

NOVEL PHOTOREARRANGEMENT OF 3-PHENYL-2-PROPENYLGERMANES

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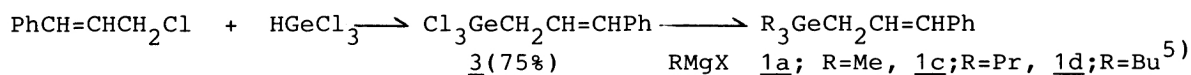
3-Phenyl-2-propenylgermanes, $R_3\text{GeCH}_2\text{CH=CHPh}$ ($R=\text{Me, Et, Pr, Bu, Ph}$) were found to rearrange to 1-phenyl-2-propenylgermanes, $R_3\text{GeCH(Ph)CH=CH}_2$ upon irradiation with low pressure mercury lamp in cyclohexane.

There have been a number of studies on the photochemical rearrangement of organosilanes.¹⁾ For example, silyl substituted phenylpropynes underwent photochemical [1,3]-rearrangement to afford silyl substituted 3-phenylpropadienes.²⁾ On the contrary, very little is known about the photochemical behavior of the organogermanium compounds.¹⁾

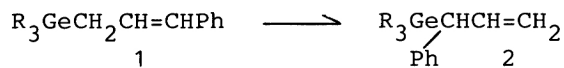
We wish to report here that irradiation of 3-phenyl-2-propenylgermanes, $R_3\text{GeCH}_2\text{CH=CHPh}$ ($R=\text{Me, Et, Pr, Bu, Ph}$), (1a-e) gave 1-phenyl-2-propenylgermanes, $R_3\text{GeCH(Ph)CH=CH}_2$, (2a-e); this is the first example of the photochemical [1,3]-rearrangement of germyl groups in germylelefins.

The starting compounds, 1b and 1e, were prepared by Grignard method.³⁾

$R_3\text{GeBr} + \text{PhCH=CHCH}_2\text{MgCl} \longrightarrow R_3\text{GeCH}_2\text{CH=CHPh}$
Compounds 1a, 1c and 1d were synthesized by reaction of 3-phenyl-2-propenyl-trichlorogermane (3), which was prepared from trichlorogermane and cinnamyl chloride (75%), with appropriate alkylmagnesium halides.



Photolysis of 3-phenyl-2-propenylgermanes (1a-e) upon irradiation with low pressure mercury lamp in cyclohexane afforded their isomers, 1-phenyl-2-propenylgermanes (2a-e).⁶⁾



For example, 3-phenyl-2-propenyltriethylgermane (1b) (0.25 mmol) was irradiated externally with 160 W low pressure mercury lamp in cyclohexane (10 ml) until 1b and 2b attained to a constant ratio (1b/2b=9/91; ca. 22 h) and the resulting mixture was analyzed by GLC. 2b was isolated by preparative GLC, and its structure was confirmed by ¹H-NMR, ¹³C-NMR, and MS spectra [2b; ¹³C-NMR, δ 111.0 (t, $J_{\text{C-H}}$ =156.9 Hz), terminal carbon of C=CH_2 ; MS, m/e =278 (M^+)].

Irradiation of 2b under similar conditions gave the mixture of 1b and 2b in almost same ratio (1b/2b=8/92; ca. 22 h). Thus, 1 and 2 are in photoequilibrium under the irradiation conditions, and the equilibrium lies toward the compound 2. While starting 1 was E-form, recovered 1 was a mixture of E-Z isomer (for example, E/Z ratio of 1b after the irradiation was 1:2.15).

The results of the photolysis of 1a-e were summarized in Table 1.

Table 1. Photorearrangement of 1 to 2^{a)}

| Entry | R | Irr. Time/h | Product ratio (<u>1/2</u>) ^{b)} |
|-------|----|-------------|--|
| 1 | Me | 21 | 19/81 |
| 2 | Et | 22 | 9/91 |
| 3 | Pr | 21 | 16/84 |
| 4 | Bu | 21 | 14/86 |
| 5 | Ph | 22 | 29/71 |

a) Irradiated with low pressure mercury lamp in cyclohexane; concentration, $2.5-3.0 \times 10^{-2}$ mol/l.

b) Since no product other than photoisomer was detected, conversion yield was considered as quantitative.

It is well known that germyl radicals easily add to olefins.⁴⁾ However, in the present photorearrangement, the multi-step reaction mechanism involving the dissociation of 1 to form germyl free radical and recombination of the geminate radical pair may be denied, since no hexyltriethylgermanes were detected by GC-MS upon irradiation in the presence of 1-hexene (5.0 mol/mol of 1) under the similar conditions to entry 2 in Table 1. In every case of the photoreaction of 1a-e, reaction is very clean and formation of by-products such as digermane was not observed by GLC. Also no thermal isomerization of 1 was observed even after heating for 41 h at 150°C in cyclohexane solution in a sealed ampoule. These facts and existence of photoequilibrium indicate the present rearrangement proceeds via orbital symmetry allowed concerted [1,3]-sigmatropic mechanism.

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References

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- 2) M. Ishikawa, H. Sugawara, L. Fabry, and M. Kumada, J. Organomet. Chem., 161, 299 (1978).
- 3) R. M. G. Roberts and Faig Ei Kassi, J. Organomet. Chem., 12, 79 (1968).
- 4) M. Lesble, P. Mazerolles, and J. Satge, "The Organic Compounds of Germanium," Wiley-interscience, New York (1971), Chap. 4.
- 5) Bp(°C/mmHg): 1a, 93-93.5/3; 1c, 122-124/0.3; 1d, 150-151/0.3. Mp: 1e, 79.5-81°C.
- 6) All products gave satisfactory spectral data. Data of 2b,e are shown as example.
2b: ¹H-NMR; δ 0.33-1.27(m, 15H), 3.33(d, J=9.6 Hz, 1H), 4.90(d, J=11.4 Hz, 1H), 4.94(d, J=16.8 Hz, 1H), 6.28(m, 1H), 7.00-7.57(m, 5H); ¹³C-NMR; δ 3.5, 8.8, 42.0, 111.0(t, J_{C-H}=156.9 Hz), 124.3, 126.8, 128.2, 129.0, 143.1. MS; m/e=278 (M⁺).
2e: ¹H-NMR; δ 4.01(d, J=10.2 Hz, 1H), 4.91(d, J=16.2 Hz, 1H), 4.94(d, J=12.6 Hz, 1H), 6.30(m, 1H), 6.83-7.77(m, 20 H); ¹³C-NMR; δ 43.3, 113.5(t, J_{C-H}=158.7 Hz), 125.3, 127.9, 128.2, 128.4, 128.9, 134.0, 135.5, 138.3, 140.8. MS; m/e=422(M⁺).

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