substituted butadienes (VI) and (VIII)

(VI) (VIII)

underwent *cis-trans* isomerism on photolysis.

The chemistry of strained cyclic organosilicon compounds has been of interest since Sommer and Baum's original work in 1954 [1]. Damrauer's excellent review article covers the silacyclobutanes thoroughly [2] and recently Seyferth reported the first synthesis of a silacyclopropane [3]. In contrast, the silabicycloalkanes have received relatively little study [4 - 9]. In this report we describe the first preparation of a silabicyclo[2.1.1]hexane. The triplet-sensitized photolysis of 2,4,4-trimethyl-4-sila-3-methylene-1,5-hexadiene (I) yielded 2,2,4-trimethyl-3-methylene-2-silabicyclo[2.1.1]hexane (II) as the only product [eqn. (1)].



(I) (II)

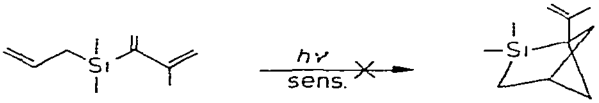
(1)

By analogy with the work of Lin and Hammond on similar all-carbon compounds [10] the above reaction presumably goes through the diradical (III), which then closes to the observed product.

(III)

The selective formation of 5-membered ring intermediates in intramolecular photoadditions is well known [11]. In our photolyses in which such intermediates were not possible (vide infra) we found that geometrical isomerization occurred rather than ring formation.

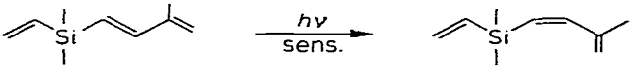
It was anticipated that on photolysis 2,4,4-trimethyl-4-sila-3-methylene-1,6-heptadiene (IV) would yield 1-isopropyl-2,2-dimethyl-2-silabicyclo[2.1.1]hexane (V) [eqn. (2)]. However, no such product was observed. In fact, under conditions where reaction (1) occurred compound (IV) remained completely unchanged. Examination of molecular models indicates that in the conformation required to produce (V) there is contact between the isopropenyl group and a silylmethyl group. The similarity between reactions (3) and (4) below suggest that this lack of reactivity of (IV) must be steric rather than electronic in origin.



(IV) (V)

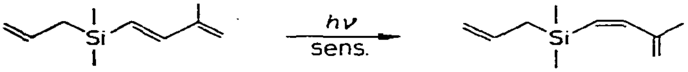
(2)

Photolyses of *trans*-2,5,5-trimethyl-5-sila-1,3,6-heptatriene (VI) and *trans*-2,5,5-trimethyl-5-sila-1,3,7-octatriene (VIII) yielded an equilibrium mixture of *cis* and *trans* isomers [eqns. (3) and (4)]. In the case of (VI) it was possible to isolate the *cis* isomer (VII) and, by its photolysis, to generate the same isomer mixture as was obtained by photolysis of (VI).



(VI) (VII)

(3)



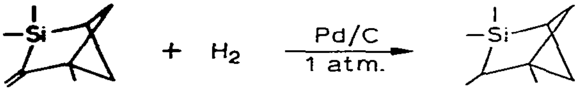
(VIII)

(4)

The structure of (II) is assigned based on the following information: (*a*), it is isomeric with triene I but it contains only one double bond so it must be bicyclic; (*b*), the IR spectrum shows a very weak absorption at 1600 cm^{-1}

indicating a vinyl silane; and (*c*), the NMR spectrum (Table 3) is generally consistent with the assigned structure and in particular shows that the methyl groups on silicon are magnetically equivalent and the vinyl protons are not.

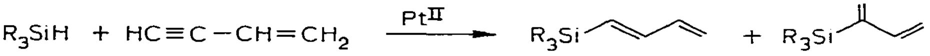
Hydrogenation of (II) under mild conditions proceeds rapidly with uptake of 1.2 moles of hydrogen to give an 80% yield of one product, viz., 1,2,3,3-tetramethyl-3-silabicyclo[2.1.1]hexane (IX) [eqn. (5)].



