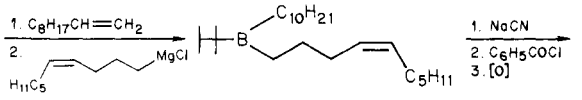
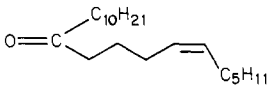
Treatment of the thexylalkylchloroboranes **3** with equimolar amounts of primary organolithium or Grignard reagents results in clean monoalkylations of boron to produce the corresponding thexyldialkylboranes **4** (Table I). They were converted into the corresponding unsymmetrically substituted ketones via the cyanidation reaction[4] to ascertain whether we were indeed dealing with mixed thexyldialkylboranes, and to demonstrate their utility in organic synthesis. This is exemplified by the preparation of (*Z*)-6-heneicosen-11-one (**6**), the sex pheromone of the Douglas fir tussock moth (eq 2).



5



(2)

6

To a solution of **2** (15 mmol) in THF at 0–5 °C was added 1-decene (15 mmol). After the reaction was maintained at 25 °C for 2 h, the resultant thexyldecylchloroborane was treated at −78 °C with a 1 M solution of (*Z*)-4-decen-1-magnesium chloride (15 mmol)[8] in ether. After the mixture was warmed to room temperature and diluted with pentane (20 mL), it was freed from precipitated magnesium chloride by transferring it directly into a second flask through a short column filled with anhydrous Na_2SO_4 (25 g).[10,11] The initial flask was washed with pentane (30 mL), the washings were also passed through the column into the second reaction flask, and the solvents were removed under reduced pressure (1 torr). The resultant organoborane **5** was diluted with THF (30 mL), treated with powdered, very dry sodium cyanide (16.5 mmol), and stirred at 45 °C for 1 h. After the addition of benzoyl chloride (18 mmol)[12] at 25 °C, the reaction mixture was stirred for 12 h at 45 °C before being oxidized with 3 N NaOH (13 mL) and 30% H_2O_2 (7.5 mL) at 40–45 °C. After the mixture was stirred at ambient temperature for 2 h, it was extracted with pentane. Distillation of the extract afforded 3.4 g (74%) of (*Z*)-6-heneicosen-11-one; bp 109–114 °C (10^{-4} torr), n^{25}_D 1.4550.

A summary of the thexyldialkylboranes prepared in this study and the yields of ketones derived from them are shown in Table I. The small amounts of thexyl-substituted ketones produced in these reactions (<5%) confirm the previous report[4] that the thexyl moiety primarily serves as an anchor group. It is important to note here that less than 1% of any symmetrical ketones was formed in these reactions, implying that the mixed thexyldialkylboranes initially formed do not undergo symmetrization under the reaction conditions used.

Thexylchloroborane (**2**) may also serve as a precursor for the preparation of a variety of thexylalkylalkenyl- and thexyldialkenylboranes. These are of considerable synthetic interest. For example, sequential treatment of **2** with 1-hexene at 0 °C, followed by stirring at 25 °C for 2 h and addition of (*Z*)-1-lithio-1-octene (−78 → 0 °C), afforded the thexylalkylalkenylborane shown in entry 5 (Table I). The trans alkenyl moiety is conveniently introduced via monohydroboration of the appropriate 1-alkyne with thexylchloroborane (1 h at 25 °C). Subsequent alkylation produces the [(*E*)-alkenyl]alkylthexylborane (entry 6). The above hydroboration–alkylation sequence may also be extended to the preparation of thexyldialkenylboranes possessing trans–trans and cis–trans alkenyl moieties as shown in entries 7 and 8.

The structures of the alkenylthexylboranes (entries 5–8) are proposed on the basis of the olefins and thexyl alcohol formed when they are protonolyzed or oxidized, respectively. Furthermore, NMR examination of the vinyl proton regions of the unsaturated organoboranes has unambiguously established that the alkylations and alkenylations have proceeded to the tri- and not to the tetrasubstituted boron compounds.

In summary, the difunctional thexylchloroborane provides for transformations involving a combination of hydroboration with alkylation steps. This novel approach possesses great flexibility and opens up a convenient route to thexyl-substituted alkyl- and alkenylboranes and to the many synthetic applications for which they can be utilized. Thus, it is apparent that thexylchloroborane strongly compliments thexylborane (**1**) for the preparation of certain organoboranes containing the thexyl moiety.

Acknowledgments. We thank the National Science Foundation for support of this investigation.

Note Added in Proof. After submitting our manuscript, Professor Brown has informed us that thexylchloroborane may also be prepared from 2,3-dimethyl-2-butene and monochloroborane–methyl sulfide. Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D., manuscript submitted for publication.

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(8) Monohydroboration of 1-chloro-4-decyne with BH_3·SMe_2 followed by protonolysis with acetic acid afforded (*Z*)-1-chloro-4-decene,[9] which was converted into the Grignard reagent in ether solvent.

(9) Kocienski, P. J.; Ostrow, R. W. *J. Org. Chem.* **1976**, *41*, 398.

