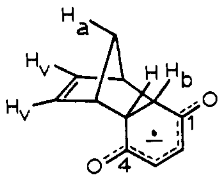
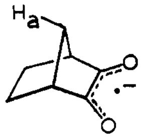
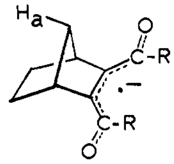


5

The splitting by H_b of 5.7 gauss indicates that $\rho_{C\text{-}1} = \rho_{C\text{-}4}$ in **5** is about $0.5\rho_{C-\pi}$ in **4a** (H_b = 10.2 gauss). On this basis one might predict for **5** that H_v = 0.5 (0.4) and H_a = 0.5 (2.7) gauss. The actual value of H_v of 0.2 gauss in **5** is in excellent agreement with this prediction. However, the experimental value of a_a^H = 0.2 gauss in **5** is surprisingly low.[8] This may indicate the importance of coplanarity of the four bonds and the p_z orbital in the hyperfine splitting of H_a in **4a** and in **5**. It is also of considerable interest that in **1a**–**4a** but not in **5** the coefficients for the carbonyl carbon atom in the highest occupied molecular orbital have the same sign. In **5** the Hückel molecular orbital coefficients for C-1 and C-4 are of opposite sign and $(c_1 + c_4)^2$ will be zero.[9] In a similar manner we predict that the value of a_a^H in **6** (a^H = 6.5 gauss[4]) will be much greater than in **7**.



6



7

Acknowledgment. Dr. G. Underwood detected the acyclic semidiones from ethyl acetate and ethyl isobutyrate in the presence or sodium–potassium alloy. These experiments led directly to the present work.

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(7) S. F. Nelsen and B. M. Trost, *Tetrahedron Letters*, 5737 (1966).

(8) The assignment of this splitting to the *anti*-hydrogen appears very questionable to us.

(9) For a discussion of the point that $a^H = Q(c_1 + c_4)^2$ and not $a^H = Q(c_1^2 + c_4^2)$ see D. H. Whiffen, *Mol. Phys.*, **6**, 224 (1963).

(10) National Aeronautics and Space Administration Predoctoral Fellow, 1965–1967.

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Germylation of Ferrocene under Friedel–Crafts Conditions. The Question of the Existence of Germonium Ions[1]

Sir:

In contrast to its carbon analog, the siliconium ion, $(C_6H_5)_3Si^+$, is not stabilized by π-orbital overlap,[2] although silicon of the SiH_3 group has been shown to withdraw electrons into its 3d orbitals from the benzene ring.[3] While the extent of delocalization in the case of silicon would be expected to exceed that to be found in the analogous case of germanium,[4] the latter, due to greater ease of ionization of the germanium–halogen bond, might be expected to form a cation more readily than silicon.[5,6] Nevertheless, several reported attempts to detect the existence of the germonium ion, $(C_6H_5)_3Ge^+$, have not been successful.[5,7,8] An investigation of dimethyldichlorogermane in water has indicated that hydrolysis may proceed *via* $(CH_3)_2Ge^{2+}$.[9]

Recently, we reported the first successful use of halosilanes in reactions analogous to Friedel–Crafts alkylation.[10] Ferrocene was silylated by chloro- and aminosilanes in the presence of anhydrous aluminum chloride, serving as evidence that siliconium ion, probably stabilized as a ferrocene π complex, can be generated under these conditions. We now report that germonium ion, presumably also in the form of a nonclassical intermediate in which $\geqslant Ge^+$ is π-bonded to the cyclopentadienyl ring of ferrocene, is capable of forming *via* the aluminum chloride catalyzed reaction of that compound with bis(N,N-dimethylamino)dichlorogermane. Germanium derivatives of ferrocene have been isolated in a combined yield of >50%.

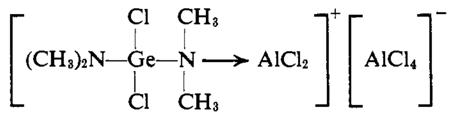
$$\mathrm{4FcH + [(CH_3)_2N]_2GeCl_2 \xrightarrow[(H_2O)]{2AlCl_3} \underset{50\%}{(Fc_2GeO)_3} + \underset{<1\%}{(Fc_3Ge)_2O}}$$

(Fc = ferrocenyl)

Silylated ferrocenes totaling only 9% were obtained from a reaction performed identically with bis(N,N-dimethylamino)dichlorosilane as reactant.

