Table I. Reactions of 1,1-Dimethyl-1-silaethene, $(CH_3)_2Si{=}CH_2$ (2), with Silicon Halides at 611° [a]
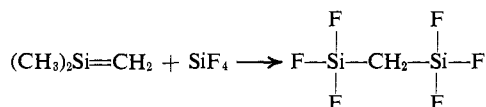
Reaction no.	$[SiMe_2]$ [b] (mmol)	Substrate	(mmol)	Products (% yield) [c]		$Me_2Si\frown SiMe_2$
				1:1 Adduct		
1	18.4	SiF_4	(~124)	$F_3SiCH_2SiMe_2F$	(44)	Trace
2	13.9	$HSiCl_3$	(49.8)	$HCl_2SiCH_2SiMe_2Cl$	(22)	Trace
3	13.3	$SiCl_4$	(20.5)	$Cl_3SiCH_2SiMe_2Cl$	(20)	3
4	14.3	$MeSiCl_3$	(38.0)	$Cl_2MeSiCH_2SiMe_2Cl$	(16)	16
5	9.76	Me_2SiCl_2	(26.4)	$ClMe_2SiCH_2SiMe_2Cl$	(13)	25
6	10.1	Me_3SiCl	(27.2)	$Me_3SiCH_2SiMe_2Cl$	(<~2) [d]	40
7	15.3	CF_4	(112)			46

[a] All experiments except for the SiF_4 and CF_4 experiments used nitrogen carrier gas. Full experimental details are given in ref 2b. [b] Precursor to 1,1-dimethyl-1-silaethene, see text. [c] All reported yields are based on amounts of material actually isolated by preparative glpc. All new compounds reported were unambiguously identified on the basis of their nmr, ir, and mass spectra. Determination of the exact mass was done on either the parent or parent minus methyl ion. The less than quantative yields are due to: ca. 20–40% wt loss during preparative glpc as verified by control experiments, a number of minor (<5%) products present in each of the reactions studied, and mechanical losses due to the small scale reactions. [d] Estimated yield is an upper limit for 1:1 adduct. Material could not be isolated in sufficient quantity for identification.

would be expected to disfavor such addition reactions in the absence of dipolar character as shown in **1**. Indeed, addition reactions of silicon fluorides with ordinary carbon–carbon double bonds are, to our knowledge, completely unknown.[4] In contrast, strong nucleophiles attack the silicon–fluorine bond quite readily.[5]

In the present study, the nucleophilic potential of the carbon component of the silicon–carbon double bond, and hence the validity of formulation **1**, was strongly indicated by the following reaction of $(CH_3)_2Si{=}CH_2$ with silicon tetrafluoride to give a 44% yield of adduct.

$$(CH_3)_2Si{=}CH_2 + SiF_4 \longrightarrow F{-}\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{Si}}{-}CH_2{-}\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{Si}}{-}F$$

As in our previous studies, $(CH_3)_2Si{=}CH_2$, 1,1-dimethyl-1-silaethene (**2**), was generated by gas-phase pyrolysis of the silacyclobutane at 611°. The details of this addition reaction, others with silicon chlorides, and the failure of CF_4 to react with **2** are summarized in Table I.

Reaction 2 in Table I provides further strong evidence for the dipolar nature of **2** and additional evidence against diradical character for this intermediate. In sharp contrast to silicon–fluorine and silicon–chlorine bonds, the silicon–hydrogen bond is well known to react *via* a radical mechanism.[4,6] Thus, diradical character of **2** should lead to addition of the silicon–hydrogen bond to **2** when the latter is generated in the presence of $SiHCl_3$. Instead, exclusive addition of the silicon–chlorine bond is found.

The structure–reactivity pattern shown by reactions 3–6, diminishing reactivity with replacement of Cl in $SiCl_4$ by methyl, is not an unexpected pattern for nucleophilic reaction at silicon.

Also, in view of the high bond energy of the silicon–fluorine bond and the lower value for the carbon–fluorine bond (116 kcal/mol),[3] it would be reasonable to expect that diradical character of **2** should lead to

addition of CF_4. As reaction 7 in Table I shows, no adduct was formed. This is in accord with lower susceptibility to nucleophilic attack of CF_4 compared to SiF_4.[5]

In addition to providing evidence for the dipolar nature of the silicon–carbon double bond, and additional evidence against a diradical structure for such intermediates, the present study also furnishes a new synthetic route to fairly inaccessible silmethylene compounds.

