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THE ACIDITIES OF GERMANE AND THE PHENYLGERMANES

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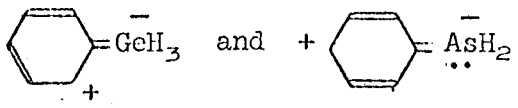
The Acidities of Germane and the Phenylgermanes

Sir:

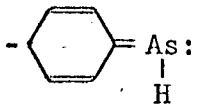
Generally, a phenyl derivative of a nonmetal hydride, $C_6H_5MH_{x-1}$, is more acidic than the parent hydride, MH_x.[1,2] For example, phenylarsine is a stronger acid than arsine, and diphenylarsine is a stronger acid than phenylarsine.[2] However, germane and the phenylgermanes constitute a puzzling exception to this rule. The phenylgermanes are weaker acids than germane - the weakness increasing with increasing phenyl substitution.[3,4] Although the exceptional acidities of the phenylgermanes has been cited as evidence for $p\pi$-$d\pi$ bonding,[3] no explanation was offered for the implied greater importance of such bonding in the phenylgermanes than in, say, the phenylarsines. The purpose of this communication is to show that the data may be explained in terms of two opposing effects of phenyl substitution: an acid-weakening effect (which we ascribe to $p\pi$-$d\pi$ bonding) and an acid-strengthening effect (mainly due to $p\pi$-$p\pi$ bonding).

The phenyl group in the molecule $C_6H_5MH_x$ can exert an acid-weakening effect if the atom M has empty valence $d\pi$ orbitals which interact with the filled $p\pi$ molecular orbitals of the phenyl ring. Such $d\pi$ orbitals are available when M is from the second or third row of the periodic table.[5] The acid-weakening effect may be ascribed to a stabilization of the acid, relative to its conjugate base. There is little such stabilization of the conjugate base because the $p\pi$-$d\pi$ interaction would cause a shift of electron density toward an atom with a formal charge

of -1. For the cases of phenylgermane[6] and phenylarsine, the effect probably has a similar magnitude, and contributing resonance structures of the following type can be written:



The acid-strengthening effect of the phenyl group in $C_6H_5MH_x$ is due (in addition to a relatively weak σ inductive effect) to a stabilization of the anion by interaction of an empty pπ molecular orbital of the phenyl ring with a filled pπ "nonbonding" orbital of the M atom. The effect is operative in the phenyl derivatives of methane and of the hydrides of elements of groups V and VI.[7] For example, in the case of phenylarsine, resonance structures of the following type can be written for the anion:



We assume that the valence orbitals of the arsenic atom in the anion are involved in bonding as follows: one pσ orbital in the As-H bond, a pσ orbital and a pπ orbital in the As-C bond, and an s orbital for the completely nonbonding lone pair. On this basis the ion should be completely planar, with a 90° C-As-H bond angle. Presumably there is little such pπ-pπ stabilization of phenylarsine; the lone pair orbital on the arsenic atom in phenylarsine probably has very little p character because of the high s^2p^3-sp^4 promotion energy.[8] (The H-As-H bond angle of 91.8° in arsine[9] is structural evidence of the "inertness" of the lone pair.)

The acid-strengthening effect is inoperative in phenylgermane[10] because the lone pair orbital on the germanium atom of the $C_6H_5GeH_2^-$ ion (like that on the arsenic atom of the isoelectronic $C_6H_5AsH_2$) has little p character. Consequently there can be no significant $p\pi$-$p\pi$ interaction between the phenyl ring and the germanium atom in the anion without an energetically unfavorable hybridization of the germanium orbitals. These conclusions are consistent with the facts that no compound is known containing a $p\pi$-$p\pi$ bond between carbon and germanium and that the germacyclopentadienide ion shows no aromatic character.[11]

Apparently whenever the π acid-strengthening effect of a phenyl group is operative, it overpowers any possible acid-weakening effect. The latter effect wins by default in the case of phenylgermanes; it probably will be found to do likewise in the case of phenylsilanes - and perhaps in the case of phenylstannanes.

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(6) Birchall and Drummond[4] have observed slight downfield nmr shifts for the ortho and para hydrogens of phenylgermane, relative to benzene. Because various complicated factors can influence the chemical shifts of ring protons, these results are difficult to interpret in terms of $p\pi$-$d\pi$ bonding. Indeed, it is not even known whether $p\pi$-$d\pi$ bonding sufficient to account for the observed acidity effects would involve enough electron withdrawal from the phenyl ring to cause a significant chemical shift in the nmr of the phenyl protons.

(7) The nonbonding electrons of the conjugate bases of these hydrides have considerable p character. This feature is a prerequisite for the π acid strengthening effect.

(8) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., 1964, New York, p. 122.

(9) W. L. Jolly, "The Chemistry of the Non-Metals," Prentice Hall, Inc., Englewood Cliffs, N. J., 1966, p. 91.

(10) Birchall and Drummond[4] have observed a slight downfield nmr shift for the ortho hydrogens of the phenylgermane anion. They have interpreted the nmr spectrum as evidence for the absence of conjugation between germanium and the ring.

(11) M. D. Curtis, J. Am. Chem. Soc., 91, 6011 (1969).

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