absorption at 456 cm^{-1} for $(CH_3)_4NMCl_3 \cdot BF_3$ (M = Ge or Sn). According to Waddington and Klanberg, such an absorption[8] is characteristic of BF_3Cl^- which should be present in IV.

Structures II and III are more difficult to eliminate, but the following data indicate that they are unlikely. (1) Long-wavelength infrared spectra in the M–Cl stretch region exhibit only two bands, an observation consistent with the C_{3v} symmetry of I but not the C_{2v} symmetry of II or low symmetry of III. However, it is possible that the other bands expected for II and III are of low intensity or lie beyond the range of the instrument, 200 cm^{-1}. Upon coordination, there is very little shift in the M–Cl stretching vibrations which indicates that framework of the MCl_3^- is not greatly distorted as is required by structure III or similar multiple bridged structures. (2) Stoichiometry of formation was determined for two acids of varying strengths and at two different temperatures (−45 and 25°), but a residual affinity which is expected for the terminal chloride of structures II and III was not observed. (3) *n*-Butyltin trichloride in methylene chloride was exposed to an excess of BF_3 for 2 hr at −45°, and the BF_3 was quantitatively removed at this temperature; thus, a stable Sn–Cl–B bridge adduct was not formed. Structure III requires that the tin accept an electron pair from the halide attached to boron, and since *n*-butyltin trichloride is a Lewis acid it should form such compounds more readily than $SnCl_3^-$. The lack of μ-SnClFB in this system indicates that III is improbable.

The remaining alternative is structure I which contains germanium–boron or tin–boron donor–acceptor bonds. Thus, π bonding does not appear to be a necessary condition for complex formation with $GeCl_3^-$ and $SnCl_3^-$. Another interesting characteristic of these metal bases is their lack of affinity for diborane under conditions which lead to boron halide addition. Precedent for this unusual order of affinity may be found in our previous work on the basicity of transition metal cyclopentadienyl hydrides.[2] Paradoxically, this order of affinity indicates Sn(II) is a hard base with boron acids, while previous synthetic studies indicate it is a soft base with transition metal acceptors. Softness and hardness are qualitative concepts which undoubtedly originate from a variety of factors.[9] Thus, we cannot expect this classification to always hold when different bonding situations are compared. With transition metal acceptors back π bonding may account for the softness of $SnCl_3^-$, but this is not possible with the boron acids.

Acknowledgment. We thank Professor F. Basolo and Paul Poskozim for suggestions, and Glenn Mack and Professor Sheldon Shore for infrared and B^{11} nmr spectra. This research was supported by Grant GP-3804 from the National Science Foundation.

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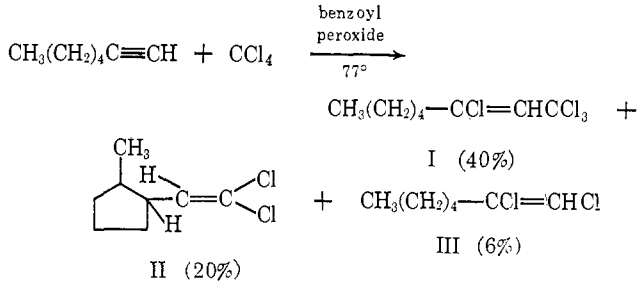
Free-Radical Isomerization. A Novel Rearrangement of Vinyl Radicals

Sir:

Intramolecular 1,5-hydrogen migration[1] in carbon radicals has been proposed in various polymerization[2] and thermal decomposition reactions,[3] but as yet no unequivocal case[4] of open-chain alkyl radical isomerization in solution has been reported. Open-chain saturated alkyl radicals, unlike their cyclic analogs[5] or corresponding oxygen[6] and nitrogen[7] radicals, do not readily abstract an internal 5-hydrogen atom. However, we wish to report that such rearrangement has now been observed with an open-chain vinyl radical.

The vinyl radical intermediate, formed by the peroxide-initiated addition of CCl_4 to 1-heptyne, has been found to abstract internal δ hydrogen, as shown by the major products isolated.



The nmr spectrum of the normal 1,2-addition product I, bp 90–92° (3 mm), contained a triplet at τ 3.5 (J = 0.7 cps, 1 H) and a multiplet at τ 7.3 (2 H) in addition to numerous peaks in the τ 8.3–9.3 region. The infrared spectrum indicated olefin absorption at 1630 cm^{-1}. The absence of any additional vinyl hydrogen peak in the nmr spectrum as well as the absence of 1618 cm^{-1} band in the infrared absorption indicates no significant contamination of I with its allylic isomer $CH_3(CH_2)_4CCl_2—CH=CCl_2$ under our experimental conditions.

Besides the normal addition product, two lower boiling compounds were isolated. The more abundant product, II, bp 77–80° (10.5 mm), consisted of two isomers in about 1.5:1 ratio as determined by vapor phase chromatography. The nmr spectrum of the major isomer showed a doublet at τ 4.35 (J = 9.7 cps, 1.0 H), a multiplet at τ 7.2 (1.0 H), broad absorption in the τ 7.8–8.8 region (7.2 H), and another doublet at τ 9.2 (J = 6.5 cps, 2.9 H). The other isomer had its low-field doublet displaced to τ 4.43 (J = 9.1 cps). The infrared spectrum of each isomer contained a sharp

