# The Reactions of a Mercurial Dichlorocarbene Precursor with Benzophenone[†]

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*Summary* Evidence is presented that the reaction of phenyldichlorobromomethylmercury with benzophenone results in the formation of carbon monoxide, dichlorodiphenylmethane, and chlorodiphenylacetyl chloride, and that the reaction may involve the intermediacy of a complex between the mercurial and the benzophenone in addition to a carbonyl ylide and/or a dichloro-oxiran.

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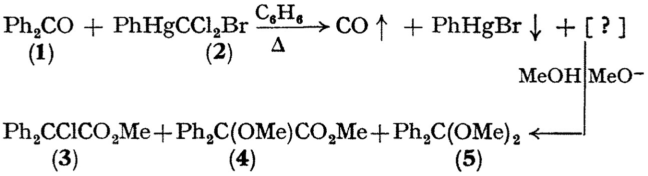
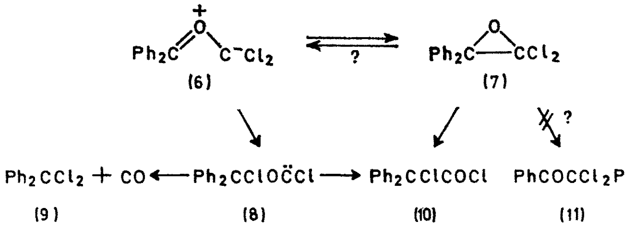
CONTRARY to published data indicating there is no reaction between benzophenone (**1**) and phenyldichlorobromomethylmercury (**2**) in hot benzene,[1] we report observations on at least two reactions which do occur and which may have some generality. Treatment of (**1**) (0·11 mol) with (**2**) (see Scheme 1) (0·066 mol) in benzene at 80° for 4 h resulted in the evolution of a 4·9% yield[‡] of carbon monoxide. That a g.l.c. peak from the crude product mixture matched the peak from a sample of chlorodiphenylacetyl chloride (**10**) and that treatment of the product mixture with a solution of sodium methoxide in methanol for several hours at reflux resulted in a mixture of methyl chlorodiphenylacetate (**3**) and methyl methoxydiphenylacetate (**4**) in the same mole ratio (*ca.* 1 : 4·3) as that obtained from an identical treatment of authentic (**10**), strongly suggests the presence of (**10**) as a product. However, the evidence does not conclusively eliminate the possibility that 2,2-dichloro-3,3-diphenyloxiran (**7**) may be present. Yields of esters (**3**) and (**4**) were 4·5 and 19·2%, respectively.[§] In addition, a 4·4% yield of dimethoxydiphenylmethane (**5**) was found which implied the presence of dichlorodiphenylmethane (**9**) in the original product mixture. The observed products together with unchanged benzophenone account for essentially all of (**1**) used in the experiment.[¶]



$$\underset{(1)}{Ph_2CO} + \underset{(2)}{PhHgCCl_2Br} \xrightarrow[\Delta]{C_6H_6} CO\uparrow + PhHgBr\downarrow + [\,?\,]$$

$$[\,?\,] \xrightarrow{MeOH \,|\, MeO^-} \underset{(3)}{Ph_2CClCO_2Me} + \underset{(4)}{Ph_2C(OMe)CO_2Me} + \underset{(5)}{Ph_2C(OMe)_2}$$

SCHEME 1



SCHEME 2

Scheme 2 shows a possible method of formation of these products. Carbonyl ylide (**6**),[2] formed initially, could break down to the alkoxyhalogenocarbene (**8**) which on the

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[‡] All stated yields are based on (**2**).

[§] In a separate reaction of (**1**) and (**2**) in which the initially formed products were hydrolysed with aqueous sodium hydroxide, a 28% yield of benzilic acid was produced.

[¶] The reaction of benzaldehyde with (**2**) in benzene has led to the identification of carbon monoxide and benzal chloride (in yields of *ca.* 27% each) in addition to evidence which suggests the presence of a small amount of chlorophenylacetyl chloride.

basis of previously published data[3] would be expected to lose carbon monoxide and form (**9**) or rearrange to the acid chloride (**10**). (**10**) could also arise from (**7**), a reaction which has been previously observed.[1] No evidence could be found for the presence of ketone (**11**).

Examination of the i.r. spectrum of a mixture of (**1**) and (**2**) in benzene revealed an additional reaction, that of reversible formation of a complex which has a separate carbonyl stretching frequency 16 $\text{cm}^{-1}$ less than that of the parent compound. Measurements of the band intensities (relative to calibrated standards) for mixtures of (**1**) and (**2**) in mole ratios of 2·75—0·55 together with the assumption of a 1 : 1 molar ratio in the complex results in an equilibrium constant for complex formation of $0{\cdot}56 \pm 0{\cdot}01$.††

Seyferth[1] has previously shown that the reaction between (**2**) and ketones containing extensive fluorine substitution adjacent to the carbonyl group results in an isolable dichloro-oxiran. Although it was suggested that the fluorine substituents on the ketone may be required for a reaction to occur, our results imply that such reactions may take place with a variety of ketones (and aldehydes), but that only those with very strong electron-withdrawing groups result in an oxiran with little tendency either to rearrange to an α-halogenoacid chloride or break down to carbon monoxide and a corresponding gem-dichloride.

Furthermore, the existence of a discrete mercurial–carbonyl complex, coupled with the observation that benzaldehyde and (**2**) evolve carbon monoxide at 25°, a temperature well below that at which (**2**) must be maintained to generate dichlorocarbene in the presence of olefins,[4] suggests the possibility that a relatively free dichlorocarbene need not be an intermediate in the aldehyde or ketone reactions.

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†† The corresponding constant for benzaldehyde complex formation with (2) was $0{\cdot}57 \pm 0{\cdot}05$.

[1] D. Seyferth and W. Tronich, *J. Organometallic Chem.*, 1969, **18**, P8.

[2] For recent information on carbonyl ylides, see: Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, 1970, **92**, 1402; D. R. Arnold and L. A. Karnischky, *ibid.*, p. 1404.

[3] J. A. Landgrebe, *Tetrahedron Letters*, 1965, 105.

[4] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, jun., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, 1965, **87**, 4259.