$$\mathrm{4FcH + [(CH_3)_2N]_2SiCl_2 \xrightarrow[(H_2O)]{2AlCl_3} \underset{4\%}{Fc_2Si(OH)_2} + \underset{5\%}{Fc_3SiOH}}$$

The greater reactivity of germanium is attributed to a combination of factors: (1) a more effective ferrocene π complexing of germanium due to its greater size and positive character;[6] (2) the (predicted) weaker bond strength of Ge–N;[11] (3) the (predicted) greater basicity of nitrogen attached to germanium[11] resulting in a more effective coordination of aluminum chloride to nitrogen. Concerning the last factor, a catalytic, dimolar aluminum chloride complex of a donor species, *e.g.*



$$\left[\mathrm{(CH_3)_2N-\underset{Cl}{\overset{Cl}{Ge}}-\underset{CH_3}{\overset{CH_3}{N}}\longrightarrow AlCl_2}\right]^+\left[\mathrm{AlCl_4}\right]^-$$

may be applicable to germanium as well as silicon,[10] but this has not yet been established. Regarding the first two factors, it is envisioned that nucleophilic attack of ferrocene on germanium *via* the ring π system occurs, in a concerted displacement of a negative ionic species, with the "pull" exerted by the catalyst.[12]

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(1) Presented at the 3rd International Symposium on Organometallic Chemistry, Munich, Aug 28–Sept 1, 1967, Abstracts, p 174.

(2) H. Gilman and G. E. Dunn, *Chem. Rev.*, **52**, 77 (1953); J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4034 (1963).

(3) L. Goodman, A. H. Konstam, and L. H. Sommer, *ibid.*, **87**, 1012 (1965).

(4) W. K. Musker and G. B. Savitsky, *J. Phys. Chem.*, **71**, 431 (1967).

(5) O. H. Johnson and E. A. Schmall, *J. Am. Chem. Soc.*, **80**, 2931 (1958).

(6) It is noteworthy, however, that a large body of evidence has been accumulated based on which germanium has been assigned an electronegativity value *higher* than that for silicon, which is contrary to prediction based on customary interpretation of the periodic table: A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958).

(7) A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

(8) M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 1238 (1961).

(9) E. G. Rochow and A. L. Allred, *J. Am. Chem. Soc.*, **77**, 4489 (1955).

(10) G. P. Sollott and W. R. Peterson, Jr., *ibid.*, **89**, 5054 (1967).

(11) K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

Analogous to the silicon case,[10] the Ge–N bond is cleaved by aluminum chloride to give Ge–Cl (see below); however, concerted displacement of dimethylamide ion appears to take precedence over that of chloride ion for the reasons discussed below. After the "push-pull" step, the transient, π-stabilized tetracoordinate germonium ion undergoes rearrangement to the ferrocene exocyclic σ complex to produce the germylated ferrocene on loss of a proton.[12]

The lower proportionate yield of tertiary product obtained in the case of germanium (see above equations) prompted an examination of the effect on that reaction of doubling the amount of aluminum chloride. No significant change in yields occurred, demonstrating that the paucity of tertiary product was *not* due to a shortage of catalyst as a result of greater utilization in the formation of secondary product. In the light of the following relative bond strengths, Ge–Cl > Si–Cl[13] > Si–N[14] > Ge–N,[11] the result is explainable on the basis that with germanium the concerted displacement of amide ion occurs rather than the displacement of chloride ion. This was supported by the finding that tetrakis(N,N-dimethylamino)germane gave tertiary products in a combined yield of 46%.

$$4\mathrm{FcH} + [(\mathrm{CH_3})_2\mathrm{N}]_4\mathrm{Ge} \xrightarrow[(\mathrm{H_2O})]{4\mathrm{AlCl_3}} \underset{21\%}{\mathrm{Fc_3GeCl}} + \underset{25\%}{(\mathrm{Fc_3Ge})_2\mathrm{O}}$$

Isolation of triferrocenylchlorogermane from this reaction demonstrated that aluminum chloride is capable of cleaving Ge–N to give Ge–Cl, and at the same time provided an explanation for the fact that no quaternary germane was obtained. Such ferrocene π-stabilized germonium species as $[(\mathrm{CH_3})_2\mathrm{N}]_3\mathrm{Ge}^+$, $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{Ge}^+\mathrm{Fc}$, and $(\mathrm{CH_3})_2\mathrm{NGe}^+\mathrm{Fc_2}$ or $\mathrm{ClGe}^+\mathrm{Fc_2}$ are considered to be generated from the tetraminogermane in a stepwise process, $(\mathrm{CH_3})_2\mathrm{NGe}^+\mathrm{Cl_2}$, $\mathrm{FcGe}^+\mathrm{Cl_2}$, and $\mathrm{Fc_2Ge}^+\mathrm{Cl}$[15] (as well as analogous species in the silicon case), from the diaminodichlorogermane.

