TABLE I
POLYHEDRAL BORANE SYNTHESES

Base–borane adduct	Temp., °C.	Products (% yield)
$(C_2H_5)_3NBH_3$	180	$B_{12}H_{12}{}^{2-}$ (>90)
$(CH_3)_3NBH_3$	175	$B_{12}H_{12}{}^{2-}$ (40–60), $B_{12}H_{11}N(CH_3)_3{}^-$ (20), $H_2B[N(CH_3)_3]_2{}^+$ (8)
$(CH_3)_3PBH_3$	175	$B_{12}H_{12}{}^{2-}$ (low), $B_{12}H_{11}P(CH_3)_3{}^-$ (60), $H_2B[P(CH_3)_3]_2{}^+$ (5)
$(CH_3)_3AsBH_3$	175	$B_{12}H_{11}As(CH_3)_3{}^-$ (40), $B_{12}H_{10}[As(CH_3)_3]$ (5), $H_2B[As(CH_3)_3]_2{}^+$ (4)
$(CH_3)_2SBH_3$	70	$B_{11}H_{14}{}^-$ (low), $B_9H_{13}S(CH_3)_2$ (low)
$(CH_3)_2SBH_3$	150	$B_{12}H_{12}{}^{2-}$ (1), $B_{12}H_{11}S(CH_3)_2{}^-$ (20), $B_{12}H_{10}[S(CH_3)_2]_2$ (30), $H_2B[S(CH_3)_2]_2{}^+$ (2)

are best effected in sealed vessels. In place of diborane, B_5H_9 has been used in reaction 1 and B_5H_9,[i] $B_{10}H_{14}$, and $B_{18}H_{22}$ have been used in reaction 2. Other substitutions, i.e., variations in solvent, base–borane complex, and temperature, lead to different products as noted below.

In dimethoxyethane rather than triethylamine, reaction 1 proceeds at 25° and 3 or more atmospheres of diborane pressure to give the triborohydride anion.

$$NaBH_4 + B_2H_6 \longrightarrow NaB_3H_8 + H_2$$
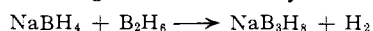
At 50° the yield of NaB_3H_8 exceeds 90%. Above 50° with ethereal solvents, $NaB_{11}H_{14}$ and $Na_2B_{12}H_{12}$ form in relative amounts that are dependent upon the particular ether employed. For example, in dimethoxyethane, the products at 120° are ~50% B_{12} and 40% B_{11}, whereas only B_{11} forms in dioxane.

The products in reaction 2 are almost wholly dependent upon the nature of the base in the base–borane adduct. Replacement of triethylamine by a donor structure in which the donor atom is less hindered leads to the formation of $B_{12}H_{12}{}^{2-}$ derivatives, e.g., $B_{12}H_{11}N(CH_3)_3{}^-$ and, in some cases, $B_9H_{14}{}^-$ derivatives, e.g., $B_9H_{13}S(CH_3)_2$. The use of less hindered bases also leads to the formation of cations of the type[2] $H_2B(base)_2{}^+$. Representative results of reaction of B_2H_6 with various base–borane adducts are listed in Table I. For simplicity, onium cations are not listed, only anions and borane cations.

In these borane syntheses, $B_3H_8{}^-$ and possibly $B_3H_7{}^-$ base appear to be important intermediates, and in fact, as noted above, moderate reaction temperature permits isolation of NaB_3H_8 in high yield.[3] Furthermore, NaB_3H_8 can be substituted for $NaBH_4$ in the synthesis of $Na_2B_{12}H_{12}$ and $NaB_{11}H_{14}$. Pentaborane(9) may also be an important intermediate. In reactions of diborane with trimethylamine, pentaborane(9) has been isolated at intermediate stages.

The new borane syntheses have no parallel in inorganic chemistry but are formally related to cracking reactions of neutral boranes and also of hydrocarbons. The simplicity of these syntheses and the high yields observed contrast sharply with the cracking reactions of neutral boranes. The difference may be a reflection of the facile formation of $B_3H_8{}^-$ in our system as contrasted to the low, steady-state concentration of the presumed B_3H_7 intermediate in the cracking of neutral boranes.

Chemical characterization of the novel derivatives of $B_{12}H_{12}{}^{2-}$ in Table I will be the subject of a separate article.

(2) N. E. Miller and E. L. Muetterties, to be published.

