Carbenoids by Deoxygenation of Carbonyl Compounds with Chloromethylsilanes

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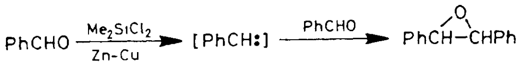
Summary Deoxygenation of benzophenone, benzaldehyde, and cyclohexanone with chloromethylsilanes and zinc–copper couple in ether is reported to yield 2,2,2-triphenylacetophenone, a mixture of deoxybenzoin and diphenylacetaldehyde, and a bicyclic ketone with the proposed 2-oxocycloheptanespirocyclohexane 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.[1] We now report results obtained *via* a modification of this procedure.

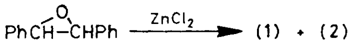
In a typical experiment, a solution of benzophenone (0·3 mol) dissolved in *ca.* 200 ml of ether was added dropwise to a mixture of dichlorodimethylsilane (0·4 mol), zinc–copper couple (0·5 g-atom), and *ca.* 100 ml of ether, producing an exothermic reaction. After continuous stirring for *ca.* 12 h 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,[2] equation (4).

$$PhCOPh + Me_2SiCl_2 \xrightarrow[\text{ether}]{\text{Zn-Cu}} Ph_3CCOPh \qquad (1)$$

$$PhCHO + Me_2SiCl_2 \xrightarrow[\text{ether}]{\text{Zn-Cu}} \underset{(1)}{PhCH_2COPh} + \underset{(2)}{Ph_2CHCHO} \qquad (2)$$

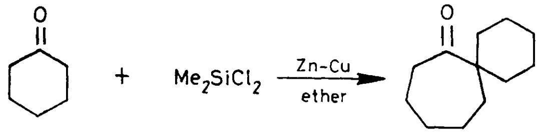


$$PhCHO \xrightarrow[\text{Zn-Cu}]{Me_2SiCl_2} [PhCH\!:] \xrightarrow{PhCHO} PhCH\overset{O}{-}CHPh \qquad (3)$$

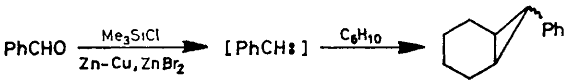


$$PhCH\overset{O}{-}CHPh \xrightarrow{ZnCl_2} (1) + (2) \qquad (4)$$

Deoxygenation of cyclohexanone under comparable conditions afforded a viscous liquid (b.p. 62—64 at 0·15 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).



(5)

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[1] W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1973, 935.
[2] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, **59**, 737.