by means of optically active transition metal complex anions.

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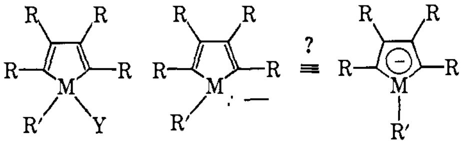
Functionally Substituted Sila- and Germacyclopentadienes. Anion Formation

Sir:

There has been much interest in whether anions (II) derived from sila- or germacyclopentadienes (I) would be stabilized by resonance since these anions have six π electrons and the resonance extremes would involve a silicon or germanium double bond to carbon. Rühlmann[1] recently prepared pentaphenylsilole (I, M = Si; R = R′ = C_6H_5; Y = H) and tetraphenylmethylsilole (I, M = Si; R = C_6H_5; R′ = CH_3; Y = H) by allowing 1,4-dilithiotetraphenylbutadiene[2] to react with phenyl- or methyldichlorosilane. Rühlmann also reported that treatment of these siloles with phenyllithium gave intense red-violet colors, but he could not decide if the color was due to an anion radical, a ring-addition product, or the silacyclopentadienide anion (II). Since the organodichlorisilanes, $RSiCl_2H$, used by Rühlmann are difficult to prepare and not readily available, a synthetic procedure employing the easily obtained $RMCl_3$ (M = Si, Ge) derivatives was sought. Such a procedure would also have the advantage that the silole or germole obtained would have Y = halogen in the structure (I), allowing for a wide variety of substitutions at the heteroatom (M).



I II

M = Si, Ge

Although attempts to prepare halogen-substituted siloles and germoles by the reaction of $(C_6H_5)_4C_4Li_2$ with chlorosilanes and -germanes have been reported to be unsuccessful,[3] it has been found that *reverse* addition of a diethyl ether suspension of 1,4-dilithiotetraphenylbutadiene[2] to a diethyl ether or tetrahydrofuran (THF) solution of $R'MCl_3$ or MCl_4 (M = Si, Ge) gives in 50–70% yield the corresponding heterocycle. Some of the new chloro-substituted siloles and germoles (I, R = C_6H_5) are: $(C_6H_5)_4C_4Si(Cl)C_6H_5$ (III), mp 181–183°; $(C_6H_5)_4C_4Si(Cl)CH_3$ (IV), mp 194–195°; $(C_6H_5)_4C_4GeCl_2$ (V), mp 197–199°; $(C_6H_5)_4C_4Ge(Cl)C_6H_5$ (VI), mp 210–211°. The chloride may be displaced by many reagents, *e.g.*, RO^-, R^-, and transition-metal carbonyl anions.[4] Of interest here are the hydrides which may be prepared in 70–90% yield by reduction with $LiAlH_4$: $(C_6H_5)_4C_4Si(H)C_6H_5$ (VII), mp 198–199°, ν_{SiH} 2120 cm^{-1}; $(C_6H_5)_4C_4Si(H)CH_3$ (VIII), mp 223–224°, ν_{SiH} 2122 cm^{-1}; $(C_6H_5)_4C_4GeH_2$ (IX), mp 192–193°, ν_{GeH} 2060 cm^{-1}; $(C_6H_5)_4C_4Ge(H)C_6H_5$ (X), mp 187–188°, ν_{GeH} 2056 cm^{-1}.

When *n*-butyllithium is added to X in THF at $-78°$, a bright red color is produced. The addition of water to this red solution regenerates the starting hydride X. If trimethylchlorosilane is added in place of water, the silyl derivative, $(C_6H_5)_4C_4Ge(C_6H_5)Si(CH_3)_3$, mp 178–180°, ν_{SiCH_3} 1250 and 850 cm^{-1}, τ_{SiCH_3} 9.77, is formed in 90% yield. Thus, the bright red color is ascribed to the germyllithium compound, $(C_6H_5)_4C_4Ge(Li)C_6H_5$ (XII).

