and decomposes near room temperature to biphenyl and copper metal.[1,2,4]

Other arylcoppers prepared by this method are *m*- and *p*-(trifluoromethyl)phenylcoppers (**2** and **3**) and *m*- and *p*-fluorophenylcoppers (**4** and **5**), all dark brown, highly soluble solids.

2 is exceedingly soluble in organic solvents (for example, 80% concentration by weight in ether), is trimeric in benzene, and does not appear to form complexes with basic solvents such as dioxane or benzonitrile. The ^{19}F nmr spectra of **4** and **5** in ether–dioxane are -0.05 and 5.37 ppm from fluorobenzene,[5] suggesting that the copper substituents exert negligible inductive effect but a relatively large resonance withdrawal, probably by p–π interaction involving empty 4p orbitals on copper.

Nonafluoro-*t*-butylcopper (**6**) was prepared by rapid exchange of *m*-(trifluoromethyl)phenylcopper and nonafluoro-*t*-butyl bromide[6] at 0° in ether–dioxane. A 2:3 complex with dioxane was isolated in 72% yield as a colorless, free-flowing powder. **6** is stable at room temperature, decomposes near 80°, and is highly ether soluble. By contrast, alkylcoppers are unstable above 0°,[1b,7] explosive,[7d] and insoluble without strong complexing agents.[8]

Fluorinated arylcoppers pyrolyze to biphenyls and copper, hydrolyze readily, and oxidize cleanly and rapidly at 0° with dry air, benzoyl peroxide, bromine, or cupric bromide to biphenyls. When the thermal and oxidative coupling reactions are run in solvents and reagents known to react with free radicals, the coupling product is still formed in high yield. This agrees with Whitesides' observation that free-radical intermediates are not formed in the coupling of vinylic copper(I) compounds.[9] Copper(II) species are reasonable intermediates.

In a reaction related to the Ullmann biaryl synthesis[10] and of potential synthetic utility, organocoppers couple with organic halides.[1b,11] For example, **1** couples easily with iodobenzene (87%), 1-bromoadamantane (93%), methyl iodide (39%), and α-bromotoluene (40%); **2** couples with *p*-nitrobenzoyl chloride (72%) and allyl bromide (68%). In the coupling with benzylic and tertiary alkyl halides, carbonium ions have been intercepted quantitatively by aromatic solvents.

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(8) (a) G. Costa, A. Camus, and N. Marsich, *J, Inorg. Nucl. Chem.*, **27**, 281 (1965); (b) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

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(10) (a) A. H. Lewin and T. Cohen, *Tetrahedron Letters*, 4531 (1965); (b) P. E. Fanta, *Chem. Rev.*, **64**, 613 (1964); (c) R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.* (London), 95 (1965).

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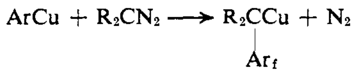
6 may be in equilibrium with unstable cuprous fluoride and perfluoroisobutylene since it reacts with 1-bromoadamantane, giving 1-fluoroadamantane[12] (98%) and CuBr (91%).

Arylcoppers, like many copper compounds,[13] react readily with diazoalkanes to form initially a new organocopper by formal insertion of a carbene[14] into the carbon–copper bond. **1** and ethyl diazoacetate (1.1 equiv) in THF at 0° gave upon hydrolysis ethyl (pentafluorophenyl)acetate (43%). In the presence of excess diazo-



$$ArCu + R_2CN_2 \longrightarrow \underset{\displaystyle Ar_f}{R_2\overset{}{C}}Cu + N_2$$

alkanes, typical carbenoid reactions occur: 200 equiv of ethyl diazoacetate gave a 1:1 mixture (82%) of diethyl maleate and fumarate; 30 equiv of bis(trifluoromethyl)diazomethane[15] in cyclohexene at 25° gave 7,7′-bis(trifluoromethyl)norcarane[15] (43%); and ethyl diazoacetate in 2-butyne at 25° gave ethyl 1,2-dimethylcyclopropene-3-carboxylate (10%).

Further studies on the synthetic utility of organocopper compounds and complete details of this work will be published soon.

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(14) We do not believe free carbenes are intermediates. An ylide, $Ar_fCu^-C^+RR'$, is the most likely intermediate for the carbon–copper reaction and possibly in methylene transfer reactions. Kirmse, *et al.*,[13a] propose an analogous intermediate for the copper salt–diazomethane reaction.

