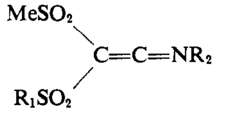
Simon, Kerek, and Ostrogovich,[3] using the Hückel molecular orbital method, estimated that the barrier to thermal racemization of ketenimines as well as of carbodiimides should not be higher than 10 kcal/mol.

Structure determinations of alkyl- or aryl-substituted ketenimines are lacking. An X-ray analysis of the crystal structure of ketenimines IIa and IIb, which have strongly electron-withdrawing sulfonyl substituents on carbon, showed a virtually linear C=C=N—C chain with an unusually short C=N bond (1.15 Å) having essentially triple bond character.[4,5] For IIc an angle of 145° between the bonds of the nitrogen atom was reported, the C=N bond (1.17 Å) being still too short for a double bond.[6]



IIa, R_1 = methyl; R_2 = methyl
IIb, R_1 = phenyl; R_2 = methyl
IIc, R_1 = methyl; R_2 = ethyl

At −99° and above the 100-MHz proton resonance spectrum[7] of a 3% solution of Ia[8-11] in 1:1 vinyl chloride–chlorodifluoromethane shows a doublet for the methyl protons with 6.6-Hz coupling to the methine protons. At −102° the lines are broadened greatly, and on further lowering of the temperature they separate into a pair of doublets with a chemical-shift difference of 4 Hz at −113° (Figure 1).

Under the same experimental conditions the ketenimine Ib[8] shows two methyl doublets with markedly temperature-dependent chemical-shift differences (3.9 Hz at −117°, 2.6 Hz at −71°), merging to one doublet (J = 6.7 Hz) at −51°.

These results confirm[12] the expected dissymmetric geometry for the ketenimines Ia and Ib and demonstrate the rapid interconversion of the enantiomers A and B at room temperature. The free energies of activation for racemization as calculated at the coalescence temperatures are 9.1 ± 0.2 kcal/mol for Ia and 12.2 ± 0.3 kcal/mol for Ib.[13]

Thus, the barriers to recemization in ketenimines are considerably higher than the barrier found for diisopropylcarbodiimide (6.7 ± 0.2 kcal/mol).[2] There seems to be a marked influence of the substituents: replacement of the phenyl group in Ia by CH_3 to give Ib raises the barrier by about 3 kcal/mol.

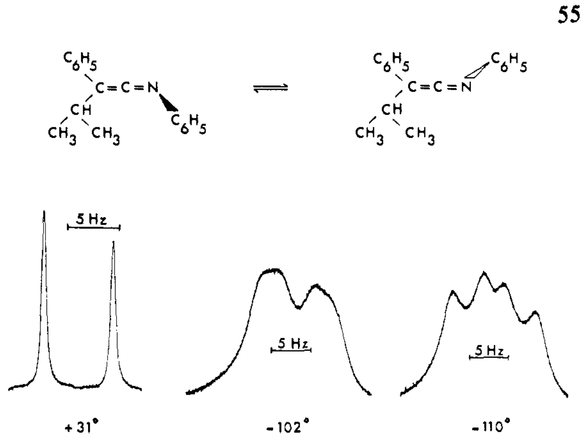
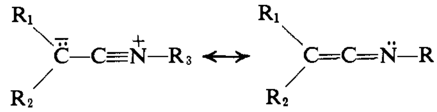


Figure 1. 100-MHz spectra of the methyl protons of phenylisopropylketene phenylimine (Ia) at various temperatures.

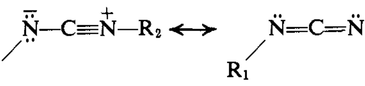
As for the racemization mechanism, a linear polar transition state symbolized by (IIIa ↔ IIIb) seems to be most likely.



IIIa IIIb

This transition state would account for the observed substituent effect. In extreme cases with strongly electronegative groups on carbon, such as IIa and IIb, the linear form (IIIa ↔ IIIb) becomes energetically favored over the bent geometry I.[4,5]

If an analogous transition state (IVa ↔ IVb) is assumed for the interconversion of carbodiimides,[14] the differences in the barriers to racemization of ketenimines and carbodiimides should reflect the



IVa IVb

difference in electronegativities of nitrogen and carbon in imines and olefins, respectively. One would also predict that the barrier to racemization of an aryl-substituted carbodiimide might be considerably lower than that found for diisopropylcarbodiimide (6.7 kcal/mol).[2]

Acknowledgment. This work was supported by the United States Public Health Service.

