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Carbenoids by Deoxygenation of Carbonyl Compounds with Chloromethylsila.  By Clifford L. Smith, James Arnett, and James Ezike	nes

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Summary Deoxygenation of benzophenone, benzaldehyde, and cyclohexanone with chloromethylsilanes and zinc-

copper couple in ether is reported to yield 2,2,2-triphenylacetophenone, a mixture of deoxybenzoin and diphenyl-

acetaldehyde, and a bicyclic ketone with the proposed 2-oxocycloheptanespirocyclohexane structure, respectively; a carbene mechanism is proposed.

A REACTION of chlorotrimethylsilane with cyclohexanone and zinc metal in ether has been reported to yield only cyclohexene in ca. 72% yield. We now report results obtained via a modification of this procedure.

In a typical experiment, a solution of benzophenone (0.3 mol) dissolved in ca. 200 ml of ether was added dropwise to a mixture of dichlorodimethylsilane (0.4 mol), zinccopper couple (0.5 g-atom), and ca. 100 ml of ether, producing an exothermic reaction. After continuous stirring for ca. 12 h at room temperature, the white precipitate formed was filtered off and washed several times with water. Recrystallization of the 'dry' solid from hot benzene yielded 2,2,2-triphenylacetophenone (70%), equation (1). A similar reaction of benzaldehyde gave deoxybenzoin (1) and diphenylacetaldehyde (2) in a total yield of 45%, equation (2). The mechanism in equation (3) involving the formation of a carbenoid and its subsequent addition across the carbonyl group of benzaldehyde yielding the intermediate trans-stilbene oxide is invoked for reaction (2). Zinc chloride induced ring-opening of this incipient epoxide, prior to a common hydride or phenyl shift, would account for the formation of compounds (1) and (2), respectively,<sup>2</sup> equation (4).

PhCOPh • 
$$Me_2SiCl_2$$
  $\xrightarrow{Zn-Cu}$  Ph<sub>3</sub>CCOPh (1)

$$PhCHO + Me_2SiCl_2 \xrightarrow{Zn-Cu} PhCH_2COPh + Ph_2CHCHO (2)$$

$$(1) (2)$$

$$PhCHO \xrightarrow{Me_2SiCl_2} PhCH^{\circ}] \xrightarrow{PhCHO} PhCH-CHPh$$
 (3)

$$PhCH-CHPh \xrightarrow{ZnCl_2} (1) + (2)$$
 (4)

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Deoxygenation of cyclohexanone under comparable conditions afforded a viscous liquid (b.p. 62-64 at  $0\cdot15$  mmHg) whose elemental analysis, molecular weight determination, and i.r. spectral data are consistent with the molecular formula  $C_{12}H_{20}O$  of a saturated cyclic ketone. Based upon the proposed mechanism of deoxygenation of benzaldehyde, but not confirmed unambiguously by its complex  $^1H$  n.m.r. spectrum, 2-oxocycloheptanespirocyclohexane is a reasonable structure for this ketone.

We have also discovered that benzaldehyde, benzophenone, and cyclohexanone may be deoxygenated in ether by chlorotrimethylsilane and zinc-copper couple in the presence of anhydrous zinc bromide, affording the same products as those obtained using dichlorodimethylsilane and zinc-copper couple, but in lower yields. In an experiment in which deoxygenation of benzaldehyde with chlorotrimethylsilane, zinc-copper couple, and a catalytic amount of zinc bromide was conducted in an excess of cyclohexene, 7-phenylnorcarane (15%) was obtained, confirming the intermediate formation of the proposed carbenoid, equation (5).

PhCHO 
$$\frac{Me_3SiCl}{Zn-Cu,ZnBr_2}$$
 [PhCH:]  $\frac{C_6H_{10}}{}$ 

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