R. D. Bush, C. M. Golino, L. H. Sommer*
Department of Chemistry, University of California, Davis Davis, California 95616
Received June 8, 1974

Substituent Effects in the n → π* Transition of Ketones

Sir:

Cd and ord spectroscopy of chiral ketones yields information not only about the energetics of the n → π* transition but also about the variation in the transition probability for the differential absorption of left and right circularly polarized light. The latter property was utilized in the derivation of the octant rule.[1] This topic has been well documented;[2] however, it is a subject of our current work on account of some serious breakdowns of the rule when the ketone is perturbed by some substituents in certain orientations.[3] In comparison, relatively little use has been made of the λ_{max} of the n → π* transition, except in the case of α-axial

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(3) J. Hudec, Chem. Commun., 829 (1970).
(4) R. C. Cookson, J. Chem. Soc., 282 (1954).

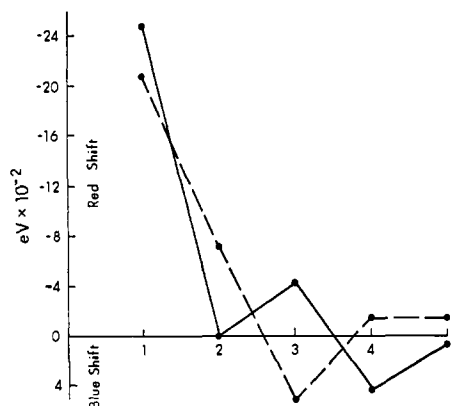**Figure 1.** Relative change in transition energy for X = F (———) and X = I (— —) in ethanol.

Cl and Br; they fall, as might be expected, between F and I in all series, except for Cl in series **1**. This alternating behavior can be extended also to compounds with *no* C–C bond between the carbonyl group and the halide, *i.e.*, acylhalides. Thus acetyl fluoride, chloride, and bromide have their respective n → π* transitions (uv) shifted to higher energy by 1.58, 0.69, and 0.51 eV relative to acetone.[12]

We believe that two factors enter into the rationalization of the striking pattern of alternation in the transition energies. First, it has been noted in theoretical studies that the inductive effect of an electronegative or electropositive substituent manifests itself not in a uniformly decreasing electron density change but in an alternation of charge along both saturated and unsaturated chains.[13,14] Thus, as in **6** and **7**, the carbonyl

haloketones[4] and certain β,γ-unsaturated ketones.[5] The former have been studied theoretically.[6,7]

We wish to report that the relative change in the transition energy in cd (or uv) of a series of ketones on substitution with F and I results in significant red or blue shifts depending on the number of intervening C–C bonds. The data presented in Figure 1 are based on cd of **1**,[8] **2**,[9] **3**,[10a] **4**,[10b] and **5**[8] in which the substituent (X = H, F, and I) is oriented in a coupling path[3] and separated from the carbonyl group by one, two, three, four, and five C–C bonds, respectively.
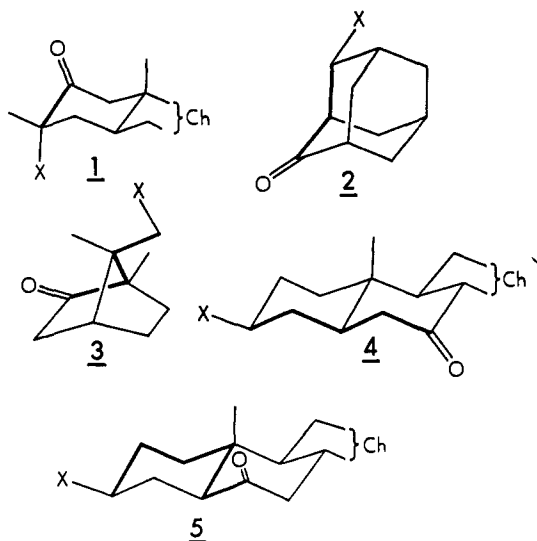
Apart from the large already rationalized[6,7] red shift (~0.2 eV) of the α-haloketones, the plot of relative transition energies shows an interesting pattern of alternation; *i.e.*, F shows larger relative red shift than I in α- and γ-substituted ketones and a relative blue shift in β and δ series.[11] We do not present the data for

carbon is effectively more shielded and deshielded, respectively, for X more electronegative than H. This should result in the destabilization and stabilization, respectively, of the n orbital on the carbonyl oxygen. The effect of σ withdrawal can be modified or even altered by π donation of X. The net effect then controls the change in the transition energy.[15] Another effect focuses on the conformationally dependent perturbation of the X substituent. In α-, γ-, and ε-substituted ketones, **8**, the σ withdrawal controls mainly the π/π* levels, while the π back-donation mainly the n level. The opposite obtains in β- and δ-substituted

