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DEOXYGENATION OF ALDEHYDES AND KETONES; A NEW GENERAL REACTION OF DIBROMOCARBENE AND DIBROMOCARBONYL YLIDES

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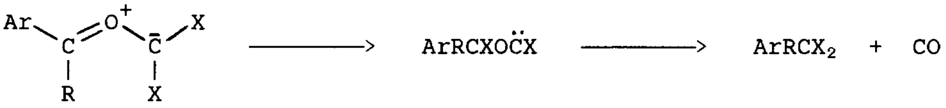
ABSTRACT: The treatment of a variety of aldehydes and ketones with phenyl(tribromomethyl)mercury results in the production of carbon monoxide from the deoxygenation of the carbonyl group by dibromocarbene.

Until now, reports of the production of carbon monoxide from the reaction of dichloro- or dibromocarbene with a carbonyl group have been limited to several substituted benzaldehydes[1] and benzophenone.[2] The published data suggest that this reaction involves the rearrangement of an initially formed carbonyl ylide **1** to alkoxyhalocarbene **2** with subsequent formation of dihalide **3** and CO.



1 **2** **3**

Alkoxyhalocarbenes, which break down to CO and other products, have been clearly implicated in the alcoholysis of haloforms under strongly basic conditions.[3]

We now report that the formation of carbon monoxide from the reaction of dibromocarbene (from the thermal decomposition of phenyl(tribromomethyl)-mercury) and various aldehydes and ketones is an extremely general reaction contrary to early publications which suggested that these mercurial carbene precursors might not react with simple aliphatic ketones.[4]

In order to verify that this type of reaction involves a deoxygenation rather than a decarbonylation of the carbonyl group, benzaldehyde-α-^{13}C with 46 ±1% isotopic label was prepared from benzoic acid-α-^{13}C as shown, and treated with phenyl(tribromomethyl)mercury in benzene at 80°.

$$Ph^{13}CO_2H \xrightarrow{THF\cdot BH_3} Ph^{13}CH_2OH \xrightarrow[CH_2Cl_2]{HPy^{+}CrO_3Cl^{-}} Ph^{13}CHO$$

$$Ph^{13}CHO + PhHgCBr_3 \xrightarrow[80^{\circ}]{C_6H_6} Ph^{13}CHBr_2 + CO + PhHgBr$$

The result was benzal bromide-α-^{13}C with 44±1% isotopic label, and CO with a natural abundance of ^{13}C as determined by mass spectrometry.

Displayed in Table I are the results of treating benzaldehyde and a variety of aliphatic aldehydes and ketones with phenyl(tribromomethyl)mercury (mole ratio 1.8 to 1) at 75-80° for 4 h. Carbon monoxide is always produced but in yields which vary from about 16% to 46%.

Prior results for the reaction of $:CCl_2$ with benzaldehydes and benzophenone,[2a] coupled with product studies for selected compounds from Table I lead to Scheme I as a reasonable sequence of steps to explain the production of CO. Important primary reaction products from the study of selected compounds from the Table by capillary GC-MS procedures include dibromide **9** and bromoalkene **10**, which arise from ion pair **8**. Further evidence for **8** is derived from the observation that norcamphor results in rearranged structures

Scheme I

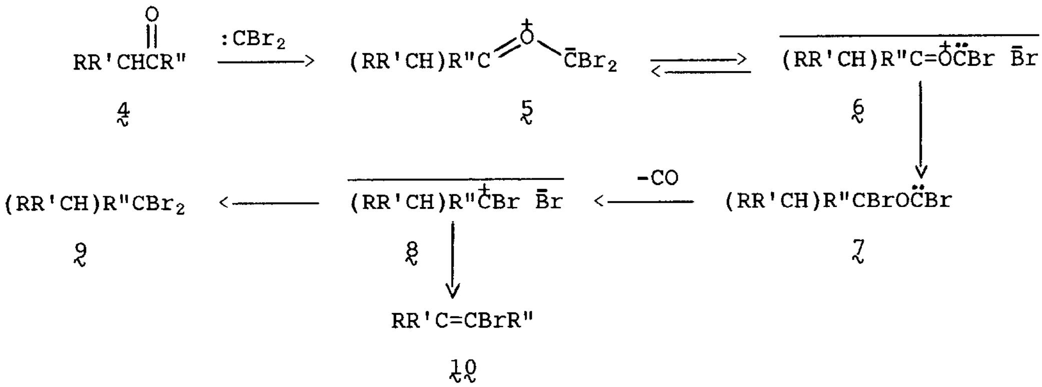


Table 1. Yields of CO in the Reaction of $PhHgCBr_3$ with RCOR'

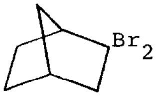
Compound	CO yield (%)[b]	No. of Runs
Aldehydes		
Benzaldehyde	46.4 ± 0.9	3
Propionaldehyde	35.0 ± 0.8	2
Isobutyraldehyde	39.3 ± 1.5	2
Pivaldehyde	18.8 ± 3.0	5
Ketones		
Acetone	15.5 ± 3.0	3
Ethyl *n*-butyl	19.0 ± 0.5	3
Methyl cyclopropyl	20.2 ± 0.7	2
Dicyclopropyl	20.3 ± 0.0	2
Cyclohexanone	37.9 ± 0.9	2
Cyclopentanone	19.4 ± 0.5	2
Norcamphor	46.0 ± 3.5	3

[a] $PhHgCBr_3$ (1.89 mmol), RCOR' (3.40 mmol), benzene (5 mL) at 75-80° for 4 h.

[b] Error reported as ± range/2.

12 and 14 in addition to dibromide 11 and bromoalkene 13. However, only products 12 and 13 were formed when dibromide 11 was treated with PhHgBr in benzene at 80° in a control experiment. Thus, bromoalkene 14 must arise from a cationic precursor of dibromide 11.

Of special mechanistic interest is the observation that the unusually high yield of CO for cyclohexanone and norcamphor relative to other ketones can be attributed to relief of torsional and bond angle strain, respectively, in the interconversion of carbene-oxonium ion pair 6 to alkoxybromocarbene 7. Among the aliphatic aldehydes the lower yield of CO from pivaldehyde is consistent with a steric effect on bromide attack in the interconversion of 6 to 7.



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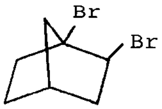

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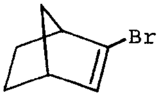

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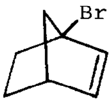

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