

polymerize on standing to give, at first, more viscous liquids and then white solids.

We have previously found that molecular weight determination on samples of *o*-phenylenedioxydiphenylsilane purified in various ways gave evidence that the monomeric and dimeric species could be separated², and corroboration for this has come from another laboratory⁶. Only dimeric values were obtained for the liquid *o*-phenylenedioxydimethylphenylsilane, however.

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Baker Laboratory, Cornell University,
Ithaca, New York (U.S.A.)

C. M. SILCON
J. J. ZUCKERMAN

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PRELIMINARY NOTES

The $n \rightarrow \pi^*$ transition of α -metal ketones

In a recent publication Harnish and West¹ proposed that the ultraviolet absorption spectra of α -silyl ketones could be explained on the basis of $d\pi-p\pi$ bonding involving the d orbitals of silicon and the π and π^* orbitals of the carbonyl group. West² has since generalized these proposals to predict the effect of metalloid substitution on the electronic transition of two- and three-atom chromophores.

Yates, Agolini and Csizmadia^{3,4} by LCAO calculations, have been able to predict the magnitude of the shifts produced in ketones of the type R_3SiCOR , R_3GeCOR , and $R_3SiCOSiR_3$ without invoking d orbital participation.

In addition they have found that in ketones of the type $(C_6H_5)_3MCO(C_6H_5)$ that the base strength of the ketone decreased in the order $Si > Ge > C$, indicating that in the ground state the predominant effect is inductive release of electrons to the oxygen atom, rather than electron withdrawal through $d\pi-p\pi$ bonding^{3,4}.

Since it is generally agreed⁵ that the amount of $d\pi-p\pi$ bonding should be successively less in germanium and tin compounds than in silicon compounds, it seemed of value to prepare a series of ketones $(C_6H_5)_3MCOCH_3$, $M = C, Si, Ge$ and Sn , to gain

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additional information on the cause of the observed shift of the position of the $n \rightarrow \pi^*$ transition.

Acetyltriphenylgermane was prepared by the addition of triphenylgermyl-lithium to acetyl chloride at -70° and by the oxidation of 1-triphenylgermylethanol.

Acetyltriphenyltin, I, was prepared by the addition of triphenyltinlithium to an excess of acetyl chloride in tetrahydrofuran at -70° . The reaction mixture was allowed to warm to room temperature and the volatile components removed under vacuum. A solution of I was obtained by extracting the residue with pentane. The pentane was removed to obtain I as a waxy solid. All attempts to purify I led to decomposition.

The identity of I was confirmed on the basis of the following observations: exposure of a solution of I to air for 5 to 10 minutes led to complete conversion to triphenyltin acetate which was identified by comparison with an authentic sample. Similar reactions have previously been reported for α -silylketones by Brook and Pierce⁶. Lithium aluminum hydride reduction of I gave 1-triphenyltinethanol, melting point $93-95^\circ$, (Anal.: Calcd. for $C_{20}H_{20}OSn$: C, 60.8; H, 5.10; found: C, 60.5; H, 5.08) identified by its infrared and nuclear magnetic resonance spectra. Finally, the ultraviolet absorption spectrum of the $n \rightarrow \pi^*$ transition was a multiplet, characteristic of the α -metal ketones.

TABLE I
CARBONYL GROUP ABSORPTION IN $(C_6H_5)_3MCOCH_3$

Compound	λ_{max} , $m\mu^a$	ν_{max} , cm^{-1}
$(C_6H_5)_3CCOCH_3$	302	1710
$(C_6H_5)_3SiCOCH_3$	363, 376, 392	1644
$(C_6H_5)_3GeCOCH_3$	352, 365, 380	1660
$(C_6H_5)_3SnCOCH_3$	363 (s), 375, 391	1670

^a In *n*-heptane; ^b in carbon tetrachloride; (s) shoulder.

