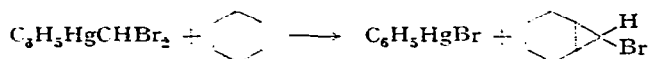


PRELIMINARY NOTES

Synthesis of monohalocyclopropanes and 1-haloolefins via phenyl-(dihalomethyl)mercury compounds

Our studies of the synthesis of *gem*-dihalocyclopropanes using $C_6H_5HgCX_2Br$ compounds as CX_2 sources¹⁻³ have been extended to an investigation of the utility of $C_6H_5HgCHXBr$ compounds* in the preparation of monohalocyclopropanes. We have found that both compounds ($X=Cl$ and Br) serve excellently in the preparation of monohalocyclopropanes. For example, 0.01 mole of $C_6H_5HgCHBr_2$ and 10 ml of cyclohexene were sealed in a nitrogen-flushed, heavy-walled Pyrex tube (*ca.* 80 ml volume) and heated for 11 h at 132° with continuous shaking. The dark yellow reaction mixture was filtered to remove 3.4 g (95%) of phenylmercuric bromide. Gas chromatographic analysis of the filtrate showed that a 1:1.16 mixture of the *trans* and *cis* isomers of 7-bromobicyclo[4.1.0]heptane** had been formed in 86% yield***.



A 1:1.14 mixture of the *trans* and *cis* isomers of 7-chlorobicyclo[4.1.0]heptane** was formed in 95% yield under similar conditions (130° for 10 h) when $C_6H_5HgCHClBr$ was used instead. Thus the previously available methods for direct preparation of monohalocyclopropanes by "carbenoid" addition to olefins—the $RLi + CH_2Cl_2$ method⁷ and the chlorodiazomethane method⁸ for $CHCl$ addition and the $CHBr_3 + Li$ method⁹ for $CHBr$ addition—are supplemented by a new procedure which does not involve use or intervention of a strongly basic reagent. These new "carbenoid" reactions of phenyl(dihalomethyl)mercury compounds are of particular value when $CHBr$ transfer is involved, since the available route to bromocarbene⁹ is not very satisfactory.

A further similarity of $C_6H_5HgCHXBr$ reagents to $C_6H_5HgCX_2Br$ compounds is seen in their reactions with triethylsilane. The reaction of $C_6H_5HgCHBr_2$ (5 mmoles) with triethylsilane (25 ml) at reflux (*ca.* 109°) under nitrogen during 27 h gave (bromo-methyl)triethylsilane ($n_D^{25} 1.4665$) in 72% yield. Dihalomethylenation of triethylsilane in high yield had been observed by us previously¹⁰.

It is not yet known whether these reactions of phenyl(dihalomethyl)mercurials

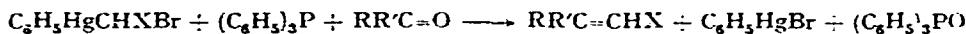
* The recent report by Reutov and Lovtsova⁴ suggest that the preparation of $C_6H_5HgCHBr_2$ by the reaction $C_6H_5HgX + CH_2Br_2 + \textit{tert}-BuOK \rightarrow gives only impure product in poor yield. This is not so; in our hands this procedure reproducibly gives yields of 70-80% of material of good purity. Phenyl(bromochloromethyl)mercury also can be prepared in good yield by this procedure using CH_2BrCl . For properties of these compounds see ref. 5.$

** Identified by comparison of g.l.c. retention times and infrared and NMR spectra with those of authentic samples⁶.

*** The optimum product yield is dependent on the reaction temperature and the reaction time: longer heating at 132° resulted in a yield decrease; lower temperatures did not allow achievement of maximum yields.

involve intermediate formation of a halocarbene or a direct reaction between mercurial and substrate. Experiments designed to distinguish between these possibilities are in progress.

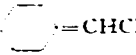
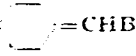
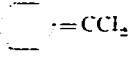
A new, general synthesis of vinylic bromides and chlorides based on (dihalo-methyl)mercurial chemistry has been developed.



The procedure used was as follows: triphenylphosphine (20 mmoles), mercurial (X = Cl or Br, 20 mmoles) and *n*-heptaldehyde or benzaldehyde (40 mmoles) were heated at reflux in 50 ml of benzene under nitrogen with stirring. The dark red color of the reaction mixture which developed as the temperature rose to 80° was discharged at 80° with simultaneous separation of C₆H₅HgBr. The mixture was refluxed for 30 min: filtration to remove phenylmercuric bromide (usually ca. 90–95%) was followed by trap-to-trap vacuum distillation of the filtrate and g.l.c. analysis for vinylic chloride or bromide. Triphenylphosphine oxide was extracted from the residue with cyclohexane. Olefin yields are given in Table I. These reactions did not occur under the above conditions when cyclohexanone was used in place of the aldehydes. However, when these reactions with cyclohexanone were carried out in *o*-xylene at reflux, the expected olefins were obtained in good yield.

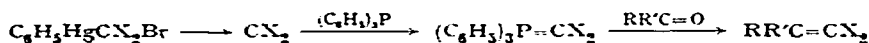
TABLE I

PHENYL(DIHALOMETHYL)MERCURY AND PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS IN OLEFIN SYNTHESIS

Mercurial	Carbonyl compound	Haliolefin produced ^a	Yield, %
C ₆ H ₅ HgCHClBr	<i>n</i> -heptaldehyde	CH ₃ (CH ₂) ₅ CH=CHCl ^b	81.5
	benzaldehyde	C ₆ H ₅ CH=CHCl	73.3
	cyclohexanone	 =CHCl	77.0
C ₆ H ₅ HgCHBr ₂	<i>n</i> -heptaldehyde	CH ₃ (CH ₂) ₅ CH=CHBr	53.0
	benzaldehyde	C ₆ H ₅ CH=CHBr	54.7
	cyclohexanone	 =CHBr	51.6
C ₆ H ₅ HgCCl ₂ Br	<i>n</i> -heptaldehyde	CH ₃ (CH ₂) ₅ CH=CCl ₂	68.0
	benzaldehyde	C ₆ H ₅ CH=CCl ₂	64.5
	cyclohexanone	 =CCl ₂	65.0

^a Identified by comparison of observed physical and spectral properties with those reported in the literature. ^b New compound; *n*_D²⁵ 1.4380, satisfactory analysis.

This general procedure also is applicable to the preparation of olefins of type RR'C=CX₂ from aldehydes and ketones. Selected results are given in Table I. One can only speculate about the mechanism of these reactions at present. An obvious possibility is the sequence



However, a direct reaction between mercurial and triphenylphosphine, with or without intervening phosphonium halide, also must be considered. Such a one-step Wittig olefin synthesis has been demonstrated for $RCH=CF_2$ (using $ClF_2CCOONa$)¹¹, but the scope of this method is limited by the availability of trihaloacetates. Similar two-step (separate formation of P-ylid, then the Wittig reaction) syntheses of halo-olefins based on carbenoid reactions are known for $RR'C=CX_2$ ¹² and for $RR'C=CHCl$ ^{13,14}. The one-step reactions of CX_4 ($X = Cl$ or Br), triphenylphosphine and carbonyl compound also produce $RR'C=CX_2$, but have the disadvantage that in many instances $RR'CX_2$ in an amount equivalent to that of the product is produced as well^{15,16}.

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