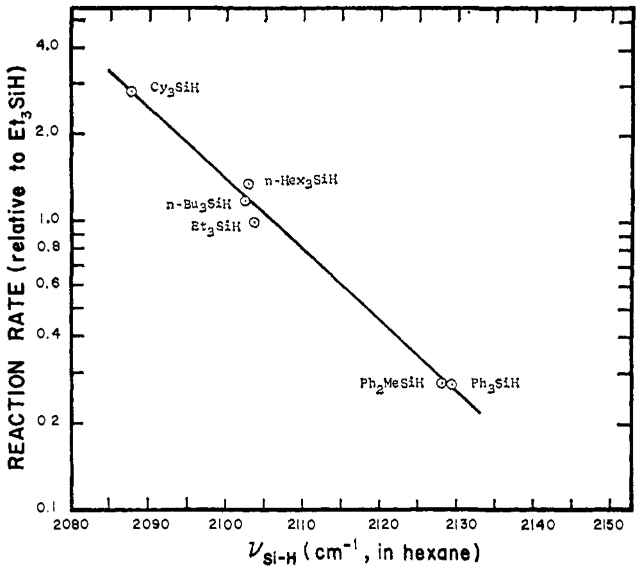

Figure 1. Logarithm of the relative rates of silane ozonolysis as a function of the Si–H stretching frequency.

sorption spectrum. Moreover, in accordance with the assumption that the spectrally significant reduced masses for the compounds studied are relatively large and constant,[3] which implies that ν_{Si-H} is a measure of the related force constant, a potential energy parameter, it might be expected that, for a given temperature, log (Si–H reactivity) should be a linear function of ν_{Si-H}.[4,5] That such a correlation is very well the case is shown in Figure 1, where the logarithms of the reaction rates of six silanes in hexane toward ozone, relative to that of triethylsilane, prove to be an excellent linear function of the Si–H stretching frequency. The slope of -0.024 implies a doubling of relative reactivity for each spectral shift of -12 cm^{-1}. This relationship and its sign is consistent with Si–H stretching being important in the reaction's rate-determining step, with the stronger bonds (those of higher frequency) possessing less reactivity.

Alternatively, the ν_{Si-H} value in a hydrosilane may be a measure of the electronic environment of the silicon atom in the molecule,[6] with the slope of the linear plot, herein described, reflecting the reaction mechanism—the response of the reactant to the increase or decrease of electronic density on the silicon atom. In this case, the stretching vibration may not be involved in the rate-determining step. This view would encompass, quantitatively, the positive slope relationship derived from the data of Hetflejš, Mareš, and Chvalovsky on the solvolyses of vinylethylsilanes,[7,8] but not of their alkoxy- and silyloxysilanes.[8]

Further studies are in progress to clarify the significance of the linear correlation.

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[3] The Si–H stretching frequency, ν_{Si-H}, is not found correlatable with the mass R in R_3SiH.

[4] J. F. Hyde, P. L. Brown, and A. L. Smith, *J. Am. Chem. Soc.*, **82**, 5854 (1960), have reported a thermodynamically significant linearity between chlorosilane hydrolysis equilibrium constants and the related hydrosilane stretching frequency but give no indication of a kinetic correlation.

[5] In accordance with a referee's suggestion, it should be emphasized that bond frequency and bond dissociation energy are not always parallel particularly for polyatomic systems.

[6] Correlations between ν_{Si-H} and substituent σ^* summation have been reported by H. W. Thompson, *Spectrochim. Acta*, **16**, 238 (1960).

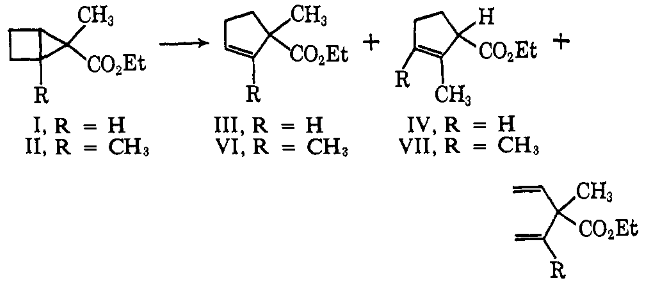
[7] J. Hetflejš, F. Mareš, and V. Chvalovsky, *Collection Czech. Chem. Commun.*, 30, 1643 (1965).

[8] J. Hetflejš, F. Mareš, and V. Chvalovsky, Scientific Communications, International Symposium of Organosilicon Chemistry, Prague, 1965, p 282.

