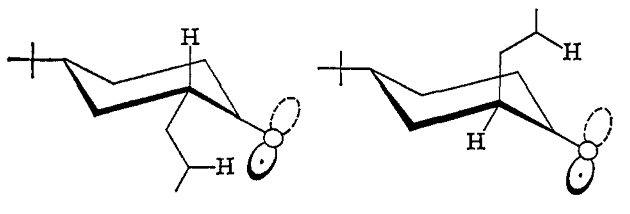
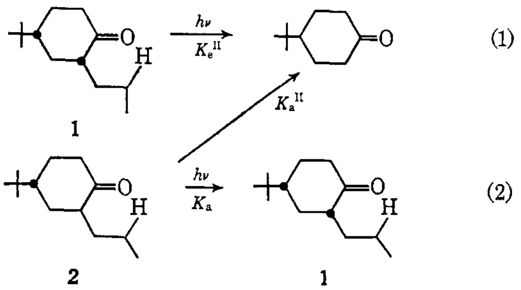


1 2

Figure 1. Most probable excited-state conformation for **1** and **2**. Notice that for **1** the formation of a cyclic six-membered transition state for hydrogen abstraction by the half-vacant n orbital is easy to achieve, while for **2** the hydrogen to be abstracted lies close to the nodal plane of the half-vacant n orbital.

A remarkable difference in the rate constants for photolysis of **1** and **2** is revealed by studies of the quenching of reactions 1 and 2 by 1,3-pentadiene.[9] Thus, reaction 1 is unaffected by addition of up to 0.9 *M* 1,3-pentadiene, which implies that either (a) nearly all of the type II split for **1** occurs in the singlet state (which is not quenched by piperylene[9]) or (b) the type II split occurs in the triplet state with a rate constant[10,12] greater than $\sim 8 \times 10^{10}$ sec^{-1}. On the other hand, the conversion of **2** to **1** is strongly quenched by 1,3-pentadiene ($k/k_\alpha \sim 60$).



We propose that the striking contrast in the photochemistry of **1** *and* **2** *results from a stereoelectronic requirement for the type II split and that this requirement probabably also exists in all photochemical hydrogen abstraction reactions by the* n,π* *states of alkyl ketones.*[14] It is clear from models of **1** that the hydrogen on the γ carbon can facilely form a six-membered transition state (for the type II split) in which the C–H bond axis is directed toward the half-vacant n orbital of the carbonyl oxygen atom (see Figure 1). It is generally assumed that the reactivity[15-17] toward hydrogen abstraction for the n,π* states of alkyl ketones derives from the electrophilic nature of the localized half-vacant n orbital. If so, then **1** should experience minor restrictions because of the relatively unrestrained approach of the n orbital by the γ-H for type II reaction and proceed faster than the analogous process for **2**, *which cannot achieve the required transition state for hydrogen abstraction without severe molecular deformations or conversion into a higher energy boat construction.*

Since the simple model of a planar n,π* suffices to explain these data, an important implication of the results reported here is that the geometry of the n,π* is not severely distorted from planarity.[18]

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[9] 1,3-Pentadiene has been shown to quench only triplet states of ketones: see ref 6 and G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961); however, 1,3-dienes are known to quench singlet states of nonketonic compounds: L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

[10] 2-Hexanone, an open-chain model for the type II split for **1** and **2**, undergoes cleavage with a rate constant[6] of 1×10^9 sec^{-1} from the triplet and 10^7–10^8 sec^{-1} from the singlet (assuming an intersystem rate constant of 10^7–10^8 for 2-hexanone[11]). A small amount of unquenchable type II cleavage also apparently occurs from **2**.

[11] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1965); *J. Am. Chem. Soc.*, **88**, 3467 (1966).

[12] Value calculated assuming the rate constant for diffusion-controlled quenching[13] in cyclohexane is 8×10^{10} l./mole sec^{-1}.

[13] F. W. Wilkinson, *Quart. Rev.* (London), **20**, 403 (1966).

[14] (a) Stereochemical requirements for the "McLafferty rearrangement," the mass spectral analog of the Type II split, have also been noted: H. Budzikiewicz, C. Fensilau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966). (b) We have found the mass spectra of **1** and **2** to be essentially identical at 75 and 12 eV. However, the source temperature (200°) unfortunately may be sufficiently high to equilibrate the molecular ions of **1** and **2** before decomposition. Experiments at lower source temperature and measurements of ionization potentials are in progress.

[15] For example, see C. Walling and M. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965); A. Pawda, *Tetrahedron Letters*, 3465 (1964).

