

- Soc.*, **4**, 133 (1983).
- (8) Y. K. Kang and M. S. Jhon, *Macromolecules* in press.
- (9) G. Del Re, *J. Chem. Soc.*, **4031** (1958).
- (10) G. Del Re, B. Pullman and T. Yonezawa, *Biochim. Biophys. Acta*, **75**, 153 (1963).
- (11) H. H. Greenwood, "Computing Methods in Quantum Organic Chemistry," Wiley, New York, 1973.
- (12) A. J. Hopfinger, "Conformational Properties of Macromolecules," Academic Press, New York, 1973.
- (13) K. S. Pitzer, *Adv. Chem.*, **2**, 59 (1959).
- (14) D. A. Brant, *Ann. Rev. Biophys. Bioeng.*, **1**, 369 (1982).
- (15) Y. K. Kang and M. S. Jhon, *Theoret. Chim. Acta* (Berl), **61**, 41 (1982).
- (16) W. J. Orville-Thomas, Ed., "Internal rotation in molecules," Wiley, New York, 1974.
- (17) R. V. Hogg and A. T. Craig, "Introduction to Mathematical Statistics," 4th Ed., Macmillan, New York, 1978.
- (18) M. Karplus and A. Maccammon, *CRC Crit. Rev. Biochem.*, **9**, 293 (1981).
- (19) M. Karplus and J. N. Kushick, *Macromolecules*, **14**, 325 (1981).
- (20) R. Fletcher, "Fortran Subroutines for Minimization by Quasi Newton Methods," A. E. R. E. Report R7, 125 (1972).
- (21) R. C. Weast Ed., *Handbook of Chemistry and Physics*, 56th Ed., CRC, Cleveland, (1975).
- (22) H. L. Friedman and C. V. Krishnan, "Water; a Comprehensive Treatise," Vol. 3. F. Franks, Ed., Plenum, New York, p. 1 1973.
- (23) A. Pullman, "The New World of Quantum Chemistry", B. Pullman and R. Parr Eds., Reidal, Dordecht, 1976, p.149.

S_H2 Reaction on Silicon-Carbon Bond in the Photoreactions of 2,3-Benzo-1,1-diphenyl(or dimethyl)-1-sila-2-cyclobutene with Carbonyl Compounds

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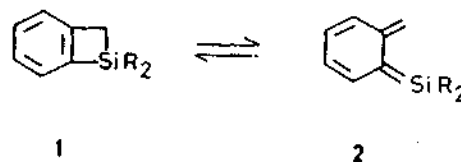
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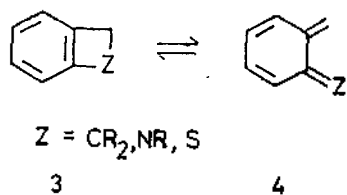
The photoreaction of 2,3-benzo-1,1-diphenyl (or dimethyl)-1-sila-2-cyclobutene (**9** or **10**) with an aldehyde or ketone results in 1:1 cycloadduct of [4+2] type. In the reactions of 2,3-benzo-1,1-dimethyl-1-sila-2-cyclobutene (**10**) with acetone and butanone, another 1:1 adducts (**13**) were also formed, respectively. The following facts indicate that the formation of adduct involves an attack of a triplet carbonyl compound on the silicon of the benzosilacyclobutene, an S_H2 process. (1) Even when the reaction of **9** with acetophenone was carried out under conditions such that more than 99 % of incident light was absorbed only by acetophenone using the filter solution of aq. cupric sulfate, the same adduct was still formed. (2) When the reaction of **9** with acetone was carried out under oxygen atmosphere, only trace amount of adduct was formed.

Introduction

In recent years, much attention has been paid to the chemistry of multiple bonds involving silicon.¹ In the course of study on the chemistry of *o*-quinonoid compounds,² we became more interested in the properties of *o*-silaquinone methide (**2**) which is unknown yet.

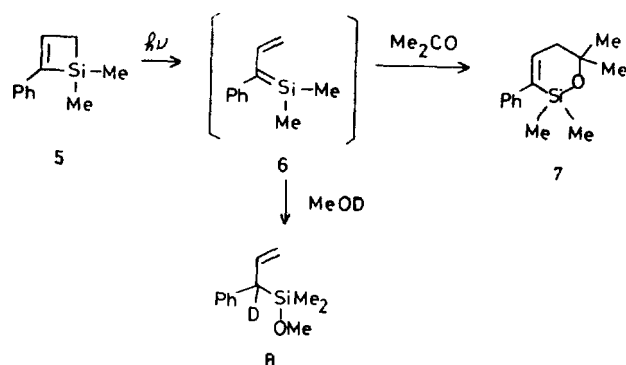


Benzocyclobutene and its heteroatom-substituted analogs (**3**) undergo thermal and photochemical ring opening to give