(10) The cyanidation reaction does not proceed in the presence of magnesium or lithium salts.

(11) The filtration is conveniently effected with the aid of a double-ended Teflon tube (0.422-cm i.d.) under nitrogen pressure.

(12) Use of trifluoroacetic anhydride[4] instead of benzoyl chloride resulted in a lower ketone recovery.

Structure of Goniomine, an Alkaloid of a New Type Biogenetically Related to Indole Alkaloid. X-Ray Analysis of Dihydrogoniomine[1]

Sir:

We have isolated goniomine (**4**) [mp 223 °C (methanol), $[\alpha]^{20}_D$ −270° (*c* 0.5, $CHCl_3$)] from *Gonioma malagasy* Mgf and P. Bt (Apocynaceae),[2] following classical alkaloid extraction and purification methods. Goniomine, $C_{19}H_{22}O_2N_2$, gave the following spectral data: mass spectrum (MS), *m/e* 310 ($M^{+\cdot}$, 80%), 200 (35), 172 (60), 158 (24), 144 (54), 143 (100), 130 (24), 124 (17), 123 (76), 95 (19); IR ($CHCl_3$) 1675, 1590 cm^{-1}; UV (ethanol, qualitative) 212, 233, 272, 305 nm; ^1H NMR ($CDCl_3$, Me_4Si δ = 0) δ 1.42 (d, 3 H, J = 6.5 Hz), 5.18 (d, 1 H, $J \simeq$ 1 Hz), 5.98 (d, 1 H, $J \simeq$ 1 Hz); ^{13}C NMR ($CDCl_3$, 22.63 MHz, Me_4Si δ = 0) δ 15.9 (q), 30.1 (t), 32.2 (t), 38.2 (d), 43.1 (t), 53.4 (t), 59.8 (s), 62 (d), 68 (s), 73.8 (d), 119.2 (t), 122.3 (d), 123.3 (d), 125.2 (d), 128 (d), 138.3 (s), 146.9 (2s), 201.7 (s).

$NaBH_4$ reduction of **4** in methanol yielded a dihydro derivative **6**, Scheme I: mp 228 °C (ethanol); exact mass *m/e* 312.1791 (calcd for $C_{19}H_{24}O_2N_2$, 312.1832); IR ($CHCl_3$) 1675, 1590 cm^{-1}; UV (ethanol, qualitative) 217, 249, 308 nm. In the ^1H NMR data ($CDCl_3$, Me_4Si δ = 0), a new signal at 1.09 (d, 3 H, J = 6.5 Hz) appears while the two olefinic protons disappear. From these data, we could establish the presence of an *exo*-methylene group conjugated with a carbonyl function. Acetic anhydride/pyridine treatment of **4** gave easily an *O*-acetyl derivative **5**: MS *m/e* 352 ($M^{+\cdot}$); IR ($CHCl_3$) 1730, 1680, 1605 cm^{-1}.

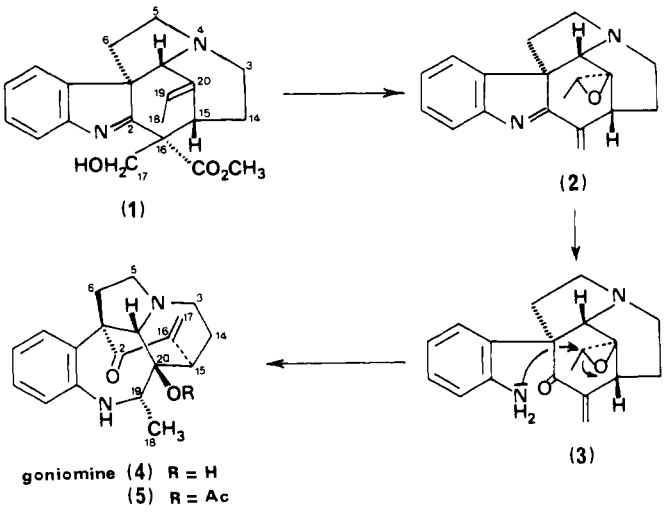
It was not possible to assign a structure fitting with the chemical results and the spectral data although it was probable that goniomine was related to indole alkaloids such as the other known alkaloids found in the same plant. We will indeed see that goniomine has quite unexpected chemical reactivity. The complete structure and relative stereochemistry of goniomine were deduced from the single-crystal X-ray study of its 16,17-dihydro derivative[3]

(1) The first communication on the structure of goniomine was given at the International Symposium on Recent Advances in the Chemistry and Biology of Alkaloids, London, April 1979.

(2) Markgraf, F.; Boiteau, P. *Adansonia* **1972**, *12*, 223–229.

