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PHOTOCHEMISTRY OF DI(9-ANTHRYL)DIMETHYLSILANE AND -GERMANE[1]

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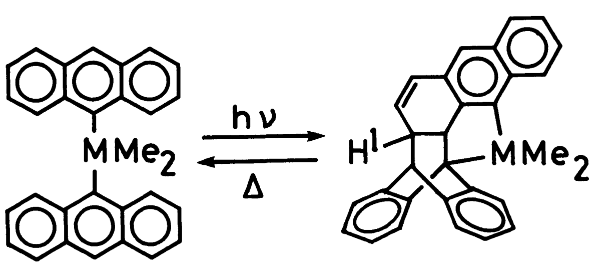
By irradiation, both di(9-anthryl)dimethylsilane and -germane afforded a new type of [4+2] intramolecular addition products that underwent quantitative cycloreversion by thermolysis. The photoproduct from the former was converted to a novel naphthotriptycene derivative.

Anthracene is known to give a photodimer (para-dianthracene) on irradiation. Also, intramolecular reactions are known. For example, di(9-anthryl)methane gave an intramolecular [4+4] addition compound (**1**) with a cyclopropane structure.[2] In view of the known high reactivity of silacyclopropane,[3] we have been interested in the photochemistry of the corresponding silicon and germanium compounds and consequently, we have found an entirely new type of intramolecular photochemical dimerization of anthracene for the title compounds.[4]

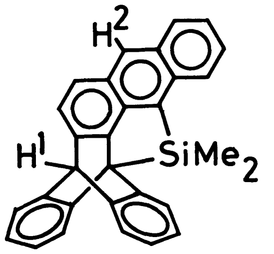
The reaction of 9-anthryllithium, prepared by the reaction of 9-bromoanthracene and t-butyllithium,[5] with dimethyldichlorosilane and dimethyldichlorogermane afforded di(9-anthryl)dimethylsilane (**2**) and -germane (**3**) in 35 and 68% yields, respectively.[6]

Irradiation of a benzene solution of **2** with a high-pressure mercury arc lamp with a Pyrex filter gave a photoproduct **4** in 90% yield.[7] The formation of **4** is formally due to the photochemical [4+2] reaction which may create a mechanistic scrutiny.[8] Expectedly, thermolysis of **4** at 250 °C for 1 h gave the starting **2** quantitatively by cycloreversion.



2: M = Si
3: M = Ge

4: M = Si
6: M = Ge



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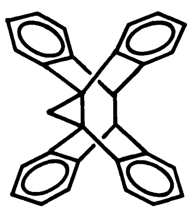

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Existence of three methine and two vinylic protons is characteristic of the structure of **4**. The proton H^1 couples with all those protons as evidenced by a decoupling experiment. Correspondingly, four sp^3 carbons other than those of SiCH$_3$ were observed as three doublets and one singlet in ^{13}C NMR. These data indicate unequivocally the structure shown in the equation.

Dehydrogenation of 4 with DDQ in refluxing chloroform gave a new naphthotriptycene derivative 5 in 70% yield.[9] Structure of 5 is verified by ^{1}H NMR, especially by signals characteristic to triptycene (H^1) and anthracene (H^2).

Irradiation of the germanium analog (3) under similar conditions gave 6 in 71% yield as colorless crystals, mp 194 °C. Similarly to 4, thermal cycloreversion of 6 at 200 °C for 1 h afforded 3 quantitatively. Photochemistry of these and related compounds is in progress. The work was supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid No. 59470013).

References

1) Chemistry of Organosilicon Compounds 203.
2) D. E. Applequist and D. J. Swart, J. Org. Chem., 40, 1800 (1975); W. R. Bergmark, G. Jones, II, T. E. Reinhardt, and A. M. Halpern, J. Am. Chem. Soc., 100, 6665 (1978) and references cited therein. For the photoreactions of anthracene, see: E. J. Bowen, Adv. Photochem., 1, 23 (1963); B. Stevens, ibid., 8, 161 (1971). Photochemistry of bichromophoric systems, see: F. C. DeSchryver, N. Boens, and J. Put, ibid., 10, 359 (1977).
3) D. Seyferth, J. Organomet. Chem., 100, 239 (1975).
4) We are informed by Dr. J-P. Desvergne that the same photoproduct 4 has been obtained from 2 in the Bordeaux group. M. Daney, C. Vanucci, J-P. Desvergne, A. Castellan, and H. Bouas-Laurent, to be published (1985).
5) This new method is better than the use of the corresponding Grignard reagent in both yields and easiness of purification and a number of related compounds were prepared by the method.
6) 2: pale yellow crystals, mp 164-165 °C; MS m/e 412 (M^+, 100); ^{1}H NMR (CCl_4) δ 1.30 (6H, s), 7.1-7.5 (8H, m), 7.8-8.0 (4H, m), 8.3-8.5 (6H, m); high resolution MS, Found: 412.1612, Calcd for $C_{30}H_{24}Si$: 412.1647. 3: pale yellow crystals, mp 166-167 °C; ^{1}H NMR (CCl_4) δ 1.39 (6H, s), 7.0-7.5 (8H, m), 7.8-8.0 (4H, m), 8.2-8.4 (6H, m); high resolution MS, Found: 458.1123, Calcd for $C_{30}H_{24}{}^{74}Ge$: 458.1090.
7) 4: colorless crystals, mp 197 °C (dec), MS m/e 412 (M^+, 100); ^{1}H NMR (CCl_4) δ 0.83 (3H, s), 1.21 (3H, s), 3.23 (1H, dddd, J=11.6, 3.2, 2.1, 1.8 Hz), 3.92 (1H, d, J=11.6 Hz), 4.22 (1H, d, J=2.1 Hz), 5.75 (1H, dd, J=9.6, 3.2 Hz), 6.11 (1H, dd, J=9.6, 1.8 Hz), 6.5-7.8 (13H, m); ^{13}C NMR ($CDCl_3$) δ -2.9 (q), 0.0 (q), 41.4 (d), 45.4 (d), 51.2 (d), 53.1 (s), 20 separated sp^2 carbon signals; ^{29}Si NMR ($CDCl_3$) δ 3.8; high resolution MS, Found: 412.1656.
8) For photochemical [4+2] cycloaddition of anthracene, see: N. C. Yang, D. M. Shold, and J. K. McVey, J. Am. Chem. Soc., 97, 5004 (1975); N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, ibid., 97, 5006 (1975); T. Okada, K. Kida, and N. Mataga, Chem. Phys. Lett., 88, 157 (1982).
9) 5: yellow crystals, mp 245 °C; MS m/e 410 (M^+, 43) ^{1}H NMR ($CDCl_3$) δ 1.27 (6H, s), 5.56 (1H, s), 6.8-7.1 (4H, m), 7.3-7.7 (8H, m), 7.8-8.2 (2H, m), 8.34 (1H, s); ^{13}C NMR ($CDCl_3$) δ 2.7 (q), 48.8 (s), 55.2 (d), 19 separated sp^2 carbon signals; ^{29}Si NMR ($CDCl_3$) δ 12.9; high resolution MS, Found: 410.1482, Calcd for $C_{30}H_{22}Si$: 410.1491.

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