On the other hand, when the silicon hydrides (VII and VIII) are treated with *n*-butyllithium in the same manner, a very intense, dark purple color is generated as was observed by Rühlmann.[1] The addition of water or D_2O to these solutions does not regenerate the starting hydrides (or deuterides) although the intense color is dispelled. Nmr spectra of the resins obtained after removal of the THF show broad unresolved absorptions in the region τ 10–7.7, and the area ratios indicate the presence of butyl groups in the resins. Furthermore, the splitting patterns of the H_2O- and D_2O-quenched reaction products are different, suggesting that H or D is incorporated in the resins. No Si–H or Si–D stretching frequencies are observed in the infrared spectra of the products, so the hydrogen or deuterium must be attached to the carbon skeleton. Unfortunately, the C–D stretching region is obscured by a weak overtone or combination band.

To determine if a hydrogen atom attached to the heteroatom was necessary to form these intensely colored solutions, *n*-butyllithium was added to the previously unreported $(C_6H_5)_4C_4Ge(C_6H_5)_2$, mp 198–199°. An intense purple color formed and this solution exhibited a very weak electron spin resonance (esr) signal at a *g* value near 2. The extreme weakness of the signal shows that radicals are not the predominant species in solution. Hence, in this case it is concluded that the butyllithium adds to the ring structure to give a conjugated C–Li derivative which is responsible for the intense colors observed.

The above results may be compared with the reactions of triphenylsilane and triphenylgermane with *n*-butyllithium. Triphenylgermane readily forms triphenylgermyllithium,[5] but triphenylsilane forms *n*-butyltriphenylsilane and lithium hydride.[6] Thus, there exists the possibility that $(C_6H_5)_4C_4Si(C_6H_5)(C_4H_9)$ (XIII) and LiH are formed when butyllithium is added to VII, and that the LiH then adds across a carbon–carbon double bond to form a highly colored C–Li derivative. This possibility was tested by adding crushed lithium hydride to a THF solution of XIII, which was prepared from III and butyllithium in benzene. No reaction was observed after stirring for 2 hr at room temperature. However, the addition of $LiAlH_4$ to a THF solution of XIII immediately causes an intense purple color. It is possible that LiH formed *in situ* is sufficiently more reactive than bulk LiH (which has a very low solubility in THF) that a direct comparison cannot be made.

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(1) K. Rühlmann, *Z. Chem.*, **5**, 354 (1965).

(2) E. H. Braye, W. Hubel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

(3) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

(4) M. D. Curtis, unpublished results.

(5) H. Gilman and C. Gerow, *J. Am. Chem. Soc.*, **78**, 5435 (1956).

(6) H. Gilman and H. W. Melvin, *ibid.*, **71**, 4050 (1949).

Although the nature of the species responsible for the intense colors has not been conclusively established, these results do show that silacyclopentadienide anions are *not* formed from treatment of the hydrides with *n*-butyllithium at low temperatures. Further studies are in progress to determine if the silacyclopentadienide anions can be prepared by other methods. The germanium hydride X does form the germyllithium derivative XII, but triphenylgermane also forms triphenylgermyllithium under the same conditions. It thus appears that the ring structure does not confer enhanced acidity to the hydrides (I, Y = H).

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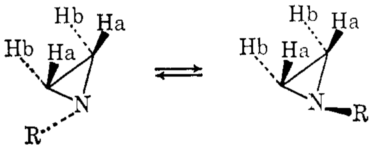
Aziridines. X. The Influence of Steric Factors on Nitrogen Inversion Rates and Ring Proton Shifts in Aziridines

Sir:

The study of nitrogen inversion in aziridines has become an active field of interest in recent years. In many aziridines, the rates of nitrogen inversion are of suitable magnitude for study by nmr spectroscopy.[1] At *ca.* 25°, the ring proton spectrum of 1-alkylaziridines (I, R = Me, Et, *i*-Pr) gives rise to an A_2B_2 pattern indicating that the rate constant (k_i) for the nitrogen inversion process (Ia ⇌ Ib) is small compared to the chemical shift, ν_{AB}. At higher temperatures, the ring proton spectrum of I (R = Et), for example, broadens and then at ~108° the coalescence temperature (T_c) collapses to a singlet. At T_c, the inversion rate constant becomes equal to $2.22\nu_{AB}$, or approximately 60 sec^{-1}.[1b] Replacing the ethyl group by methyl, benzyl, phenethyl, or cyclohexyl does not greatly affect the latter value. On the other hand, the bulky *t*-butyl group appears to increase the rate of nitrogen inversion dramatically. Thus, Bottini and Roberts[1b] report that the 40-Mc/sec nmr spectrum of 1-*t*-butylaziridine (II) even at −77° possesses only a single sharp line for the ring protons, "indicating that inversion occurs too rapidly for measurement." The lower inversion barrier was ascribed[1b] to nonbonded interactions between the ring protons and the *t*-butyl group in the ground state of II.[2]



Ia Ib

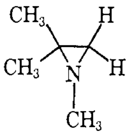
In this communication we present new data concerning nitrogen inversion in 1-*t*-butylaziridine (II) and discuss the factors which govern the magnitude of ν_{AB} in 1-alkylaziridines.

