undoubtedly caused by ice and some of the 3365 cm.$^{-1}$ absorption in D by ammonia, it should be noted that the addition of NH_3 in passing from B to C increases the relative intensity of the 3220 cm.$^{-1}$ peak. It follows therefore that NH_3 also absorbs in this region.

Structural Conclusions

It seems clear that neither hydrate of ammonia contains ammonium ions. In addition to the reasons previously outlined, the presence of NH_4^+ ion would imply OH^- or O^{--} ions. In the former case a frequency higher than any observed would be expected (OH^- absorption occurs at 3638 cm.$^{-1}$ in NaOH[9]); in the latter there is no explanation for the two highest frequencies.

$NH_3 \cdot H_2O$ is a bimolecular crystal. There are five H atoms and only three unshared electron pairs per mole, so at least two H atoms must be either nonbonded or very weakly bonded. If, as in crystalline NH_3, three weak hydrogen bonds are formed to the single electron pair of NH_3, only two strong bonds can be formed. From the spectrum it can be concluded that a strong $NH \cdots O$ bond is formed (2.8 Å. or less from the magnitude of the frequency shift observed) and that both hydrogens from H_2O are involved in at least weak hydrogen bonds (since free H_2O absorbs near 3700 cm.$^{-1}$). This implies at least one $O\text{–}H \cdots N$ bond.

$2NH_3 \cdot H_2O$ is a trimolecular crystal. The two NH_3 molecules appear to be non-equivalent. The structure includes at least one strong $NH \cdots O$ bond and all of the hydrogens from H_2O are hydrogen bonded.

[9] W. Busing, Symposium on Molecular Structure and Spectroscopy, The Ohio State University, June, 1953.

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A New Reaction of Organogermanium Compounds

BY ROBERT WEST

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Among organometallic compounds, those of arsenic have long been considered to be unique in that primary and secondary derivatives can be reduced to mono- or dialkylarsines, $RAsH_2$ or R_2AsH, by zinc and hydrochloric acid.[1] We have found that organogermanium compounds can be reduced to the corresponding hydrides under similar conditions. This reaction is interesting since all attempts to reduce organotin or organosilicon compounds to the hydrides in the same way have been unsuccessful. Thus a solution of triphenylgermanium bromide, when treated with amalgamated zinc and aqueous HCl, is readily reduced to triphenylgermane. The product can be identified easily by the strong Ge–H fundamental stretching vibration at 2400 cm.$^{-1}$ in the infrared spectrum.[2] However, under similar conditions triphenyltin chloride or iodide gave no material showing Sn–H absorption (at 1870 cm.$^{-1}$)[3]; and diphenyldichlorosilane and triphenylchlorosilane gave no products showing Si–H absorption (at 2100 cm.$^{-1}$).[4]

The reduction of organogermanium compounds to hydrides in this way parallels the known reaction of inorganic germanium compounds with alkali and aluminum, in which small amounts of GeH_4 are formed.[5] The reason for the anomalous easy formation of Ge–H bonds in reductions of this type is not known, but it is interesting to note that such reduction is consistent with Sanderson's recent conclusion that germanium is actually more electronegative than either silicon or tin.[6] The evidence found by Johnson and Harris for the metalation of triphenylgermane by phenyllithium[7] is another possible indication of abnormally high electronegativity for germanium.

Experimental

Triphenylgermane.—To 15 g. of amalgamated zinc dust was added 2 g. of triphenylgermanium bromide[8] dissolved in 100 ml. of 1:1 ethanol–ethyl ether. Over two hours, 50 ml. of 12 *N* aqueous HCl was added, with occasional stirring. The solution was then decanted and partitioned between water and ether; the organic layer was washed with water, dried and evaporated to give 0.6 to 1.0 g. of oily material, principally triphenylgermane. This crude product contained about 15% of tetraphenylgermane, m.p. 230°, which could be obtained by washing with methanol.

Crude triphenylgermane from two such runs was passed through an alumina chromatographic column in cyclohexane solution; the cyclohexane was then evaporated and the residual oil was crystallized from methanol to give 0.5 g. of triphenylgermane as transparent hexagonal plates of the β-form, m.p. 27°.[7,8] The infrared absorption spectrum in chloroform solution showed bands at 4200, 3030, 2040, 1950, 1880, 1818, 1726, 1610, 1490, 1433, 1382, 1338, 1308, 1260, 1098, 1068, 1027 and 1002 cm.$^{-1}$.

