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GENERATION AND REACTIVITY OF BIS(2,6-DIETHYLPHENYL)GERMANIUM(II)

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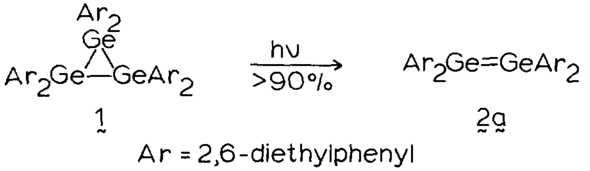
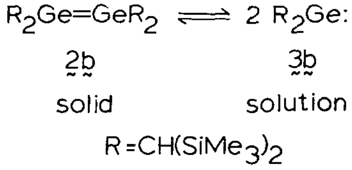
Abstract: The title intermediate (3a) is produced on photolysis of hexakis(2,6-diethylphenyl)cyclotrigermane (1) or bis(2,6-diethylphenyl)bis(trimethylsilyl)germane (4) as evidenced by trapping experiments, and thermally dimerizes to tetrakis(2,6-diethylphenyl)digermene (2a). Diarylgermylenes such as 3a do not form stable triethylamine adducts (e.g. 5a) as has been previously reported.

We recently reported the crystal structure of the first, stable tetraaryldigermene, tetrakis(2,6-diethylphenyl)digermene (2a), obtained by the exceptionally clean photolysis of hexakis(2,6-diethylphenyl)cyclotrigermane (1) (eqn. 1).[1] Compound 2a maintains its dimeric structure in solution unlike the recently characterized tetrakis[bis(trimethylsilyl)methyl]digermene 2b, which dissociates to the corresponding germylene, bis[bis(trimethylsilyl)methyl]germanium(II) (3b) in solution (eqn. 2).[2]



Equation 1

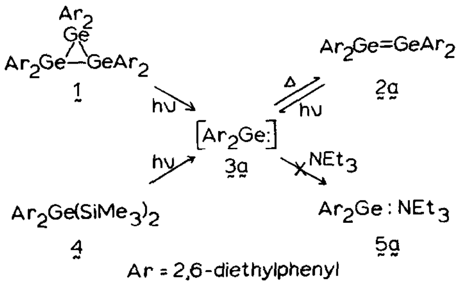


$$R_2Ge{=}GeR_2 \rightleftharpoons 2\ R_2Ge{:}$$

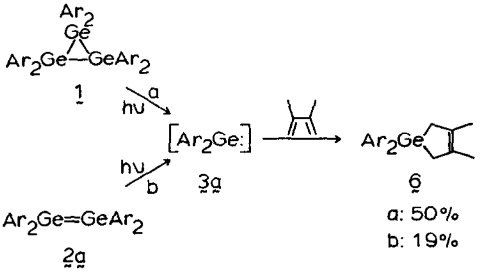
Equation 2

We describe herein that 1) bis(2,6-diethylphenyl)germanium(II) (3a) is produced during the photolysis of cyclotrigermane 1 or on irradiation of digermene 2a,[3] 2) germylene 3a is also generated by photolysis of bis(2,6-diethylphenyl)bis(trimethylsilyl)germane (4) and thermally dimerizes to form digermene 2a,[4] and 3) compounds such as 3a do not form stable adducts (e.g. 5a) with triethylamine as has been previously claimed. (Scheme I on next page).[5]