(3) D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963), report a similar synthesis of NaB_3H_8.

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Structural Studies by Nuclear Magnetic Resonance. VI. The Stereospecificity of Coupling between Protons Separated by Five Bonds and Conformations of Some Aromatic Aldehydes

Sir:

In unsaturated systems proton couplings through five bonds are well documented.[1] When these systems are rigid[1a,b,c,i] the interacting protons are *trans-trans* coplanar. We wish to discuss system I, where X is an sp^2 hybridized carbon, nitrogen, or oxygen, and to point out, with emphasis on benzaldehydes, the dependence of $J_{H_1H_4}$ on the dihedral angle formed by the H_1XC and

I
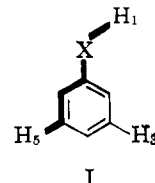
XCH_5 planes.

We have examined at 60 Mc. the n.m.r. spectra of 65 benzaldehydes in several solvents and concentrations varying from neat to 5%. Table I summarizes a few representative data.[2] By varying Y, the carbonyl group can be forced to assume different conformations, e.g., salicylaldehydes (Y = OH) have conformation II;

II   III   IV
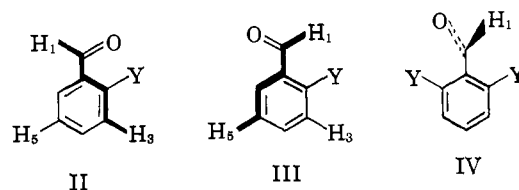
when Y = NO_2, F, Cl, Br, OCH_3 the carbonyl group assumes conformation III.[3]

From the data we draw several conclusions: (a) H_1 couples only with hydrogens *meta* to the carbonyl group. (b) The coupling constant is independent of substituent electronic effects. (c) When the interacting protons are *trans-trans* coplanar (dihedral angle 180°), e.g., H_1–H_3 in II and H_1–H_5 in III, the apparent coupling constant is about 0.7 c.p.s.; when they are *cis-trans* coplanar (dihedral angle 0°), e.g., H_2–H_5 in II and H_1–H_3 in III, $J = 0$. Assuming that *para*-monosubstituted benzaldehydes are planar[4] with sufficiently fast flipping of the carbonyl group about the carbon–carbon single bond to make H_3 and H_5 equivalent, the apparent coupling should be the average of *trans-trans* and *cis-trans*. Indeed, for *para*-monosubstituted benzaldehydes H_1 is a triplet with spacings of 0.35 c.p.s. (d) For benzaldehydes substituted at both *ortho* positions, H_1 couples (triplet) with the hydrogens *meta* to the carbonyl with $J = 0.35$ c.p.s. If in these compounds the

(1) (a) J. E. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963); (b) F. A. L. Anet, *J. Chem. Phys.*, **32**, 1274 (1960); (c) R. J. Tuite, H. R. Snyder, A. L. Porte, and H. S. Gutowsky, *ibid.*, **35**, 187 (1961); (d) J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, **55**, 518 (1959); (e) S. Gronowitz and R. A. Hoffman, *Acta Chem. Scand.*, **13**, 1687 (1959); (f) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **36**, 266 (1962); (g) T. Schaefer, *ibid.*, **36**, 2235 (1962); (h) J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959); (i) G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and S. Ratka, *J. Am. Chem. Soc.*, **85**, 2784 (1963); (j) R. Freeman, N. S. Bhacca, and C. A. Reilly, *J. Chem. Phys.*, **38**, 293 (1963).

(2) *J* values were computed from first-order analysis with reasonably good first-order spectra being obtained for most disubstituted and trisubstituted benzaldehydes. For monosubstituted benzaldehydes, especially *ortho* and *meta*, the complex aromatic region (ABCDX systems) was usually not analyzed and *J* values were computed from the first-order appearance of the H_1 doublet. In all cases $\delta(H_1H_5)/J_{H_1H_5}$ = 200–500.

(3) The conformation of o-nitrobenzaldehyde has been shown to be III; see K. E. Calderbank and R. J. W. LeFèvre, *J. Chem. Soc.*, 1463 (1949).

(4) Benzaldehyde is planar according to R. Bramley and R. J. W. LeFèvre, *ibid.*, 56 (1962).

