Carbonyl Ylides as Possible Intermediates in Reactions of a Mercurial Dichlorocarbene Precursor with Benzaldehyde

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Summary The intermediacy of a carbonyl ylide is used to explain why treatment of benzaldehyde with phenyl(bromodichloromethyl)mercury produced phenylmercuric bromide, carbon monoxide, benzal halide, and methyl 2,4-diphenyl-3,5-dioxahexanoate as major products.

RECENT evidence for the intermediacy of carbonyl ylides in the photolysis of epoxides[1] prompts us to report on the likelihood of similar intermediates being responsible for the intriguing products which result from the reaction of phenyl(bromodichloromethyl)mercury (**1**) with benzaldehyde (**2**) and to compare these observations with our reported work on benzophenone.[2]

The treatment of benzaldehyde with mercurial (**1**) (3·04 : 1 mole ratio) in benzene at 75—80° resulted in precipitation of phenylmercuric bromide (**3**) and evolution of carbon monoxide (**4**) over a 3—4 h period. Addition of methanol and pyridine to the filtered benzene solution resulted in the formation of products (**5**)—(**10**) with yields based on (**1**) as shown under the structure. An isolated

$$PhHgCCl_2Br + PhCHO \xrightarrow[\Delta]{PhCHO} PhHgBr + CO +$$

(**1**) (**2**) (**3**) (92%) (**4**) (29·7%) [products]

$$[Products] \xrightarrow[Pyridine]{MeOH} PhCHCl_2 + PhCHClBr +$$

(**5**) (**6**)

$$PhCH(OMe)OCH(Ph)CO_2Me +$$

(**7**)

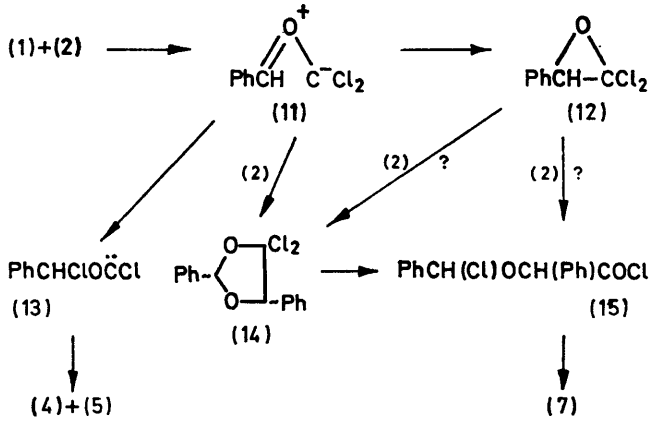
threo + *erythro* (42%)

$$PhCHClCO_2Me + PhCHOHCO_2Me + PhCH(OMe)_2$$

(**8**) (1·8%) (**9**) (2·7%) (**10**) (5·4%)

sample of acetal (**7**) isomers gave a satisfactory C and H analysis as well as characteristic spectral data. The relative areas of individual aliphatic n.m.r. peaks due to the two diastereomers show that the isomer ratio is 1·8 : 1. All other products were unambiguously identified by spectroscopic and g.l.c. comparison with authentic samples.

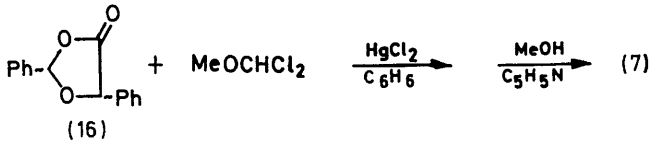
The Scheme provides an outline of paths to account for several of the major products. Because prior work has established the ease with which alkoxyhalogenocarbenes such as (**13**) break down with loss of carbon monoxide,[3] and because the origin of (**13**) is difficult to envisage except from carbonyl ylide (**11**), the intermediacy of (**11**) is strongly suggested.



SCHEME

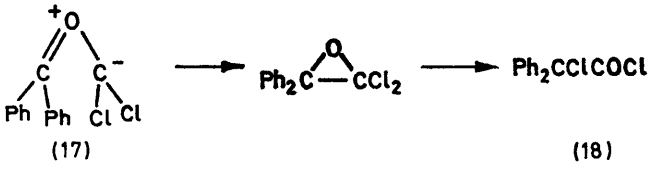
That both (**5**) and (**6**) result from the breakdown of (**13**) and its monobromo-analogue is shown by the reproducible equality of the collective yield of (**5**) plus (**6**) *versus* evolved carbon monoxide, and the fact that a control reaction of (**2**), (**3**), (**5**), and chlorophenylacetyl chloride failed to produce (**6**).

Although a 1,3-dipolar addition of benzaldehyde to (**11**) should readily form (**14**), a convenient precursor of the observed acetal ester (**7**), formation of (**14**) from (**12**) cannot be completely excluded. An attempt to generate (**14**) and/or (**15**) by treatment of (**16**) with methyl dichloromethyl ether, a type of reaction for which there is a precedent,[4] did produce (**7**) after treatment of the reaction mixture with methanol and pyridine, and thus provides additional evidence for the structure of (**7**) as well as the path suggested for its formation.



Further evidence for the intermediacy of (**11**) is provided by the observation that a strong electron-withdrawing group (*m*-CF_3) on benzaldehyde substantially increases the corresponding yield of the analogue of (**7**) while an electron-donor group (*p*-OMe) decreases that yield, consistent with the expected electronic effects of these substituents on the stability (and lifetime) of the carbonyl-ylide. Similar effects have been noted in the dipolar addition of substituted ketocarbenes to benzonitrile.[5]

In contrast to these results for benzaldehyde are the reported results for benzophenone[2] in which carbon monoxide and dichlorodiphenylmethane and/or bromochlorodiphenylmethane [the analogues of (**5**) and (**6**)] were formed in only 4·5% yield while the major products were derived from chlorodiphenylacetyl chloride (**18**), the analogue of which in the benzaldehyde case leads to the formation of (**8**) in at best 2% yield. We suggest that the difference in behaviour between benzaldehyde and benzophenone may be partly due to steric interactions between *ortho*-hydrogen and halogen in (**17**) which promote rapid conrotatory closure to the oxiran. Once formed, the oxiran would be expected to open readily to (**18**).[6]



That an i.r. spectrum of a fresh solution of (**1**) and (**2**) revealed a new carbonyl absorption at a frequency 12 cm^{-1} lower than that of (**2**),‡ suggests that the mechanism of

† A control reaction involving (**2**), (**3**), (**5**), and chlorophenylacetyl chloride followed by treatment with methanol and pyridine failed to produce (**7**).

‡ Measurement of band intensities over a range of relative concentrations of (**1**) and (**2**) and the assumption of a **1 : 1** complex revealed an equilibrium constant for its formation of 0·57 ± 0·05.[2]

breakdown of the mercurial in the presence of aldehydes and ketones could be different than that normally assumed when an olefin is the substrate.[7] However, treatment of (**1**), (**2**), and mixtures of simple olefins produced (in addition to the products expected from benzaldehyde) dichlorocyclopropyl derivatives of the olefins in identical relative yields to those found when benzaldehyde was absent. Therefore, dichlorocarbene remains a likely intermediate.

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