Reactions of Bicyclo[2.1.0]pentanes. I. Thermal Rearrangement Involving an Unprecedented 1,2 Carbethoxyl Migration[1]

Sir:

Current interest in the properties of bicyclo[2.1.0]pentanes[2] prompts us to communicate our observations concerning the thermal behavior of the bicyclo[2.1.0]pentanecarboxylates I and II. Both of these were generated photochemically from their appropriate cyclopropylacrylic ester precursors. Compound II has previously been derived from such a photolytic rearrangement,[3] while I was produced in good yields from the irradiation of ethyl 2-methyl-3-cyclopropyl-2-propenoate. Compound I was converted at temperatures above 300° to four products, A–D, formed in the ratio 1:5:1:10.[4] Of these, B, C, and D were found to be esters isomeric with I.[5] Ester C, formed only as a minor product, was demonstrated to have structure III by means of spectral comparison with an authentic sample of III prepared by an independent route.[6] The structure of the major product D was established as IV by comparison with a sample of IV prepared from the photochemical or thermal vinylcyclopropane rearrangement of ethyl 3-cyclopropyl-2-butenoate as previously reported by us.[7]



I, R = H
II, R = CH_3

III, R = H
VI, R = CH_3

IV, R = H
VII, R = CH_3

V, R = H
VIII, R = CH_3

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[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P25.

[2] (a) P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965); (b) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967); (c) T. H. Kinstele, R. L. Welsh, and R. W. Exley, *J. Am. Chem. Soc.*, **89**, 3660 (1967); (d) W. G. Dauben and J. R. Wiseman, *ibid.*, **89**, 3545 (1967); (e) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964); (f) J. P. Chesick, *ibid.*, **84**, 3250 (1962); (g) M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962); (h) R. T. Lalonde, *ibid.*, **87**, 4217 (1965); (i) R. T. Lalonde and L. S. Forney, *ibid.*, **85**, 3767 (1963); (j) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

[3] M. J. Jorgenson, *J. Am. Chem. Soc.*, **88**, 3463 (1966).

[4] The amount of C and C′ formed was strongly dependent on the reaction scale, diminishing substantially when the reaction was scaled down. The ratios reported for both I and II are those for the pyrolysis under identical conditions of a 25-mg sample.

[5] Compound A exhibited no carbonyl stretching absorption in the infrared but revealed strong absorption at 1210 cm^{-1}, compatible with an ether structure for A; it was not further characterized.

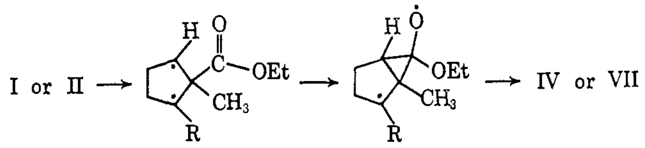
[6] C. Ouannes, M. Dvolaitzky, and J. Jacques, *Bull. Soc. Chim. France*, 776 (1964).

[7] M. J. Jorgenson and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965).

Ester B is assigned structure V on the basis of its distinctive ir and nmr spectra [$\nu(CCl_4)$ 3100 (w), 1740 (s), 1630 (w), and 920 (s) cm^{-1}; $\tau(CCl_4)$ 3.6–4.3 (complex absorption, two protons), 4.7–5.3 (complex absorption, four protons), 5.92 (quartet, two protons), 8.67 (singlet, three protons), and 8.77 (triplet, three protons)].

While the formation of III can be accounted for by a 1,3 hydrogen shift in the diradical E (R = H), the mechanistic origin of IV is less clear. It could arise either *via* a methyl migration, followed by a series of isomerizations, or much more simply by a 1,2 carbethoxyl shift. Decisive information concerning this mechanistic question was gleaned from the thermal rearrangement of the bicyclo[2.1.0]pentane II. Pyrolysis of II gave rise to three isomeric esters, B′, C′, and D′, formed in a ratio of 1:3:4.[4] Ester C′ was identified as VI. Compound VI has been previously reported by us as a photochemical vinylcyclopropyl rearrangement product of ethyl 2-methyl-3-cyclopropyl-2-butenoate;[3] it was also synthesized by an established route.[8] Spectral examination revealed B′ to be VIII. The major product, D′ [$\nu(CCl_4)$ 1740 (s) cm^{-1}; $\tau(CCl_4)$ 5.95 (quartet, two protons), 6.77 (broad triplet, one proton), 7.5–8.3 (complex absorption, four protons), 8.4 (broad singlet, six protons), and 8.77 (triplet, three protons)], was identical with the photochemical vinylcyclopropyl rearrangement product of ethyl 3-(1-methylcyclopropyl)-2-butenoate whose structural designation as VII is secure by analogy.[7]

