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Preliminary communication

Reactions of phenyl(bromodichloromethyl)mercury with α-dicarbonyl compounds

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We have reported the preparation of oxiranes by the reaction of phenyl(trihalomethyl)mercury compounds with highly fluorinated acetones, *e.g.*, $(CF_2X)_2C{=}O$ (X = Cl and F)[1]. In exploratory reactions designed to investigate the scope of this novel oxirane synthesis, no stable oxirane products were obtained when phenyl(bromodichloromethyl)mercury was heated in the presence of phosgene, benzophenone, hexanone-3 and hexachloroacetone. In our further research we have found examples where other products are isolated to the exclusion of the expected oxirane or where other products are formed in addition to the expected oxirane. The cases of benzil and oxalyl chloride are illustrative.

Treatment of 30 mmol of benzil with 30 mmol of phenyl(bromodichloromethyl)mercury in benzene at reflux for 6 h gave phenylmercuric bromide in 93% yield. Evaporation of the filtrate and extraction of the oil obtained with pentane to leave behind a small quantity of unconverted benzil was followed by evaporation of the pentane extracts. A pale yellow solid, (I), melting range 42–50°, $\nu(C{=}O)$ 1678 and 1782 cm^{-1}, which was very sensitive to moisture, was isolated. Treatment of the latter with methanol in the presence of an equimolar quantity of pyridine gave α-chloro-α-carbomethoxy-α-phenylacetophenone in 89% yield; m.p. 110–111°; $\nu(C{=}O)_{melt}$ 1680 and 1755 cm^{-1}; NMR (CCl_4) δ 3.75 (s, 3) and 7.2–7.9 ppm (m, 10). Hydrolysis of I (sodium acetate buffer in THF/water) at 25° afforded α-benzoylbenzyl chloride in 68% yield. These reactions indicate that I was the acid chloride shown in Scheme 1.

Another example was provided by the reaction of oxalyl chloride with phenyl(bromodichloromethyl)mercury (3 h at 65° in benzene). Here the product mixture contained both the initially formed oxirane, 2,3,3-trichloro-2,3-epoxypropenoyl chloride (II) (15%), and products in principle derived from it, trichloropyruvyl chloride (III) (46%) and trichloroacetyl chloride (1.2%) (by GLC). The IR spectrum of the oxirane showed a sharp $\nu(C{=}O)$ at 1790 cm^{-1}, while the IR spectrum of the characteristically pale yellow trichloropyruvyl chloride showed a broad peak at 1765 cm^{-1}. In addition to these products, some higher boiling compounds (unresolved) were present in low yield. Their

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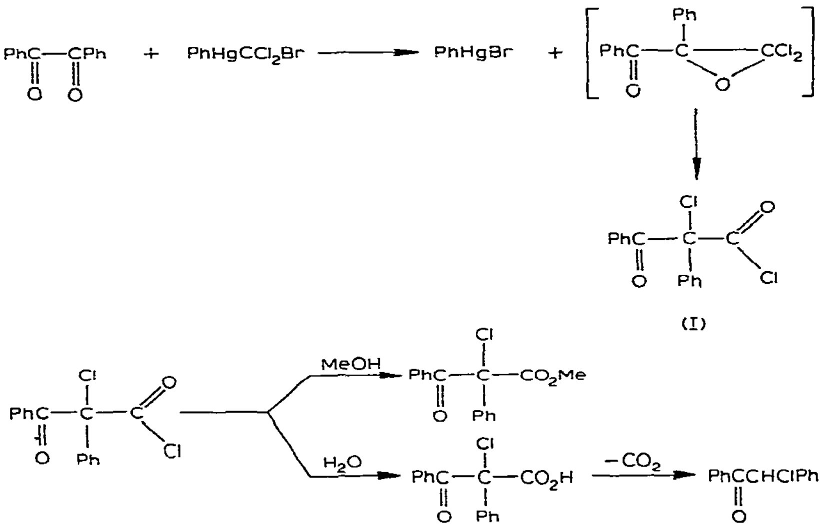
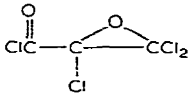
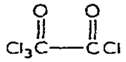