In contrast to the study of Bottini and Roberts,[1b] we have found that the ring protons in the 40- and 60-Mc/sec spectrum of II as the neat liquid or a 50% CCl_4 solution form *two peaks* separated by ~2 and 3 cps, respectively, at room temperature. The magnitude of ν_{AB} was found to be solvent and concentration dependent. For example, the proton spectrum of II as a 20% benzene solution (w/v) exhibits an A_2B_2 pattern with $\nu_{AB} \approx 11$ cps at 34° and lower.

On heating a benzene solution of II the ring proton spectrum broadens and then collapses to a single band at about 52°, the coalescence temperature.[3] The thermodynamic parameters for the inversion process in 1-*t*-butylaziridine-2,2-d_2 ($T_c \approx 52°$) are currently being assessed from the deuterium-decoupled spectra in various solvents.

The present study clearly demonstrates that steric factors do indeed accelerate the nitrogen inversion process in 1-alkylaziridines.[4] However, the rate of nitrogen inversion in the case of 1-*t*-butylaziridine (II) is far less than that previously claimed by Bottini and Roberts.[1b]

Of particular relevance is the similarity of the present data and those reported for 1-alkyl-2,2-dimethylaziridines (iii,[1b] III[1c,e]) and *trans*-1-ethyl-2,3-dimethylaziridine[1b,e] (IV). Such similarities strongly imply that the degree of steric assistance to the inversion process in these molecules is comparable.[6]



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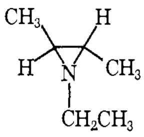

IV

In addition to accelerating the nitrogen inversion process, steric factors also play a prominent role in determining the magnitude of ring proton shifts (ν_{AB}) in aziridines.

In harmony with our earlier studies[7] on styrenimines (2-phenylaziridines), we find that ring protons *cis* to the magnetically anisotropic N-alkyl bond in I (R = Me, Et, *i*-Pr) are shifted over 25 cps upfield relative to the ring protons in aziridine (I, R = H). A comparison of the ν_{AB} values for the 1-alkylaziridines recorded in

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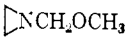
(1) (a) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, 70, 786 (1958); (b) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958); (c) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960); (d) T. J. Bardos, V. Szantay, and C. K. Navada, *ibid.*, **87**, 5796 (1965); (e) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967); (f) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967); (g) V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Opt. Spectry.* (USSR), **19**, 122 (1965).

(2) After completion of this paper, Anet and Osyany[1e] suggested that the effect of the *t*-butyl group could not be regarded as firmly established because the ring protons still formed a single band at −77°. If ν_{AB} is about 0–3 cps, the authors[1e] argue that, as a result of coupling, a single line would result regardless of the value of k_i. An explanation for this unusually small ν_{AB} value for II, however, was not proposed by Anet and Osyany.[1e]

(3) Interestingly, 1-(1-adamantyl)aziridine as a 20% benzene solution exhibited a coalescence temperature of about 41°.

(4) In several instances, the presence of heteroatoms on the alkyl chain allegedly increases k_i *via* an electronic effect.[1g] Thus, Bystrov and co-workers[1g] report T_c values of approximately 30 and 57° for



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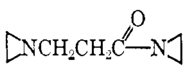
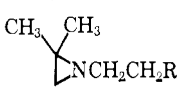


ii



iii

i and ii,[5] respectively.

(5) The very similar T_c values of 57 and 55° reported for ii[1g] and iii (R = CH_2OH, CO_2Et),[1b] respectively, cannot be easily rationalized.

(6) Arguing that steric repulsions were not very different in II, III, and IV, as shown by molecular models, Anet and Osyany[1e] recently proposed that the rate of nitrogen inversion in these three compounds would be similar.

(7) S. J. Brois, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, No. O-72.