While the formation of IV from I can be rationalized, albeit deviously, in terms of a methyl shift, the production of VII from II demands a carbethoxyl migration.[9] One possible pathway can be envisaged to proceed *via* a "carbethoxyl participation" mechanism by way of the transition state or intermediate F (R = CH_3).[10]



E F

A comparison of our thermal reactions with those of other bicyclo[2.1.0]pentanes is significant. The parent hydrocarbon affords primarily cyclopentene, with only 0.5% 1,4-pentadiene being detected.[2e] Recently, methyl 3,3-dimethyl-1-bicyclo[2.1.0]pentanecarboxylate has been reported to yield cyclopentene products[2c] also accountable by 1,2 hydrogen migrations from the bridge position. Our bicyclo[2.1.0]pentanes I and II, lacking abstractable hydrogens at the bridge carbon, choose alternate pathways for rearrangement. The formation of large amounts of cyclobutane cleavage products (V and VIII) is novel for a bicyclo[2.1.0]pentane system; 1,3 hydrogen shifts, which account for the formation of III and VI,[11] although not thoroughly substantiated, have been previously invoked in free radical chemistry,[12] while the 1,2 carbethoxyl migration, established here as giving rise to IV and VII, is without analogy in free radical or thermal chemistry.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 2445-A1,3). Part of this work was carried out while holding a Special Fellowship, awarded by the National Institutes of General Medical Sciences to M. J. J., at the University of Leiden, The Netherlands, 1967–1968.

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(8) R. Granger and H. Techer, *Compt. Rend.*, **250**, 1282 (1960).

(9) Methyl migration to either radical carbon of E will result in two cyclopentenecarboxylates which are structurally different from VII.

(10) The diradical intermediate E is invoked in this mechanistic scheme solely in analogy with the accepted mechanism which gives rise to cyclopentene from the parent hydrocarbon.[2e] The possibility of a concerted pathway is not ruled out.

(11) It is worth noting that VI can be derived as well from the diradical E by way of a 1,2 carbethoxyl migration to the more stable tertiary position. No such mechanism is possible for the formation of III from I, and a 1,3 hydrogen shift is therefore favored.

(12) R. Kh. Freidlina, *Advan. Free Radical Chem.*, 1, 211 (1965).

(13) To whom inquiries should be addressed.

(14) Summer visitor from Humboldt State College on a National Science Foundation program for college teachers, 1967.

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Intramolecular Chlorine–Tin Coordination in an Organotin Derivative of Seven-Coordinate Molybdenum

Sir:

Reaction of tetracarbonylbipyridylmolybdenum with methyltin trichloride has very recently been reported[1] to yield bipy(OC)$_3$ClMoSnCH$_3$Cl$_2$. On the basis of its stoichiometry and low conductivity, the compound was formulated as a seven-coordinate molybdenum derivative in which an electron-pair donating carbonyl group had been replaced by univalent chloride and methyldichlorotin ligands. We now communicate some results of an X-ray diffracton study which establish the coordination geometry about molybdenum and reveal also an unexpected and novel five-coordinate state for the tin atom.

Crystal data are $a = 6.73 \pm 0.02$ Å, $b = 11.14 \pm 0.01$ Å, $c = 24.46 \pm 0.03$ Å, $\beta = 90.5 \pm 0.2°$, space group $P2_1/c$, four molecules per unit cell. Data from seven levels about the *a* axis were collected on a PAILRED automated diffractometer using crystal monochromatized Mo Kα radiation and a moving-crystal stationary-counter scanning procedure. Within these seven levels 3606 unique reflections were measured, and of these 1924 were considered to be significantly above background ($I \geq 2.6\sigma(I)$ where $\sigma(I)$ was based on counting statistics). The data then extend to a resolution of 1.1 Å in the *a* direction and 0.7 Å in directions perpendicular to this. The structure was solved by conventional heavy-atom procedures. All nonhydrogen atoms have been located and their coordinates refined by least squares to a present *R* index (with isotropic thermal motion assumed for all atoms) of 0.098.

The molecular structure is shown in Figure 1, in which the more important bond lengths are indicated. The coordination of molybdenum may be termed a "capped octahedron"[2] comprised of an approximately octahedral bipy(OC)$_3$ClMo grouping with the tin atom located over the octahedral face defined by the chlorine atom and two of the carbonyl ligands. This

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(1) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 7, 310 (1968).

(2) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), 21, 130 (1967).