m.p. 84–90°, C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>, m.p. 102–124°, and  $C_{21}H_{21}N_3O_3$ , m.p. 108–114°. Structure 3, assigned to the first alkaloid, has been confirmed by its synthesis from tryptamine and 1f under Bischler-Napieralski conditions (5). Present data, which include  $\lambda_{max}$  (MeOH) 224 ( $\epsilon$  40700), 276 ( $\epsilon$  9500), 290 m $\mu$  (sh,  $\epsilon$  7900),  $\lambda_{max}$ (CHCl<sub>3</sub>) 5.80  $\mu$ , a methyl singlet at  $\tau$  6.14, and signals from 4 indole protons near  $\tau$  2.7 and 3 pyridine protons at  $\tau$  1.03 (d,  $J \sim 2$  Hz), 1.48 (d,  $J \sim 2$ Hz), and 1.89 (3 lines, splitting  $\sim$  2 Hz) in the nuclear magnetic resonance spectrum, indicate that the second is a tetracyclic secondary amine (acylable) and contains a simple indole unit and an isolated 5-substituted methyl nicotinate unit. The third appears, on the basis of data of a similar nature, to be a pentacyclic tertiary amine and to contain a simple indole unit and a disubstituted (probably 4,5-) methyl nicotinate unit.

### (iv) Other Alkaloids

At least 6 other bases are present in the extract, including  $C_{18}H_{17}N_3O_2$ , m.p. 229–232° and  $C_{21}H_{26}N_2O_4$ , m.p. 209–211°; the former probably belongs in group (*iii*), but it appears structurally more complex than those already assigned to that group. All extractions afforded a considerable amount of a component which had the characteristics of a high molecular weight polyhydroxy base.

The composition of the total extract was variable and appeared to depend on factors such as the age of the tree from which the bark was obtained. The question of whether pyridines are

true alkaloids or artifacts produced by reaction of a precursor with ammonia during isolation has been raised previously (6). Our earlier procedures did employ ammonia in the extraction and chromatography steps, but, in a control isolation which carefully avoided ammonia at every stage, we obtained the same pyridine as in the former procedure; unfortunately, none of the more complex alkaloids was isolated by either procedure on this occasion.

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## Reaction of trialkylboranes with diazoacetaldehyde. A new synthesis of aldehydes

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A new aldehyde synthesis has been developed, based on the reaction of organoboranes with diazoacetaldehyde.

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Previous publications have described syntheses of ketones (1), nitriles (2), esters (2), and diketones (3), in which olefins, via their organoborane derivatives, have been simultaneously functionalized and homologated. We have expanded this versatile method to include a new, mild aldehyde synthesis which permits a 2-carbon-atom extension (ethanalation) of olefins by the reaction of trialkylboranes with diazoacetaldehyde (eq. [1]).

$$[1] \qquad R_3B + N_2CHCHO \xrightarrow{-N_2} RCH_2CHO$$

This process conveniently augments the repertory of organoborane-based aldehyde syntheses, which to date have been limited to 1- (4) and 3carbon-atom (5) chain-lengthening reactions.

Some typical examples are summarized in Table 1. The reactions of organoboranes derived from 1-alkenes as well as cyclopentene proceed in good yield (77–98 %); yields are lower, however, for sterically-hindered trialkylboranes. Triarylboranes also react successfully, as exemplified by the conversion of triphenylborane to phenylacetaldehyde (76%).

Although the hydroboration of monosubstituted terminal olefins produces approximately 94% primary and 6% secondary alkyl groups (6), the product from reaction of the trialkylborane derived from 1-butene was hexanal; no evidence (gas-liquid phase chromatography (g.l.p.c.)) for the formation of 3-methylpentanal was observed. Since a similar migrational preference of primary over secondary alkyl groups has also been noted in the organoborane-diazoacetic ester reaction (2), these developments permit the synthesis of functional derivatives free of isomeric contaminants. By way of contrast, the 3-carbon aldehyde homologation, involving reaction of trialkylboranes with acrolein (5), gives products derived from preferential migration of the secondary alkyl groups in the organoborane.<sup>1</sup>

Functional diazo substrates react with organoboranes to produce intermediates which undergo hydrolysis with extreme ease (2). The g.l.p.c. analysis of a crude tributylborane-diazoacetaldehyde reaction mixture after complete consumption of diazo compound, but prior to the addition of water, revealed the presence of some hexanal. The infrared (i.r.) spectrum exhibited absorption at 1730 (aldehyde carbonyl) and 1670  $cm^{-1}$  (enol ether ?); the latter disappeared at the

### TABLE 1

Conversions of olefins into aldehydes by the reaction of the corresponding trialkylboranes with diazoacetaldehyde in the presence of water

Olefin*	Product	Yield† (%)
Ethylene <sup>‡</sup>	Butanal	88
1-Butene	Hexanal	77
Cyclopentene	Cyclopentylacetaldehyde	98
Isobutylene	4-Methylpentanal	67
2-Butene	3-Methylpentanal	33