(15) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 3617 (1966).

Allan Cairncross, William A. Sheppard
Contribution No. 1377, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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Correlation between Si–H Reactivity and Infrared Stretching Frequency in the Silane–Ozone Reaction

Sir:

The Eyring absolute rate theory[1] postulates that reactions proceed through transition states wherein one degree of vibrational freedom is transformed into the translation path for reaction. This implies that for suitable systems, a bond's reactivity should be relatable to its stretching frequency, yet we have not found such thinking or pertinent examples in the literature.

In extension of studies on the silane–ozone reaction first described by us,[2] wherein

$$R_3Si\text{-}H + O_3 \longrightarrow R_3Si\text{-}OH + O_2$$

it has now been found that the reactivity of the Si–H bond toward ozone in the case of a number of trisubstituted silanes (all of those examined) is a monotonically decreasing function of the wave number of the corresponding Si–H stretching frequency in the infrared ab-

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(1) H. Eyring, *Chem. Rev.*, **17**, 65 (1935), and related papers.

(2) L. Spialter and J. D. Austin, *J. Am. Chem. Soc.*, **87**, 4406 (1965); *Inorg. Chem.*, **5**, 1975 (1966).

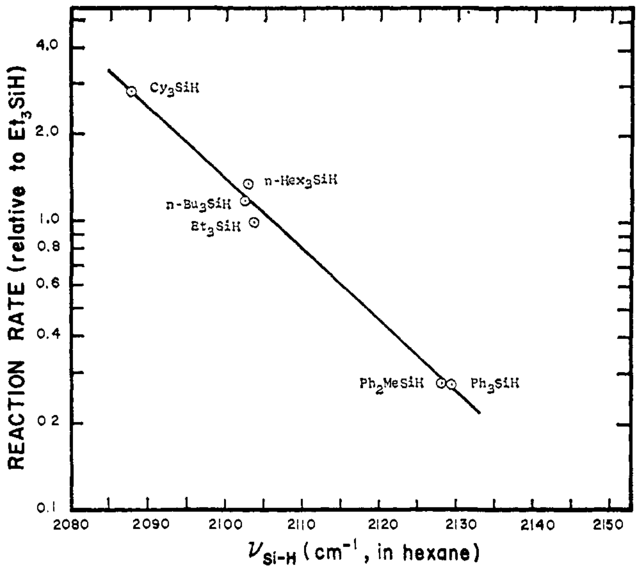

Figure 1. Logarithm of the relative rates of silane ozonolysis as a function of the Si-H stretching frequency.

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 $\nu_{\mathrm{Si-H}}$ 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 $\nu_{\mathrm{Si-H}}$.[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 $\nu_{\mathrm{Si-H}}$ 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.

Leonard Spialter, William A. Swansiger
Chemistry Research Laboratory, Aerospace Research Laboratories
U. S. Office of Aerospace Research
Wright-Patterson Air Force Base, Ohio 45433

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(3) The Si-H stretching frequency, $\nu_{\mathrm{Si-H}}$, is not found correlatable with the mass R in R$_3$SiH.

(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 $\nu_{\mathrm{Si-H}}$ and substituent σ^* summation have been reported by H. W. Thompson, *Spectrochim. Acta*, **16**, 238 (1960).

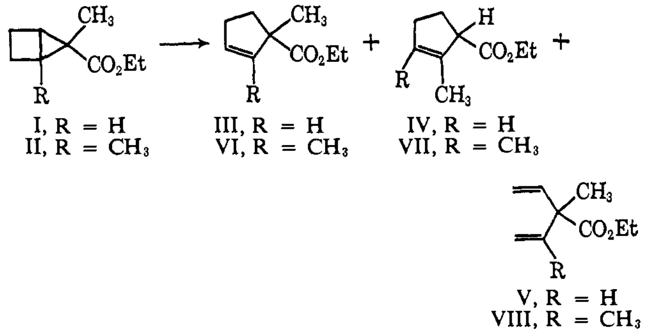
(7) J. Hetflejš, F. Mareš, and V. Chvalovsky, *Collection Czech. Chem. Commun.*, 30, 1643 (1965).

(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.

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(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).

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