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Phenyl(iododichloromethyl)mercury: A useful room temperature dichlorocarbene precursor

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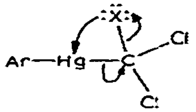
Phenyl(bromodichloromethyl)mercury is a very useful dichlorocarbene precursor. However, temperatures around 80° are required to obtain a rapid rate of CCl_2 extrusion[1], and at room temperature this process is extremely slow[2]. Thus a reagent which is an effective source of dichlorocarbene at room temperature and at the same time has all the other advantages associated with the $PhHgCX_3$ reagents[1] would be most welcome.

Several years ago we considered the possibility of the indirect synthesis of phenyl(iododichloromethyl)mercury via $PhHgCCl_3$ [3]. We expected $PhHgCCl_2I$ to be a more reactive CCl_2 source than $PhHgCCl_2Br$ since the latter reagent was in turn much more reactive than $PhHgCCl_3$. This expectation was given further support by the results of kinetic studies of $ArHgCCl_2Br$/olefin reactions, which indicated that a concerted, cyclic process was involved in the CCl_2 extrusion step[4,5]:

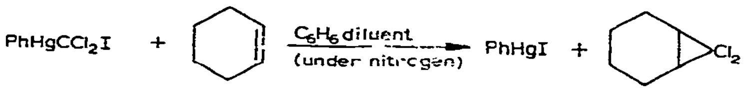


The much more rapid elimination of PhHgBr (as compared to PhHgCl) was explained in terms of two factors: the greater nucleophilicity of Br *vs.* Cl and the weaker C—Br bond strength, compared to that of the C—Cl bond. On this basis, $PhHgCCl_2I$ would be expected to be an extremely reactive CCl_2 generator. Our present studies have shown this to be the case.

Phenyl(iododichloromethyl)mercury was prepared by a variation of our procedure generally used for the synthesis of the $PhHgCCl_nBr_{3-n}$ (n = 0—3) reagents[6]. One equivalent of iododichloromethane[7] was added with stirring to a reagent mixture maintained at −55° under nitrogen which had been prepared from approximately molar equivalents of phenylmercuric chloride slurried in diethyl ether and unsolvated potassium tert-butoxide dissolved in THF. Immediately upon completion of the addition, the resulting mixture was evaporated at reduced pressure and the colored solid residue was treated with water and dichloromethane. Evaporation of the organic layer was followed by crystallization of the residue from dichloromethane/pentane at −78°. We emphasize that it is necessary to carry out the reaction and work-up procedure as rapidly as possible in order to obtain reasonable yields of phenyl(iododichloromethyl)mercury in acceptable purity.

Phenyl(iododichloromethyl)mercury was obtained as a micro crystalline yellow solid which melts with instant decomposition at 72° (Found: C, 17.09; H, 1.08; I, 25.72. $C_7H_5Cl_2IHg$ calcd.: C, 17.24; H, 1.03; I, 26.04%). Its stability as a solid at room temperature is only fair and it is best stored in a freezer. It is much less stable in solution and in most preparations is contaminated with variable amounts of phenylmercuric iodide resulting from its decomposition. A useful procedure for assessing the concentration of active reagent in such samples is based on the decomposition of a weighed sample of the crude solid at 40° in cyclohexene solution, evaporation of the volatiles and weighing of the residual PhHgI. The assumption that the observed weight loss represents CCl_2 lost allows calculation of the purity of the crude $PhHgCCl_2I$ sample. In the experiments mentioned below, yields are based on the $PhHgCCl_2I$ content of the mercurial samples used; typically, the purity thus determined was 75–90% by weight.

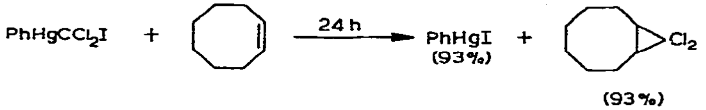
As we had expected, phenyl(iododichloromethyl)mercury is an extremely reactive CCl_2 generator. Reactions of this mercurial with cyclohexene (1/3 molar ratio) (eqn. 1) served to show this very effectively. At 80°, the reaction to give 7,7-dichloronorcarane (in 85% yield) occurred instantaneously. The reaction was best carried out by adding a benzene solution of $PhHgCCl_2I$ to the refluxing olefin solution over a period of a few minutes. The yellow color of the mercurial solution was discharged within 10 sec of its addition. Phenyl(iododichloromethyl)mercury is particularly useful as a room temperature CCl_2 reagent. Reaction (1) was complete (to give 7,7-dichloronorcarane in 89% yield) within 24 h at 24°. This new organomercury reagent can even be used at lower temperatures. At 0°, reaction (1) proceeded to give 7,7-dichloronorcarane in 71% yield within 8 days.



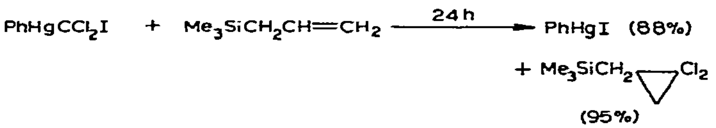
(1)

The progress of these reactions can be monitored by thin layer chromatography[1] or, more easily, by noting the disappearance of the yellow color of the mercury reagent. The work-up procedure is simple, consisting of filtration to remove the insoluble phenylmercuric iodide and isolation or estimation of the organic product by distillation or GLC.

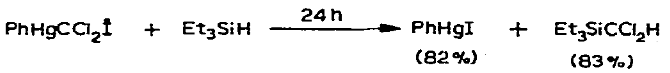
Several other room temperature reactions of $PhHgCCl_2I$ were examined (eqn. 2–4).



(2)



(3)



$$PhHgCCl_2I + Et_3SiH \xrightarrow{24\,h} \underset{(82\%)}{PhHgI} + \underset{(83\%)}{Et_3SiCCl_2H} \quad (4)$$

It is apparent that in $PhHgCCl_2I$ we have a very useful new dichlorocarbene precursor. We expect that it will find unique synthetic application and it should be especially applicable to those reactions where the product of CCl_2 addition or insertion is both thermally labile and base sensitive.

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