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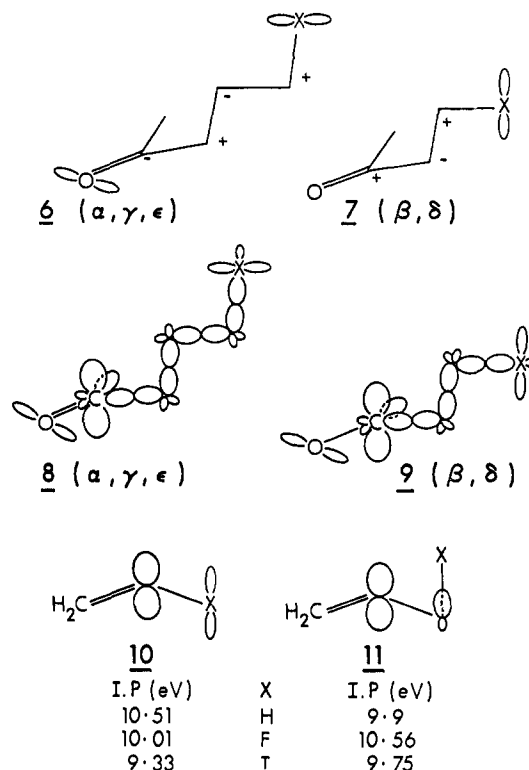
(8) Unpublished data.

(9) G. Snatzke and G. Eckhardt, *Tetrahedron* **24**, 4543 (1968).

(10) (a) M. T. Hughes and J. Hudec, *Chem. Commun.*, 805 (1971); (b) G. P. Powell and J. Hudec, *Chem. Commun.*, 806 (1971).

(11) The five bond (ε-substituted ketones) series are not good models as they must have some three-bond character (noninteracting) mixed in (*via* the C-3, C-4, C-5 bonds). An ideal system would be D-homo-6α-substituted-androstan-17a-one.

(12) K. Yates, S. L. Klemenko, and I. G. Csizmadia, *Spectrochim. Acta, Part A*, **25**, 765 (1969).

(13) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970); *J. Amer. Chem. Soc.*, **92**, 2191 (1970); J. A. Pople, *Accounts Chem. Res.*, **3**, 217 (1970).

(14) L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, **96**, 1370 (1974).

(15) This amounts to σ withdrawal when X is more electronegative and σ donation where X is more electropositive (+ and − in **6** and **7** refer to decreased and increased shielding, respectively, produced by more electronegative X).

ketones, 9. The effect on the π-system is illustrated by the measured ionization potentials, I_π, of vinyl and allyl halides 10^{16} and $11.^{16,17}$ Increased π-donation (F → I) in 10 raises the energy of the π level in 10, just as decreased σ withdrawal (F → I) in 11 accomplishes the same.

The relative roles of the alternating charge effect and the conjugative through-bond interaction remain to be elucidated in both theoretical and experimental studies.

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Edgar E. Ernstbrunner, John Hudec*

Chemistry Department, The University
Southampton SO95NH, England

sym- and *unsym-*Benzoferroles. Ferroles from a Cyclobutadieneiron Tricarbonyl

Sir:

It has recently been reported[1] that the reaction of 1,7-cyclododecadiyne (1) with $Fe(CO)_5$, unexpectedly, affords the ferrole 2, rather than the ferrole 3 which had been proposed[2] earlier and which could have been more reasonably expected.

1   2

3   4
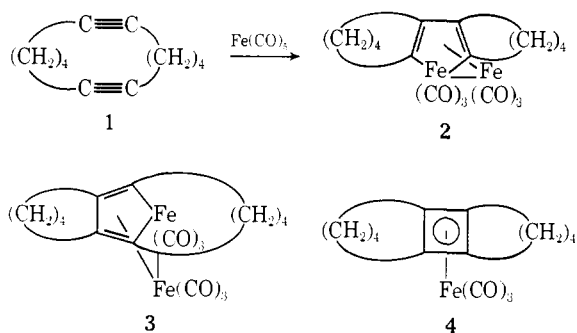
One possible mechanism for the conversion of diyne 1 to the ferrole 2 involves initial formation of the isomeric ferrole 3, then isomerization of 3 to 2, perhaps through a cyclobutadiene diiron complex. There exists, however, no experimental evidence for the interconversion of metallocycles of type 2 and 3.

