

for  $sp^3$  hybridized  $C^{13}$  has values of about 4.0 c.p.s. The data presented here show that for  $sp^3$  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.<sup>5</sup> 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<sup>1</sup> consisted of slowly dropping a heavy water solution containing 2.5*F* NaOD, 0.5*F*  $K_2SbO(C_4H_9O_6)$ , and 0.4*F*  $KBH_4$  into a heavy water solution 2*F* 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<sup>2</sup> 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<sup>3</sup> 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  $\nu_1$  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<sup>4</sup> 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<sup>5</sup> is formed from borohydride ion; and diborane has exchangeable<sup>6</sup> 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.

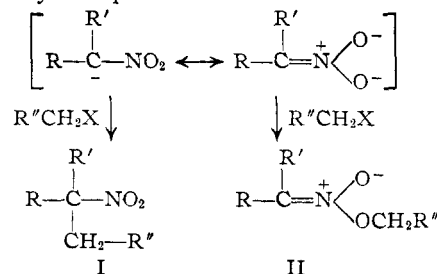
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#### THE LEAVING GROUP AS A FACTOR IN THE ALKYLATION OF AMBIDENT ANIONS

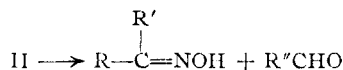
Sir:

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



it is generally assumed that they arise from the nitronic ester.<sup>1</sup>

(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).



Haas and Bender,<sup>1</sup> who studied the reaction of nine *para*-substituted benzyl halides with the sodium salt of 2-nitropropane, showed that only *p*-nitrobenzyl chloride gives carbon-alkylation; all the other benzyl halides examined yield aldehydes, evidently arising from oxygen-alkylation.

It now has been found that the uniqueness of the *p*-nitrobenzyl system depends not only on the *p*-nitro group but also, and in a dramatic way, on the leaving group. For example, whereas *p*-nitrobenzyl chloride gives 95% carbon-alkylation the use of *p*-nitrobenzyl iodide results in 81% oxygen-alkylation; Table I summarizes our findings. Such dependence of the reaction course on the nature of the leaving group has not been demon-

TABLE I

NATURE OF REACTION OF  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$  WITH THE LITHIUM SALT OF 2-NITROPROPANE IN DMF AT  $-16^\circ$  AS A FUNCTION OF X<sup>a</sup>

$\text{X}$	C, %	O, %
$\text{NMe}_3^b$	93	0
	93	0
Cl	95	1
OTos	40	32
Br	17	65
I	7	81

<sup>a</sup> All reactions were run to completion using 0.25 molar  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$  and 0.5 molar lithium salt except for the pentachlorobenzoate ester reaction which was 0.035 molar in ester and 0.07 molar in lithium salt. All yields refer to pure products isolated except for the % 0 in runs employing the tosylate, bromide and iodide; here the aldehyde yields are by gas chromatography and are *ca.* 10–15% higher than the yields of pure *p*-nitrobenzaldehyde 2,4-dinitrophenylhydrazone isolated. Reaction times range from *ca.* 35 hr.

for  $\text{X} = \text{NMe}$  (slowest) to 0.5 hr. for  $\text{X} = \text{I}$  (fastest). Repetition of the *p*-nitrobenzyl iodide experiment using the  $\text{X} = \text{Cl}$  reaction time (20 hr.) did not alter the yield of carbon alkylate. <sup>b</sup> Run at  $25^\circ$ .

strated before, either in the alkylation of nitroparaffin salts, or in the alkylation of any other ambident<sup>2</sup> anions.

In contrast, the unsubstituted benzyl system shows no leaving group effect. The reactions of benzyl chloride, bromide, iodide or tosylate with the lithium salt of 2-nitropropane in DMF all give 82–84% yields of benzaldehyde and *ca.* 1% yields of the carbon alkylate (2-benzyl-2-nitropropane).

It is noteworthy that whenever carbon alkylation is observed in the *p*-nitrobenzyl system the reaction rate is much faster than for the corresponding benzyl compound whereas when the *p*-nitro group is unable to effectuate carbon alkylation of the 2-nitropropane anion it simultaneously fails to produce a large increase in rate relative to the corresponding benzyl compound (Table II).

This suggests that oxygen alkylation, the usual mode of reaction of a nitroparaffin anion, derives

(2) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

TABLE II

Reaction rates $\frac{p\text{-O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{X}}{\text{C}_6\text{H}_5\text{CH}_2\text{X}}$	
$\text{NMe}_3$	>100
	>100
Cl	>100
OTos	8
Br	6
I	3

simply from nucleophilic displacement by the oxygen of the anion on the benzylic carbon; however, in the *p*-nitrobenzyl series, when X is a difficultly displaced group, a second mode of attack by the nitroparaffin anion has a chance to compete and it is this second process which is productive of carbon alkylation. The matter of mechanism is currently under investigation.

Aside from its obvious significance as regards the alkylation of other ambident anions, the properties herein reported for the *p*-nitrobenzyl system may very well be important in reactions involving non-ambident nucleophiles and this possibility is being explored.

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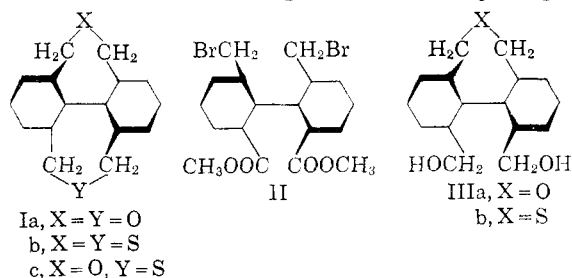
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#### A MODEL FOR ANGLE STRAIN CALCULATIONS. OPTICALLY ACTIVE SYMMETRICALLY BRIDGED BIPHENYLS<sup>1,2</sup>

*Sir:*

The architecture of molecules of type I is uniquely suited for a comparison of theoretical and experimental evaluations of angle strain. A high degree



of constitutional symmetry in cases where  $\text{X} = \text{Y}$  minimizes the assumptions ordinarily entailed in calculations for less symmetrical molecules.<sup>3</sup> We wish to report that calculated angle deformation energies in the transition state conformations for racemization of Ia and Ib account for the experimentally observed energy barriers.

(1) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the Alfred P. Sloan Foundation for partial support.

(2) Satisfactory elemental analyses were obtained for all substances reported. Chemical shifts are expressed for solutions in  $\text{CDCl}_3$ , with reference to external benzene.

(3) *E.g.*, K. E. Howlett, *J. Chem. Soc.*, 1250 (1955); *cf.* F. H. Westheimer, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956, Chapter 12.