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PRELIMINARY COMMUNICATION

Generation of fluorochlorocarbene by the mercurial route

The recent intense interest in the reactions of fluorochlorocarbene with olefins, as evidenced by six publications on this subject this year[1-6], prompts us to report concerning the generation of this species by thermolysis of phenyl(fluorodichloromethyl)mercury, $C_6H_5HgCCl_2F$, in refluxing benzene solution. The previous procedures for CFCl generation used the action of strong base on $RCCl_2F$ derivatives such as fluorodichloromethane[6,7,8], methyl fluorodichloroacetate[4,9] and *sym*-difluorotetrachloroacetone[1,2,5,9,10], or the high temperature (150°) reaction of fluorodichloromethane with ethylene oxide in the presence of a catalytic quantity of tetraethylammonium bromide[3]. While these procedures find useful application in many cases, the requirements of strongly basic reaction conditions or of higher temperature limit their more general application, and in some cases the mercurial route will be the only applicable one.

The mercurial reagent can be prepared by the reaction of phenylmercuric chloride with fluorodichloromethane and potassium tert-butoxide (the tert-butanol monosolvate[11]) in 1 : 6.5 : 2 molar ratio, respectively, in anhydrous diethyl ether at *ca.* −30° *with high speed stirring*. In this variation (in solvent and temperature) of our

$$C_6H_5HgCl + CHCl_2F + \text{tert-BuOK} \rightarrow C_6H_5HgCCl_2F + \text{tert-BuOH} + KCl \qquad (1)$$

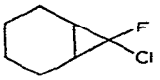
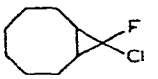
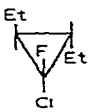
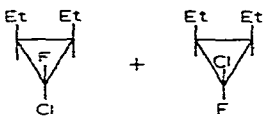
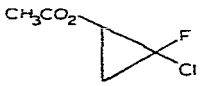
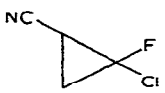
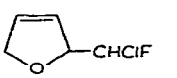
published procedure for $C_6H_5HgCX_3$ compounds[12] pure $C_6H_5HgCCl_2F$ was never obtained in the many runs carried out*. In all cases an unresolvable, roughly 1 : 4 mixture of diphenylmercury and the desired mercurial was obtained in 40–50% yield. The presence of the $Hg–CCl_2F$ moiety was demonstrated by hydrogen chloride cleavage of the mercury compound mixture to give phenylmercuric chloride and $ClHgCCl_2F$, m.p. 149–151°. Exhaustive brominolysis of the mercurial mixtures and GLPC determination of the bromobenzene and fluorodichlorobromomethane produced served excellently in the quantitative analysis of these mixtures. These mixtures then were used in the reactions with the substrates indicated in Table 1; the diphenylmercury contaminant did not interfere. In general, the reactivity of $C_6H_5HgCCl_2F$ approximates that of phenyl(trichloromethyl)mercury[13] in that reaction times of *ca.* 48 h in refluxing benzene solution were required to obtain the product yields listed. The general experimental procedure used in $C_6H_5HgCX_3$/olefin reactions[13] was applicable.

Examination of Table 1 makes apparent several points of interest concerning mercurial-derived CFCl. As with the $C_6H_5HgCCl_nBr_{3-n}$ reagents, base-sensitive olefins can be converted to dihalocyclopropanes, *e.g.*, the examples of acrylonitrile and vinyl acetate. The 1-fluoro-1-chlorocyclopropanes are produced in generally excellent yields, in contrast to the generally poorer yields obtained by the other methods

* It may be noted that use of benzene as solvent, as described in ref. 12, gave only minor amounts of $C_6H_5HgCCl_2F$ when the reaction described by eqn. 1 was attempted.