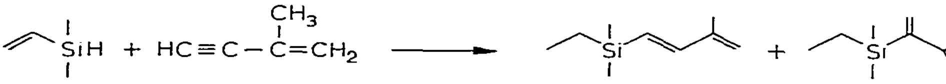
(II) (IX) (5)

Compound (IX) has a molecular weight of 154, its IR spectrum shows no unsaturation and its NMR spectrum (Table 3) is consistent with the proposed structure, i.e., the methyl groups on silicon are not magnetically equivalent and the 2-methyl group is part of an AB_3 pattern similar to the AB_6 pattern observed in our laboratory in the spectrum of isopropyltrimethylsilane. Saturation of the vinyl group on going from (II) to (IX) causes a large upfield shift of the *exo* protons (which are nearer the methylene group than the *endo* protons). The result is that the factors causing the separation of the *endo* and *exo* protons in the all-carbon analogues of (IX) are offset by the proximity of the silicon atom to the *exo* protons which results in an overlapping of the *exo* and *endo* proton signals.

The preparation of the starting materials in this study was accomplished by adaptation of known reactions. A.A. Petrov and co-workers studied the hydrosilylation of 1-buten-3-yne and found that 1-silyl-1,3-butadiene was the major product along with a minor amount of 2-silyl-1,3-butadiene [eqn. (6)] [12]. Similarly, we found that about 90% of the distillate obtained in the Pt^{II} catalyzed addition of vinyldimethylsilane to 2-methylbut-1-en-3-yne was (VI), with the other 10% being (I) [eqn. (7)]. This was a useful preparative method for (VI) but (I) was prepared in a different manner. Similar results were obtained in the preparation of (VIII).

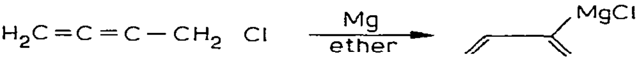


(6)



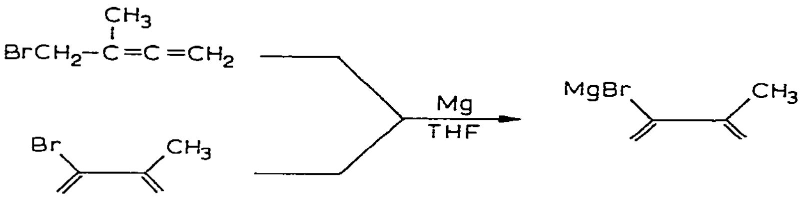
(VI) (I) (7)

Compound (I) was prepared by a coupling reaction between vinyldimethylchlorosilane and the appropriate Grignard reagent. Aufdermarsch showed that 2-(1,3-butadienyl)-magnesium chloride forms on treatment of 4-chloro-1,2-butadiene with magnesium in ether [eqn. (8)] [13]. Traynard and



(8)

Pasternak [14] have reported that in THF both 4-bromo-3-methyl-1,2-butadiene and 2-bromo-3-methyl-1,3-butadiene form the same Grignard reagent [eqn. (9)]. Since these two compounds are the main products of the hydro-



(9)

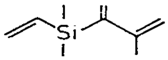
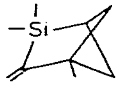
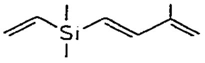
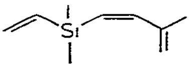
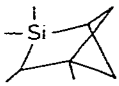
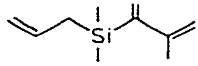
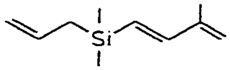
bromination of 2-methylbut-1-en-3-yne [15] we were able to convert the hydrobromination mixture to a Grignard solution without separation of the isomers. Details are given in the Experimental section.

Experimental

The compound 2-methylbut-1-en-3-yne was obtained from Farchan Research Labs, Willoughby, Ohio. Elemental analyses were performed by the Schwarzkopf Microanalytical Labs, Woodside, New York. The NMR spectra reported here were obtained using a JEOL 4H-100 spectrometer. The compounds were examined as 30% solutions in carbon tetrachloride using benzene as an internal standard.