highly reactive *o*-quinonoid intermediates(4).³

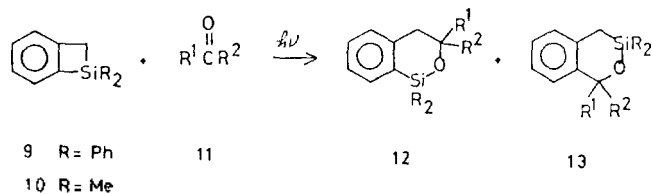
Valkovich and Weber communicated that the photoreaction of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene (5) with acetone leads to [4+2] adduct, 7, probably *via* 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene (6).⁴ Further evidence for the presence of 6 as an intermediate was provided by these authors. Photolysis of 5 in methanol-O-d₁ yielded dimethylmethoxy-(1-d₁-1-phenyl-2-propenyl)silane (8) as a major product.⁵ Methanol is an effective trapping reagent for unstable silicon-carbon double bond compounds generated both by gas phase pyrolysis⁶ and solution photolysis.⁷ These facts strongly suggest that benzosilacyclobutene (1) could be a reasonable precursor of 2.



We now wish to report here that the photoreactions of benzosilacyclobutenes (1) with aldehydes or ketones result in the formation of 1:1 adducts of [4+2] type as in the case of the silacyclobutene (5) but the reactions proceed *via* attack of excited carbonyl compounds to the benzosilacyclobutene (1), not *via* *o*-silaquinone methide intermediate (2).⁸

Results and Discussion

An aldehyde or ketone solution of 2,3-benzo-1,1-diphenyl (or dimethyl)-1-sila-2-cyclobutene (9 or 10) in a quartz tube was irradiated with a 100 W medium pressure mercury lamp through a Vycor filter to give 1:1 adducts, benz [C] [1,2] oxasilacyclohexenes (12).



It was observed that the rates of these reactions vary considerably depending on the concentration of benzosilacyclobutene. The amount of carbonyl compounds were adjusted such that the concentration of benzosilacyclobutene should be between 0.1 and 0.2 mole per liter. Dichloromethane was used as the solvent in the reaction of 9 with acetophenone or propiophenone. The yields (Table 1) are calculated based on

TABLE 1: The Yield of 12

| 12 | R | R ¹ | R ² | yield (%) |
|----|----|----------------|---------------------------------|-----------|
| a | ph | Me | Me | 52 |
| b | ph | Me | Et | 69 |
| c | ph | Et | Et | 40 |
| d | ph | | (CH ₂) ₄ | 82 |
| e | ph | | (CH ₂) ₅ | 42 |
| f | ph | Et | H | 68 |
| g | ph | <i>n</i> -Pr | H | 53 |
| h | ph | Me | ph | 25 |
| i | ph | Et | ph | 31 |
| j | Me | Me | Me | 52 |
| k | Me | Me | Et | 57 |
| l | Me | Et | Et | 41 |
| m | Me | | (CH ₂) ₄ | 77 |
| n | Me | | (CH ₂) ₅ | 45 |
| o | Me | Et | H | 46 |
| p | Me | <i>n</i> -Pr | H | 41 |
| q | Me | Me | ph | 29 |

TABLE 2: NMR Spectra* (δ) of 12a-q and 13j in Carbon Tetrachloride

| Compound | Benzylic | R ¹ | R ² | Si-Methyl |
|----------|--------------|---------------------------|-----------------------|--------------------|
| 12a | 2.87(s) | | 1.35(s) | — |
| 12b | 2.84(q) | 1.27(s) | 0.93(r) 1.3-1.9(m) | — |
| 12c | 2.81(s) | | 0.84(r) 1.61(q) | — |
| 12d | 2.97(s) | | 1.3-2.2(m) | — |
| 12e | 2.81(s) | | 0.8-2.0(m) | — |
| 12f | 2.6-3.2(m) | 1.03(r) 1.4-1.9(m) | 3.9-4.4(m) | — |
| 12g | 2.6-3.2(m) | 0.75-1.2(m) 1.2-1.9(m) | 4.0-4.5(m) | — |
| 12h | 3.21(q) | 1.59(s) | — | — |
| 12i | 3.25(br,s) | 0.67(r) 1.83(q) | — | — |
| 12j | 2.79(s) | | 1.22(s) | 0.27(s) |
| 12k | 2.76(q) | 1.13(s) | 0.89(r) 1.71(q) | 0.25(s) 0.27(s) |
| 12l | 2.72(s) | | 0.81(r) 1.44(q) | 0.26(s) |
| 12m | 2.85(s) | | 1.3-2.1(m) | 0.23(s) |
| 12n | 2.71(s) | | 0.9-1.9(m) | 0.27(s) |
| 12o | 2.55-2.97(m) | 0.97(r) 1.51(q) | 2.88(quin) | 0.27(s) 0.30(s) |
| 12p | 2.5-3.05(m) | 0.7-1.2(m) 1.2-1.8(m) | 3.7-4.2(m) | 0.28(s) |
| 12q | 3.0-3.2(m) | 1.44(s) | — | 0.31(s) 0.37(s) |
| 13j | 2.06(s) | | 1.52(s) | 0.09(s) |

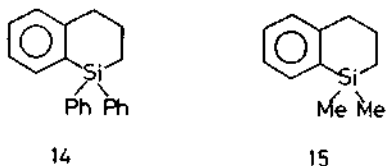
* The chemical shifts of the aromatic protons are not included in the Table (see Experimental).

consumed benzosilacyclobutene.

