absence of moisture, relatively stable. From their complicated reaction with water, no **14** or other pseudobasic carbinol, but some **4**, can be recovered.

Interesting is the base-catalyzed air oxidation of **14** to **4**. Whereas, *e.g.*, an oxygen-free DMF solution of **14** and $KOC(CH_3)_3$, 0.5 *M* in each, is stable at room temperature, upon admission of air **4** is rapidly and exclusively formed.

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## 7,12-Dihydropleiadenes. III. Conformational Preferences in 7-Alkyl-7,12-dihydropleiadenes

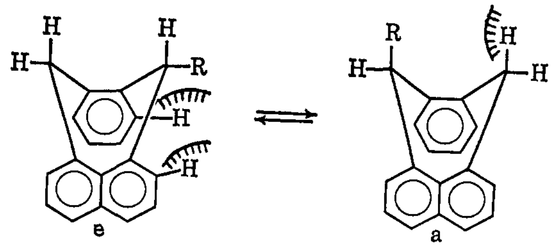
*Sir:*

The effective steric bulks of methyl, ethyl, and isopropyl groups are generally considered[1,2] to be of comparable magnitude and substantially less than the corresponding bulk of the spherically symmetrical *t*-butyl group, due to the ability of the unsymmetrical ethyl and isopropyl substituents to rotate in such a way that their β-methyl groups are removed from compression with proximal atoms.[1,2] The resulting small decrease in entropy produces only minor changes in the conformational energies of these alkyl groups on cyclohexanes[1,2] and their effect on acid–base equilibria[3,4] and nucleophilicity of 2-alkylpyridines.[3,4] We wish to report on the conformational preferences of 7-methyl-, 7-ethyl-, and 7-isopropyl-7,12-dihydropleiadenes,[5] noting that there are great differences in their conformational equilibria, contrary to the usually encountered similarities.

The two conformers of each 7-alkyl-7,12-dihydropleiadene were clearly evident in the low-temperature (*ca.* −20 to −40°) nmr spectra[6] and were characterized by the appropriate $C_7$-methine proton signal. We have previously shown that equatorial $C_7$ and $C_{12}$ protons in 7,12-dihydropleiadenes (DHP) resonate at higher field than the axial protons.[7] Comparison of $\delta_{C_7\text{-}H}$ with the chemical shifts of axial and equatorial $C_{12}$ protons in the 7-alkyl-DHP's thus allows one to deduce the position of the methine proton, and consequently the alkyl group as well. Pertinent nmr data are presented in Table I.

The following conclusions emerge from the chemical shift data and integrated peak areas. (1) The major $C_7$-methine quartet in 7-methyl-DHP appears at low field relative to the minor quartet. The former signal corresponds to the *axial* $C_{12}$-methylene proton and the latter with the *equatorial* $C_{12}$ proton, these assignments having been established previously. Thus the main conformer has the $C_7$-methyl group equatorial,[8] with $\Delta F°_{253}$

Table I. Low-Temperature Nmr Spectra of Conformational Isomers of 7-Alkyl-7,12-dihydropleiadenes[a]



| Compd | $\delta_{C_7\text{-}H}$ | $C_7$-R | [a]/[e] | $\Delta F°_{253}$, kcal/mole |
|---|---|---|---|---|
| 7-Methyl-7,12-DHP-12,12-$d_2$ | e 303 ($J \sim 7$)<br>a 259 ($J \sim 7$) | .... | 0.13[b] | +1.0 |
| 7-(Ethyl-α,α-$d_2$)-7,12-DHP | e 293<br>a 240 | e 64<br>a 54 | 1.05[c] | 0.0 |
| 7-(Ethyl-α,α-$d_2$)-7,12-DHP-12,12-$d_2$ | e 294<br>a 242 | e 66<br>a 55 | | |
| 7-Isopropyl-7,12-DHP | a 209 ($J$ [10]) | .... | ≥20[d] | −1.5[d] |

[a] Measurements were made at $T = -20 \pm 2°$ on an A-60 spectrometer equipped with A-6040 variable temperature controller; chemical shifts (probable accuracy ±1 cps) are reported in cycles per second downfield from internal TMS in $CDCl_3$ solvent. The axial $C_{12}$-proton doublet appears at 306 ± 6 cps in all compounds not $C_{12}$ deuterated, whereas the equatorial $C_{12}$ protons showed up at 229 ± 7 cps (all geminal coupling constants *ca.* 15 cps). All $\Delta F°$ values reported are estimated to be accurate to ±0.1 kcal/mole. [b] Integrated area of $C_7$-proton signals. [c] Integrated area ratio of methyl signals (in $C_7\text{–}CD_2CH_3$). [d] No detectable signal for conformer e (therefore, ≪5% present, if any).