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(7) Varian HA-100 spectrometer.

(8) Ketenimines Ia and Ib were synthesized in 60 and 62% yields from 2-phenyl-3-methylbutanoic acid[10] and 2,3-dimethylbutanoic acid,[11] respectively, *via* the iminochlorides according to the general method described by Stevens and French.[9] Ketenimine Ia is a yellow oil, bp 112–113° (0.18 mm). Ib is a greenish yellow oil, bp 57–58° (0.16 mm).

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(12) Interpretation of the results in terms of restricted rotation about the isopropyl–ketenimine C–C single bond can be discarded since this barrier to hindered rotation should be less than 5 kcal/mol.

(13) The errors given for the $\Delta F^{\ddagger}$ values are based on estimated maximal errors in the temperature of ±3° and an estimated uncertainty in chemical-shift differences of ±0.5 Hz.

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(15) On leave from Max-Planck-Institut für Medizinische Forschung, Heidelberg, Germany.

(16) Carbodiimides. VI. Carbodiimides. V: see ref 2.

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Received April 10, 1970

Hexa(dimethylgermanium)tetraphosphide. A New Germanium–Phosphorus Cage Molecule

Sir:

We wish to report the preparation and characterization of hexa(dimethylgermanium)tetraphosphide,

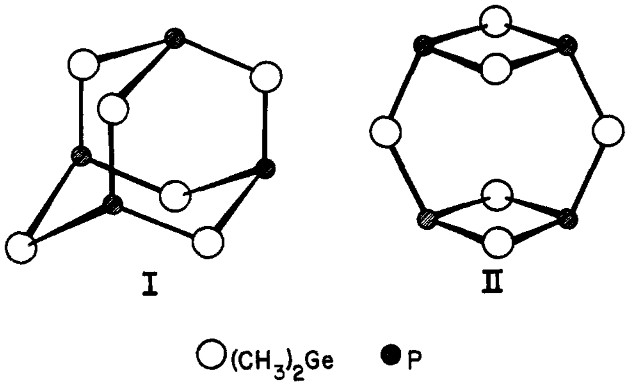

Figure 1. Proposed structures for $[(CH_3)_2Ge]_6P_4$.

$[(CH_3)_2Ge]_6P_4$. This molecule appears to be the first example of what may be an entire series of new germanium–phosphorus cage molecules.

Hexa(dimethylgermanium)tetraphosphide is formed in greater than 95% yield in the mercury-catalyzed thermal decomposition of $(CH_3)_2Ge(PH_2)_2$.[1] Reaction proceeds according to eq 1 and is essentially complete

$$6(CH_3)_2Ge(PH_2)_2 \longrightarrow 8PH_3 + [(CH_3)_2Ge]_6P_4 \qquad (1)$$

after 24 hr at 100°. Upon completion of the reaction, the white solid product is sublimed under high vacuum from the reaction vessel at *ca.* 200°. No residue is left in the reaction vessel. Repeated sublimation yields analytically pure product. *Anal.* Calcd for $C_{12}H_{36}Ge_6P_4$: C, 19.48; H, 4.90; P, 16.72. Found: C, 19.32; H, 4.77; P, 17.00. The product is thermally stable *in vacuo* up to 300°, is oxidized slowly in air, and hydrolyzes slowly at ambient temperature. The $[(CH_3)_2Ge]_6P_4$ is slightly soluble in chloroform and benzene.

The characterization of $[(CH_3)_2Ge]_6P_4$ is based on data obtained from elemental analysis (see above), ir, ^{1}H nmr, and mass spectral measurements, and reactions with HCl and DCl. From these data, the compound stoichiometry has been established and the structures shown in Figure 1 can be proposed.

The polyisotopic mass spectrum of $[(CH_3)_2Ge]_6P_4$ is complex owing to the large number of atoms involved and the presence of six naturally occurring isotopes of germanium (^{70}Ge–^{76}Ge). The spectrum exhibits a series of closely spaced peak envelopes ranging from *m/e* 12 to 754. The envelope of most intense peaks occurs at *m/e* 115–121 and is assigned to $GePCH_2^+$ fragment ions. The cutoff in the mass spectrum occurs at *m/e* 754; however, the most intense peaks in the parent envelope occur at *m/e* 734–746. Comparison of the relative intensities of these peaks with the intensities calculated for the 13 most intense peaks in a Ge_6 envelope shows excellent agreement. The highest mass Ge_6 species which is abundant enough to detect under our conditions occurs at *m/e* 450. Therefore, the highest mass peak at *m/e* 754 in the observed spectrum can be assigned to a $C_{12}H_{36}Ge_6P_4^+$ parent ion.