From the reactions of 10 with acetone and butanone other adducts (13j and 13k) were also formed. On the basis of the high resolution mass spectra, 13j was found to be the isomer of 12j. 12j and 13j showed the parent peak at *m/e* 206.

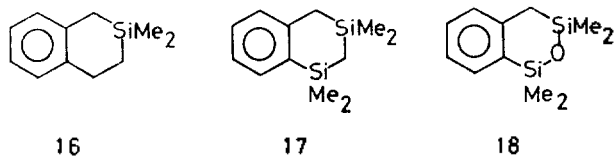
1151 and m/e 206. 1137 (Calcd for $C_{12}H_{18}OSi$: 206. 1127), respectively.

The NMR spectrum (CCl_4) of **12** (Table 2) showed that the chemical shifts of benzylic protons correspond closely to the reported values of δ 2.87 and 2.89 for the benzylic protons of the similar compounds **14**⁹ and **15**¹⁰, respectively.



For **12h**, **12i** and **12q**, the benzylic protons exhibit a slight downfield shift, indicating the anisotropy of the benzene ring of R^2 .

In the NMR spectrum of **13j**, the benzylic protons appear at a much higher field (δ 2.06) than those of **12**. This value of chemical shift, however, corresponds closely to the reported values of δ 1.92, 2.04, and 2.14 for the benzylic protons of similar compounds **16**,¹¹ **17**,¹⁰ and **18**,¹², respectively.

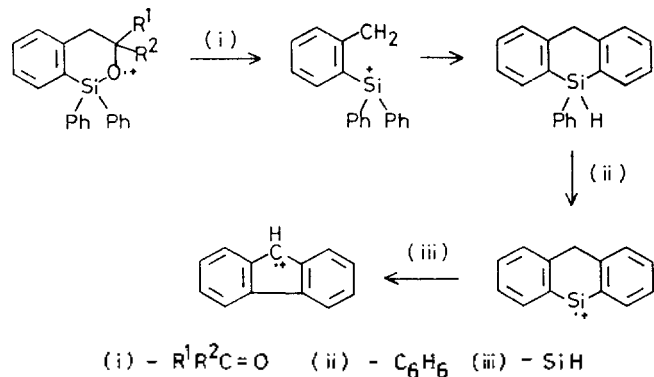


The silicon-attached methyl protons of **12j-p** appear at about δ 0.28 compared with δ 0.09 for **13j**. This upfield shift in **13j** indicates that the silicon-attached methyl protons of **13j** are free from the anisotropy of benzene ring, which is responsible for **12j-p**.

These data as well as the reported values of δ 0.02, 0.09 ($PhCH_2SiMe_2$) and δ 0.29, 0.31 ($PhSiMe_2$) for the similar compounds **17**¹⁰ and **18**,¹², indicate that the assignments of **12** and **13** are reasonable.

The mass spectrum of **12** showed the peaks at m/e 194 [$M - R^1R^2C=O - C_6H_6$]⁺ and m/e 165 [$M - R^1R^2C=O - C_6H_6 - SiH$]⁺ in high abundance, ranging from 22–100%. This is in good agreement with the reasonable fragmentation pattern involving considerable rearrangements¹³ (Scheme 1).

Formation of 1:1 adduct (**12**) could be rationalized in terms of two mechanistic alternatives. One (Scheme 2) is that photoexcited **1** opens to **2**, which then undergoes a



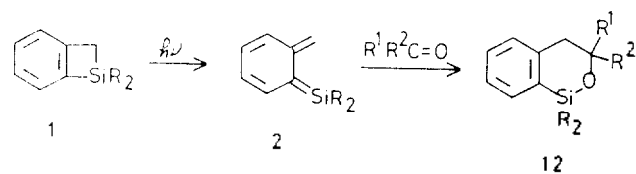
Scheme 1.

[4+2] cycloaddition reaction with carbonyl compounds to yield **12**. Another (Scheme 3) is that the oxygen atom of the triplet excited state of carbonyl compounds resulting from photoexcitation attacks the silicon atom of **1** to open the silacyclobutene ring. In other words, a bimolecular homolytic substitution (S_H2) reaction could take place.