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(1) (a) E. L. Eliel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 761 (1965); (b) E. L. Eliel and T. J. Brett, *J. Am. Chem. Soc.*, **87**, 5039 (1965).

(2) (a) N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **31**, 894 (1966); (b) N. L. Allinger and S. E. Hu, *ibid.*, **27**, 3417 (1962).

(3) V. Gold, *Progr. Stereochem.*, **3**, 172, 191 (1962).

(4) H. C. Brown, *J. Chem. Educ.*, **36**, 424 (1959).

(5) All compounds gave satisfactory elemental analyses and had spectral properties consistent with their structures.

(6) A variety of dihydropleiadenes show free energy barriers for ring inversion of *ca.* 13.5–15 kcal/mole (P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Am. Chem. Soc.*, **88**, 1477 (1966)). Thus, whereas isolation and study of diastereomeric conformers of 7-alkyl-DHP's are virtually impossible, it is nevertheless quite simple to "freeze out" ring inversion, on the nmr time scale, at temperatures of *ca.* −10° and below.

(7) P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *ibid.*, **88**, 1482 (1966).

(8) Additional evidence for the equatorial preference of methyl comes from base-catalyzed equilibration studies of *cis*- and *trans*-7,12-dimethyl-7,12-dihydropleiadenes, where it was shown that the former isomer (diequatorial) predominates at equilibrium. By contrast, *trans*-7,12-dimethoxy-7,12-DHP predominated over the *cis* isomer after acid-catalyzed equilibration in methanol, as predicted from the previously observed *axial* preferences of the methoxyl group. These studies will be discussed further in the full paper.

$\simeq$ 1.0 kcal/mole for the equilibrium equatorial $CH_3 \rightleftarrows$ axial $CH_3$. (2) In 7-ethyl-$\alpha,\alpha$-$d_2$-7,12-dihydropleiadene, the high-field methyl singlet is assigned to the *axial* $C_7$–$CD_2CH_3$ group, as in the 7-methoxy-7,12-dihydropleiadene conformers,[7] and the $C_7$-methine signals (seen clearly in the $C_{12}$-$d_2$ compounds) assigned as above, with the high-field signal arising from the equatorial proton. $K_{eq}$ varies somewhat with temperature and is *ca.* 1.1 at $-20°$, giving $\Delta F°_{253} \simeq 0.0$ kcal/mole.[9] The noteworthy result is that the ethyl group has no substantial preference for either position, whereas the methyl group greatly preferred the equatorial position. (3) Only one conformer was detectable in 7-isopropyl-7,12-dihydropleiadene. Since the single $C_7$-methine doublet ($J \simeq 10$ cps) corresponds closely with the equatorial $C_{12}$ proton, the $C_7$-isopropyl group is therefore overwhelmingly axial! Assuming $K_{eq} \geq 20$, $\Delta F°_{253} \leq -1.5$ kcal/mole.

The above preliminary results show that the conformational energies of methyl, ethyl, and isopropyl groups in dihydropleiadenes differ by at least 2.5 kcal/mole. At present, we wish mainly to note that conformational preferences of simple alkyl groups in various molecular arrays can be quite different from each other, in sharp contrast with the situation in simple cyclohexanes.[10]

**Acknowledgment.** We are grateful to the National Science Foundation for generous support of this research.

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[9] More accurate measurements are needed to give meaningful values for $\Delta H°$ and $\Delta S°$ for 7-ethyl-DHP, although preliminary results suggest that *axial* 7-ethyl-DHP has the greater entropy.

[10] This has already been observed to an extent in 2-alkylcyclohexanones but the effect is smaller than in our examples; see also R. D. Stolow, *J. Am. Chem. Soc.*, **86**, 2170 (1964).