The $[(CH_3)_2Ge]_6P_4$ reacts quantitatively with HCl to yield $(CH_3)_2GeCl_2$ and PH_3 according to eq 2. Sub-

$$[(CH_3)_2Ge]_6P_4 + 12HCl \longrightarrow 6(CH_3)_2GeCl_2 + 4PH_3 \qquad (2)$$

stitution of DCl for HCl results in the formation of PD_3 as the phosphine product. These data, along with the independent elemental analysis and mass spectral data, confirm the proposed compound formulation. Also, it is clear that the structure of the molecule is one in which the four phosphorus atoms are trigonally bonded to dimethylgermanium groups and in which there are no germanium–germanium or phosphorus–phosphorus bonds. No migration of CH_3 groups from germanium to phosphorus occurs.

The infrared spectrum of $[(CH_3)_2Ge]_6P_4$ (KBr pellet) exhibits absorptions at 3070 (w), 3030 (w), 1234 (s), 1226 (s), 808 (vs), 735 (w, sh), 586 (s), 566 (s), 476 (w), 454 (w), 438 (w), and 420 (w) cm^{-1}. The absorptions at 3070, 3030, and 2960 cm^{-1} can be assigned to C–H stretching modes[2,3] and the peaks at 586 and 566 cm^{-1} can be assigned tentatively to Ge–C stretching modes.[4] The absence of absorptions in the region 2150–2160 cm^{-1} clearly precludes the presence of P–H bonds in the molecule. A complete analysis of the infrared and Raman spectra is planned and will be reported later.

The 60.0-MHz ^{1}H nmr spectrum of $[(CH_3)_2Ge]_6P_4$ in $CDCl_3$ exhibits a single symmetrical resonance at τ 9.55 ppm which can be assigned readily to the methyl protons by comparison with data reported for other methyl(phosphino)germanes.[1] The resonance shows fine structure ($J \sim 2$ Hz) which, due to the limited sample solubility and resultant low signal-to-noise ratio, has not yet been amenable to a more detailed analysis. The presence of only one spectral resonance strongly supports a structure for $[(CH_3)_2Ge]_6P_4$ in which all methyl groups are equivalent.

Structures I and II can be considered for $[(CH_3)_2Ge]_6P_4$. Structure I is of the adamantane type, *e.g.*, analogous to P_4O_6[5] or $P_4(NCH_3)_6$,[6] consisting of a tetrahedral arrangement of phosphorus atoms joined by bridging dimethylgermanium groups located along the six tetrahedral edges. Structure II consists of two four-membered germanium–phosphorus rings joined at the phosphorus atoms by dimethylgermanium groups. In both I and II all phosphorus atoms are equivalent. In I the dimethylgermanium groups are equivalent. In II the dimethylgermanium groups in the rings are different from those connecting the rings. Based on the ^{1}H nmr data, the possible formal analogy with P_4O_6 and $P_4(NCH_3)_6$, and the likelihood that the four-membered rings in II would result in a more highly strained system, it is proposed that I is the correct structure for $[(CH_3)_2Ge]_6P_4$.

In the absence of mercury, thermal condensation of $(CH_3)_2Ge(PH_2)_2$ proceeds more slowly and leads to the formation of stable species containing three and four germanium atoms along with $[(CH_3)_2Ge]_6P_4$. Further studies to characterize the products of these reactions, to determine the role of mercury in the condensation process, and to establish unequivocally the structure of $[(CH_3)_2Ge]_6P_4$ are in progress currently and will be reported later.

Acknowledgment. This work was supported by Grant No. GP-8090 of the National Science Founda-

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tion. The assistance of Mr. David Fox in calculating theoretical mass spectra is gratefully expressed.