TABLE 1

ELEMENTAL ANALYSES[a], MOLECULAR WEIGHTS AND BOILING POINTS OF NEW COMPOUNDS

Compound		C	H	Si	M/e	B.p.(°C/mm)
(I)		70.81 (71.05)	10.46 (10.52)	18.00 (18.42)	152	55/35
(II)		70.71 (71.05)	10.54 (10.52)	18.16 (18.42)	152	37/15
(VI)		70.93 (71.05)	10.68 (10.52)	18.21 (18.42)	152	42—43/15
(VII)		70.95 (71.05)	10.29 (10.52)	18.80 (18.42)	152	
(IX)		69.93 (70.12)	11.70 (11.68)	18.27 (18.18)	154	
(IV)		72.27 (72.28)	10.64 (10.84)	16.92 (16.86)	164	57—58/15
(VIII)		72.03 (72.28)	10.87 (10.84)	16.59 (16.86)	164	50/15

---

[a] Found (calcd.) (%).

Tables 1, 2 and 3 contain the pertinent analytical data on the new compounds reported here.

The starting materials used in this work were prepared as follows:

Trans-2,5,5-trimethyl-5-sila-1,3,6-heptatriene (VI). To 10 g (0.15 mol) of 2-methylbut-1-en-3-yne in 15 ml of heptane was added a few drops of Speier's catalyst [16]. The mixture was heated to reflux and 12 g (0.14 mol) of vinyldimethylsilane was added over a period of 30 min. The mixture was refluxed until the pot temperature reached 80° and then a reduced pressure distillation

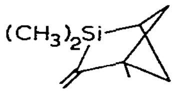
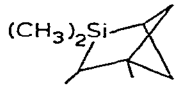
TABLE 2

SELECTED IR DATA OF NEW COMPOUNDS

Compound	Unsaturated CH stretch	C=C stretch butadienyl	C=C stretch allyl or vinyl	Unsaturated CH wag
(I)	3045, 3030, 3025	1610 s, 1565 m	1585 m	1000, 940, 920, 880
(II)	3020		1600 vw	900
(VI)	3085, 3050	1615 m, 1580 s	1595 (sh)	1010, 990, 950, 890
(VII)	3085, 3050	1620 m, 1565 s	1585 s	1010, 950, 890
(IV)	3085 (sh), 3080 s, 3055 (sh)	1610 (sh), 1565 w	1620 s	980, 920, 880
(VIII)	3080, 3055	1615 (sh), 1570 s	1630 s	980, 920, 880

TABLE 3

NMR DATA OF NEW COMPOUNDS

Compound		Signals (τ) and assignments[a]
(I)	$CH_2{=}CH(CH_3)_2Si(CH_2{=})C(CH_3)C{=}CH_2$ 1,2 3 4 5,6 7 8,9	3.83(3) m (1,2,3); 4.14(1) s (5), 4.43 (1) s (6); 4.95 (2) s (8,9); 7.89 (3) s (7); 9.58(6) s (4)
(II)		4.35(1) d, 4.63(1)d methylene protons; 7.73(2) m, *exo* protons; 8.28(3) m, *endo* protons plus bridgehead proton; 8.60(3), bridgehead methyl; 9.48(6) s, silyl methyls
(IX)		7.93—8.63(5)m all the cyclobutyl protons; 8.63—9.13(7)m α-CH plus α-methyl (unsymmetrical doublet at 8.83) plus bridgehead methyl (singlet at 8.75) 9.63, 9.73(6) two singlets, silyl methyls.
(VI)*t*	$CH_2{=}CH(CH_3)_2SiCH{=}CH(CH_3)C{=}CH_2$ 1,2 3 4 5,6 7 8,9	3.33(1) d, *J* 20Hz(6); 4.18(1) d, *J* 20Hz(5); 4.13(3) m (1,2,3); 4.90(2) s (8,9); 8.08(3) s (7); 9.70(6) s (4).
(VII)*c*	$CH_2{=}CH(CH_3)_2SiCH{=}CH(CH_3)C{=}CH_2$ 1,2 3 4 5 6 7 8,9	3.23(1) d, *J* 15Hz(6); 4.46(1) d, *J* 15Hz(5); 4.13(3) m (1,2,3); 5.00(1) s (8); 5.05 (1) s (9); 8.08(3) s (7), 9.70(6) s (4).
(IV)	$CH_2{=}CHCH_2(CH_3)_2Si(CH_2{=})C(CH_3)C{=}CH_2$ 1,2 3 4 5 6,7 8 9,10	4.21(1) m (3); 4.21(1) s (6); 4.55 (1) s (7); 5.06 (3) s (1,9,10); 5.20(1) s (2); 8.03 (3) s (8); 8.30 (2) d, *J* 6Hz(4); 9.75 (6) s (5)
(VIII)*t*	$CH_2{=}CHCH_2(CH_3)_2SiCH{=}CH(CH_3)C{=}CH_2$ 1,2 3 4 5 6 7 8 9,10	3.30(1) d, *J* 19Hz(7); 4.18(1) d, *J* 19Hz (6); 4.18(1) m (3); 4.68, 4.80, 5.00 (4) broad singlets (1,2,9,10); 8.08(3) s (8); 8.35 (2) d, *J* 6Hz(4); 9.80(6) s (5).