[11] Alfred P. Sloan Foundation Fellow, 1963–1967.

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## Reaction of Recoiling Silicon Atoms with Phosphine and Silane

*Sir:*

We wish to report our observations on the chemistry of recoiling silicon atoms in gaseous phosphine and phosphine–silane mixtures. These experiments represent a beginning toward the exploration of the hitherto unknown chemistry of atomic silicon.[1] Our goals in this study are a knowledge of the scope and fundamental mechanisms of silicon atom reactions and an understanding of the roles of electronic structure and kinetic energy as factors determining the reaction of silicon atoms.

In these experiments free silicon atoms were produced from phosphine by nuclear techniques. Gaseous phosphine at *ca.* 2 atm pressure in quartz ampoules was irradiated with a flux of *ca.* $10^8$ neutrons/cm$^2$ sec from the nuclear transformation $Be^9(d,n)B^{10}$ induced by a 20-$\mu$a current of 6-Mev deuterons accelerated by the Washington University Medical Cyclotron. The fast-neutron irradiation of $P^{31}$ (natural abundance 100%) is known to yield $Si^{31}$ (half-life 2.62 hr) from the nuclear transformation $P^{31}(n,p)Si^{31}$ with calculated cross-section 77 mbarns. The recoil energy of a $Si^{31}$ atom formed under these conditions is *ca.* $6 \times 10^5$ ev, thus ensuring the breakage of all bonds present in the precursor molecule. Calculations based on the adiabatic principle[2] indicate that $Si^{31}$ atoms should reach the energy region of chemical reactions as neutral species.

When pure phosphine was irradiated, the sole radioactive product which was eluted by helium from a variety of vapor-chromatographic columns at room temperature was silane ($SiH_4$). The silane contained *ca.* 60% of the total volatile radioactivity in the reaction vessel as determined by the analytical system consisting of two flow counters monitoring respectively the gas stream entering and the gas stream leaving the vapor chromatograph.[3] Reaction products were identified by comparison of retention times on at least two different chromatographic columns with those of authentic samples. It may be safely assumed that the only radioactivity detected in these experiments was the $\beta$-decay of $Si^{31}$.

Addition of cold silane to the reaction mixture prior to neutron irradiation resulted in an increase in the yield of radioactive silane and the appearance of a new radioactive product, disilane ($Si_2H_6$). The presence of even a few per cent of cold silane in the reaction mixture was accompanied by a tenfold increase in the total yield of volatile radioactivity. Increasing the amount of cold silane in the reaction mixture to 50% increased the total yield of volatile radioactivity only slightly and did not seem to have a further effect on the yield of radioactive silane. The yield of radioactive disilane did, however, increase with increasing pressure of cold silane in the reaction mixture. The fraction of the total volatile activity contained in the silane plus disilane also increased with increasing pressure of cold silane in the reaction mixture. The results of a series of experiments at fixed phosphine pressures and varying silane pressures are shown in Table I.

In an effort to determine whether thermal energy silyl radicals ($\cdot SiH_3$) were necessary precursors to radioactive silane produced in these reactions, a 1:1 mixture of phosphine and ethylene was irradiated with neutrons. Ethylene is known to be an efficient scavenger for thermal energy silyl radicals.[4] The yield of radioactive silane was only slightly (<40%) reduced in this experiment. In addition to radioactive silane, other volatile radioactive products were detected which resulted from attack on ethylene by silicon-containing species. These products will be described in a future report.

When a small amount (2%) of ethylene was added to a mixture of silane and phosphine ($SiH_4:PH_3 = 0.82$) prior to neutron irradiation, in order to scavenge ther-

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[1] For recent reports in which the possible occurrence of silicon atoms is considered, see (a) M. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964); (b) D. Snediker and W. W. Miller, "Recoil and Radiation Chemistry of Silanes," in "A Report of Current Research Activities of the Department of Chemistry," The Pennsylvania State University, July 1965; (c) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).

[2] (a) H. S. W. Massey, and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p 441; (b) M. A. El-Sayed, P. J. Estrup, and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

[3] The analytical method is essentially a two-counter version of that described by R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

[4] D. G. White and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 3897 (1954).