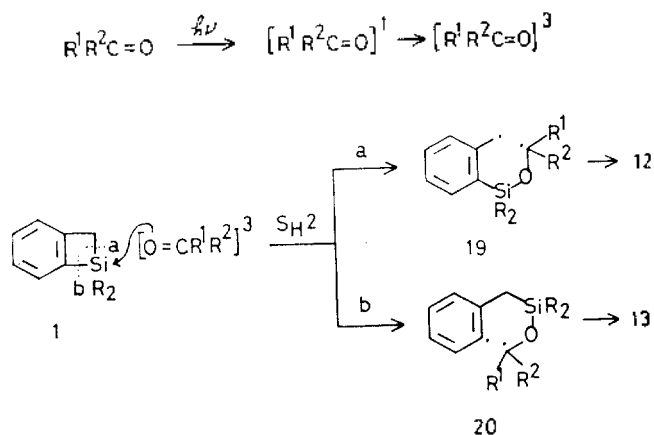
In order to clarify which mechanism is operating for the above 1:1 adduct formation, it has to be investigated which of the two reactants, benzosilacyclobutene or carbonyl compounds, initially absorbs light. A solution of **9** and acetophenone in dichloromethane was irradiated with light filtered with an aqueous cupric sulfate solution.

1,1-Diphenyl-1-silabenzocyclobutene (**9**) does not absorb light of wavelength longer than 300 nm, while the aqueous cupric sulfate filter solution absorbs light of wavelengths shorter than 300 nm. Moreover, the concentration of acetophenone was about ten times higher than that of **9**. Consequently, in the reaction using the aqueous cupric sulfate filter solution, light is completely absorbed by acetophenone. The photoreaction using the filter solution under otherwise identical conditions to those for direct irradiation also resulted in the formation of **12h**, although the yield was somewhat lower. This observation strongly suggests that Scheme 3 is an actual pathway for the present reactions. The triplet states of carbonyl compounds attack the silicon atom of **1** in S_H2 fashion to give diradical **19** which further reacts to give the final product (**12**). It is well-established that the reactivity of $n-\pi^*$ triplet of excited carbonyl compound is comparable with that of an alkoxyl radical.¹⁴

An acetone solution of **9** gave 1:1 adduct, **12a**, in less than 3% yield when oxygen was bubbled into the solution throughout irradiation. Over 90% of the starting material, **9**, remained unreacted. This is in marked contrast with over 60% yield of 1:1 adduct from the same reaction in the absence of oxygen. Molecular oxygen is known to quench triplet acetone efficiently. This implies the involvement of triplet state



Scheme 2.



Scheme 3.

of acetone in the above photoreactions. Therefore, it is safe to conclude that S_{H2} reaction mechanism is operating in the reaction of benzosilacyclobutene with not only aromatic carbonyl compounds but also aliphatic ones.

In the reactions of **10** with acetone and butanone, other types of 1:1 adducts, **13j** and **13k**, were also formed, respectively. The reason why the isomeric adducts were obtained only in these cases is obscure. The most reasonable explanation of this observation is that the reaction proceeds *via* diradical intermediate **20**, which undergoes cycloaddition to **13** (the path *b* in Scheme 3). It is believed that this is supportive evidence for the S_{H2} mechanism presented above for the formation of **12**.

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 the Si-Si bond.¹⁵

In summary, the photoreactions of benzosilacyclobutenes (**9** and **10**) with aldehydes and ketones result in the formation of 1:1 adduct of [4+2] type as in the case of the silacyclobutene (**5**) but the reactions proceed *via* attack of excited carbonyl compounds to the benzosilacyclobutene, not *via* *o*-silaquinone methide (**2**) intermediate.

Experimental

NMR spectra were recorded in carbon tetrachloride with Hitachi R-24B and Varian EM360A and EM390 spectrometers unless otherwise stated.

UV and IR spectra were recorded on Hitachi ESP-3 and EPI G-2 spectrometers, respectively. Mass spectra were determined on a Hitachi RMU-6L mass spectrometer (70eV). High resolution mass spectra were taken with a JEOL JMS-D300 spectrometer. For gas chromatographic separation, JEOL-750 and Shimadzu GC-6A gas chromatographs, and a column (2 mm×2 m) packed with SE-30 were used. Melting points were not corrected.