\*Each olefin was converted to the corresponding trialkylborane

following the procedure of ref. 6. †By g.l.p.c. analysis. Yield based on diazoacetaldehyde. The molar ratio of diazoacetaldehyde:trialkylborane:water was 1:1.5:10, although we have not determined that these excesses are necessary. A 1:1 molar ratio of organoborane to diazo compound gives somewhat lower yields. ‡Triethylborane was obtained from Alfa Inorganics, Inc.

expense of the former after addition of water. This observation is highly reminiscent of the formation of enol borinates (5) from the 1,4addition of trialkylboranes to acrolein, and implies a similar intermediate.<sup>2</sup>

Rather than conduct the hydrolysis in a separate stage, however, we have observed that higher yields of aldehydes and an experimentally more convenient procedure is achieved by adding water to a solution of organoborane in THF prior to the addition of diazo compound. This permits the rapid, in situ hydrolysis of the functional boron intermediate.

The straightforward experimental procedure is illustrated for the preparation of cyclopentylacetaldehyde.<sup>3</sup> To a mixture of tricyclopentylborane (47 mmole) in 23 ml THF and 1.8 ml (100 mmole) of water, was added (60 min) 8.4 mmole of diazoacetaldehyde4 in 10 ml THF at

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<sup>&</sup>lt;sup>1</sup>A limitation of the R<sub>3</sub>B-diazo reaction at present, a difficulty also encountered in the propanalation process, is that but one alkyl moiety is utilized. Although B-alkyl-9-borabicyclo[3.3.1]nonane (B-R-9-BBN) derivatives have recently been very effectively employed to circumvent this difficulty in the carbonylation reaction and the alkylation of  $\alpha$ -halocarbanions (7), diazo substrates react with B-R-9-BBN derivatives with preferential -cyclooctyl bond migration (8, 9).

However, B-R-9-BBN derivatives fail to react with acrolein.

<sup>&</sup>lt;sup>2</sup>Also, trialkylboranes react with diazo ketones and esters in the presence of deuterium oxide to furnish  $\alpha$ -deuterio ketones and esters with incorporation of one deuterium atom in high yield and isotopic purity (10). The interesting consequences of these developments, suggestive of a mechanistic convergence of the R<sub>3</sub>B-diazo and R<sub>3</sub>B-carbonyl systems, warrant further detailed elaboration, although at present our primary concerns have been focused on the novel synthetic aspects of the

 $R_3B$ -diazo reaction. <sup>3</sup>Organoboranes derived from 1-alkenes react at 0–10°, boranes from 1,1-disubstituted olefins at 40°, whereas those derived from 1,2-disubstituted olefins require a brief reflux period before nitrogen evolution ceases

<sup>&</sup>lt;sup>4</sup>Prepared according to the method of Z. Arnold (11) from  $\beta$ -(*N*-methylanilino)-acrolein and *p*-toluenesulfonyl azide. Caution! Although we experienced no difficulties in numerous reactions of this material, adequate safety precautions should be observed in its preparation and isolation. Arnold reports that diazoacetaldehyde detonates very violently when overheated.

We have also synthesized this material in a convenient manner by reacting formic acetic anhydride with excess diazomethane. (Unpublished results of G. F. Morrison.) usg. prep

25°. Nitrogen evolution was quantitative after an additional stirring period of 60 min at 25°; g.l.p.c. analysis indicated a 98% yield of product.<sup>5</sup> In a duplicate experiment (98% yield), the crude mixture was first processed with aqueous sodium borohydride, then alkaline hydrogen peroxide. The isolated yield of 2-cyclopentylethanol was 72%.

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# Mechanism of silicon hydride addition to hydridocarbonyltris(triphenylphosphine)iridium(I)

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The discovery of the oxidative addition of simple covalent molecules to transition metal complexes has led to major advances in the field of homogeneous catalysis (1, 2). Our interest has been directed towards the reactions of silicon hydrides (3-5) in the hope that a detailed under-

standing of their oxidative addition reactions would help to solve one of the outstanding problems in homogeneous catalysis, namely, the activation of saturated hydrocarbons.

We have previously reported (5) reaction [1], which was shown to result in *cis* addition of the silicon hydride.



The only definitive reaction mechanism that has thus far been demonstrated for oxidative addition to a five-coordinate  $d^8$  complex is that shown in reactions [2] and [3], according to Collman and Roper (1)



[1]

[2]

<sup>&</sup>lt;sup>5</sup>Lower yields were obtained by attempting to distill the sensitive product directly from the crude reaction mixture. Other workers (5) have also observed that direct distillation of aldehydes from residual boron-containing materials leads to product loss. Consequently, we have employed g.l.p.c. to determine yields and isolate pure samples in the preliminary study of this new process.