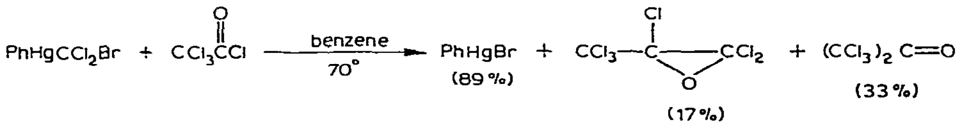
Scheme 1

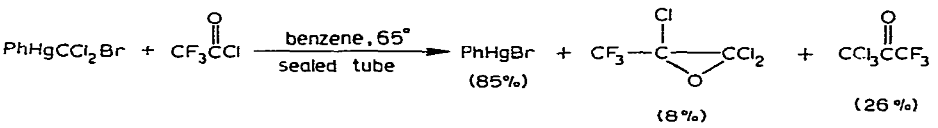
yellow color and the broad absorption in their IR spectrum at 1780 cm^{-1} is suggestive of the presence of hexachlorobiacetyl.


(II)

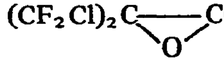

(III)

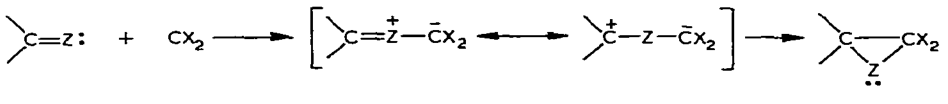
Two other cases of the isolation of both the oxirane and its rearrangement product were encountered with trichloroacetyl chloride and trifluoroacetyl chloride:





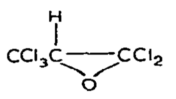
While it is fairly certain that the rearranged products in the case of benzil were formed during the course of the reaction at 80°, there is no guarantee that this is the case with rearrangement products from the reactions of oxalyl chloride and the trihaloacetyl chlorides. GLC analysis and isolation were carried out under the mildest possible conditions, but injection port and detector temperatures of 100–110° were used, thus possibly causing rearrangement at that stage.

The pyrolysis of a stable chloro-oxirane has been shown to give a carbonyl compound (*e.g.*,  $(CF_2Cl)_2\underset{O}{C{-}{-}CClBr} \rightarrow (CF_2Cl)_2BrCCOCl$ [1]), but it does not follow that in the reactions under present discussion the carbonyl products are derived from thermolysis of the oxirane also isolated. As Gilchrist and Rees[2] have pointed out, it is likely that in the case of carbene addition to C=O, C=S and C=N bonds an ylide-type mechanism prevails:



If this is the case, then it is possible that the formal rearrangement product could be formed directly from the ylide without intervention of the oxirane[*,**]. In this connection we note that such a possibility, product formation via an ylide intermediate without going through a ring-closed intermediate, was indicated as an alternative route in our 1966 report concerning the reaction of phenyl(bromodichloromethyl)mercury with carbodiimides[7].

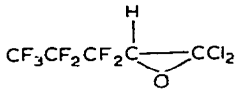
In contrast to the reactions of the trihaloacetyl chlorides with phenyl(bromodichloromethyl)mercury, reactions of the aldehydes CCl_3CHO and $n\text{-}C_3F_7CHO$ with this organomercury reagent gave only the oxiranes IV and V in yields of 46% and 43%, respectively. Oxirane V was very stable, surviving unchanged a 1 h heating period at 230° in a capillary tube.



(IV)

n_D^{25} 1.4938

δ 4.18 ppm (s)



(V)

n_D^{25} 1.3361

δ 3.78 ppm(t,J = 9.5 Hz)

In conclusion, we take note of related studies reported by Landgrebe[9] which demonstrate that $PhHgCCl_2Br$ does indeed react with benzophenone. The expected oxirane was not isolated, but treatment with sodium methoxide in methanol gave products derivable from $Ph_2ClCCOCl$ in ca. 28% yield.

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[*] A carbonyl ylide, $Me_2\overset{+}{C}{-}O{-}\overset{-}{C}H_2$, was implicated in the reaction of methylene (via photolysis of diazomethane) with acetone by Bradley and Frey[3], and other workers[4] have shown that a carbonyl ylide can cyclize to the oxirane.

[**] That these reactions proceed via a carbene mechanism is by no means established. As we have pointed out previously, the reactions of $PhHgCCl_2Br$ with substrates containing good donor atoms, *e.g.*, triphenylphosphine[5], tertiary amines[6], carbodiimides[7] and thiocarbonyl compounds[8], very possibly involve a direct transfer of CX_2 from the mercurial to substrate without intervention of a free carbene. Such a possibility also must be considered in the case of carbonyl compounds, especially those which are known to be good donor molecules.

ACKNOWLEDGMENTS

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