Scheme I



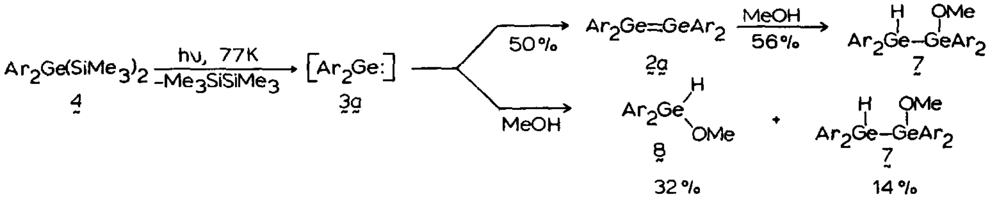
Scheme II



Irradiation of cyclotrigermane 1 in the presence of excess 2,3-dimethyl-1,4-butadiene provided 1,1-bis(2,6-diethylphenyl)-3,4-dimethyl-1-germacyclopent-3-ene (6) in 50% isolated yield.[6] If the course of this reaction was monitored by ^{1}H-NMR spectroscopy, signals due to compound 6 and digermene 2a were observed at the initial stage of photolysis. After the starting material (1) had been consumed, further irradiation led to the disappearance of digermene 2a and concomitant formation of additional 6. Germacyclopentene 6 was also produced and was isolated in 19% yield when digermene 2a (prepared from 1) was irradiated in the presence of 2,3-dimethylbutadiene. These results indicate germylene 3a is generated by photolysis of compound 1 or digermene 2a and is trapped[7,8] under these conditions by the butadiene to provide compound 6 (Scheme II).

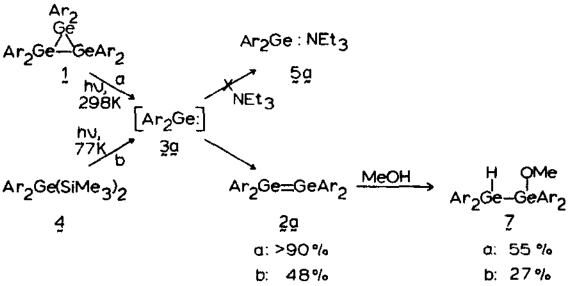
Germylene 3a was independently prepared by photolysis of disilagermane 4[6] as follows: Irradiation of compound 4 in methylcyclohexane-d_{14} glass at 77K for 10 min led to red coloration of the glass which on annealing to room temperature dissipated to give a yellow solution containing digermene 2a and hexamethyldisilane in addition to 4. Repetitive photolysis at 77K, followed by annealing, for 6 h produced digermene 2a in 50% yield at 48% conversion. The formation of digermene 2a was further confirmed by quenching the photolysate with methanol which furnished methoxydigermane 7[1] in 28% yield based on starting material (Scheme III). If disilagermane 4 was photolyzed in frozen methanol: THF-d_8 mixture as described above for 7.5 h, compound 7 and bis(2,6-diethylphenyl)methoxygermane (8)[6] were formed in 14% and 32% yield at 60% conversion, respectively (Scheme III). These results are consistent with the following interpretation: Photolysis of compound 4 provides germylene 3a which undergoes thermal dimerization to form digermene 2a. In the presence of methanol, species 3a is partly trapped as methanol adduct 8.[9]

Scheme III



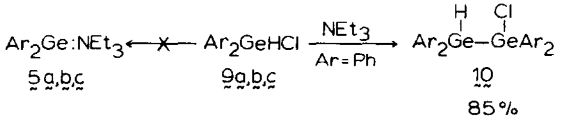
Having established that germylene 3a is produced by photolysis of cyclotrigermane 1 or disilagermane 4, the photolyses of these compounds were conducted in the presence of triethylamine in order to stabilize monomeric 3a by complex formation (i.e. 5a).[5] Irradiation of compound 1 at 298K or disilagermane 4 at 77K in the presence of excess triethylamine did not lead to the formation of adduct 5a in detectable amounts and, as described above, provided digermene 2a in >90% or 48% yield at 90% or 52% conversion, respectively. Treatment of the photolysates with methanol furnished methoxydigermane 7 in 55% or 27% yield based on compounds 1 or 4, respectively (Scheme IV).