Further elution of the chromatogram with 1:1 benzene–chloroform gave 0.3 g. of solid material, m.p. 130°, probably triphenylgermanol.[8]

Dimethylgermane.—To 20 g. of amalgamated zinc dust was added 4.0 g. of dimethylgermanium sulfide[9] dissolved in 50 ml. of ethanol. Over 1 hour, 50 ml. of 12 *N* HCl was added. The gaseous products were condensed in a trap held at −78°. The contents of the trap (dimethylgermane, ethanol and hydrogen sulfide) were separated by bulb-to-bulb distillation on a vacuum chain to give 0.2 g. of dimethylgermane; mol. wt. calcd. 105, found 97, 99 (vapor density). The gas had strong infrared absorption bands at 2985 (C–H), 2060 (Ge–H) and 844 cm.$^{-1}$ (Ge–C), as well as weaker bands at 898 and 882 cm.$^{-1}$.

A similar reaction was carried out using methylgermanium trichloride instead of dimethylgermanium sulfide. No methylgermane was found in the trap, which was held at −120° during the reaction.

Attempted Reduction of Tin and Silicon Compounds.—These reactions were carried out similarly to the reduction of triphenylgermanium bromide, except that the crude products were not chromatographed. Diphenyldichlorosilane and triphenylchlorosilane were treated with amalgamated zinc and gaseous HCl in absolute ethanol to prevent irreversible hydrolysis. The only compounds found in the products from these reactions were diphenylsilanediol and triphenylsilanol, respectively.

Triphenyltin chloride and iodide were treated in the same way as triphenylgermanium bromide, except that the reactions were carried out under nitrogen to prevent any oxida-

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[1] A. W. Palmer and W. M. Dehn, *Ber.*, **34**, 3594 (1901); W. M. Dehn, *Am. Chem. J.*, **33**, 101 (1905); **40**, 88 (1908); W. M. Dehn and B. B. Wilcox, *ibid.*, **35**, 1 (1906).

[2] W. B. Steward and H. H. Nielsen, *Phys. Rev.*, **48**, 861 (1935); J. W. Straley, C. H. Tindal and H. H. Nielsen, *ibid.*, **62**, 161 (1942).

[3] D. R. Lide, Jr., *J. Chem. Phys.*, **19**, 1605 (1951).

[4] J. A. Hawkins and M. K. Wilson, *ibid.*, **21**, 360 (1953); R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

[5] J. H. Müller and N. H. Smith, THIS JOURNAL, **44**, 1909 (1922).

[6] R. T. Sanderson, *ibid.*, **74**, 4792 (1952).

[7] O. H. Johnson and D. M. Harris, *ibid.*, **72**, 5566 (1950).

[8] C. A. Kraus and L. S. Foster, *ibid.*, **49**, 457 (1927)

[9] E. G. Rochow, *ibid.*, **70**, 1801 (1948).

tion of Sn–H bonds. The reaction products were apparently mixtures, containing no detectable amount of triphenylstannane.

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COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF AN ARGINYL PEPTIDE

Sir:

The synthesis of peptides containing arginine has presented unusual difficulties, and only a few dipeptides have been reported. No peptide in which the carboxyl group of arginine is linked to another amino acid has been synthesized.[1] It has now been found that the pyrophosphite method[2] can be used for this purpose.

Carbobenzoxy-L-arginine hydrobromide[3] (0.010 mole) and methyl L-leucinate (0.010 mole) were added to 7 cc. of diethyl phosphite, then tetraethyl pyrophosphite (0.020 mole) was added. After 30 minutes heating on a steam-bath, methyl carbobenzoxy-L-arginyl-L-leucinate hydrobromide hydrate was precipitated as a gum by 100 cc. of anhydrous ether. This was crystallized by dissolving in 5 cc. of methanol, bubbling in hydrogen bromide a moment, then adding 40 cc. of anhydrous ether; yield 3.06 g. (57%). A further 0.47 g. was obtained from the original filtrate on dilution with ether, giving 3.53 g. in all (66%). Solution in 10 cc. of methanol and dilution with 40 cc. of water yielded 2.79 g. (52%), m.p. 90–92°,[4] $[\alpha]^{23}\text{D}$ −20.3° (*c* 2, methanol).