TABLE I

SPIN–SPIN COUPLING (C.P.S.) IN SUBSTITUTED BENZALDEHYDES

Benzaldehyde	Solvent	H_1	Half-width of H_1	$J_{H_1H_3}$	$J_{H_1H_5}$
2-OH	CH_2Br_2	Doublet		0.6	0
2-OH, 5-Cl, Br, NO, NO_2	CH_2Br_2, CCl_4	Doublet		0.60	0
2-OH, 4-OH	Acetone	Doublet		0.55	0
2-Cl, 4-Cl	CH_2Br_2, DMSO	Doublet		0	0.70
2-NO_2, 4-NO_2	CH_2Br_2, DMSO	Doublet		0	0.65
2-OCH_2, 4-OCH_3	CH_2Br_2	Doublet		0	0.60
2-OCH_3, 5-OCH_3	CH_2Br_2, acetone	Singlet	0.5	0	...
2-NO_2, 5-OH	Acetone	Singlet	0.5	0	...
2-OH, 3-Cl, 5-Cl	CH_2Br_2	Singlet	0.6	...	...
2-NO_2, 4-OCH_3, 5-OCH_3	CH_2Br_2	Singlet	0.5	0	...
3-OMe, 4-OH, 5-NO_2	DMSO	Singlet	0.5	...	...
2-Cl	CH_2Br_2	Doublet		0	0.6
2-OCH_3	CH_2Br_2, DMSO	Doublet		0	0.7
4-NO_2	Acetone	Triplet		0.35	
4-OCH_3	Acetone, CCl_4	Triplet		0.35	
2,4,6-Trimethyl	CCl_4, acetone	Triplet		0.3	
2,6-Dichloro	C_6H_6	Triplet		0.35	
2-OH, 5-Cl, Br, NO, NO_2	CCl_4 + DMSO				
	(1.0 m aldehyde/0.5 m DMSO)	Doublet		0.50	
	(1.0 m aldehyde/2.0 m DMSO)	Doublet		0.40	
	(1.0 m aldehyde/2.0 m DMSO)	Singlet	0.65		
2-OH, 5-Cl, Br, NO, NO_2	DMSO	Singlet	0.50		
2-OH, 5-Cl, Br, NO, NO_2	D_2O (alkaline)	Singlet	0.7		
2-OH, 3-NO_2	C_6H_6, acetone, CCl_4	Doublet			0.60
3-NO_2	CCl_4, C_6H_6, acetone	Doublet			0.45–0.50
3-NO_2, 4-OH	Acetone, C_6H_6	Doublet			0.55–0.60
3-Br or 3-Cl	CCl_4, C_6H_6, acetone	Doublet			0.40–0.45
3-OCH_3	Acetone, CCl_4, C_6H_6	Singlet	0.6		
3-OH	Acetone, C_6H_6	Singlet	0.7		
3-OCH_3, 4-OCH_3	Acetone, C_6H_6, CH_2Br_2	Singlet	0.7		
Piperonal	Acetone, C_6H_6, CH_2Br_2	Singlet	0.7		
3-CH_3	Acetone	Doublet			0.2

plane of the carbonyl group is almost perpendicular to that of the ring (IV), the coupling for a 90° dihedral angle is probably 0.35 c.p.s.

When X = nitrogen (I), $J_{H_1H_5}$ = 0.7 c.p.s. (2,4-dinitrophenylhydrazones, o-nitrophenylhydrazones, and 2,-4-dinitrophenylhydrazine),[1i] 0.6 c.p.s. (N-phenyl-2,4-dinitroaniline), 0.5 c.p.s. (o-nitroacetanilide), and 0.4 c.p.s. (p-acetoxy-o-nitroacetanilide). When X = oxygen (I), $J_{H_1H_5}$ = 0.45 c.p.s. for methyl salicylate[1j] and less than 0.2 c.p.s. for about 20 other phenols that we have examined. For methyl mercaptosalicylate, X = sulfur (I), $J_{H_1H_5} < 0.1$ c.p.s. For 2,4-dichlorobenzaldoxime $J_{H_1H_3}$ = 0.65 c.p.s. In all cases $J_{H_1H_3}$ (cis–trans coupling) is zero.

From the above stereospecific couplings we can draw conclusions regarding the conformations of several aromatic aldehydes.

