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Preliminary communication

Cyclohexyl(trihalomethyl)mercury compounds: very reactive dihalocarbene precursors

DIETMAR SEYFERTH and CAROL K. HAAS

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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SUMMARY

The cyclohexyl(trihalomethyl)mercurials, $RHgCCl_3$, $RHgCCl_2Br$, $RHgCClBr_2$ and $RHgCBr_3$ (R = cyclohexyl), have been prepared and have been found to be excellent dihalocarbene sources. They transfer their CX_2 very rapidly at 80° and within 2–3 days at room temperature.

We have reported recently concerning phenyl(iododichloromethyl)mercury, which is an exceptionally reactive source of dichlorocarbene[1]. This reagent transfers CCl_2 to a carbenophile within a few minutes at 80° and within 24 h at room temperature. However, this compound is difficult to prepare and, because of its high reactivity, has poor stability on storage, even as the solid. Phenyl(bromodichloromethyl)mercury transfers CCl_2 fairly rapidly at 80° (within 2 h), but only very slowly at room temperature (within 18 days)[2]. An organomercury CCl_2 transfer reagent with a reactivity intermediate between that of $PhHgCCl_2I$ and $PhHgCCl_2Br$, one that transfers its CCl_2 very rapidly at 80° and within a few days at 25°, was considered a worthwhile objective for further research.

An indication that such a reagent might be found within the class of the alkyl(trihalomethyl)mercury compounds was provided by some interesting observations by Shcherbakov[3]. It was reported that n-$C_3H_7HgCCl_2Br$ can be isolated as an unpurifiable liquid which decomposes within 2–3 days at room temperature. A three day reaction of this material with cyclohexene at room temperature gave 7,7-dichloronorcarane in 70% yield and n-C_3H_7HgBr (80%). A similar reaction carried out at 40° gave the norcarane in 85% yield within a 5 h period. N-Propyl(trichloromethyl)mercury, a liquid, also had enhanced CCl_2 transfer reactivity (compared to $PhHgCCl_3$), giving 7,7-dichloronorcarane in 82% yield after reaction with cyclohexene at 80° for 8 h. The higher toxicity of alkylmercurials (*vs.* aryl derivatives) makes work with the relatively volatile n-propyl compounds

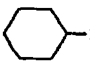
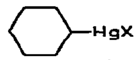
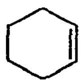
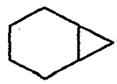
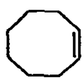
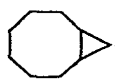
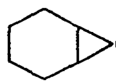
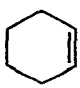
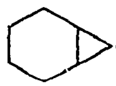
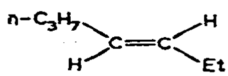
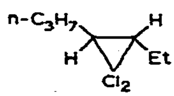
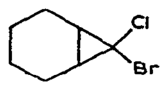
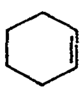
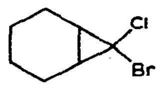
TABLE 1

APPROXIMATE REACTION TIMES FOR CX_2 TRANSFER FROM $RHgCX_3$

	R = phenyl		*R = cyclohexyl*	
	room temp.	*80°*	*room temp.*	*80°*
CCl_3		40 h		8 h
CCl_2Br	18 days	2 h	2 days	< 10 min
$CClBr_2$	16 days	2 h	3 days	< 10 min
CBr_3	15 days	2 h	2 days	< 10 min

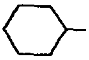
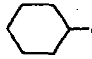
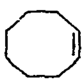
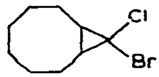
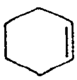
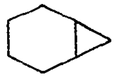
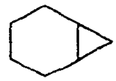
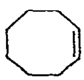
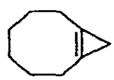
TABLE 2

REACTIONS OF CYCLOHEXYL (TRIHALOMETHYL) MERCURIALS

CX_3 in $HgCX_3$	Reactant	Reaction conditions [a]	Product (% yield) [b]	 (% yield) [c]
CCl_3		6.5 h / 80°	 Cl_2 (92)	
CCl_3		8 h / 80°	 Cl_2 (90)	98
CCl_3	Et_3SiH	8 h / 80°	Et_3SiCCl_2H (88)	97
CCl_2Br		6 min / 80°	 Cl_2 (96)	95
CCl_2Br		49 h / 25°	 Cl_2 (95)	85
CCl_2Br		50 h / 25°	 (88)	80
CCl_2Br	Et_3SiH	50 h / 25°	Et_3SiCCl_2H (80)	89
$CClBr_2$		7 min / 80°	 (85)	90
$CClBr_2$		3 days / 25°	 (87)	91

(to be continued)

