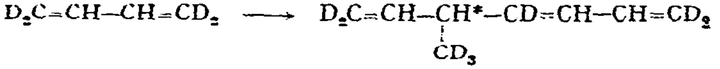
product. The product of butadiene-1,1,4,4-d_4 dimerization was confirmed by its NMR spectrum together with other evidence to be 3-methyl-d_3-hepta-1,4,6-triene-1,1,4,7,7-d_5. The NMR spectrum of the deuterio-methylheptatriene as compared with that of 3-methylhepta-1,4,6-triene indicated the absence of the doublet (τ 8.90) assigned to the methyl protons, the change of the sextet (τ 7.15) into the doublet assigned to H* and the simplification of the multiplets of vinyl protons. The result suggests that the hydrogen transfer in the linear dimerization of butadiene by the cobalt complex catalyst occurs only at 1- and 4-positions of butadiene.



$$D_2C{=}CH{-}CH{=}CD_2 \longrightarrow D_2C{=}CH{-}\underset{CD_3}{CH^*}{-}CD{=}CH{-}CH{=}CD_2$$

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Halogenated organotin compounds as CX_2 transfer agents

We have expended considerable effort on studies of the CX_2 transfer reactions of phenyl(trihalomethyl)mercury compounds[1], and it seemed of interest to evaluate trihalomethyl compounds of other metals as dihalocarbene sources. The earlier work of Clark and Willis[2] showed trimethyl(trifluoromethyl)tin to be a source of CF_2 at 140–150°. This suggested that other trihalomethyltin compounds should undergo thermal α-elimination of trimethyltin halide to give dihalocarbenes, and we chose to commence our investigation of this aspect of halomethyl metal chemistry with a study of trimethyl(trichloromethyl)tin and trimethyl(bromodichloromethyl)tin. The preparation of the former was accomplished in 62 % yield using the reaction of trimethyltin chloride with trichloromethyllithium[3–5] (eqn. 1). A route to $(CH_3)_3SnCCl_2Br$ was provided

$$(CH_3)_3SnCl + LiCCl_3 \xrightarrow{-110^\circ} (CH_3)_3SnCCl_3 + LiCl \tag{1}$$

by our discovery that CCl_2 (as generated by the mercurial route) is capable of inserting into the mercury-halogen linkage[6]. This suggested that CCl_2 insertion into the tin–halogen linkage also should be possible. Confirmation appeared to be provided by the

$$(CH_3)_3SnBr + C_6H_5HgCCl_2Br \xrightarrow{C_6H_6, 80^\circ} \underset{(63\%)}{(CH_3)_3SnCCl_2Br} + \underset{(95\%)}{C_6H_5HgBr} \qquad (2)$$

reaction shown in eqn. 2. Tetrachloroethylene also was formed in 17 % yield. However, reaction of phenylbromodichloromethylmercury with trimethyltin chloride gave a mixture of the expected $(CH_3)_3SnCCl_3$ and $(CH_3)_3SnCCl_2Br$ in a ratio of 1.45. Thus in the latter case both CCl_2 insertion into the Sn–Cl bond and alkylation of tin by the Hg–CCl_2Br compound appear to have occurred. It then is, of course, not possible to determine whether insertion or alkylation is responsible for the formation of product in reaction 2, or if both routes contributed to formation of trimethyl(bromodichloromethyl)tin.

Both trimethyl(trihalomethyl)tin compounds are solids with melting points just above room temperature. Their volatility enables their purification by gas–liquid partition chromatography (GLPC). Both are very susceptible to hydrolysis, brief exposure to moist air sufficing to convert small samples quantitatively to the respective haloform and trimethyltin hydroxide. Anhydrous ammonia in ether also cleaves the trihalomethyl groups from tin. Thus the usual methods for separating trimethyltin halides from $(CH_3)_3SnR$ compounds are not applicable, and a combination of high vacuum distillation and GLPC was required to separate these products from unconverted trimethyltin halide. Both $(CH_3)_3SnCCl_3$ and $(CH_3)_3SnCCl_2Br$ have been characterized by means of elemental analysis and their NMR* and infrared spectra; both have been found to be good CX_2 transfer agents.

GLPC analysis of a cyclohexene solution (3 ml) of trimethyl(bromodichloromethyl)tin (0.65 mmole) that had been heated at reflux (*ca.* 80°) for 92 h showed the presence of 7,7-dichloronorcarane (42 %), trimethyltin bromide, starting tin compound (8 %) and very small amounts of 7-bromo-7-chloronorcarane and trimethyltin chloride. A faster reaction occurred at 140°: when a solution of trimethyl(trichloromethyl)tin (7.7 mmoles) in cyclooctene (20 ml) was heated at reflux for 3 h, the starting tin compound was consumed completely and 9,9-dichlorobicyclo[6.1.0]nonane was formed in 94 % yield. A similar reaction of 7.3 mmoles of $(CH_3)_3SnCCl_2Br$ with cyclooctene at reflux gave both the expected 9,9-dichlorobicyclo[6.1.0]nonane (66 %) and 9-bromo-9-chlorobicyclo[6.1.0]nonane (5 %) (eqn. 3). An authentic sample of the latter was prepared by the reaction of $C_6H_5HgCClBr_2$ with cyclooctene in benzene at 80°.