Anal. Calcd. for $C_{21}H_{36}N_5O_6Br$: C, 47.2; H, 6.79; N, 13.1; Br, 15.0. Found: C, 47.4; H, 6.99; N, 13.3; Br, 15.2.

Carbobenzoxy-L-arginyl-L-leucine was obtained by heating 2.83 g. of the methyl ester hydrobromide hydrate on a steam-bath in 28 cc. of *N* hydrobromic acid for an hour, making slightly alkaline with ammonium hydroxide and chilling. The crystalline product was recrystallized from 30 cc. of *N*/6 hydrobromic acid by the addition of ammonium hydroxide; yield 1.20 g. (54%), m.p. 223–224° dec., $[\alpha]^{24}\text{D}$ −26° (*c* 2, 0.4 *N* HBr). *Anal.* Calcd. for $C_{20}H_{31}N_5O_5$: C, 57.0; H, 7.41; N, 16.6. Found: C, 57.2; H, 7.64; N, 16.6.

L-Arginyl-L-leucine hydrobromide hydrate was obtained by hydrogenation with a palladium catalyst of 1.06 g. of the carbobenzoxy derivative in 40 cc. of water plus 2.5 cc. of 1.04 *N* HBr. A crystalline product obtained by evaporation of the filtered solution under vacuum was washed out with acetone, then recrystallized by dissolving in 4 cc. of water and slowly adding 40 cc. of acetone; yield 0.78 g. (80%), m.p. 162–163° dec., $[\alpha]^{24}\text{D}$ +8.6° (*c* 2, water).

Anal. Calcd. for $C_{12}H_{28}N_5O_4Br$: C, 37.3; H, 7.3; N, 18.1; Br, 20.7. Found: C, 37.1; H, 7.2; N, 18.2; Br, 20.7.

Paper chromatography gave an R_f value of 0.58 in a butanol–water–acetic acid (5:4:1) system, and showed the presence of arginine and leucine in an acid hydrolysate.

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[1] J. S. Fruton, "Advances in Protein Chemistry," Vol. V, Academic Press, Inc., New York, N. Y., 1949, p. 64.

[2] G. W. Anderson, J. Blodinger and A. D. Welcher, THIS JOURNAL, **74**, 5309 (1952).

[3] Prepared by R. Janice Joyce, of these laboratories; m.p. 177–179.5°, $[\alpha]^{24}\text{D}$ −6.9° (*c* 2, water); calcd. for $C_{14}H_{21}N_4O_4Br$: 20.8% Br. Found: 20.6% Br.

[4] Melting points were taken on a calibrated Fisher–Johns block.

TWO DIMENSIONAL PHASE TRANSITION OF ETHANE ON SODIUM CHLORIDE

Sir:

The chief evidence for first-order phase transitions of films adsorbed on solid surfaces has been the adsorption isotherms measured by Jura, *et al.*, for *n*-heptane on graphite,[1] ferric oxide[2] and reduced silver powder.[3] Adsorption isotherms for *n*-heptane on the same solids (but not the same samples) have subsequently been repeated by Smith[4] and by Young, Beebe and Bienes,[5] who report that their work provides no evidence of first-order phase transitions in those systems. Their papers support the trend to interpret all experimentally observed discontinuities in adsorption isotherms as caused by slow rates or diffusion inside the sample or errors in the apparatus.

The chief remaining evidence for a first-order phase transition of an adsorbed film on a solid surface now devolves on the adsorption isotherms of ethane on sodium chloride and on potassium chloride crystals at 90°K., reported by Ross and Boyd,[6] and since verified in this laboratory on a different sample of sodium chloride at 90°K. by Mr. W.

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[1] G. Jura, W. D. Harkins and E. H. Loeser, *J. Chem. Phys.*, **14**, 344 (1946).

[2] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *ibid.*, **14**, 117 (1946).

[3] Jura, *et al.*, *ibid.*, **13**, 535 (1945).

[4] R. N. Smith, THIS JOURNAL, **74**, 3477 (1952).

[5] D. M. Young, R. A. Beebe and H. Bienes, *Trans. Faraday Soc.*, **49**, 1086 (1953).

[6] S. Ross and G. E. Boyd, "New Observations on Two-Dimensional Condensation Phenomena," MDDC Report 864, 1947,