for sp³ hybridized C^{13} has values of about 4.0 c.p.s. The data presented here show that for sp³ hybridized C^{13}, $J_{C^{13}-C-C-H}$ is either equal or considerably greater than the corresponding $J_{C^{13}-C-H}$ in the same compound. Such anomalies—spin-spin coupling constants do not decrease monotonically with the number of bonds separating the interacting nuclei—have been observed in various metal alkyls.[5] The general impression has been that J_{M-C-H} is abnormally small. We wish to suggest that perhaps, as in the case of C^{13}, $J_{M-C-C-H}$ is abnormally large, and more intensive studies on J's between interacting nuclei separated by three bonds may explain decreases which are not monotonic with the number of separating bonds.

(5) (a) P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960); (b) R. E. Dessy, T. J. Flautt, H. H. Jaffé and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959); (c) E. B. Baker, *ibid.*, **26**, 960 (1957).

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ANOMALOUS HYDROGEN–DEUTERIUM DISTRIBUTION IN STIBINE PREPARED FROM ANTIMONY(III) AND BOROHYDRIDE IN HEAVY WATER

Sir:

We wish to report an unexpected deuterium–hydrogen distribution in the preparation of stibine. This preparation yielded SbH_3 to SbD_3 in a ratio of about 15:1 with no partially deuterated stibine detectable. The synthesis[1] consisted of slowly dropping a heavy water solution containing $2.5F$ NaOD, $0.5F$ $KSbO(C_4H_4O_6)$, and $0.4F$ KBH_4 into a heavy water solution $2F$ in D_2SO_4 while vigorously bubbling nitrogen through the reaction mixture at 11 cm. total pressure. The total exchangeable hydrogen was 97% deuterium. The gaseous stibine was trapped and purified as recommended by Jolly.

The infrared spectrum of our preparation showed peaks in the rock salt region at 1945, 1882, 1825, 1406, 1362, 1320, 832 and 775 cm.$^{-1}$. These eight peaks, the only peaks in the spectrum of our sample, are in agreement[2] with the four fundamental vibrations of SbH_3 and the two fundamental vibrations of SbD_3 which were in the range of the prism used. Although the intensity[3] measurements could not be used to determine the relative amounts of SbH_3 to SbD_3 it should be mentioned that the relative absorbancy of v_1 for SbH_3 to SbD_3 was about 10:1.

Mass spectrometric analysis of the stibine showed a broad peak in the 120–130 region, no oxygen, a little water with H_2O greatest and D_2O least, and small amounts of H_2, HD and D_2 with an H to D ratio of about 15.

The sample was decomposed in the gas phase by an electrical discharge, using an ordinary Tesla coil leak detector external to the glass system. The ratio of H to D was estimated from measure-

(1) W. L. Jolly, *J. Am. Chem. Soc.*, **83**, 335 (1961); S. R. Gunn, W. L. Jolly and L. G. Green, *J. Phys. Chem.*, **64**, 1334 (1960).

(2) W. H. Haynie and H. H. Nielsen, *J. Chem. Phys.*, **21**, 1839 (1953); D. C. Smith, *ibid.*, **19**, 384 (1951); American Petroleum Institute Spectra No. 315.

(3) B. L. Crawford, Jr., *J. Chem. Phys.*, **20**, 977 (1952).

ments of the mass peak heights for H_2, HD and D_2 in the completely decomposed sample. Assuming the hydrogen originated only from SbH_3 and SbD_3, our preliminary results gave a ratio of 15:1 for the hydride to the deuteride ratio.

Most of the readily conceivable mechanisms for the reactions producing stibine would be expected to yield SbH_3, SbH_2D, $SbHD_2$ and SbD_3 in ratios which would be predicted statistically from the over-all H to D ratio in the stibine. For our experiment, a statistical distribution would correspond to the most abundant deuterated product being SbH_2D. Hence, it was surprising to find SbD_3 as the only deuterated product. The D in the stibine did not originate from borohydride since the hydrogens of borohydride ion are known not to exchange[4] with the hydrogen of an aqueous solvent.

One possibly is the existence of two independent paths, one resulting in SbH_3 and the other SbD_3. The path leading to hydride formation would involve reactions only with BH_4^-. The second path leading to the deuteride would involve reactions of deuteriodiborane with Sb(III). In concentrated sulfuric acid some diborane[5] is formed from borohydride ion; and diborane has exchangeable[6] hydrogens. Such a two-path mechanism can be used to explain the appearance of SbD_3 (without other deuterio species) in addition to the expected SbH_3.

Work is in progress to elucidate the mechanism of this deuteration and to study the analogous reactions with the corresponding As, Sn and Ge compounds.

We wish to acknowledge assistance of Mr. N. Neunke and thank Dr. H. Papazian for measuring the infrared spectrum.

(4) P. R. Girardot and R. W. Parry, *J. Am. Chem. Soc.*, **73**, 2368 (1951).

(5) H. G. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959).

(6) S. Kaye and T. Freund, unpublished results.

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THE LEAVING GROUP AS A FACTOR IN THE ALKYLATION OF AMBIDENT ANIONS

Sir:

The reaction of nitroparaffin salts with alkyl halides may occur as carbon-alkylation or as oxygen-alkylation. The latter is productive of nitronic esters (II) which are not isolated; instead the carbonyl compound and oxime are obtained and

I　　　　　　　　　　II
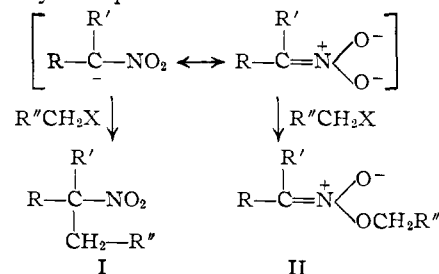
it is generally assumed that they arise from the nitronic ester.[1]

(1) L. Weisler and R. W. Helmkamp, *J. Am. Chem. Soc.*, **67**, 1167 (1945); H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767, 3482 (1949).