space group is Pbca, with $a = 16.9$, $b = 18.9$, $c = 14.7$ A. The formula weight from these data and the observed density is 611 (±1%) (calcd for $[PtCl(CO)(P(C_2H_5)_3)_2]SiF_5$: 618; calcd for $0.5[PtCl(CO)(P(C_2H_5)_3)_2]_2SiF_6$: 566).

Although the previous conclusions[1] are now known to be incorrect, the reactions described above are remarkable in several ways. (a) The formation of a platinum carbonyl and BF_4^- under such mild conditions, presumably by interaction of C_2F_4 with the glass surface in contact with the hydride, is remarkable. It can be related to, but is more extreme than, the ability of the isoelectronic Ir(I) and Rh(I) systems to abstract carbon monoxide from oxygen-containing organic solvents.[2,6] (b) The cation is isoelectronic with Vaska's compound[2] and may show similar properties. These are being investigated. (c) This is the first reported isolation of the SiF_5^- ion. Further detailed studies of this species are currently in progress.

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Opening the $B_{10}H_{10}^{2-}$ Cage to Produce $B_{10}H_{12}(Et_2S)_2$

Sir:

The preparations of $B_{10}H_{12}(base)_2$ derivatives have been reported from reactions of decaborane with soft bases.[1,2] These have been converted further to the $B_{10}H_{10}^{2-}$ structure by action of more or harder base.[3] We wish to report the synthesis of $B_{10}H_{12}(Et_2S)_2$ from $(NH_4)_2B_{10}H_{10}$, which is the first time, to our knowledge, that the $B_{10}H_{10}^{2-}$ cage has been opened to clearly reestablish the decaborane skeleton.

This reaction takes on further significance with the recent preparation in these laboratories of the $B_{10}H_{10}^{2-}$ ion from simple borohydrides.[4] $B_{10}H_{12}(Et_2S)_2$, other $B_{10}H_{12}(base)_2$ compounds,[2,3] and carboranes,[5] for example, can now be prepared from simple starting materials, by-passing decaborane as an intermediate.

The product is obtained from the reaction of $(NH_4)_2B_{10}H_{10}$ and anhydrous HCl in ethyl sulfide (eq 1).

$$3(NH_4)_2B_{10}H_{10} + 2HCl + 2Et_2S \longrightarrow B_{10}H_{12}(Et_2S)_2 + 2NH_4Cl\cdot(NH_4)_2B_{10}H_{10} \quad (1)$$

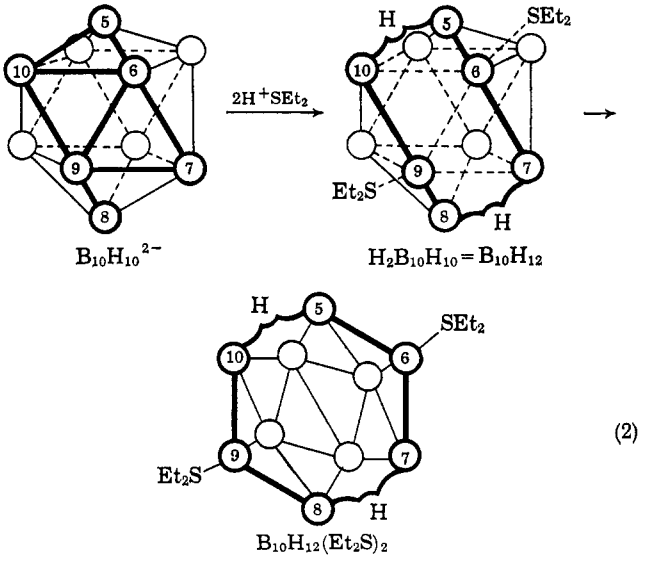
Reaction occurs readily at room temperature. A double salt, $NH_4Cl\cdot(NH_4)_2B_{10}H_{10}$, insoluble in ethyl sulfide, is produced as the by-product. $B_{10}H_{12}(Et_2S)_2$ is recovered in approximately 92% yield based on the above equation from the filtrate by vacuum evaporation of the excess ethyl sulfide. Infrared, X-ray, and nmr comparisons with authentic samples left no doubt as to its identity. The product was somewhat impure but gave elemental analyses approximating the desired compound.

Anal. Calcd for $[(C_2H_5)_2S]_2B_{10}H_{12}$: B, 36.0; C, 31.9; H, 10.6; S, 21.3. Found: B, 34.7; C, 29.6; H, 10.3; S, 20.3.

Work on recovery of the $(NH_4)_2B_{10}H_{10}$ from the double salt by use of other solvents is in progress. With large excesses of HCl the reaction gives some free NH_4Cl and correspondingly higher quantities of $B_{10}H_{12}(Et_2S)_2$. Several samples have been allowed to react with propargyl bromide, and the expected bromomethylcarborane derivative was obtained.[5]

Muetterties has reported obtaining a bridge-hydrogen structure from the $B_{10}H_{10}^{2-}$ ion.[6] Dehydration of an aqueous solution of $(H_3O)_2B_{10}H_{10}$ gave a white solid from which a material could be sublimed. The sublimate showed evidence for bridge hydrogens in its infrared pattern. The unknown had the approximate composition of $B_{10}H_{12}OH_2$. He concluded that the solid belonged to the $B_{10}H_{12}$(base) or $B_{10}H_{13}^-$ structural class. A referee has pointed out that the formation of $B_{18}H_{22}$ from $B_{20}H_{18}^{2-}$ plus acid involves opening $B_{10}H_{10}$ cages. However, degradation with loss of boron also obviously occurred.[7]

