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REVERSIBILITY IN THE HOMOLYTIC AROMATIC SUBSTITUTION WITH SILYL AND GERMYL RADICALS[#,1)]

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The 3,6-bis(trimethylsilyl)cyclohexadienyl radical (**1**), generated from the corresponding cyclohexadiene, gave the expected *p*-bis(trimethylsilyl)benzene (**4**) at 0°C. At 130°C, however, the reaction afforded trimethylsilylbenzene, **4**, and *m*-bis(trimethylsilyl)benzene in 62, 17, and 5% yield, respectively. The suggested elimination of the trimethylsilyl radical from the cyclohexadienyl radical is demonstrated by ESR.

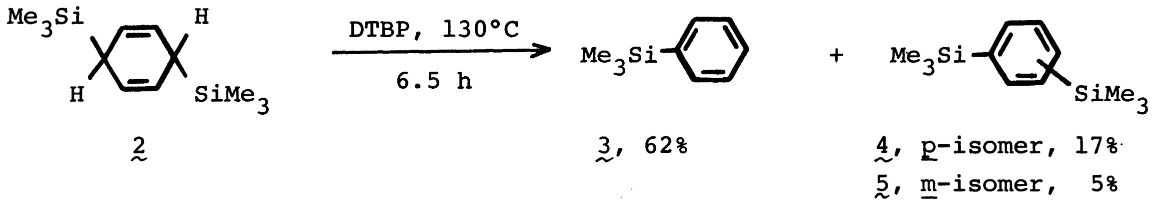
There is a substantial body of evidence for addition of free radicals to aromatics leading to aromatic substitution.2) One notable example is the homolytic aromatic arylation in which roles of the intermediate aryl-substituted cyclohexadienyl radicals as well as the directive effect of substituents have been disclosed by pioneering works of Hey and coworkers3) and Simamura and coworkers.4) Some years ago, by our hands, the homolytic aromatic silylation was studied also5) and later, the intermediate silyl-substituted cyclohexadienyl radicals were detected directly by ESR.6) The structure of the intermediate radicals has been elucidated both experimentally7) and theoretically.7,8)

However, the problem whether the step of free-radical addition to aromatics is reversible or not remains unsolved, no decisive evidence for the reversibility in the addition of carbon-centered radicals being found up to date.2) On the other hand, Eaborn et al. have suggested the reversible addition of a silyl radical to benzene on the basis of the temperature dependence of the yields in the reaction of bis(trimethylsilyl)mercury with benzene.9) They also reported that a germyl radical does not undergo addition to aromatics.10) Jackson interpreted such a difference in the behavior of group IVB radicals toward aromatic substitution reactions on the basis of the difference of C-M bond energies among C-C, C-Si, and C-Ge bonds.11) In this paper, we report the chemical and ESR spectroscopic evidence for the reversible addition of silyl and germyl radicals in homolytic aromatic substitution for the first time.

As demonstrated by ESR,7) the 3,6-bis(trimethylsilyl)cyclohexadienyl radical (**1**) exists as a paramagnetic species of the highest steady-state concentration during the reaction of 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene (**2**) and photochemically generated *tert*-butoxy radicals at a low temperature. In order to shed light on the fate of this interesting radical, we have investigated the products of the reaction of **2** with *tert*-butoxy radicals in details.

[#] Dedicated to Professor Osamu Simamura on the occasion of his 70th birthday.

When a 1:1 mixture of **2** and di-*tert*-butyl peroxide (DTBP) was heated in a sealed tube under nitrogen at 130°C for a period of 6.5h, the main products were analyzed to be phenyltrimethylsilane (**3**), *p*- (**4**), and *m*-bis(trimethylsilyl)benzene (**5**) in 62, 17, and 5% yield, respectively. No *o*-isomer was obtained.

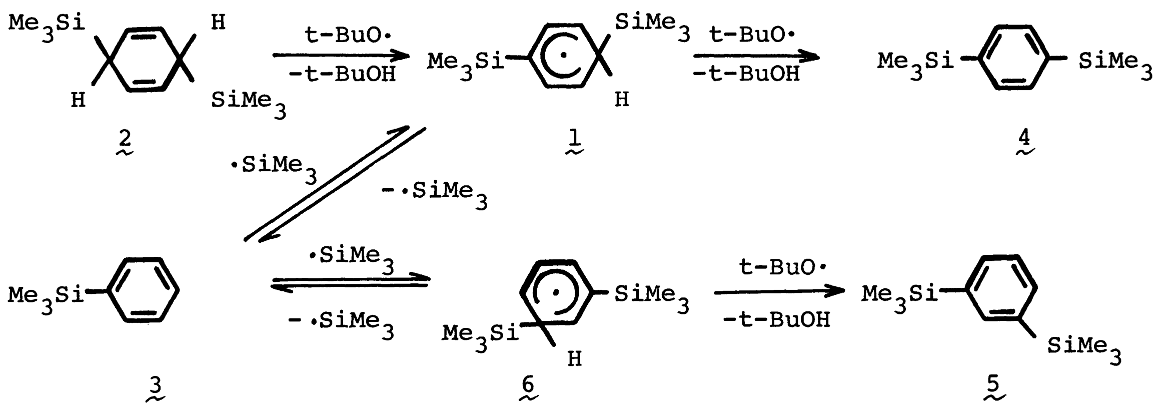


The total yield of products based on **2** was over 80%. In contrast, the photochemical reaction of **2** with DTBP in hexane at 0°C for a period of 3.5h resulted in the remarkably different product distribution:

$$\mathbf{2} \xrightarrow[\text{3.5 h}]{\text{DTBP, HP-lamp}} \underset{1\%}{\mathbf{3}} + \underset{35\%}{\mathbf{4}} + \underset{0\%}{\mathbf{5}}$$