TABLE 2 *(continued)*

CX_3 in $-HgCX_3$	Reactant	Reaction conditions [a]	Product (% yield) [b]	$-HgX$ (% yield) [c]
$CClBr_2$		3 days/25°	 (83)	90
$CClBr_2$	Et_3SiH	3 days/25°	$Et_3SiCBrClH$ (70)	90
CBr_3		10 min/80°	Br_2 (40)	90
CBr_3		48 h/25°	Br_2 (50)	80
CBr_3		48 h/25°	Br_2 (34)	80

[a] In general, reactions were carried out with 10 mmol of the mercury reagent and 30 mmol of the reactant in 7–10 ml of dry benzene, with stirring under nitrogen. In room temperature experiments and in the 80° experiments with cyclo-$C_6H_{11}HgCCl_3$, the benzene solution of the reactants simply was stirred for the stated length of time. In the other 80° experiments, the mercury reagent, dissolved in benzene, was added during 3 min to the preheated substrate and the resulting mixture was heated for the remaining part of the stated reaction time.
[b] Determined by GLC.
[c] Obtained by filtration of the reaction mixture after it had been cooled to 5°.

undesirable. Furthermore, crystalline, more readily purified alkyl(trihalomethyl)mercurials would be much more practical for synthetic applications. Accordingly, we have searched for alkyl(trihalomethyl)mercury compounds with these desirable properties.

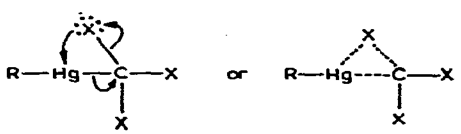
We have found the cyclohexyl(trihalomethyl)mercurials to be reactive dihalocarbene transfer reagents whose ready application at room temperature makes them particularly attractive. These mercurials were prepared in good yield by the reaction of cyclohexylmercuric chloride, the appropriate haloform and potassium tert-butoxide in THF at –60 to –65°. Their high reactivity requires a rapid work-up of the reaction mixture and storage of the product at 0°. An excess of base must be avoided in these preparations or else pure materials cannot be isolated. These mercurials are subject to autoxidation, hence should be handled under nitrogen. All were obtained as analytically pure, crystalline solids: cyclo-$C_6H_{11}HgCCl_3$, m.p. 50–52° (lit.[4] m.p. 52–55°); cyclo-$C_6H_{11}HgCCl_2Br$, m.p. 44–46°, dec. 85°; cyclo-$C_6H_{11}HgCClBr_2$, m.p. 60–63°; cyclo-$C_6H_{11}HgCBr_3$, m.p. 53–56°.

All of these organomercury reagents except the tribromomethyl compound gave excellent yields of carbene-derived products on decomposition in the presence of a suitable carbenophile in much shorter reaction times than do the analogous phenyl(trihalomethyl)-mercurials (Table 1). Each cyclohexyl(trihalomethyl)mercurial was allowed to react with several olefins and with triethylsilane. The results of these experiments are shown in Table 2. Cyclohexyl(trichloromethyl)mercury is shown to be a fairly reactive CCl_2 source at 80°, while cyclohexyl(bromodichloromethyl)mercury reacts very rapidly at 80° but still is quite reactive (compared to $PhHgCCl_2Br$) at room temperature. Cyclohexyl(dibromochloromethyl)mercury, a CClBr source, is of comparable reactivity. Unaccountably, cyclohexyl-(tribromomethyl)mercury gave good yields of cyclohexylmercuric bromide in comparable reaction times, but the yields of CBr_2 transfer product were not good, at room temperature or at 80°. The formation of a grey color during these cyclo-$C_6H_{11}HgCBr_3$ reactions may indicate an alternate mode of decomposition which does not release dibromocarbene.

An advantage of these reagents is the relatively poor solubility of the cyclohexylmercuric halides in benzene in the concentrations used at room temperature. The cyclohexylmercuric halide yields given in Table 2 represent the material which was filtered from the reaction mixtures after cooling to 5°. At 80°, the cyclohexylmercuric halides were found to be soluble in these reaction mixtures.

These cyclohexyl(trihalomethyl)mercury reagents should prove quite useful in special applications (when the carbenophile is thermally labile or low-boiling or when the product is not thermally stable). It is noteworthy that a relatively reactive organomercury CCl_2 source can now be obtained from the commercially available and inexpensive chloroform.

The acceleration of the rate of CX_2 extrusion from $RHgCX_3$ compounds when R is changed from an aryl group to an alkyl substituent very likely is related to the electron-releasing properties of the latter. Transition state I has been suggested for this extrusion process[5]. While aryl substitution on mercury should facilitate nucleophilic attack at



(I)

mercury by X, alkyl substitution should assist the heterolysis of the mercury—carbon bond, and it appears that the latter is the more important effect.

We are investigating the potential application of the cyclohexyl-for-phenyl variation to some of our other organomercury divalent carbon transfer reagents[5]. Variations in R, the alkyl substituent on mercury, also are being examined.

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