Scheme IV



These results indicate that triethylamine does not prevent dimerization of germylene 3a (by stable adduct formation) under photochemical or thermal conditions. These results appeared to conflict with the behavior of other unstable diarylgermylenes, which were reported to form triethylamine complexes upon dehydrochlorination of diarylchlorogermanes.[5] Thus, reactions of bis(2,6-diethylphenyl)chlorogermane (9a),[6] dimesitylchlorogermane (9b)[6] and diphenylchlorogermane (9c)[6] with triethylamine were investigated. Treatment of either chlorogermane 9a or 9b with excess triethylamine (2.4 or 4.0 equiv.) in dry benzene-d_6 at room temperature did not provide germylene complexes 5a or 5b; in fact, no reaction was observed (^{1}H-NMR, 250 MHz) after 63 and 24 h, respectively. In contrast, addition of excess triethylamine (4.4 equiv) to chlorogermane 9c in C_6D_6 (0.05 M) led to the precipitation of triethylamine hydrochloride. A ^{1}H-NMR spectrum (250 MHz) of the mixture revealed that starting material was completely consumed after 12 h at room temperature. The major product, which was present at the initial stage of this reaction, was tetraphenylchlorodigermane (10),[6,10] formed in 85% yield. In addition, two other unidentified Ge-H compounds were produced and together with compound 10 accounted for the total amount of diphenylchlorogermane initially present (Scheme V).

Scheme V



a: Ar = 2,6-diethylphenyl
b: Ar = mesityl
c: Ar = phenyl

At no time during this reaction were significant amounts of complex 5c present. We can offer no explanation for the discrepancy between our results and those previously reported.[5] We note that the results of many trapping reactions, performed at elevated temperatures that were cited as evidence for the formation of compound **5c** at room temperature,[5] can also be rationalized by the intermediacy of digermane **10**. It has been reported that this compound decomposes to chlorogermane **9c** and poly(diphenylgermylene) on heating.[10]

In conclusion, we have presented evidence for the formation of germylene **3a** by photolysis of cyclotrigermane **1** or disilagermane **4**. In the absence of trapping agents, germylene **3a** dimerizes to form digermene **2a**. Triethylamine does not prevent the latter process under thermal or photochemical conditions. Finally, we have obtained no evidence for the formation of *stable* triethylamine complexes of diarylgermylenes under conditions previously reported for their preparation.[11]

References and Footnotes

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4. For studies involving related trisilanes see a) Fink, M.J.; Michalczyk, M.J.; Haller, K.J.; Michl, J.; West, R., *Organometallics*, *1984*, **3**, 793. b) Orahnak, T.S.; Michl, J. ; West, R., *J. Am. Chem. Soc.*, *1979*, **101**, 5427.
5. a) For a recent review see: Satge, J., *Pure & Appl. Chem.*, *1984*, **56**, 137. b) Riviere, P.; Castel, A.; Satge, J., *J. Organomet. Chem.*, *1982*, **232**, 123. c) Riviere, P. Satge, J.; Castel, A., *C.R. Hebd. Seances Acad. Sci. Ser. C.*, *1975*, **281**, 835.
6. All compounds were identified by their IR, ^{1}H-NMR (250 MHz) and mass spectra. Full experimental details are available from the authors on request.
7. The thermal cycloadditions of other unstable germylenes to butadienes have been reported. a)Schriever, M.; Neumann, W.P., *J. Am. Chem. Soc.*, *1983*, **105**, 897. b) Ma, E.C.-L.; Kobayashi, K.; Barzilai, M.W.; Gaspar, P.P.; *J. Organomet. Chem.*, *1982*, **224**, C13 and references therein.
8. Photolysis of **1** very likely generates **2a** and **3a** directly.
9. Reaction of germylene **3b** with methanol and ethanol provides analogous products. Lappert, M.F.; Miles, S.J.; Atwood, J.L.; Zaworotko, M.J.; Carty, A.J., *J. Organomet. Chem.*, *1981*, **212**, C4.
10. Riviere, P.; Satge, J., *Helv. Chim. Acta.*, 1972, **55**, 1164.
11. S.C.: National Sciences and Engineering Research Council NATO Postdoctoral Fellow. Financial Support: The National Science Foundation, U.S.A. Yoshitomi Industries Ltd., and Kao Corporation, Japan. High resolution mass spectra: NIH Grant RR00317 (principal investigator, Professor K. Biemann).

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