

Independent synthesis of compound (III) was accomplished by first forming the lithium alkoxide of tricarbonyl(hydroxytetraphenylcyclopentadienyl) manganese, (IV), then allowing it to react with a stoichiometric amount of triphenyltin chloride. Both the product obtained by treating the lithium salt of (IV) with triphenyltin chloride and that obtained by heating a mixture of (I) and tetraphenylcyclopentadienone melted at 206–207° with decomposition. Both of the infrared spectra were identical between 2–15  $\mu$ . Investigation of the mechanism of this novel rearrangement is not planned.

### Experimental

Compound (IV) was prepared by a procedure described previously<sup>4</sup>. Ethyllithium in benzene was obtained from Lithium Corporation of America. Tetrahydrofuran (THF) was distilled from NaAlH<sub>4</sub> before use. Melting points are corrected. All glassware was dried at 125° and flushed with nitrogen while being assembled. Reactions were carried out under a nitrogen atmosphere.

*Tricarbonyl[(triphenylstannoxy)tetraphenylcyclopentadienyl]manganese, (III)*. A 50-ml 3-necked flask was charged with 1.0 g (1.91 mmoles) of (IV) in 30 ml of THF. To this stirred solution was added slowly 2.1 ml of 0.88 *N* ethyllithium in benzene by syringe over a 6-min period while cooling the reaction mixture at –10°. Subsequently, the mixture was warmed to 10° and 0.8 g (2.03 mmoles) of triphenyltin chloride was added. The mixture was warmed at 40° for 15 min and then the solvents were evaporated under reduced pressure (water aspirator). The residual oil was dissolved in dichloromethane and some solids were filtered off. The solvent was evaporated and the residue was fractionally crystallized from a mixture of dichloromethane and *n*-hexane to give 0.88 g (53%) of (III), m.p. 204–208° (decomp.). Recrystallization from the same solvent pair raised the melting point to 206–207° (decomp.). The melting point was not depressed when admixed with the product from the thermal reaction.

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### Bis-silyl and bis-germyl ketones

The structure and spectra of  $\alpha$ -silyl and  $\alpha$ -germyl ketones have been the subject of considerable study and comment<sup>1–5</sup>.

As a further contribution in our study of these compounds we wish to report the synthesis of bis(triphenylsilyl)ketone, (I), and bis(triphenylgermyl)ketone, (II). Both of these compounds although lacking any extended conjugation are colored, the former being a red-violet solid, melting point  $155-58^{\circ}$ , and the latter a orange-pink solid, melting point  $152^{\circ}$ .

The ketones were prepared by the oxidation of the corresponding disubstituted methanol obtained from the addition of methyl formate to the triphenylmetallithium reagent. Although both ketones are stable over several weeks as solids they are quite unstable in solution. Thus (I) in cyclohexane rapidly undergoes photolysis to hexaphenyldisilane, and presumably carbon monoxide, while (II) gives hexaphenyl-digermane.

The ultraviolet absorption spectra of these bis and related ketones is given in Table I. Extinction coefficients are not reported since the rapid decomposition of the ketones in solution made it difficult to obtain reproducible values.

TABLE I  
ULTRAVIOLET ABSORPTION SPECTRA OF KETONES

Compound	Phenyl $m\mu$	$C=O, n \rightarrow \pi^*$	kcal/mole <sup>a</sup>
		$m\mu$	
$CH_3COCH_3$		279	103
$Ph_3SiCOCH_3$	260-272	300, 372, 384 ( $C_6H_{12}$ )	77
$Ph_3SiCOSiPh_3$ (I)	262-273	478, 524, 554 ( $CCl_4$ ) 517, 545 (EtOH)	53
$Ph_3GeCOGePh_3$ (II)	262-273	451, 483, 513 ( $C_6H_{12}$ )	

<sup>a</sup> Energy value given corresponds to the average of the observed wavelengths.

It is noteworthy that replacement of the methyl groups of acetone by silyl groups appears to give additive changes in the  $n \rightarrow \pi^*$  transition energy of the carbonyl group. Thus replacement of the first methyl group of acetone by a triphenylsilyl group lowers the energy of the  $n \rightarrow \pi^*$  transition by 26 kcal per mole, and replacement of the second methyl group lowers the energy by a further 24 kcal per mole.

The infrared carbonyl group absorption for the bis-silyl ketone, (I), appears to be a weak band at  $6.43 \mu$  while that for the bis-germyl ketone, (II), is a strong band at  $6.19 \mu$ .

Further investigation into the physical and chemical properties of these and related compounds is at present underway.

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