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PHOTOREACTIONS OF BENZOSILACYCLOBUTENES WITH CARBONYL COMPOUNDS. S_H2 REACTION ON Si-C BOND BY TRIPLET CARBONYL COMPOUNDS

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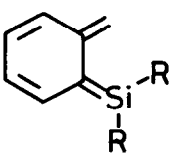
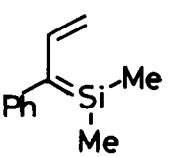
Summary: Photoreaction of 2,3-benzo-1,1-diphenyl(or dimethyl)-1-sila-2-cyclobutene with an aldehyde or ketone results in 1:1 cycloadduct of [4+2] type, the formation of which is accountd for in terms of S_H2 process, i.e., attack of a triplet carbonyl compound on the silicon of the benzosilacyclobutene.

In recent years, much attention has been paid to the chemistry of multiple bonds involving silicon.[1] In continuation of our study on the chemistry of o-quinonoid compounds,[2] we became interested in the properties of an unknown species, o-silaquinone methide (1).



1



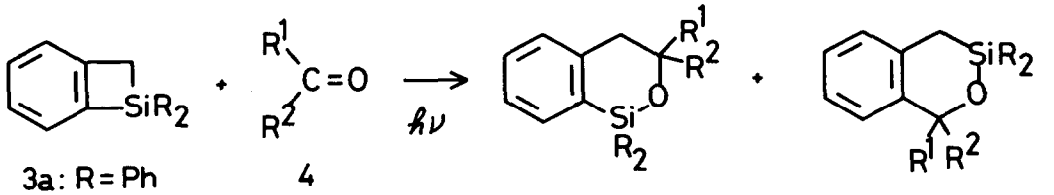
2

Valkovich and Weber recently communicated that the photoreaction of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene with acetone leading to [4+2] adduct, 2,2,6,6-tetramethyl-1-oxa-3-phenyl-2-silacyclohexene, and proposed the intermediacy of 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene (2).[3] This result suggests that benzosilacyclobutene would be a reasonable precursor of 1.

We report here that the photoreactions of benzosilacyclobutenes with ketones and aldehydes result in the formation of 1:1 adducts of [4+2] type as in the case of the silacyclobutene but the reactions proceed via attack of excited

carbonyl compounds to the benzosilacyclobutene, not via o-silaquinone methide intermediate.

2,3-Benzo-1,1-diphenyl(or dimethyl)-1-sila-2-cyclobutene (3) (1-2 mmol) was dissolved in a ketone or aldehyde (4) (2-10 ml) with a quartz tube, and the solution was irradiated by a medium pressure mercury lamp (100 W) through a Vycor filter (9-15 h) to give the corresponding benzoxasilacyclohexenes (5) (and 6 in some cases).



3a: R=Ph
3b: R=Me
4
5
6

The results are summarized in Table. The structure was identified by spectral data (NMR and MS) and elemental analyses.

Table Yield of the photoproducts

Entry	Benzosila-cyclopropene	Carbonyl compd (4) R^1	Carbonyl compd (4) R^2	Yield (%)[a]
1	3a	Me	Me	52
2	3a	Me	Et	69
3	3a	$(CH_2)_4$		82
4	3a	Et	H	68
5	3a	n-Pr	H	53
6	3a	Ph	Me	25
7	3b	Me	Me	52[b]
8	3b	Et	Me	57[c]
9	3b	Et	H	46
10	3b	n-Pr	H	41

a) In some cases a small amount of 3 was recovered, the yield being based on unrecovered 3. b) The isomer 6 was also obtained in 5% yield along with 5. See Text. c) See note 7).

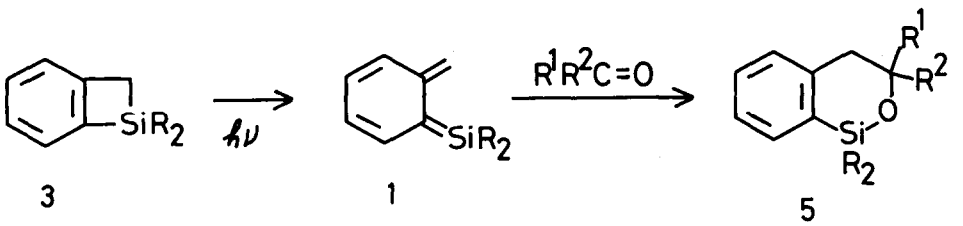
There are two possible reaction pathways, Schemes 1 and 2, for the formation of 5; the former involves the o-silaquinone methide (1) which undergoes [4+2] cycloaddition with 4, while the latter invokes the triplet state of

4 which attacks the silicon of 3 in S_H2 (bimolecular homolytic substitution) fashion to give diradical 7, hence 5 as a final product. It is well established that the reactivity of n-π* triplet carbonyl compound approximates to that of an alkoxyl radical.[4,5]

The following facts indicate that Scheme 2 is actually operative in the present reactions. 1) Even when the reaction of 3a with acetophenone was carried out under conditions such that more than 99% of the incident light was absorbed only by acetophenone using the filter solution of aq. cupric sulfate, 5 (R=R^1=Ph, R^2=Me) was still formed in 19% yield (cf. Entry 6 in Table). 2) In the reaction of 3b with acetone, there was obtained another 1:1 adduct which was identified as 6 (R=Ph, R^1=R^2=Me; 5%).[6,7] The formation of 6 can only be accommodated with the intermediacy of diradical (8).[8] To the best of our knowledge, this is the first example of S_H2 reactions occurring on the Si-C bond although such a process has been reported for Si-Si bond.[9]