Mechanistically the synthesis of $B_{10}H_{12}(Et_2S)_2$ from $(NH_4)_2B_{10}H_{10}$ can be pictured as just the reverse of the $B_{10}H_{12}(base)_2$ conversion to $B_{10}H_{10}^{2-}$ derivatives. Hawthorne suggests that this latter conversion occurs by the removal of protons from the bridge positions in the $B_{10}H_{12}(base)_2$ structure, and that the resulting filled two-center orbitals undergo a nucleophilic displacement of the coordinated bases. In our reaction, protons which are presumably supplied *via* the ethylsulfonium ion, Et_2SH^+, probably attack in the apex region of the $B_{10}H_{10}^{2-}$ cage. Nmr studies with deuterium chloride have established that hydrogen exchange occurs at the apex borons.[6,8,9] Single crystal X-ray



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studies on $Cu_2B_{10}H_{10}$ also show bonding with the Cu^+ ions along apex-equatorial boron edges.[10]

Presumably cage-opening occurs *via* the formation of bridge hydrogens between apex and equatorial borons. Bond rupture and coordination of ethyl sulfide between the equatorial borons result with the ethyl sulfide coordinated borons now becoming the 6 and 9 positions of the resulting $B_{10}H_{12}(Et_2S)_2$ structure. A plausible mechanism is depicted in eq 2 (the numbering system used is that for decaborane and only the "mouth" borons are numbered). The rupture of the cage bonds may involve a multicenter reaction with the Et_2SH^+ ion or simple displacement by some solvent ethyl sulfide.

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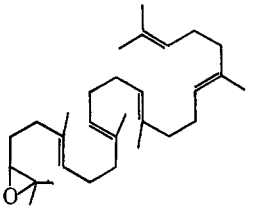
Enzymic Synthesis of β-Amyrin from 2,3-Oxidosqualene

Sir:

Recent studies have demonstrated that lanosterol is synthesized in the mammalian liver from 2,3-oxidosqualene (**1**)[1-3] under the influence of an enzyme, 2,3-oxidosqualene–sterol cyclase, which can be obtained from liver microsomes in a partially purified water-soluble form.[4] The separation of the squalene-to-sterol conversion into discrete oxidation and cyclization steps suggests a similar possibility for the biosynthesis of pentacyclic triterpenes and, therefore, a powerful experimental approach for studying the details of the remarkable rearrangement processes which are supposed to lead from the lupanyl[5] system to the triterpenes of the oleanane (β-amyrin), ursane (α-amyrin),[6] friedelane,[7] and other series. Since it has been shown that β-amyrin (**2**) is formed enzymically from squalene in a homogenate from germinating peas (*Pisum sativum*),[8] this system was selected for initial study. We report here an investigation which demonstrates that 2,3-oxidosqualene is indeed a precursor of β-amyrin in *Pisum sativum* and that the cyclizing enzyme can be obtained in water-soluble form.



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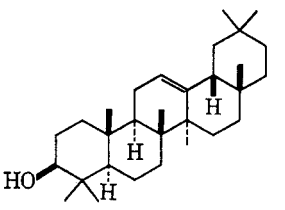

2

Anaerobic incubation for 24 hr at 37° of ^{14}C-labeled 2,3-oxidosqualene with a cell-free homogenate from *Pisum sativum* led to isolation of a product which showed upon thin layer chromatography on silica gel about 35% of the radioactivity in a band with an R_f equal to that of β-amyrin. That this material was in fact primarily β-amyrin was demonstrated by the following experiments. Recrystallization (*ca.* 2 mμ-moles, 6000 counts/min) from ethanol–water with carrier β-amyrin (50 mg) led to a constant specific activity after the first crystallization (131, 106, 105, 104, 108 counts/min per mg). The combined fractions from this recrystallization experiment were acetylated with acetic anhydride in pyridine and chromatographed. The radioactivity was found in the zone characteristic of β-amyrin acetate using a thin layer of silica gel and 5% ethyl acetate–benzene for development. In addition, thin layer chromatography of acetylated biosynthetic material on a 20% silver nitrate–silica gel plate (3:2, chloroform–petroleum ether) showed the absence of labeled lanosterol and an R_f for the radioactive product identical with that of β-amyrin acetate. Vapor phase chromatography of acetylated labeled biosynthetic product using a glass column packed with 2% Epon 1001 on Diatoport S at 235° capable of separating α- and β-amyrin acetates showed >95% of the radioactivity in the β-amyrin acetate peak.

The intermediacy of squalene 2,3-epoxide in the biogenesis of β-amyrin is further supported by an experiment using 2,3-iminosqualene, which has been shown to be a potent inhibitor of enzymic cyclization of 2,3-oxidosqualene to lanosterol.[9] Incubation of ^{14}C-labeled squalene in the presence of 2,3-iminosqualene with a cell-free homogenate from *Pisum sativum* capable of converting squalene to β-amyrin[8] led to isolation by chromatography of about 2% of the radioactivity in a band of R_f equal to that of 2,3-oxidosqualene (using silica gel with 3% ethyl acetate–benzene as solvent). Dilution of this material with carrier 2,3-oxidosqualene and treatment with perchloric acid in aqueous glyme led to a product which upon chromatographic separation (using silica gel with 20% ethyl acetate–benzene as solvent) manifested radioactivity almost totally in the band of R_f corresponding to 2,3-dihydroxylated squalene.[2]

The solubilization and partial purification of this 2,3-oxidosqualene–β-amyrin cyclase from *Pisum sativum* has been effected by a procedure similar to that used in the purification of the 2,3-oxidosqualene–lanosterol cyclase from hog liver.[4] The cell-free homogenate[8] in pH 7.4 phosphate buffer (without added sucrose or glutathione) was treated at 0° with just sufficient sodium desoxycholate solution to effect clarification,

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