Photoreaction of 9 with Acetone. A dry acetone solution (180 ml) of **9**¹⁶ (559 mg, 2.05 mmol), through which nitrogen was passed, was irradiated for 7 h with a 100 W medium pressure mercury lamp through a Vycor filter at ca. 5°C. Most of the acetone was evaporated and the residue was subjected to DCC (dry column chromatography) [silica gel, CH_2Cl_2 - CCl_4 (1:7)] and then PLC (preparative layer chromatography) (silica gel, CH_2Cl_2 - CCl_4 (1:5)) to give **12a** (353 mg, 52%). An analytical sample was obtained by recrystallization from ethanol-methanol. **12a**: mp 111–112.5°C; NMR: δ 1.35 (6H, *s*), 2.87 (2H, *s*), 6.9–7.8 (14H, *m*); MS: *m/e* 330 (M^+ , 14%), 315 (M^+ - CH_3 , 39), 272 (M^+ - CH_3COCH_3 , 29), 252 (41), 237 (39), 194 (100), 165 (22); Found: C, 80.15; H, 6.89%. Calcd for $\text{C}_{22}\text{H}_{22}\text{OSi}$: C, 79.95; H, 6.71%.

Photoreactions of 9 with Butanone and 3-Pentanone. The following is typical of the procedure used in the photoreactions of benzosilacyclobutenes (**9** and **10**) and carbonyl compounds.

In three carefully dried quartz NMR tubes was placed a butanone solution (3 ml) of **9** (404 mg, 1.48 mmol). A stream of dry argon was passed through each solution to displace the air, and each tube was sealed with a cap and paraffin film.

The tubes were then irradiated externally with a medium pressure mercury lamp (100 W) through a Vycor filter for 15.5 h. After removal of the solvent, the residue was subjected to PLC (silica gel, CCl_4), to give **12b** (300 mg, 59%) and unreacted **9** (55.6 mg, 14%).

A 3-pentanone solution (6 ml) of **9** (200 mg, 0.74 mmol) was irradiated for 10 h. The reaction mixture was subjected to DCC and then PLC (silica gel, hexane-ether (15:1)), to give **12c** (68 mg, 26%) and unreacted **9** (70 mg, 35%). **12b**: mp: 103–104.5°C (ethanol); NMR: δ 0.93 (3H, *t*, $J=7.2$ Hz), 1.3–1.9 (2H, *m*), 1.27 (3H, *s*), 2.56, 2.82, 2.86, 2.92 (2H, $J=15.6$ Hz), 6.8–7.8 (14H, *m*); MS: *m/e* 344 (M^+ , 3%), 329 (4), 315(98), 272(24), 238(100), 194(60), 165(24), 105(22); Found: C, 80.17; H, 7.14%. Calcd for $\text{C}_{23}\text{H}_{24}\text{OSi}$: C, 80.18; H, 7.02%. **12c**: mp: 108–110°C (ethanol); NMR: δ 0.84 (6H, *t*, $J=7.2$ Hz), 1.61 (4H, *q*, $J=7.2$ Hz), 2.81 (2H, *s*), 6.9–7.7 (14H, *m*).

Photoreactions of 9 with Cyclopentanone and Cyclohexanone.

Using the above procedure, **9** (410 mg, 1.51 mmol) in 3 ml of cyclopentanone was irradiated externally for 15.5 h. The reaction mixture was subjected to DCC (silica gel, CCl_4) to give **12d** (176 mg, 33%) and unreacted **9** (190 mg, 46.5%).

In another experiment, a cyclopentanone solution (2 ml) of **9** (83 mg, 0.31 mmol) was irradiated externally for 9 h. The reaction conditions were maintained same as the above, except the concentration of **9** in cyclopentanone. The reaction mixture was subjected to DCC (silica gel, CCl_4) to give **12d** (61 mg, 56%) and unreacted **9** (26 mg, 31%). **12e** was similarly prepared. **12d**: mp: 110–111.5°C (ethanol); NMR: δ 1.3–2.2 (8H, *m*), 2.97 (2H, *s*), 6.9–7.9 (14H, *m*); MS: *m/e* 356 (M^+ , 100%), 327(8), 272 (16), 250(39), 237(58), 194(35), 165(22); Found: C, 81.00; H, 6.83%. Calcd for $\text{C}_{24}\text{H}_{24}\text{OSi}$: C, 80.85; H, 6.78%. **12e**: mp: 114–115.5°C (ethanol); NMR: δ 0.8–2.0 (10H, *m*), 2.81 (2H, *s*), 6.8–7.7 (14H, *m*).

