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ON THE NATURE OF "GERMIRENE" DERIVATIVES

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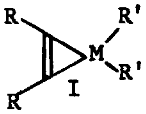
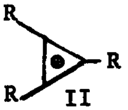
A recent well-amplified publication[1] reports the synthesis of new classes of aromatic compounds having the general structure I (M = Ge or Si). These


I


II

were claimed to be heterocyclic analogs of the cyclopropenyl cation[2] (II) and their aromatic character was ascribed to p π-orbital interaction of the double bond with an empty d-orbital of the heteroatom, rather than the purely p π-orbital interactions in II.

However, three discrepancies, listed below, which appeared in the Russian paper led us to reinvestigate the nature of the products.

a) The "aromatic character" of the synthesized products was based on the stability of the systems to the action of bromine, alkali, and strong acids and lack of hydrogen addition in a catalytic process.

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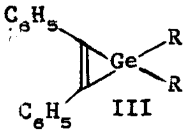
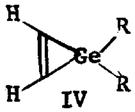
(1) M. E. Vol'pin, Yu. D. Koreshkov, V. G. Dulova and D. N. Kursanov, Tetrahedron, 18, 107 (1962).
(2) R. Breslow, J. Am. Chem. Soc. 79, 5318 (1957).

In addition, stability to heat and oxidation were cited.

These properties with the exception of inertness to bromine are common, however, to many organometallic systems which are not hetero-aromatic, especially in the organo-germanium series[3] and to many substituted organo-silicon compounds.[4] With regard to the action of bromine on I ($R = C_6H_5$; $R' = CH_3$; $M = Ge$) our results are at variance with those of Vol'pin[1]. We have found that while absorption of bromine is not rapid, decolorization is almost complete after an hour at room temperature, in carbon tetrachloride solution.

b) The molecular weight cited (635) for the iodide III ($R = I$) was determined cryoscopically in benzene and was in poor agreement with the


III


IV

theoretical value (505). The dimethyl derivative III ($R = CH_3$) was determined to have a molecular weight of 299.9 at 1% concentration in camphor, which at 10% concentration rose to almost 600. In this case an accurate value could be obtained only by extrapolation to zero concentration of III ($R = CH_3$). Similar results were obtained with IV ($R = CH_3$) and the variations in molecular weight were ascribed to, "...a marked association often observed with germanium compounds".

While the latter may be true for inorganic germanium compounds and perhaps even for such substances as III ($R = I$) it is scarcely convincing for the purely organic derivatives of germanium. Surprisingly, no attempts appear to have been made to use more modern techniques for molecular weight determination, and the Russian results cannot then eliminate dimeric forms such as V.

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(3) G. E. Coates, "Organometallic Compounds", John Wiley and Sons, Inc., New York, New York, p. 164ff (1960).

(4) C. Eaborn, "Organosilicon Compounds.", Butterworth's Scientific Publications, London, p. 122ff (1960).

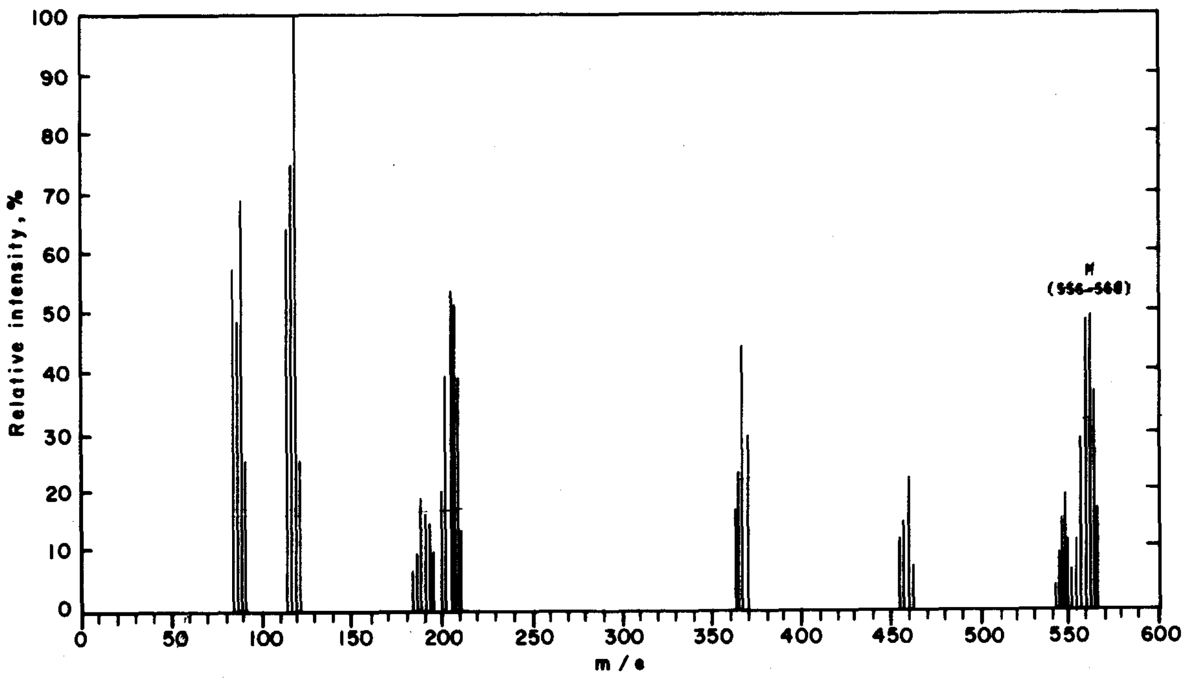
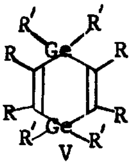
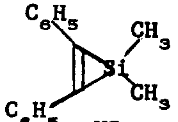