The positions of the ultraviolet and infrared absorption maxima for the carbonyl group for $(C_6H_5)_3MCOCH_3$ are given in Table I.

These results suggest that the primary cause of the shift in the position of the $n \rightarrow \pi^*$ transition is the inductive effect of the metal rather than $d\pi-p\pi$ bonding.

Preliminary results on the addition of triphenyltinlithium to a variety of other acid chlorides indicate that the reaction is general. Thus, reaction with methyl chloroformate gives a product with ν_{max} 1628 cm^{-1} . Further research to characterize this product and others is currently underway.

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Department of Chemistry, University of Alberta,
Edmonton, Alberta (Canada)

G. J. D. PEDDLE

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Reactions of pentafluorophenyllithium and cyclopentadienyliron carbonyl cations

The reactions of $C_5H_5Fe(CO)_3^-BPh_4^-$ and $C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]^-Cl^-$ with sodium borohydride¹ provide a contrast which illustrates an effect of substitution of triphenylphosphine for carbon monoxide in a metal complex. The former reaction yields $[C_5H_5Fe(CO)_2]^-$ presumably via the hydride $C_5H_5Fe(CO)_2H$, whereas the latter yields a cyclopentadiene derivative, $C_5H_6Fe(CO)_2^+[(C_6H_5)_3P]^-$.

We have also observed a contrast in reactions of these two cyclopentadienyliron carbonyl cations with pentafluorophenyllithium. The reaction of this lithium reagent (prepared from butyllithium and bromopentafluorobenzene in diethyl ether² at -78°) and a slurry of $C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]^-I^-$ in tetrahydrofuran was run at 0° for 2 h. After removing solvent the residue was chromatographed on an alumina column, with a single yellow band eluting with benzene. This band was collected and evaporated giving a yellow solid. Crystallization from a benzene-octane mixture gave the yellow crystalline cyclopentadiene-iron compound *exo*- $C_6F_5-C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]^-$, m.p. $132.5-134.0^\circ$, in 59.4% yield; this product was characterized by analysis (Calcd. for $C_{21}H_{20}FeO_2PF_5$: C, 61.4; H, 3.33; F, 15.7; P, 5.11; Mol. wt., 666. Found: C, 61.6; H, 3.50; F, 15.4; P, 5.00; mol. wt., 610).

The infrared spectrum of this compound in carbon tetrachloride contained bands characteristic of the pentafluorophenyl group and the triphenylphosphine ligand, and contained also two strong carbonyl stretching frequencies at 1960 and 1925 cm^{-1} (compared to 1978 and 1912 cm^{-1} in a Nujol mull spectrum of $C_5H_6Fe(CO)_2^+[(C_6H_5)_3P]^-$). The presence of a single isomer, the *exo*-form, was clear from this spectrum which showed a C-H stretching frequency at 2940 cm^{-1} characteristic of the *endo*-C-H but which lacked an absorption at ~ 2750 cm^{-1} which would be expected* for an *exo*-C-H. The proton NMR spectrum of this complex contained broad peaks at 2.70 τ (multiplet), 5.03 τ , 5.85 τ , and 7.40 τ of relative intensities 15:2:1:2. These resonances are assignable to the protons C_6H_5 , H_A , H_{endo} , H_B respectively (Fig. 1).

When a diethyl ether solution of pentafluorophenyllithium was reacted with a slurry of $C_5H_5Fe(CO)_3^+PF_6^-$ in tetrahydrofuran at 0° for 2 h a reaction was again

* There appears some doubt in the literature regarding the geometry of substituted cyclopentadiene complexes of metals. The most definitive work is found in a crystal structure determination^{1a} of *exo*-1- $C_6H_5C_5H_2CoC_5H_5$. The infrared band at 2952 cm^{-1} in this compound could logically be assigned to the *endo*-CH-, contrary to the assignment originally made for this compound^{2b}, and contrary to most other assignments made in other substituted cyclopentadiene complexes.