[16] M. Kasha in "Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins University, Baltimore, Md., 1961, p 31.

[17] H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

[18] Independent evidence for this conclusion is difficult to obtain. Formaldehyde is severely puckered and has a pyramidal shape in its n,π* states.[19] However, a substantial degree of this bending probably originates from H–H *bonding* in the n,π* state.[20]

[19] D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966); J. C. D. Brand and D. G. Wilkinson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963).

[20] E. W. Abrahamson, J. G. F. Littler, and K. P. Vo, *J. Chem. Phys.*, **44**, 4082 (1966).

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Fluorinated Organocopper Compounds

Sir:

We have isolated several fluorinated organocopper compounds and found that they are highly soluble in organic solvents, more thermally stable than their hydrocarbon analogs, and useful synthetic intermediates.

We have prepared solutions of fluorinated arylcopper(I) compounds by the metathetical reaction of Grignards with cuprous halide in ether. The magnesium salts are removed as their insoluble dioxane complexes and the arylcoppers isolated by concentration in an inert atmosphere.

$$C_6F_5MgX + CuX \longrightarrow \underset{\mathbf{1}}{C_6F_5Cu} + MgX_2$$

By this method, pentafluorophenylcopper (**1**) is isolated in 70% yield as colorless 1:1 and 2:1 dioxane complexes which are freed of dioxane by heating at 130° (1 μ) for 5 hr.

Anal. Calcd for C_6F_5Cu: C, 31.3; F, 41.2; Cu, 27.6. Found: C, 31.2; F, 39.8; Cu, 27.8.

1 dissolves in most aprotic solvents except alkanes, hydrolyzes and oxidizes slowly in moist air, and decomposes above 200° to form decafluorobiphenyl and copper metal. For comparison, phenylcopper,[1] a colorless solid, is difficult to obtain in pure state,[2] complexes weakly with ether,[2] is soluble in the presence of strong complexing agents,[1a,3] is very difficult to handle,[2]

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[1] (a) R. Reich, *Compt. Rend.*, **177**, 322 (1923); (b) H. Gilman and J. M. Straley, *Rec. Trav. Chim.*, **55**, 821 (1936).

[2] G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organometallic Chem.* (Amsterdam), **5**, 568 (1966).

[3] G. Costa, A. Camus, N. Marsich, and L. Gatti, *ibid.*, **8**, 339 (1967).

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.

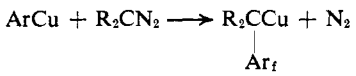
Nonafluoro-*t*-butylcopper (**6**) was prepared by rapid exchange of *m*-(trifluoromethyl)phenylcopper and nonafluoro-*t*-butyl bromide[6] at 0° in ether–dioxane. A 2:3 complex with dioxane was isolated in 72% yield as a colorless, free-flowing powder. **6** is stable at room temperature, decomposes 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.

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 diazoalkanes, 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%).



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

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

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(4) H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966).

(5) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963); (b) *ibid.*, **85**, 3146 (1963).

(6) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *J. Org. Chem.*, **28**, 184 (1963).

(7) (a) H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, **65**, 435 (1943); (b) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); (c) C. E. H. Bawn and F. J. Whitby, *Discussions Faraday Soc.*, 228 (1947); (d) G. Costa, A. M. Camus, and E. Pauluzzi, *Gazz. Chim. Ital.*, **86**, 997 (1956); (e) G. Costa and G. De Alti, *Atti Accad. Nazl. Lincei VIII*, **28**, 1 (1960); (f) G. Costa, G. De Alti, and S. Lin, *ibid.*, **31**, 265 (1961); (g) G. Costa, G. De Alti, L. Stefani, and G. Boscarato, *Ann. Chim.*, **52**, 289 (1962).

(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).

(9) G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88**, 4541 (1966).

(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).

(11) (a) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1967); (b) C. Björklunk and M. Nilsson, *Tetrahedron Letters*, 675 (1966); (c) N. Nilsson, *ibid.*, 679 (1966); (d) C. E. Castro and R. D. Stephens, *J. Org. Chem.*, **28**, 2163 (1963); (e) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **31**, 4071 (1966).

(12) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

(13) (a) W. Kirmse, M. Kapps, and R. B. Hager, *Chem. Ber.*, **99**, 2855 (1966); (b) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron Letters*, 5239 (1966); (c) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).

(14) We do not believe free carbenes are intermediates. An ylide, $\mathrm{Ar_fCu^{-}C^{+}RR'}$, 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).

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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

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

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).