Poor material balance of the latter reaction may originate in the competitive photochemical isomerization of **2**, which was revealed by an independent experiments in the absence of DTBP.[12)] It should be noted that **3**, produced by the elimination of a trimethylsilyl radical from the intermediate radical **1**, was detected only in the reaction at a high temperature, while the yield of **3** amounted to only 1% in the reaction at 0°C.

The following scheme may explain the reaction pathways of the radical (**1**) reasonably.



Generation of **1** from **2** has been verified by an ESR experiment,[7)] so that the formation of **3** is best explained by spontaneous elimination of the trimethylsilyl radical from **1**. Reversible addition of the trimethylsilyl radical to phenyltrimethylsilane (3) accounts for the formation of m-bis(trimethylsilyl)benzene satisfactorily, although direct rearrangement from 1 to 2,6-bis(trimethylsilyl)cyclohexadienyl radical (6) can not be excluded completely at this moment. The results also indicate that the spontaneous elimination of the trimethylsilyl radical from 1 is preferred to the hydrogen abstraction to afford 4 at a high temperature, while the former reaction is not important at a low temperature.

The actual intermediacy of the trimethylsilyl radical in the reaction of 1 to give 3, was proved by spin-trapping experiments. When a mixture of 2, DTBP, and 1,1-di-tert-butylethylene as a spin-trap was photolyzed in an ESR cavity at temperatures lower than 60°C, the ESR spectrum of 1 was observed, but at temperatures higher than 60°C only the ESR spectrum of the silyl-radical adduct to 1,1-di-tert-butylethylene (7) was detected by ESR with high signal intensity. A similar experiment with thermally generated tert-butoxy radicals from di-tert-butyl peroxyoxalate gave an ESR spectrum of 7 at 40°C, although the signal intensity was rather low. The hfsc values of 7 were 15.6G for two β-methylene protons and 0.35G for 18 protons of two tert-butyl groups, in good agreement with those reported previously by Griller and Ingold.[13)]

$$\text{t-BuO}\cdot + \mathbf{2} \longrightarrow \mathbf{1}$$

$$\mathbf{1} \longrightarrow \mathbf{3} + \mathrm{Me_3Si}\cdot$$

$$\mathrm{Me_3Si}\cdot + (\text{t-Bu})_2\mathrm{C{=}CH_2} \longrightarrow (\text{t-Bu})_2\dot{\mathrm{C}}\text{-}\mathrm{CH_2SiMe_3}$$

7

These facts lead to the conclusion that the cyclohexadienyl radical (1) becomes kinetically unstable at temperatures higher than 40-60°C and eliminates the trimethylsilyl radical which can be trapped successfully by 1,1-di-tert-butylethylene to give 7. Thus, the results of ESR experiments coincide with those of the product study quite nicely.

Similarly, when a mixture of 3,6-bis(trimethylgermyl)cyclohexadiene (8), 1,1-di-tert-butylethylene, and DTBP in hexane was photolyzed, the ESR spectrum of the expected 3,6-bis(trimethylgermyl)cyclohexadienyl radical (9) was obtained only at temperatures below -110°C. However, above the temperature, the adduct radical, $(\text{t-Bu})_2\dot{\mathrm{C}}\text{-}\mathrm{CH_2GeMe_3}$, was detected as a sole paramagnetic species. Apparently, the trimethylgermyl radical was eliminated from 9 at a much lower temperature than the trimethylsilyl radical from 1. The ready dissociation of the trimethylgermyl radical from the cyclohexadienyl radical explains the inertness of the germyl radical toward the homolytic aromatic substitution.

These chemical and ESR spectroscopic studies clearly demonstrate that the addition reaction of both trimethylsilyl and trimethylgermyl radicals to benzene is reversible. Elimination of the trimethylsilyl radical from the cyclohexadienyl radical becomes important only at a relatively high temperature so that homolytic aromatic silylation can proceed rather efficiently under the condition of a high concentration of peroxide. It would be predictable that homolytic aromatic germylation would be feasible if we could carry out the reaction at a very low temperature.

We have already demonstrated experimentally7) and theoretically8) that the 6-silyl group in silyl-substituted cyclohexadienyl radicals occupies the axial position of an envelope form of the cyclohexadienyl radical at the preferred conformation where substantial spin delocalization to the C-Si bond is noted. The out-of-plane angle was estimated to be +4° by CNDO/27) and +4.3° by ab initio calculations.8) The analyses of hfsc by using the Heller-McConnell equation,14) the out-of-plane angles of both 1 and 9 were estimated to be 6-7° and 10°, respectively.12) The distorted structures of 6-silyl and 6-germyl radicals with considerable spin delocalization onto the C-Si and C-Ge bonds may be related to the reversibility of the addition of silyl and germyl radicals to aromatics.

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