0002-7863/80/1502-5920$01.00/0

Scheme I



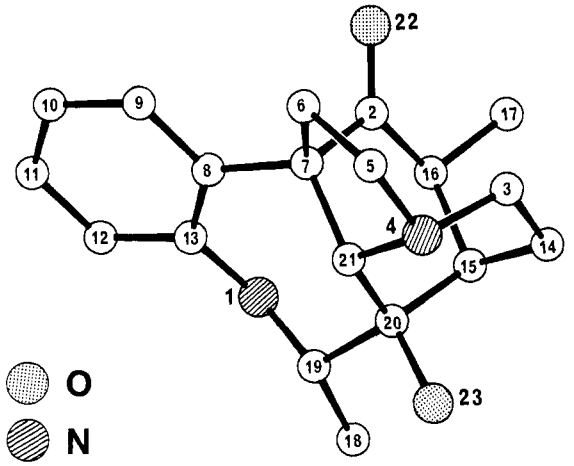
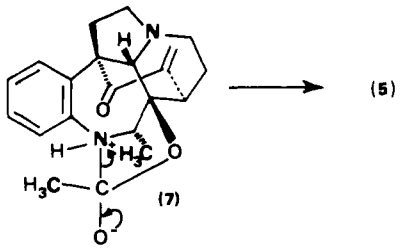


Figure 1. Perspective drawing of dihydrogoniomine (**6**).

(**6**) because crystals of goniomine itself were not suitable for such an analysis.

Crystals of **6** belonged to the monoclinic system, space group $P2_1$, with two molecules ($Z = 2$) in the unit cell of dimensions $a = 8.209$ (9), $b = 10.006$ (21), $c = 9.920$ (9) Å, $\beta = 102.0$ (1)°, $V = 797.02$ Å^3. A total of 1504 data were measured on a Philips PW 1100 diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) and the $\theta/2\theta$ scan technique. Of these reflections, 808 having $I > 3\sigma(I)$, σ deduced from counting statistics, were considered as observed. The coordinates of the nonhydrogen atoms were derived by using the direct-methods program MULTAN 77.[4] All the hydrogen atoms were located on successive difference electron-density maps. The structure was refined by the full-matrix least-squares methods with anisotropic thermal factors for the nonhydrogen atoms and the hydrogen atoms fitted geometrically. Those of the methyl and of the hydroxyl groups were located on a difference Fourier map. For the observed reflections, $\sum||F_o| - |F_c||/\sum F_o$ was 0.044. Figure 1 shows a perspective view of the molecule with the labeling of the atoms. The seven- and the five-membered rings are in chair and half-chair conformations, respectively. An intramolecular hydrogen bond of 2.75 Å is observed between the nitrogen atom N(4) and the hydroxyl group O(23)-H (N···H = 2.0 Å, N···H-O = 128°). The nitrogen atom N(1) (sp^3) is hydrogen bonded to the keto group O(22) of another molecule (N···O = 3.07 Å, O···H = 2.22 Å, N-H···O = 142°). Further crystallographic details can be found in the supplementary data.

Scheme II



The formation of **5** from goniomine (**4**) in Ac_2O/pyridine is remarkable for two reasons: N(1) is not acetylated in conditions where this would be expected, and a tertiary O-acetyl derivative is formed. This result can be explained by the formation of an intermediate oxazolidine (**7**), the opening of which, during workup, leads to the *O*-acetyl derivative **5** (Scheme II).

A reasonable biogenetic hypothesis (Scheme I) starting from precondylocarpine (**1**) can be proposed for goniomine (**4**), involving the intramolecular opening of the 19,20-epoxide by attack of the primary amine formed by the cleavage of the N(1)-C(2) imine bond. With this hypothesis, The absolute configuration of goniomine should be that depicted in Scheme I, related to the condylocarpine series.[5]

Goniomine represents a new type of alkaloid derived from the tetrahydro-1*H*-1-benzazepine ring system and is almost certainly biogenetically related to monoterpenoid indole alkaloids. Until now, the only alkaloids following the same biosynthetic pathway and no longer having an indole nucleus were the quinoline alkaloids quinine and camptothecin.[6]

Acknowledgments. We thank Drs. A. Ahond and B. C. Das for fruitful discussions concerning the spectral data of goniomine and its derivatives.

Supplementary Material Available: Fractional coordinates (Table I), anisotropic thermal factors (Table II), bond distances and angles (Table III), principal torsional angles (Table IV), observed and calculated structure factors (4 pages) (Table V) (9 pages). Ordering information is given on any current masthead page.

(3) Biogenetic numbering has been used: Le Men, J.; Taylor, W. *Experientia* **1965**, *21*, 508-510.

(4) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J.-P. MULTAN 77, 1977. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. University of York (England) and Louvain-la-Neuve (Belgium).

(5) Klyne, W.; Buckingham, J. "Atlas of Stereochemistry", Oxford University Press: London, 1974; p 151.

(6) Wall, M. E.; Wani, M. C.; Cook, C. E.; Palmer, K. H.; McPhail, A. T.; Sim, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 3888-3890.

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Persulfonium Salts: The Reaction of a Difluoropersulfurane with Lewis Acids

Sir:

We report evidence for stable, cationic, and pentacoordinate (10-S-5)[1] organosulfur species which we propose to call per-