---

[a] The number in parentheses is the number of protons, the letter describes the signal i.e., s = singlet, d = doublet, m = multiplet and the last bracket indicates the assignments.

was carried out. The fraction collected at 66 - 70°/40 mm weighed 12 g (57% yield). Analysis on a 12′ × 1/8″ APL on Chrom W gas chromatography column at 150° and 10 ml/min flow rate showed this material to be 90% (VI) and 10% (I). It was possible to obtain pure (VI) by distillation of this mixture through an 8″ glass helix-packed column but not pure (I).

Trans 2,5,5-trimethyl-5-sila-1,3,7-octatriene (VIII). The above hydrosilylation procedure was carried out using allyldimethylsilane in place of vinyldimethylsilane. A 57% yield of distillate boiling from 79 - 83°/40mm was obtained. Gas chromatographic analysis on the above column at 150° and 10 ml/min flow rate showed the mixture to be 80% (VIII) and 20% (IV). Distillation of this mixture through an 8″ glass helix-packed column yielded pure (VIII) but not pure (IV).

2,4,4-Trimethyl-4-sila-3-methylene-1,5-hexadiene (I). Eighty grams (1.2 mol) of 2-methylbut-1-en-3-yne was placed in a 500 ml, three-necked Morton flask equipped with an air driven stirrer and a dropping funnel. The enyne was cooled to −10° and 200 ml of saturated (62%) aq. HBr (2.2 mol) was added during a period of one hour, during which the pot temperature was kept below 0°. After the addition was complete the mixture was stirred for one additional hour as it warmed to room temperature. The unused enyne (35 g) was recovered from the reaction mixture by distillation into a dry ice trap at 20 mm. The monobrominated mixture (60 g, 61% yield) was collected by distillation into a dry ice trap at 1 mm. (Caution, this mixture contains a lachrymator.)

Into a 200 ml three-necked flask equipped with a magnetic stirrer, a condenser and an addition funnel was placed 6.4 g (0.26 mol) of magnesium and 75 ml of THF. To this was added dropwise 39 g (0.26 mol) of the above-prepared bromobutadiene. After the addition was complete and the reaction mixture had cooled to room temperature, 32 g (0.26 mol) of vinyldimethylchlorosilane was added to this mixture and the resulting mixture was refluxed overnight. Subsequent hydrolysis, drying and distillation yielded 16 g (0.11 mol, 41% yield) of distillate boiling at 37 - 39°/20 mm. Gas chromatographic analysis of this material using the above column and conditions showed it to be 80% (I) along with three other components which were not identified.

2,4,4-Trimethyl-4-sila-3-methylene-1,6-heptadiene (IV). Using the above procedure the Grignard reagent formed from 25 g (0.17 mol) bromobutadiene was treated with 22 g (0.16 mol) of allyldimethylchlorosilane and after workup there was obtained 7 g (0.04 mol, 25% yield) of distillate boiling at 48 - 56°/20 mm. Gas chromatographic analysis using the above column and conditions showed the mixture to contain 70% (IV) and three other components which were not identified.