TABLE 1

REACTIONS OF PHENYL(FLUORODICHLOROMETHYL)MERCURY[a]

Substrate	Product[b] (% Yield)	n_D^{25}	Comments
cyclohexene	 (86)	1.4591	mixed isomers, lit.[3] n_D^{20} 1.4603
cyclooctene	 (91)	1.4707	mixed isomers, lit.[3] n_D^{20} 1.4712
trans-EtCH=CHEt	 (97)	1.4071	
cis-EtCH=CHEt	 (86) (1:12 ratio)	1.4129 (mixed isomers)	
$CH_3CO_2CH=CH_2$	 (86)	1.4113	mixed isomers
$CH_2=CHCN$	 (40)	1.4276	mixed isomers
	 (75) +  (8)	1.4483	mixed isomers
Et_3SiH	$Et_3SiCClFH$ (83)	1.4351	
$Me_3SnSnMe_3$	$Me_3SnCClFSnMe_3$ (36)	1.5253	by products include $Me_3SnCCl_2SnMe_3$ (8%), Me_3SnCl, Me_3SnPh, Me_2SnPh_2

[a] Substrate/$PhHgCCl_2F$ ratio = 3. Reactions in refluxing benzene for 48 h. [b] Satisfactory microanalyses were obtained for all products. Their IR and/or NMR spectra were in agreement with the structure written.

mentioned[1-10]. The mercurial-derived CFCl adds to olefins in a stereospecific manner*. In agreement with the greater selectivity of CFCl when compared with CCl_2

* The same observation was made in the addition of CFCl, produced by the $(CFCl_2)_2CO$/base reaction, to olefins by Moss and Gerstl[1]. Our structural assignments for the isomeric fluorochlorocyclopropanes produced from *cis*- and *trans*-3-hexene (via ^{19}F NMR) parallel their assignments in the case of *cis*- and *trans*-2-butene.

in olefin reactions[2], we find that CFCl is much more selective than CCl_2 with respect to C=C addition *vs.* C–H insertion. In the case of 2,5-dihydrofuran, the ratio of C=C addition to α C–H insertion was nearly equal to one for CCl_2[13], but this ratio was 9 in the case of fluorochlorocarbene. Furthermore, CFCl insertion into the very reactive (to CCl_2) β C–H bond of $PhMe_2SiCH_2CHMe_2$[14]* was not observed. However, CFCl is capable of undergoing insertion reactions into more reactive single bonds, as evidenced by its reactions with triethylsilane and hexamethylditin. These reactions with the C–H bond of 2,5-dihydrofuran, the Si–H bond and the Sn–Sn bond are the first CFCl insertion reactions to be reported.

As with phenyl(trichloromethyl)mercury[16], the action of sodium iodide on $C_6H_5HgCCl_2F$ produces a more rapid release of carbene from the mercurial. For example, the reaction of $C_6H_5HgCCl_2F$ with slightly more than one equivalent of anhydrous sodium iodide in the presence of cyclohexene in 1,2-dimethoxyethane (DME) at 85° gave 7-fluoro-7-chloronorcarane in 70% yield after a reaction time of only 3 h. In the case of the $C_6H_5HgCCl_3$/NaI reagent system, reactions with acrylo-

nitrile and vinyl acetate served to implicate the trichloromethyl anion as an intermediate, since among the products obtained were $CCl_3CH_2CH_2CN$ and CH_3CO_2-$CH(CH_3)CCl_3$, respectively[16]. Similar reactions were carried out between the C_6H_5-$HgCCl_2F$/NaI reagent and these functional olefins, but here no CCl_2F^- derived products were obtained. Only the expected fluorochlorocyclopropanes (in 33 and 70% yield, respectively) could be detected. This finding does not speak against nucleophilic displacement of CCl_2F^- by I^- in processes such as reaction (2), rather, in our opinion, it is best interpreted in terms of the instability of the fluorodichloromethyl anion (as compared to CCl_3^-) with respect to chloride ion loss to form fluorochlorocarbene. It has been noted that a fluorine substituent destabilizes a trihalomethyl anion but stabilizes the derived dihalocarbene[17].

The results of this work have clearly demonstrated the utility of phenyl-(fluorodichloromethyl)mercury as a CFCl transfer agent. Our efforts in this area are continuing and details of this work will be provided at a later date.

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* See the preliminary communication on this general type of reaction (Ref. 15).

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