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NOVEL PHOTOREARRANGEMENT OF 3-PHENYL-2-PROPENYLGERMANES

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3-Phenyl-2-propenylgermanes, $R_3GeCH_2CH=CHPh$ (R=Me, Et, Pr, Bu, Ph) were found to rearrange to 1-phenyl-2-propenylgermanes, $R_3GeCH(Ph)CH=CH_2$ 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, $R_3GeCH_2CH=CHPh$ (R=Me, Et, Pr, Bu, Ph), (1a-e) gave 1-phenyl-2-propenylgermanes, $R_3GeCH(Ph)CH=CH_2$,(2a-e); this is the first example of the photochemical [1,3]-rearrangement of germyl groups in germylolefins.

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

$$R_3GeBr + PhCH=CHCH_2MgCl \longrightarrow R_3GeCH_2CH=CHPh$$

Compounds 1a, 1c and 1d were synthesized by reaction of 3-phenyl-2-propenyltrichlorogermane (3), which was prepared from trichlorogermane and cinnamyl chloride (75%), with appropriate alkylmagnesium halides.

$$PhCH=CHCH_2Cl + HGeCl_3 \longrightarrow \underset{3\,(75\%)}{Cl_3GeCH_2CH=CHPh} \xrightarrow{RMgX} R_3GeCH_2CH=CHPh$$

1a; R=Me, 1c;R=Pr, 1d;R=Bu[5]

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]

$$\underset{1}{R_3GeCH_2CH=CHPh} \longrightarrow \underset{Ph}{R_3GeCHCH=CH_2}\ \ \underset{2}{}$$

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 ^{1}H-NMR, ^{13}C-NMR,and MS spectra [2b;^{13}C-NMR, δ 111.0 (t, J_{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 (1/2)[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 x 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. Sugasawa, 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: ^{1}H-NMR; δ0.33-1.27(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); ^{13}C-NMR; δ3.5, 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: ^{1}H-NMR; δ4.01(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); ^{13}C-NMR; δ43.3, 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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