Tetrahedron Letters,Vol.28,No.3,pp 343-344,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

A STABLE AND LONG-LIVED GERMAIMINE

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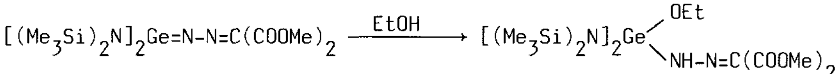
Spectroscopic identification of the first reported stable germaimine is provided, together with an analysis of its bond structure; it exists in cisoid and transoid forms.

Germaimines, $R_2Ge{=}NR'$ are reported to be unstable compounds, detected only by trapping experiments.[1] We have recently shown that reactions of the electron-rich germylene $[(Me_3Si)_2N]_2Ge$ with diazo-compounds $N_2CR^1R^2$ provided products which, on the basis of trapping experiments, are best considered to be germyleneazines, *e.g.* (I), which with ethanol gave the adduct (II).[2]



$$[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Ge{=}N{-}N{=}C(COOMe)_2} \xrightarrow{\mathrm{EtOH}} [(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Ge}\genfrac{}{}{0pt}{}{\diagup\,\mathrm{OEt}}{\diagdown\,\mathrm{NH{-}N{=}C(COOMe)_2}}$$

(I) (II)

This germaimine is stable in solution in benzene in the absence of air, in that whether the ethanol was added 3 h or 23 h after the diazomalonic ester and germylene had been mixed makes little difference to the yield of isolated purified adduct (II) which was obtained, demonstrating that the azine (I) remained largely unchanged during this period.

Spectroscopic evidence is now presented for the structure of germyleneazine (I).

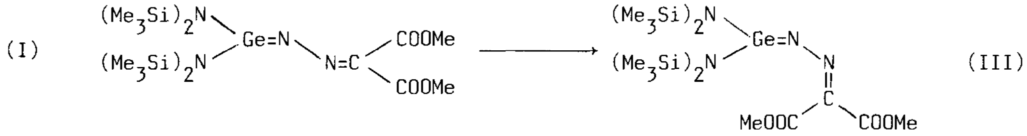
A solution in benzene of a 1:1 mixture of $[(Me_3Si)_2N]_2Ge$ and $N_2C(COOMe)_2$ provides the following n.m.r. spectra: ^1H: δ 0.24 [36H, $(Me_3Si)_2$], 3.39 (3H, OMe), 3.72 (3H, OMe); ^{13}C: δ 4.9 (Me_3Si), 51.1 and 52.2 (OMe), 119.6 [$C(COOMe)_2$], 157.5 and 165.8 (CO). Signals ascribable to the original reactants are not observed; the spectra of separate solutions of these reactants are unchanged for several days.

These spectra are consistent with the formation of the germaimine (I). The presence of two distinct signals for the ester groups indicates that rotation about the C=N bond is restricted at ambient temperatures; the appearance of only one sharp signal for the trimethylsilyl groups implies, however, that rotation takes place about the Ge=N bond.

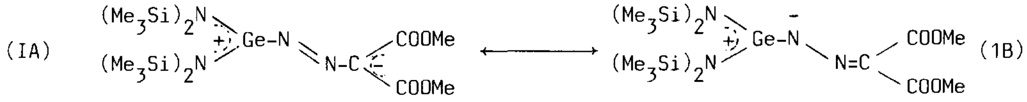
When a solution of the initial germaimine (I) is kept at room temperature, n.m.r. spectra of the solution show that it slowly changes into another compound (III), whose spectra are: ^1H: δ 0.19 [36H, $(Me_3Si)_2$], 3.02 (3H, OMe), 3.48 (3H, OMe); ^{13}C: δ 4.9 (Me_3Si), 43.4 and 52.1 (OMe), 123.0 [$C(COOMe)_2$]. After two days at room temperature (I) and (III) were present in approximately equimolar quantities; after 7 days (I) has been completely converted into (III).

The rate of conversion was markedly influenced if excess diazo-compound or germylene were present. When a 1:2 molar ratio of diazo-compound and germylene were mixed the initial n.m.r. spectra were a summation of the spectra of (I) and of the excess germylene. In this case (I) was completely converted into (III) in less than 2 days. In contrast, when a 2:1 molar ratio of diazo-compound and germylene were mixed, the n.m.r. spectra, which were the sum of those of (II) and the excess diazo-compound, did not change, even after the mixture had been kept for 7 days. The observation of separate resonances for (I) and the excess germylene or diazo--compound shows that no exchange occurred of $[(Me_3Si)_2N]_2Ge$ or $N_2C(COOMe)_2$ groups between (I) and the other components in the mixtures.

The close similarity of the spectra of (I) and (III) and the clean conversion of (I) into (III) suggests that they are isomeric forms, *viz.*



The spectroscopic data further indicate that rotation about the C-N bond is very inhibited, that rotation about the Ge-N bond is fast and about the N-N bond occurs slowly. This suggests that the structures of (I) and (III) are best represented as hybrids of (A) and (B), with (B) dominant, *e.g.*

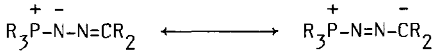


The chemical shifts of the signal for the unique carbon atoms in (I) and (III) are also consistent with such structures.

MNDO calculations, with fully optimised geometry, on the simple model compound $(H_2N)_2Ge{=}N^{a}{-}N^{b}{=}C^{c}(CHO)_2$, (IV), support this interpretation and confirm that (B) is the dominant form, but that (A) is also important. The net calculated atomic charges are Ge + 1.80; N^a -0.77; N^b -0.04; C^c -0.21.

In addition the calculations show that for (IV) the cisoid isomer is more stable than the transoid, and on this basis, the transoid structure is assigned to the initial product (I) and the cisoid structure to the isomer (III).

A similar hybrid structure has been postulated for the structurally similar phosphinazines (V).[3]



$$R_3\overset{+}{P}\text{-}\overset{-}{N}\text{-}N{=}CR_2 \longleftrightarrow R_3\overset{+}{P}\text{-}N{=}N\text{-}\overset{-}{C}R_2 \qquad (V)$$

Addition reactions of ethanol,[2] and other weak acids HX[4] with the germaimine (I) are all 1,2-additions across the Ge-N bond; hence their course, and the final products, are not affected by the isomerisation of (I) to (III).

References

1. For a review, see J. Satge, *Adv. Organomet. Chem.*, 1982, **21**, 291.
2. C. Glidewell, D. Lloyd and K. W. Lumbard, *J. Chem. Soc., Dalton Trans.*, in the press.
3. See A.W. Johnson, "Ylid Chemistry", Academic Press, New York, 1966, p.241
4. C. Glidewell, D. Lloyd and K. W. Lumbard, to be published.

(Received in UK 21 November 1986)