Reactions in this work were performed (0.05 mole of germane or silane; 20 hr of reflux in 350 ml of *n*-octane) similarly to those previously reported for the silylation of ferrocene.[10] Products[16] were isolated *via* chromatography on silica gel: $(\mathrm{Fc_2GeO})_3$, orange crystals from benzene, mp 338–340°; $(\mathrm{Fc_3Ge})_2\mathrm{O}$, golden-tan platelets from ethanol, mp 205–206°; $\mathrm{Fc_3GeCl}$, golden platelets from *n*-heptane, mp 224–226° dec (heating 10°/min); $\mathrm{Fc_2Si(OH)_2}$, yellow-orange powder from *n*-heptane, mp 167–168.5°; $\mathrm{Fc_3SiOH}$, short orange-brown needles from *n*-heptane, mp 193.5–195°.

For the most part, organogermanium compounds are prepared by means of organometallic reagents.[17] The few previously reported germanium derivatives of ferrocene have been prepared in this manner.[18] The germylation of ferrocene under Friedel–Crafts conditions offers a new, facile method of establishing bonds between germanium and ferrocene carbon without the need to prepare an intermediate metallic derivative of ferrocene. Investigations are in progress to determine the scope, and to verify several aspects of the mechanism.

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[12] *Cf.* silylation of ferrocene.[10]

[13] H. A. Skinner, *Trans. Faraday Soc.*, **41**, 645 (1945).

[14] A. E. Beezer and C. T. Mortimer, *J. Chem. Soc., Sect. A*, 514 (1966).

[15] This species is questionable, however, since it requires cleavage of the Ge–Cl bond. The small quantity of tertiary product isolated may have been generated *via* disproportionation.

[16] Satisfactory analytical data including molecular weights were obtained; infrared spectra taken with Nujol mulls were consistent with assigned structures.

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[18] D. Seyferth, H. P. Hofman, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1**, 227 (1962); H. Rosenberg and R. V. Schenk, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 8–13, 1963, p 76Q.

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Chemical Shift Anisotropies from Nuclear Magnetic Resonance Studies in Liquid Crystals

Sir:

The anisotropy in the nuclear magnetic shielding in a molecule can be determined from the shift in the nuclear magnetic resonance signal that arises from partial molecular alignment in a magnetic field.[1] Such alignment can be easily achieved for liquid crystals[2] and for molecules dissolved in liquid crystals.[3] In order to determine a chemical shift anisotropy, two pieces of experimental information are required: (1) the degree of alignment of the molecule and (2) the shift of the magnetic resonance between the partially aligned state and the isotropic state of the molecule. In a nematic liquid crystal, the degree of alignment is obtained from measurements of the direct nuclear dipole–dipole interactions which appear in the spectrum as averages over the anisotropic motion of the molecule. The spectral shift between the partially aligned and the isotropic states is usually obtained by measuring the shift of the observed spectrum as the liquid-crystal solvent changes from the nematic state to the isotropic state.

The position of the spectrum is determined with respect to some reference compound. TMS has generally been used as an internal reference for proton chemical shift anisotropies with the assumption that bulk susceptibility and solvent contributions to the proton magnetic shielding will be the same for a partially aligned molecule as for a nonaligned molecule. These contributions were originally thought to be small because it was found that the proton chemical shift anisotropy appeared to be -23 ± 4 ppm when internally referenced with TMS, while it changed to an apparent -28 ± 3 ppm when externally referenced with TMS.[4]

Recently it has been pointed out[5] that the bulk susceptibility of the liquid-crystal solvent and other environmental effects that change when the nematic to isotropic phase transition occurs are not negligible and would account for the unusually large shift anisotropy reported for $\mathrm{CH_3F}$ externally referenced with TMS.[6]

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[2] R. D. Spence, H. A. Moses, and P. L. Jain, *J. Chem. Phys.*, **21**, 380 (1953).

[3] A. Saupe and G. Englert, *Phys. Rev. Letters*, **11**, 462 (1963).

[4] B. J. Lavery, Ph.D. Thesis, The Pennsylvania State University, 1967.

[5] A. D. Buckingham and E. E. Burnell, *J. Am. Chem. Soc.*, **89**, 3341 (1967).