At present nothing is known about the mechanism of these CX_2 transfer reactions. We are in favor of a carbene mechanism, in which CCl_2 and CClBr are released from the trihalomethyltin compound in a rate-determining step, but lack definitive proof. Noteworthy, in any case, is the fact that the $(CH_3)_3SnCCl_2Br$ + cyclooctene reaction gives a significant amount of the CClBr adduct. In contrast, when C_6H_5Hg-CCl_2Br was added to refluxing cyclooctene, 9-bromo-9-chlorobicyclo[6.1.0]nonane was formed in only trace amounts (< 1 %), if at all[7].

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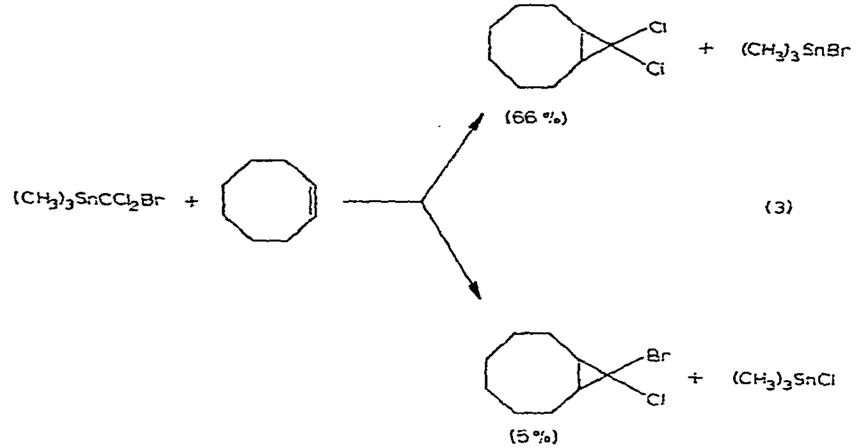
* $\delta(CH_3)_3Sn$ in ppm downfield from TMS (CS_2 solution): $(CH_3)_3SnCCl_3$: 0.48 [$J(^{117}Sn-^1H) = 51$ cps, $J(^{119}Sn-^1H) = 55$ cps]; $(CH_3)_3SnCCl_2Br$: 0.49 [$J(^{117}Sn-^1H) = 52$ cps, $J(^{119}Sn-^1H) = 55$ cps].

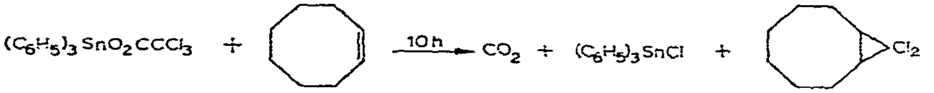
The somewhat difficult purification of these trihalomethyltin compounds and their facile hydrolysis prompted us to investigate the possible use of organotin trihaloacetates as CX_2 transfer agents. The thermal decarboxylation of some organotin esters



(3)

is known to occur, *e.g.*, $(C_4H_9)_3SnO_2CCH_2CN \longrightarrow (C_4H_9)_3SnCH_2CN$[8] and $(C_4H_9)_3SnO_2CH \longrightarrow (C_4H_9)_3SnH$[9], to mention two recent examples, and thus it seemed possible that decarboxylation and CX_2 transfer could be effected by heating an $R_3SnO_2CCX_3$ compound in the presence of an olefin. This procedure, if successful, would have the advantage of using stable, easily prepared and purified organotin starting materials. Such a route to *gem*-dihalocyclopropanes could be realized, but the product yields were only moderate due to competing side reactions.

It was found that triphenyltin trichloroacetate was stable when heated in refluxing cyclohexene (~ 80°), but that decarboxylation and CCl_2-transfer took place when this tin ester was heated in cyclooctene at reflux (~ 140°) under nitrogen. Gas evolution occurred, and subsequent analysis of the reaction mixture using GLPC showed that 9,9-dichlorobicyclo[6.1.0]nonane had been formed in 56 % yield (eqn. 4).



(4)

Benzene (39 %) also was present, and this suggests that a competing radical decomposition of the tin ester had occurred. Reaction of cyclooctene and the tin ester in 5:1 ratio in a solvent (chlorobenzene or diglyme, at reflux) gave only slightly diminished yields of the dichlorocyclopropane product. Very similar results were obtained with trimethyltin trichloroacetate. The reaction of triphenyltin tribromoacetate with cyclooctene at reflux for 3 h gave 9,9-dibromobicyclo[6.1.0]nonane in 36 % yield. Attempts to effect CF_2 transfer to olefins with triphenyltin trifluoroacetate or chlorodifluoroacetate were unsuccessful. Studies are in progress which hopefully will reveal whether R_3SnCCl_3 and R_3SnCBr_3 are intermediates in these reactions or whether decarboxylation and CX_2 transfer to olefin occur simultaneously in a concerted fashion.

It is readily apparent that phenyl(trihalomethyl)mercury compounds are to be preferred as CX_2 transfer agents. They are easily prepared and purified, are stable toward hydrolysis and their somewhat diminished stability allows rapid transfer of CX_2 to olefins and other substrates to be carried out at 80°.

Details of this work will be presented at a later date. We publish our present findings at this time in view of the current interest in trihalomethyl derivatives of the Group IV elements, notably the previously reported $(C_4H_9)_3SnCCl_3$[10], $(C_6H_5)_3PbCCl_3$[11,12] and $(C_6H_5)_3PbCBr_3$[12].

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