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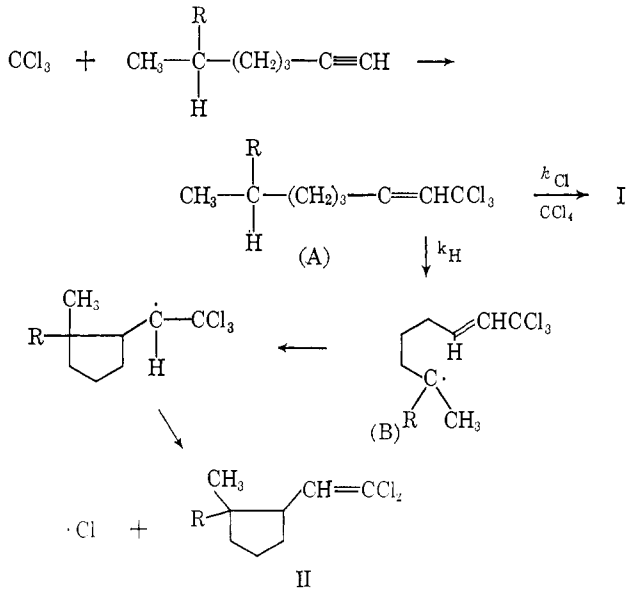
band at 1618 cm^{-1}, indicative of a $-C{=}CCl_2$ linkage.[8] *Anal.* (of the isomer mixture): Calcd for $C_8H_{12}Cl_2$: C, 53.63; H, 6.76; Cl, 39.6. Found: C, 53.33; H, 6.87; Cl, 39.1.

The skeletal structure of the rearranged product II was confirmed by quantitative hydrogenation of the isomer mixture, in the presence of Raney nickel and alcoholic KOH,[9] to a mixture of *cis*- and *trans*-1-methyl-2-ethylcyclopentane, with the *cis* isomer predominating. The vpc retention times of these products as well as their mass spectra were identical with those of authentic samples.

The other major product, III, bp 45–50° (8 mm), was shown to be the Cl_2 addition product of 1-heptyne. Its nmr spectrum and vpc retention time were identical with those of an authentic sample.

When 6-methyl-1-heptyne was used in place of 1-heptyne, the ratio of rearranged cyclic product over the normal 1:1 adduct (R:N) increased to more than 6:1, based on nmr analysis of the crude reaction product as well as on actual isolated yields. The rearranged product, bp 86–89° (10 mm), consisted of a single isomer. *Anal.* Calcd for $C_9H_{14}Cl_2$: C, 55.95; H, 7.31; Cl, 36.7. Found: C, 55.90; H, 7.32; Cl, 36.6. Its nmr spectrum contained a doublet at τ 4.3 (J = 9.7 cps, 1 H) as well as two peaks at τ 9.0 (3 H) and 9.2 (3 H), in addition to broad absorption in the τ 7.3–8.8 region.

The formation of compound II as a major product can best be explained by the free-radical chain mechanism



This mechanism displays three reaction steps involving free radicals: first, intramolecular 1,5-hydrogen abstraction, followed by internal cyclization *via* addition to a double bond,[10] and finally halogen elimination from a β-halo radical.[11] This halogen elimination is considerably faster than Cl transfer from CCl_4 in our system.

The ratio of R:N obtained with 1-heptyne increased with increasing reaction temperature. The activation energy difference was found to be $E_H - E_{Cl} = 2.7 \pm 0.5$ kcal/mole with log $A_H/A_{Cl} = 1.4 \pm 0.3$.

The following points can be deduced from our results: (1) the low ratio of the frequency factors (A_H/A_{Cl}) is in accord with a cyclic six-membered transition state in which the hydrogen from C_5 is abstracted in preference to any other hydrogen; (2) the observed 1,5-hydrogen shift in vinyl radicals, while completely absent from the corresponding secondary alkyl radicals, must be due to the greater reactivity of vinyl radicals which is in accord with the relatively high vinyl carbon–hydrogen dissociation energy.[12] With secondary alkyl radicals the activation energy difference ($E_H - E_{Cl}$) would be expected to be greater than 2.7 kcal/mole and hence the rate of chlorine transfer from CCl_4 would greatly exceed that of internal 1,5-hydrogen shift.

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Biosynthesis of Arthropod Secretions. III. Synthesis of Simple *p*-Benzoquinones in a Beetle (*Eleodes longicollis*)[1]

Sir:

While the composition of arthropod defensive secretions has been the subject of much investigation,[2] little attention has been given to the origin of their repellent components. We have recently shown that two monoterpenes which play a defensive role among insects are synthesized from acetate.[3] Simple *p*-benzoquinones are also widespread components of such defensive secretions and we now wish to report that these quinones appear to arise *via two independent pathways*. The first of these involves utilization of the preformed aromatic ring of tyrosine or phenylalanine, a mechanism which finds analogy in ubiquinone biosynthesis in animals.[4] The second involves building up of the quinone ring from acetate units, a well-known microbiological mechanism for aromatic ring biosynthesis,[5] only recently considered to occur in animals.[4,6]

For the initial study of the biosynthesis of *p*-benzoquinones in arthropods, we chose to investigate the

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(4) J. Glover in "Biochemistry of Quinones," R. A. Morton, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 7.
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(6) For recent evidence of aromatic biosynthesis from aliphatic precursors in a nematode worm (*Caenorhabditis briegsae*) and in a female cockroach (*Periplaneta americana*), see M. Rothstein and G. Tomlison, *Biochim. Biophys. Acta*, **63**, 471 (1962); P. C. J. Brunet, *Nature*, **199**, 492 (1963). Since our experiments were carried out with entire, intact beetles, the results obtained apply to this animal *including* any symbiotic organisms to which the beetle is normally a host, a limitation also applicable to the above cited study of *P. americana*.