Pure samples of both (I) and (IV) were obtained by preparative gas chromatography using a 20′ × 3/8″ FFAP on Chrom W column at 180° and 60 ml/min flow rate. While it was determined in separate experiments that the impurities obtained in the syntheses of (I) and (IV) do not photolyze under the conditions used, the observations reported below were made on pure samples.

The photolyses were carried out in a Rayonet reactor using 3500 Å lamps. The concentration of organosilicon compound in the solutions photolyzed was 2%, the solvent was hexane, the solutions were degassed and glass containers were used. Benzophenone and β-acetonaphthone were used as sensitizers with identical results.

Photolysis of 2.4 g of (I) in 100 ml of hexane and 0.2 g of β-acetonaphthone for 14 h followed by distillation (36 - 38°/15 mm) yielded 1.6 g (II).

Photolysis of 2.0 g of (VI) for 14 h yielded 1.5 g of distillate which, by gas chromatographic analysis on a 12'X 1/8" APL column, was a 57/43 mixture of (VII)/(VI). Isolation of (VII) using a 20' X 3/8" FFAP gas chromatographic column and subsequent photolysis of it yielded a 64/36 ratio of (VII)/(VI).

Photolysis of 2.0 g of (VIII) yielded 1.5 g of distillate which showed a single gc peak on both the 12' X 1/8"APL column and the 20' X 3/8" FFAP column under a variety of temperatures and flow rates. However, the NMR spectrum of the distillate contained new signals at 3.18 and 4.43 τ which were doublets (J 15Hz). The intensity ratio of these signals and those of the *trans* protons indicated that it was approximately a 50/50 mixture of the *cis* and *trans* isomers of (VIII).

Hydrogenation of (II) was carried out in a closed system using 10% Pd on charcoal as a catalyst. A gas buret was used to measure the hydrogen uptake. Recovery of the product was done by quantitative distillation in a high vacuum system. In a typical experiment 0.191 g (1.25 mmol) of (II) took up 1.50 mmol of H_2 and 0.180 g (1.15 mmol) of (IX) was recovered.

Acknowledgement

The author would like to thank Professor Timothy Thomas for his help in obtaining the mass spectra reported here, and Mr. K.L. Lee of the Dow Corning Corporation, Midland, Michigan for his generous gift of vinyldimethylchlorosilane.

References

1 L.H. Sommer and G.A. Baum, J. Amer. Chem. Soc., 76 (1954) 5002.
2 R. Damrauer, Organometal. Chem. Rev. A, 8. (1972) 67.
3 R.L. Lambert, Jr., and D. Seyferth, J. Amer. Chem. Soc., 94 (1972) 9246.
4 L.H. Sommer and O.F. Bennett, J. Amer. Chem. Soc., 79 (1957) 1008.
5 L.H. Sommer and O.F. Bennett, J. Amer. Chem. Soc., 81 (1959) 251.
6 L. Birkofer and D. Prustel, J. Organometal. Chem., 32 (1971) C75.
7 J.W. Connolly and P.F. Fryer, J. Organometal. Chem., 30 (1971) 315.
8 E. Rosenberg and J.J. Zuckerman, J. Organometal. Chem., 33 (1971) 321.
9 M. Lesbre, G. Manuel, P. Mazerolles, and G. Canquy, J. Organometal. Chem., 40 (1972) C14.
10 R.H.S. Lin and G.S. Hammond, J. Amer. Chem. Soc., 89 (1967) 4936.
11 R. Srinivasan and K.H. Carlough, J. Amer. Chem. Soc., 89 (1967) 4932.
12 T.M. Sleta, M.D. Stadnichuk, A.A. Petrov, Zh. Obshch. Khim, 38 (1968) 374.
13 C.A. Aufdermarsh, Jr., J. Org. Chem., 29 (1964) 1994.
14 Y. Pasternak and J.C. Traynard, Bull. Soc. Chim., Fr., (1966) 356.
15 J.C. Traynard, Bull. Soc. Chim., Fr., (1962) 19.
16 J.L. Speier, J.A. Webster and G.H. Barnes, J. Amer. Chem. Soc., 79 (1957) 974.