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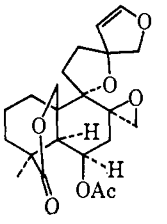
Received May 29, 1970

The Structure of Nepetaefolin, a Prefuranoid Diterpene

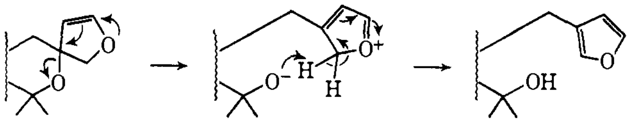
Sir:

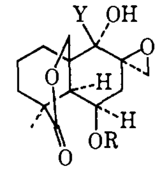
The plant *Leonotis nepetaefolia* R. Br. (family *Labiatae*) is widespread throughout the West Indies, South America, and the African continent, and has attributed to it a variety of salutary physiological effects.[1] In an earlier study of *L. nepetaefolia*, components of the seed oil were characterized,[2] but leaves and stems, wherein the more interesting medicinal properties reside, were not investigated. During a survey of leaf constituents of this plant, we have encountered several diterpenes of novel structure and wish to report evidence leading to stereostructure **1** for one of these, nepetaefolin.



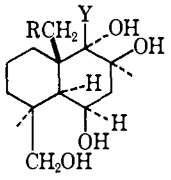
1

Nepetaefolin, mp 260° dec, $[\alpha]^{25}\mathrm{D}$ −14.6° (*c* 0.90, $CHCl_3$), is an unstable substance of composition $C_{22}H_{28}O_7$ and, on warming in $CHCl_3$, isomerizes quantitatively to nepetaefuran (**2**), mp 241–242°, $[\alpha]^{25}\mathrm{D}$ +32.3° (*c* 1.35, MeOH), which is also present in the plant extract. The transformation is characterized by disappearance of nmr signals due to a vinyl ether[3] (δ 5.09, 1 H, d, $J = 3$ Hz; 6.53, 1 H, d, $J = 3$ Hz) and the appearance of a mono-β-substituted furan (δ 6.29, 1 H, t, $J = 0.5$ Hz; δ 7.27, 1 H, m; δ 7.38, 1 H, t, $J = 1$ Hz; mass spectral base peak at m/e 81[4]); a hydroxyl group which could not be acetylated was produced concomitantly. The conversion of nepetaefolin (**1**) to nepetaefuran (**2**) thus involves elimination from a 1,2-dihydrofuran, and is rationalized as

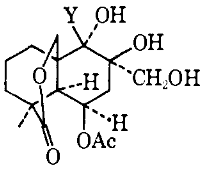




2, R = Ac
3; R = H



4, R = OH
7, R = H



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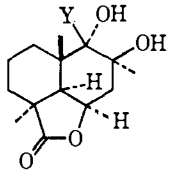

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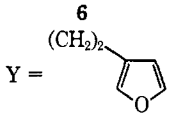
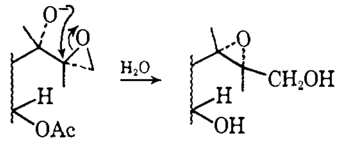


Sharp 3 H singlets at δ 2.07 and 1.96 in the spectra of **1** and **2**, respectively, suggested the presence of acetoxyl groups, and these functionalities were probed in hydrolytic experiments. Saponification of **1**, followed by acidic work-up, gave a substance (**3**), $C_{20}H_{26}O_6$, mp 202–203°, $[\alpha]^{25}\mathrm{D}$ +34.0° (*c* 1.01, MeOH), which, after treatment with Ac_2O–pyridine, afforded nepetaefuran. Base treatment of nepetaefuran, on the other hand, gave a deacetyl compound, mp 196–198°, $[\alpha]^{25}\mathrm{D}$ +29.6° (*c*, 1.29 MeOH), which was isomeric with the C_{20} product from **1**; the appearance of a new AB quartet at δ 3.48 and 3.62 indicated that a primary alcohol had been generated in this reaction. Acetylation of this material in the cold gave a primary monoacetate $C_{22}H_{28}O_7$, mp 165–166° (δ 4.06 and 4.18, 2 H, AB quartet, $J = 12$ Hz); more strenuous acetylation furnished a diacetate which showed no hydroxyl absorption. Since nepetaefuran itself does not contain a primary alcohol and the tertiary hydroxyl initially present has been lost, the transformation occurring upon treatment with base can be formalized as



Proof of the terminal epoxide moiety was obtained by hydrogenolysis of **2** with $LiAlH_4$ in THF, which gave a reduction product (**4**), $C_{20}H_{32}O_6$, mp 137–138°, $[\alpha]^{25}\mathrm{D}$ +21.4° (*c* 0.76, MeOH), containing a new CH_3

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