Photoreactions of 9 with Propanal and Butanal. A propanal solution (5 ml) of **9** (301 mg, 1.10 mmol) was irradiated for 13 h. The reaction mixture was subjected to DCC (silica gel, CCl_4) to give oily substance (502 mg) and unreacted **9** (80 mg, 27%). The former was triturated with ethanol to give colorless crystals of **12f** (180 mg, 50%). **12g** was prepared in a similar way. **12f**: mp: 86.5–87°C (ethanol); NMR: δ 1.03 (3H, *t*, $J=7.2$ Hz), 1.4–1.9 (2H, *m*), 2.6–3.2 (2H, *m*), 3.9–4.4 (1H, *m*), 6.9–7.9 (14H, *m*); MS: *m/e* 330 (M^+ , 5%), 301(48), 271(18), 252(50), 223(100), 194(43), 165(21); Found: C, 80.06; H, 6.60%. Calcd for $\text{C}_{22}\text{H}_{22}\text{OSi}$: C, 79.95; H, 6.71%. **12g**: mp: 91–92°C (ethanol); NMR: δ 0.75–1.2 (3H, *m*), 1.2–1.9 (4H, *m*), 2.6–3.2 (2H, *m*), 4.0–4.5 (1H, *m*), 7.0–8.0 (14H, *m*); MS: *m/e* 344 (M^+ , 4%), 315(2), 301(45), 266(41), 223(100), 194(35), 165(19); Found: C, 80.26; H, 7.04%. Calcd for $\text{C}_{23}\text{H}_{24}\text{OSi}$: C, 80.18; H, 7.02%.

Photoreactions of 9 with Acetophenone and Propiophenone.

A dichloromethane solution (4 ml) of **9** (289 mg, 1.06 mmol) and acetophenone (1.1 g, 84 mmol) was irradiated for 18 h. The reaction mixture was subjected to DCC and then PLC (silica gel, C_6H_{14} - Et_2O (10:1)), to give **12h** (106 mg, 25%). **12i** was also prepared in this way. **12h**: mp: 105–105.5°C (ethanol); NMR: δ 1.59 (3H, *s*), 2.93, 3.19, 3.23, 3.49 (2H, $J=15.6$ Hz),

6.8–7.8 (19H, *m*); MS: *m/e* 392 (M^+ , 68%), 377(78), 299(59), 272(17), 271(48), 194(100), 165(36), 105(32); Found: C, 82.44; H, 5.93%. Calcd for $C_{27}H_{24}OSi$: C, 82.61; H, 6.16%. **12i**: NMR: δ 0.67 (3H, *t*, $J=7.2$ Hz), 1.83 (2H, *q*, $J=7.2$ Hz), 3.25 (2H, *br s*), 6.9–7.8 (19H, *m*).

Photoreaction of 10 with Acetone. A dry acetone solution (15 ml) of **10**⁹ (414 mg, 2.80 mmol) was irradiated for 8.5 h in a similar manner to that described for the photoreaction of **9** with butanone. The reaction mixture was subjected to DCC (silica gel, $C_6H_{14}-Et_2O$ (12:1)) to give a mixture of **12j** and **13j** (333 mg, 58%). The ratio of **12j** to **13j** was found to be about 10:1 by NMR. **12j** and **13j** were isolated by preparative gas chromatography (column temp., 110°C). **12j**: δ 0.27 (6H, *s*), 1.22 (6H, *s*), 2.79 (2H, *s*), 6.8–7.4 (4H, *m*); MS: *m/e* 206 (M^+ , 27%), 191(100), 133(60); Found: C, 69.68; H, 9.13%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%. **13j**: NMR: δ 0.09 (6H, *s*), 1.52 (6H, *s*), 2.06 (2H, *s*), 6.9–7.3 (4H, *m*); MS: *m/e* 206 (M^+ , 4%), 191(100), 132(4); Found: C, 69.68; H, 9.30%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

Photoreaction of 10 with Butanone. A butanone solution (11 ml) of **10** (283 mg, 1.91 mmol) was irradiated for 8 h. The reaction mixture was subjected to DCC (silica gel $C_6H_{14}-Et_2O$ (10:1)) to give a mixture of **12k** and **13k** (240 mg, 57%) and unreacted **9** (24 mg, 8.5%). The presence of **13k** in this mixture was observed by NMR (δ 0.07 (6H, *s*) and 2.01 (2H, *s*)); other peaks are superimposed on those of **12k**. But it was impossible to isolate **13k** because the retention time of **13k** was very close to that of **12k**, and because the relative proportion of **13k** was very low. **12k**: NMR (90 MHz): δ 0.25 (3H, *s*), 0.27 (3H, *s*), 0.89 (3H, *t*, $J=6.6$ Hz), 1.13 (3H, *s*), 1.71 (2H, *q*, $J=6.6$ Hz), 2.56, 2.73, 2.79, 2.96 (2H, $J=15.3$ Hz), 6.85–7.4 (4H, *m*); MS: *m/e* 220 (M^+ , 2%), 205(16), 191(100), 133(25); Found: C, 70.84; H, 9.50%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