(1) In dimethyl sulfoxide salicylaldehydes exist in conformation VI and the equilibrium shown is fast. Also, in aqueous solution the carbonyl of the anion has
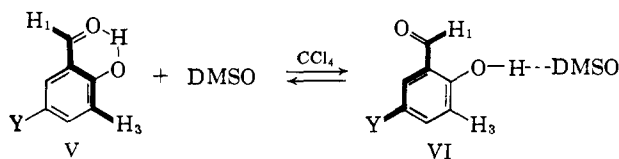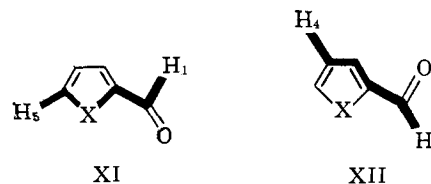

conformation VI.

(2) In solution 3-nitrosalicylaldehyde exists in conformation VII, not VIII.

(3) Assuming that meta-substituted benzaldehydes are planar, when Y = NO_2, Cl, or Br, conformation X contributes 60–70% and IX 30–40% (for 3-nitro-4-hydroxybenzaldehyde X contributes 80–85%); when Y = OCH_3 or OH, X contributes 10–20% and IX 80–90%; when Y = CH_3, IX contributes at least 70%. From
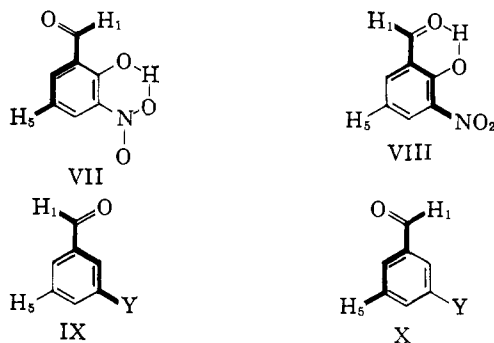
the calculated dipole moments[3] of m-nitrobenzaldehyde for IX (5.3 D.) and X (1.8 D.), and the experimental value (3.3 D.), one calculates 70% contribution by X and 30% by IX (benzene solution); from our values in benzene we also calculate 70% and 30%.

(4) H_1 of furfuraldehyde and thiophene-2-carboxaldehydes[5,6] couples only with H_5 ($J_{H_1H_5}$ about 1 c.p.s.). We find that pyrrole-2-carboxaldehyde ($J_{H_1H_5}$ = 1.2 c.p.s.) and N-methylpyrrole-2-carboxaldehyde ($J_{H_1H_5}$ = 1.0 c.p.s.) behave similarly. We suggest therefore that

these compounds exist in conformation XI, not XII

(5) L. B. Leane and R. E. Richards, Trans. Faraday Soc., 55, 518 (1959).
(6) S. Gronowitz and R. A. Hoffman, Acta Chem. Scand., 13, 1687 (1959).
(7) P. H. Cureton and C. G. LeFèvre, J. Chem. Soc., 4447 (1961), have shown that furfuraldehyde has conformation XI.

(5) H_1 of pyridine-4-carboxaldehyde is a triplet with $J = 0.35$ c.p.s. $J_{H_1H_4}$ of pyridine-2-carboxaldehyde is 0.60 c.p.s. in dimethyl sulfoxide and 0.50 c.p.s. in carbon tetrachloride. $J_{H_1H_5}$ of pyridine-3-carboxaldehyde is 0.44 c.p.s. in carbon tetrachloride[8]; we find it to be 0.50 c.p.s. in dimethyl sulfoxide. If these aldehydes are planar, then pyridine-2-carboxaldehyde exists 70–85% as XIII and 15–30% as XIV. Similarly, pyridine-3-

XIII   XIV   XV   XVI
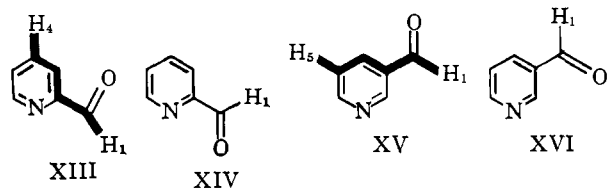
carboxaldehyde exists approximately 70% as XV and 30% as XVI.

The preference of certain conformations over others can be readily explained in terms of competitive hydrogen bonding and dipole, electrostatic, and resonance interactions.

(8) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **36**, 266 (1962).

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Preparation of Solutions of Pure Nitrous Acid

Sir:

The existence of solutions of pure nitrous acid has not been previously reported in the literature and the following technique for their production has been developed. Solutions of sodium nitrite in mixtures of water and ethylene glycol dimethyl ether (glyme) are ion exchanged at $-30°$ to produce effluent solutions of relatively pure nitrous acid.