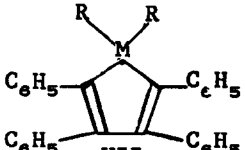
Figure 1 Mass Spectrum of Dimer of "Dimethylgermirene" M = 562



V



VI



VII

c) One of the methods used to prepare the silirene derivative VI, that of reacting dichlorodimethyl silane and sodium in the presence of diphenylacetylene, was very similar to the procedure used by ourselves[5] and others[6] for the preparation of the metalloles VII. This suggested that the silirene might be, in fact, a silole, despite the excellent elemental analytical data presented. In addition the formation of the silirene VI was accompanied by 1,2,3-triphenylnaphthalene, a by-product that we had sometimes observed in the preparation of VII.

In order to obtain information that would unequivocally distinguish between such structures as I or V and VII for the germanium compounds, the iodide III (R = I) was analyzed by x-ray absorption and fluorescence techniques for germanium and iodine. The values obtained (Found: Ge, 14.0; I, 51.0% $C_{14}H_{10}GeI_2$ requires: Ge, 14.39; I, 50.29%) were in good agreement with those found by Vol'pin et al[1]. The nuclear magnetic resonance spectrum of III (R = C_2H_5) showed aromatic proton absorption as a multiplet at -420 cps and aliphatic proton absorption at approximately -45 and -65 cps (with respect to TMS at 0 cps). The integral gave a ratio for these two types of protons that approximated 1:1. These results thus eliminate structure VII as a possibility for the germanium compounds.

In order to differentiate between structure I and dimers such as V, the mass spectrum of the parent compound III (R = CH_3) was obtained at a temperature of 100-110°C[7] by introducing the sample directly into the ion source of the mass

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(5) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, J. Am. Chem. Soc. 82, 5099 (1960).

(6) E. H. Braye, W. Hubel and I. Caplier, ibid, 83, 4406 (1961).

(7) When the spectrum was run at 170-180° the only molecular ion observable was that of hexaphenylbenzene.

spectrometer utilizing a technique to be described elsewhere. The mass spectrum so obtained is shown in Fig. 1. The group of ions at the right-hand side of the graph corresponds to the molecular ions of the compound and indicates that its molecular weight is 562 (for the most abundant of the polyisotopic molecular ions). The complete absence of ion peaks in the mass range of 278-284 emphatically excludes the possibility that the structure of this compound is of the germirene type.

The same technique was utilized to obtain the mass spectra of the diethyl and diiodo compounds III (R = C_2H_5 and I). The mass spectra indicated the expected polyisotopic molecular ion groups at m/e 618 (R = C_2H_5) and at m/e 1010 (R = I), establishing that these compounds too are dimeric in form. Again the complete lack of ion fragments at the masses corresponding to the germirene structure (III) precludes the possibility of there being present compounds of the latter type.

Molecular weight determinations of III (R = I) and III (R = C_2H_5) also were carried out using the isopiestic method. It is interesting to note that at 1% concentrations of these materials in toluene (the concentration at which largely three-membered ring monomer was claimed to be present in solution) the molecular weights found were 995 and 621 respectively.

We can only conclude from the above results that the "germirene" compounds are in reality, dimeric in nature probably of the type V. Other structures cannot be eliminated, however, and further work is underway to determine the exact nature of the ring systems involved in these and the silicon compounds.

These results, together with more detailed analyses of the mass spectra will be published at a later date.

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