An alternative explanation for the appearance of 2 involves formation of the cyclobutadieneiron tricarbonyl complex[3] 4 from 1 and $Fe(CO)_5$, and further reaction of the cyclobutadiene–$Fe(CO)_3$ complex with $Fe(CO)_5$ to yield 2.

In support of this latter proposal we now report evidence indicating that in fact cyclobutadieneiron tricarbonyl compounds can be converted to ferroles

(1) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5068 (1973).

(2) R. B. King and I. Haiduc, *J. Amer. Chem. Soc.*, **94**, 4044 (1972).

(3) A trace amount of the cyclobutadieneiron tricarbonyl complex was in fact obtained.[2]

under conditions comparable to those employed for the conversion of diyne 1 to ferrole 2. Furthermore, two isomeric ferroles have been isolated and have been found not to interconvert under similar conditions.

Benzocyclobutadieneiron tricarbonyl (5) and excess $Fe_3(CO)_{12}$ in hydrocarbon solvents react at 120° to afford a mixture of the *sym-* and *unsym-*benzoferroles, 6 and 7, respectively.[4] *sym-*Benzoferrole (6) forms orange crystals from pentane: mp 86–87°, ir (Skelly B) 2078, 2043, 2005, 2000, 1955 cm^{-1}, nmr (CS_2) τ 2.7 (s), 2.55–2.8 (m).[5] *unsym-*Benzoferrole (7) has been recently prepared by alternative routes,[6] and our physi-

5   6   7
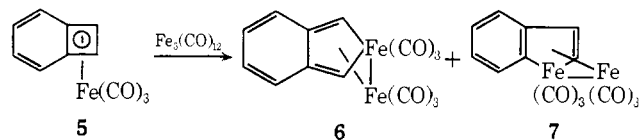
cal and spectroscopic data are in agreement with those reported. X-Ray crystallographic analysis confirms the proposed structures.

Compound 6, crystallized from pentane, is triclinic $P1$, $a = 8.734$, $b = 14.926$ Å, $c = 12.174$ Å, $\alpha = 99.04°$, $\beta = 102.06°$, $\gamma = 68.96°$, and $Z = 4$. Of the 5057 independent reflections whose intensities measured ($2\theta(max) = 50°$ with Mo $K\alpha$ radiation), 3337 were used in the structure solution and refinement. This structure, which includes two molecules per crystallographic asymmetric unit, has been refined to $R = 0.063$, $R_w = 0.055$.

Crystals of 7 from pentane are monoclinic $P2_1/c$, $a = 8.076$ Å, $b = 14.188$ Å, $c = 12.408$ Å, $\beta = 113.57°$, and $Z = 4$. Three-dimensional single-crystal intensity data were collected with Mo $K\alpha$ radiation to the limit $2\theta = 52.5°$. Of the 2854 independent reflections measured, 2093 were included in the refinement. The structure was refined to $R = 0.072$, $R_w = 0.058$.

The two benzoferroles are not interconverted or decomposed in hydrocarbon solvents at 120°, suggesting that in the diyne work ferrole 3 is probably not being converted to ferrole 2 under the reaction conditions. Instead, our results suggest that the formation of ferrole 2 from diyne 1 could more reasonably stem from the conversion of a transient cyclobutadieneiron tricarbonyl complex to the observed ferrole in the presence of $Fe(CO)_5$.

If indeed the results of the diyne studies and of our present work can be extended to a discussion of the mechanism of alkyne disproportionation ($R_1C\equiv CR_1 + R_2C\equiv CR_2 \rightleftharpoons 2R_1C\equiv CR_2$),[7] we conclude that cyclobutadiene metal complexes could conceivably be involved in this latter process. Such species, however, could be formed directly and reversibly (leading to disproportionation), and the intermediate formation or

(4) (a) With a reaction time of 7 hr the relative yields of 5, 6, and 7 were 24, 38, and 38%, respectively; no other products were observed. (b) Complex 6 and 7 have also been obtained from 5 by photolysis with pentacarbonyliron: R. Victor and R. Ben-Shoshan, *J. Chem. Soc., Chem. Commun.*, 93 (1974).

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