The process was originally used for the preparation of pure polyamine nitrites by direct neutralization, but can also be used to prepare the nitrites of other cations or for nitrosation and diazotization reactions.

Following is a typical example of the generation of nitrous acid solutions: A 1 × 16-cm. column of acid form Dowex 50W-X4 was equilibrated at $-30°$ with a 66% solution of glyme in water. Through this column at $-30°$ was passed 0.284 g. (4.12 mequiv.) of $NaNO_2$ as a 3% solution in 66% glyme–water. Flow rate was 12 ml./min. which gave a column residence time of about 24 sec. The nitrite solution was followed by 30 ml. of glyme–water.

Column effluent was collected in water containing 5.57 mequiv. of KOH, and back titration of the effluent solution showed a recovery of 97% of theoretical acidity.

Recovery of NO_2^- was determined by the following methods. The neutralized effluent was purged with N_2 through a gas diffusion tube to eliminate the possible presence of dissolved nitrogen oxide gases. A sample of neutralized and purged effluent was then titrated with ceric sulfate which showed a recovery of 94% of the NO_2^-. Evaporation of a portion of the neutralized effluent gave a weight balance which also corresponded to a 94% recovery of HNO_2. Less than 4 p.p.m. of sodium was found in the effluent solution (about 0.01 mequiv.). These results indicate that the production of nitrous acid is nearly quantitative, allowing for a

small amount of column holdup and analytical inaccuracies. If the difference between 97% acidity recovery and 94% nitrite recovery is real, then this may represent decomposition of HNO_2 to HNO_3 and NO. However, the solids recovered are entirely accountable for as KNO_2, which refutes the decomposition. The fate of about 3% of the HNO_2 therefore remained uncertain.

Yost and Russell[1] report the rate of decomposition of nitrous acid as being proportional to the fourth power of nitrous acid concentration, and very temperature dependent. This extreme dependence of rate on concentration and temperature showed the importance of operating at low temperatures and concentrations in order to prepare pure HNO_2.

The effect of concentration is illustrated by the 98% recovery of nitrous acid at as high a temperature as $0°$ when the $NaNO_2$ concentration was reduced to 1.17%.

The applicability of this technique is limited mainly by the need for a nonreactive solvent system which will hold usable amounts of nitrite salts at low temperature. In this work, the glyme–water system was found most useful, although three-component freezing-point diagrams were also explored for $NaNO_2$–water with dimethyl ether, dimethyl sulfoxide, acetone, and methanol. It is quite possible that the reactivities of the last three toward HNO_2 would limit their usefulness. Temperatures of phase separation for the $NaNO_2$–glyme–water system are shown in Table I.

TABLE I

Composition, %			Temperature of
$NaNO_2$	Glyme	Water	phase separation, °C.
7	45	48	−35
8	60	32	− 5
8.68	41.3	50	−34
10	50	40	−26
10	40	50	−29
14	30	56	−20

For those interested in extremely low temperatures, the following may be useful: A $-44°$ freezing point is achieved with 12% $NaNO_2$, 40% dimethyl sulfoxide, and 48% water. A $-50°$ freezing point is achieved with 12% $NaNO_2$, 38% methanol, and 50% water.

(1) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1946, pp. 58–61.

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             RECEIVED SEPTEMBER 14, 1963

Optically Active Vinyl Polymers. X. Synthesis of Optically Active Poly-α-olefins from Racemic Monomers by Asymmetric Catalysts

Sir:

Although the resolution of the polymers of some racemic α-olefins in fractions having optical activity of opposite sign[1] seems to indicate that the polymerization rate of the two antipodes on a single catalytic center is remarkably different, no asymmetric catalyst which electively polymerizes one of the two antipodes of racemic α-olefins has been described.[2]

The polymerization of racemic 3,7-dimethyl-1-octene and 3-methyl-1-pentene has been investigated now using catalysts prepared from $TiCl_4$ and bis[(S)-2-methylbutyl]zinc having $[\alpha]^{25}D$ +9.93° (optical purity 96%).[3]

(1) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Am. Chem. Soc.*, **84**, 1487 (1962).

(2) P. Pino, F. Ciardelli, and G. P. Lorenzi, paper presented at the International Symposium of Macromolecular Chemistry, Paris, July 1–6, 1963.