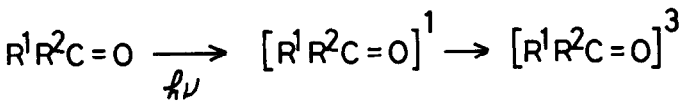
In summary, the benzosilacyclobutene undergoes bimolecular homolytic substitution (S_H2) on the Si-C bond by a triplet carbonyl compound to give a

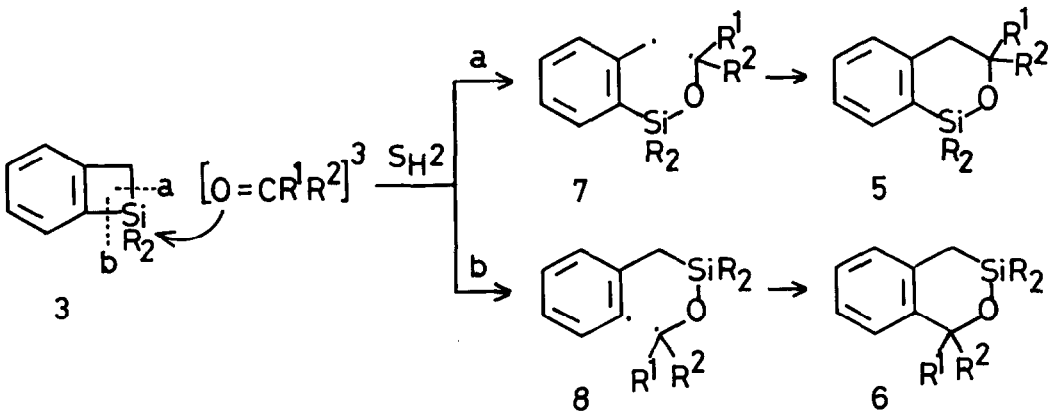
Scheme 1



3 1 5

Scheme 2





3 7 5 8 6

formal [4+2] cycloadduct.[10] This seems to suggest that S_H2 process may be operative also in the case of the afore-mentioned photoreaction[3] of the silacyclobutene with acetone where silabutadiene intermediate was claimed to be involved.[11]

References and Notes

1) P. Jutzi, Angew. Chem. Int. Ed. Engl., 14, 232 (1975); H. Sakurai, Kagaku No Ryoiki, 29, 742 (1975); L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdokin, Acc. Chem. Res., 8, 18 (1975); L. E. Gusel'nikov and N. S. Nametkin, Chem. Rev., 79, 529 (1979).

2) R. Okazaki, K. Sunagawa, M. Kotera, and N. Inamoto, Tetrahedron Lett., 3815 (1976); R. Okazaki, K. Sunagawa, K.-T. Kang, and N. Inamoto, Bull. Chem. Soc. Jpn., 52, 496 (1979); K.-T. Kang, R. Okazaki, and N. Inamoto, ibid., 52, 3640 (1979).

3) P. B. Valkovich and W. P. Weber, Tetrahedron Lett., 2153 (1975).

4) A. Padwa, Tetrahedron Lett., 3456 (1964); S. G. Cohen and R. J. Baumgarten, J. Am. Chem. Soc., 87, 2996 (1965); C. Walling and M. J. Gibian, ibid., p. 3361.

5) We previously reported that triplet benzophenone, like an alkoxyl radical, undergoes S_H2 reaction with diphosphine. R. Okazaki, K. Tamura, Y. Hirabayashi, and N. Inamoto, J. C. S. Perkin Trans. 1, 1924 (1976).

6) The isomers 5 ($R=R^1=R^2=Me$) and 6 were separated by gas chromatography and had the following spectral characteristics: 5, NMR (CCl_4, δ): 0.27 (6H, s), 1.22 (6H, s), 2.79 (2H, s), and 6.8-7.4 (4H, m); high resolution MS: m/e 206.1151 (calcd for $C_{12}H_{18}OSi$: 206.1127); 6, NMR (CCl_4, δ): 0.09 (6H, s), 1.52 (6H, s), 2.06 (2H, s), and 6.9-7.3 (4H, m); high resolution MS; m/e 206.1137.

7) The presence of an isomeric 1:1 adduct was also revealed in the reaction of Entry 8 by the NMR spectrum, but its isolation was unsuccessful so far. The reason why the isomer was obtained only in the cases of Entries 7 and 8 is not clear at present.

8) The concerted process of $[_\sigma2 + _\pi2]$ involving C-Si and C=O bonds is also possible but seems much less likely.

9) S. H. Band and I. M. T. Davidson, Trans. Farady Soc., 66, 406 (1970); A. Hosomi and H. Sakurai, J. Am. Chem. Soc., 94, 1384 (1972); idem., Chem. Lett., 193 (1972); H. Sakurai, "Free Radicals" Ed. by J. K. Kochi, Vol. 2, Chapter 25, John Wiley & Sons, New York (1973).

10) At present, concomitant occurrence of Scheme 1 along with Scheme 2 can not rigorously be eliminated.

11) We are grateful to Shin-etsu Chemical Industry Co. Ltd., for providing the chlorosilanes.

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