Photoreactions of 10 with 3-Pentanone, Cyclopentanone, Cyclohexanone, Propanal, and Butanal. Following the procedure described above, **12l-p** were prepared from the photoreactions of **10** with appropriate aldehydes and ketones. **12l**: NMR: δ 0.26 (6H, *s*), 0.81 (6H, *t*, $J=6.6$ Hz), 1.44 (4H, *q*, $J=6.6$ Hz). **12m**: NMR: δ 0.23 (6H, *s*), 1.3–2.1 (8H, *m*), 2.85 (2H, *s*), 6.8–7.5 (4H, *m*). **12n**: NMR: δ 0.27 (6H, *s*), 0.9–1.9 (10H, *m*), 2.7 (2H, *s*), 6.7–7.4 (4H, *m*). **12o**: NMR (90 MHz): δ 0.27 (3H, *s*), 0.30 (3H, *s*), 0.97 (3H, *t*, $J=6.6$ Hz), 1.51 (2H, *q*, $J=6.6$ Hz), 2.55–2.97 (2H, *m*), 2.88 (1H, *quint*, $J=6.6$ Hz), 6.9–7.4 (4H, *m*); NMR (C_6D_6) (90 MHz): δ 0.33 (6H, *s*), 0.96 (3H, *t*, $J=6.6$ Hz), 1.3–1.8 (2H, *m*), 2.4–2.9 (2H, *m*) 3.7–4.0 (1H, *m*) 6.85–7.4 (4H, *m*); MS: *m/e* 206 (M^+ , 21%), 191(56), 187(100), 161(21), 133(45); Found: C, 69.69; H, 8.70%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%. **12p**: NMR: δ 0.28 (6H, *s*), 0.7–1.2 (3H, *m*), 1.2–1.8 (4H, *m*), 2.5–3.05 (2H, *m*), 3.7–4.2 (1H, *m*), 6.7–7.4 (4H, *m*); MS: *m/e* 220 (M^+ , 6%), 205(36), 177(100), 161(18), 133(29); Found: C, 70.77; H, 9.45%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

Photoreaction of 9 and Acetophenone with an aq. Cupric Sulfate Filter Solution. A dichloromethane (6 ml) solution of **9** (300 mg, 1.10 mmol) and acetophenone (1.3 g, 11 mmol) was irradiated externally through a cupric sulfate filter solution (80 g

$CuSO_4 \cdot 5H_2O / 1 H_2O$) for 18 h. The other experimental conditions were the same as those for the direct irradiation of **9** and acetophenone. The reaction mixture was subjected to DCC (silica gel, $C_6H_{14}-Et_2O$ (10:1)) twice to give **12h** (83 mg, 19%). The adduct, **12h**, thus obtained was confirmed by NMR and IR spectroscopy. The same adduct was obtained with and without cupric sulfate filter solution.

The UV spectra (CH_2Cl_2) of **9** and acetophenone are as follows: **9**: UV: λ_{max} (ϵ); 264 (2100), 270 (2650), 277.5 nm (1980). Acetophenone: UV: λ_{max} (ϵ); 241 (1530), 279 (1710), 287(sh, 1520), 310 nm(1030).

Photoreaction of 9 with Acetone under Oxygen Atmosphere. A dry acetone solution (200 ml) of **9** (570 mg, 2.1 mmol) in the photoreactor equipped with a dry-ice condenser was irradiated for 7 h. Dry oxygen was bubbled into the solution throughout the irradiation. The reaction mixture was column chromatographed (acidic alumina, hexane) to give **12a** in only 2% (17 mg) yield. Over 91% of **9** (515 mg) was recovered intact.

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References

- (1) For reviews, see (a) L. Jutzi, *Angew. Chem. Int. Ed. Engl.*, **14**, 232 (1975); (b) H. Sakurai, *Kagaku No Ryoiki*, **29**, 742 (1975); (c) L. E. Gusel'nikov, N. S. Nametkin and V. M. Vdokin, *Acc. Chem. Res.*, **8**, 18 (1975); (d) L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979); (e) H. F. Schaefer III, *Acc. Chem. Res.*, **15**, 283 (1982).
- (2) (a) R. Okazaki, K. Sunagawa, K.-T. Kang and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **52**, 496 (1979); (b) K.-T. Kang, R. Okazaki and N. Inamoto, *ibid.*, **52**, 3640 (1979).
- (3) For reviews, see (a) R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **34**, 439 (1976); (b) W. Oppolzer, *Synthesis*, 793 (1978); (c) R. L. Funk and K. P. C. Vollhardt, *Chem. Soc. Rev.*, **9**, 41 (1980); (d) T. Kametani and H. Nemoto, *Tetrahedron*, **37**, 3 (1981).
- (4) P. B. Valkovich and W. P. Weber, *Tetrahedron Lett.*, 2153 (1975).
- (5) D. Tzeng, R. H. Fong, H. S. D. Soysa and W. P. Weber, *J. Organometal. Chem.*, **219**, 153 (1981).
- (6) G. Bertrand, G. Manuel and P. Mazerolles, *Tetrahedron Lett.*, 2149 (1978), T. J. Barton, G. T. Burns, E. V. Arnold and J. Clardy, *ibid.*, **7** (1981).
- (7) (a) M. Ishikawa, T. Fuchikami and M. Kumada, *J. Organometal. Chem.*, **118**, 166 (1976); (b) *Idem, ibid.*, **149**, 37 (1978); (c) M. Ishikawa, H. Sugisawa, K. Yamamoto and M. Kumada, *ibid.*, **179**, 377 (1979).
- (8) Preliminary report: R. Okazaki, K. T. Kang and N. Inamoto, *Tetrahedron Lett.*, 235 (1981).
- (9) C. Eaborn, D. R. M. Walton and M. Chan, *J. Organometal. Chem.*, **9**, 251 (1967).
- (10) H. Sakurai, A. Hosomi and M. Kumada, *Tetrahedron Lett.*, 1757 (1969).

- (11) S. O. A. Rizvi, B. D. Gupta, W. Adcock, D. Doddnel and W. Kitching, *J. Organometal. Chem.*, **63**, 67 (1973).
- (13) C. S. Chundy, M. F. Lapport and T. R. Spalding, *J. Chem. Soc. Dalton*, 558 (1976).
- (14) A. Padwa, *Tetrahedron Lett.*, 3456 (1964); S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **87**, 2996 (1965); C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965); R. Okazaki, K. Tamura, Y. Hirabayashi and N. Inamoto, *J. Chem. Soc. Perkin Trans.*, **1**, 1924 (1976).
- (15) S. H. Band and I. M. T. Davison, *Trans. Faraday Soc.*, **66**, 406 (1970); A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, **94**, 1384 (1972); *ibem, Chem. Lett.*, 193 (1972); H. Sakurai, "Free Radicals," Ed. by J. K. Kochi, Vol. 2, Chapter 25, John Wiley & Sons, New York, 1973.
- (16) H. Gilman and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 5589 (1964).

Molecular Orbital Calculation for Polymeric Beryllium Hydride, Polyethylene and Polymeric Boron Hydride According to the Pseudo-Lattice Method

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The pseudolattice calculations in the CNDO/2 level of approximation are carried out for polymeric beryllium hydride, polyethylene and polymeric boron hydride. Since there is no evidence on the geometry for polymeric boron hydride, the two possible geometries are assumed. One is a polyethylene-type geometry and the other is a polymeric beryllium hydride-type geometry. In order to compare their relative stability, we calculate polyethylene and polymeric beryllium hydride and then compare with polymeric boron hydride having the assumed structures. The total energy calculation indicates that a polymeric beryllium hydride-type geometry is more stable than a polyethylene-type geometry. Our results obtained for polyethylene are in good agreement with those given by CNDO/2 crystal orbital. From the convergence problem with respect to the number of unit cells (M), the calculation with value of 4 for M can be considered to give the convergence limit results.

Introduction

The molecular orbital methods at various levels have been used to discuss the conformational energy of "polymers" by starting with the monomer and adding monomer unit one by one.¹

Even though one can make a guess for a high-molecular weight polymer by continuing this process, the calculation becomes prohibitively difficult as the polymer grows and one never reaches a really large polymer. The polymer has been assumed to be an infinite chain of monomers having translational symmetry. Hence, the pseudolattice method can be also applied to polymeric systems.

In this study, polyethylene, polymeric beryllium hydride and polymeric boron hydride are adopted as model compounds for polymeric systems.

As a first example for our model studies, the polymeric beryllium hydride is treated. Because of experimental difficulties the structure of polymeric beryllium hydride has not yet been determined. It has been suggested² that a hydrogen bonded polymer might be a conceivable structure which could exist in polymeric beryllium hydride. Recent quantum mechanical calculations³ supported this point of view.

Next, we employed the experimental result^{4,5} that polyethylene is planar zig zag in the single crystal. Polyethylene has been studied by the *ab initio* MO method^{6,7} and CNDO/2

crystal orbital.⁸⁻¹⁴ Our MO calculation using the pseudolattice method is performed and compared with that of CNDO/2 crystal orbital.

Finally, polymeric boron hydride is chosen. This model is assumed to have the two possible geometries.

In order to determine the relative stability of these two possible geometries, MO calculations for both geometries are carried out and compared with each other. In this study, the coulomb lattice sums are involved in our MO calculations for polymeric system and because of computational limitation of *ab initio* method, CNDO/2 approximation¹⁵⁻¹⁷ is used.

Theory

(A) *Pseudolattice method.* The pseudolattice method proposed by No and Jhon was applied to several ices¹⁸ and solid HF.¹⁹ In order to give the same environment for all molecules in a chosen cluster, overlap and coulomb integral matrices are composed of the submatrices which are obtained by making use of translational symmetry of molecules.

The pseudolattice method is therefore set up as follows.

(i) If the distances between two molecules is more larger than the interaction range considered (R_c), the overlap and coulomb integrals between the molecules are neglected. Hence, the matrix elements expressed in the atomic basis set can be written as follows.