−3.90 ppm, respectively. In each compound the two peaks are of equal intensity. The broader downfield peak is assigned to the CH_2 groups *cis* to the halogen, in accordance with the general observation that halogens tend to produce downfield shifts for protons in close proximity,[2] with the fact that bromine produces larger shifts than chlorine in boron cations,[3] and with the fact that the perturbation of the chemical shift of the CH_2 protons should differ slightly depending on whether the proton is above or below the six-membered ring, relative to the halogen.

The formation of the norbornane structure apparently proceeds through ring closure by intramolecular displacement of iodide from the intermediate N,N′-dimethylpiperazine–iodoborane. This general reaction type is now well established.[4–6] It is, however, somewhat surprising that ring closure, with the formation of an undoubtedly strained structure, is preferred over intermolecular reaction leading to a bisamine cation.

Substantial strain in the bicyclic structure becomes evident when one compares the results of transamination by pyridine for the norbornane homomorph and the analogous bis(trimethylamine) ion. The dihydro cation reacts cleanly at 23–25° in 0.13 *M* pyridine solution to produce N,N′-dimethylpiperazine, as evidenced by the appearance of the corresponding absorptions in the nmr spectrum. The reaction is first order in the cation with an approximate rate constant of 6×10^{-5} sec^{-1}. In contrast, bis(trimethylamine)dihydroboron(1+) ion does not react noticeably after 8 days under identical conditions. With a conservative lower limit of detection of free trimethylamine corresponding to 0.25% reaction, an upper limit for the first-order transamination rate constant is calculated as 2×10^{-9} sec^{-1} for the trimethylamine cation. In the absence of ring strain one would have expected quite similar reactivity since dimethylpiperazine and trimethylamine have comparable base strengths, and since both amines, in their cations, should produce substantially the same steric interactions with a nucleophile approaching boron. The observed minimum rate factor of 3×10^4, however, would correspond to at least 6-kcal/mol activation energy difference favoring transamination of the norbornane homomorph, if the activation entropies are similar. We attribute this decrease in activation energy to relief of strain when the N–B–N bridge is broken.[7]

The chloro and bromo derivatives IIa and IIb still react more rapidly than the bis(trimethylamine) cation, though much more slowly than the dihydro derivative I. The times required for 10% reaction at 100° in 0.13 *M* pyridine solution were 12, 25, and 70 min, respectively, for IIa, IIb, and the bis(trimethylamine) ion.

Substantial differences in reactivity between the norbornane homomorph and bis(trimethylamine)boronium ion are also observed in halogenation. For example, chlorination of the bicyclic structure was not quite complete in 20 hr, whereas the noncyclic compound reacted completely in less than 2 hr. This *decrease* in reactivity of the bicyclic compound is either due to the greater bulk of the new halogen substituent destabilizing the new structure or to a reluctance of the bridging boron to form a radical by hydrogen atom loss.[8] Whatever the explanation, the results support the general proposition that the reactions leading to breaking of the bridge are enhanced and reactions involving substitution on the bridging atom with retention of the bridge are retarded relative to analogous noncyclic compounds. This parallels the reluctance of norbornane derivatives to undergo substitution on the bridging carbon.[9]

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Phenyl(trifluoromethyl)mercury, a New and Useful Reagent for the Generation of Difluorocarbene under Mild Conditions. Preparation *via* a Novel Fluorination Reaction using Phenylmercuric Fluoride

Sir:

We have reported recently concerning the trimethyl(trifluoromethyl)tin–sodium iodide reagent, which is one of the mildest difluorocarbene sources available.[1] This reagent converts olefins to *gem*-difluorocyclopropanes in generally very good yields, and these reactions proceed at a preparatively useful rate in neutral medium at 80–85°. The very successful application of phenyl(trihalomethyl)mercury compounds of type $PhHgCCl_nBr_{3-n}$ (n = 0–3) to *gem*-dihalocyclopropane synthesis[2,3] led us to consider organomercury routes to CF_2 as well. The compounds CF_3HgI and $(CF_3)_2Hg$ have been known for 20 years.[4] Their preparation was accomplished as shown in eq 1 and 2. However, a synthesis

$$CF_3I + Hg \xrightarrow{\text{uv, sealed tube}} CF_3HgI \quad (1)$$

$$CF_3I + Cd\text{-}Hg \xrightarrow{\text{room temperature, sealed tube, 24 hr}} (CF_3)_2Hg \quad (2)$$

not based on the gaseous, expensive iodotrifluoromethane and metallic mercury seemed desirable. We report here concerning a new route to fluoromethylmercurials which is based on the now easily prepared phenyl(trihalomethyl)mercury reagents.[5]

The desired mercurial, phenyl(trifluoromethyl)mercury, can be prepared in good yield by the fluorination of phenyl(tribromomethyl)mercury with phenylmer-

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curic fluoride (eq 3). The reaction is carried out by

$$PhHgCBr_3 + 3PhHgF \longrightarrow PhHgCF_3 + 3PhHgBr \quad (3)$$

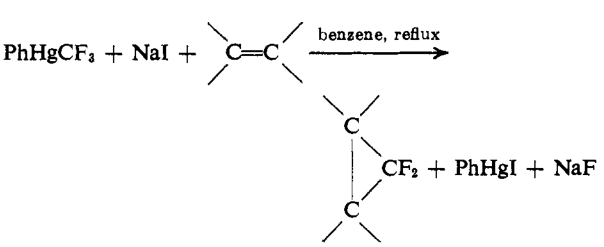
adding a solution of 1 molar equiv of $PhHgCBr_3$[5] in toluene (5 ml per mmol of mercurial) dropwise with stirring to a solution, cooled to −65°, containing 3 molar equiv of phenylmercuric fluoride[6] and a small (*ca.* 0.05 ml/mmol of $PhHgCBr_3$) quantity of 48% aqueous HF[7] in toluene (*ca.* 1.6 ml/mmol of PhHgF). The reaction mixture is warmed slowly to room temperature, stirred for an additional hour, and filtered from precipitated solids.[8] Evaporation of the filtrate followed by crystallization of the solid residue from hexane gives small, dense, white needles of phenyl(trifluoromethyl)mercury, mp 140–143°. Yields of 70–75% are typical.

An analogous reaction of phenylmercuric fluoride with phenyl(trichloromethyl)mercury did not occur under these conditions. However, when such a 3PhHgF–1$PhHgCCl_3$ reaction mixture was heated at 90° for *ca.* 90 min after the initial low-temperature addition step, phenyl(trifluoromethyl)mercury was produced in 53% yield. Better yields have not been achieved to date. This obvious difference in reactivity between C–Br and C–Cl bonds in phenyl(trihalomethyl)mercury compounds toward fluorination by phenylmercuric fluoride has permitted the selective fluorination of phenyl(bromodichloromethyl)mercury to the difficult to prepare phenyl(fluorodichloromethyl)mercury[9] (eq 4).

$$PhHgCCl_2Br + PhHgF \longrightarrow PhHgBr + PhHgCCl_2F\ (70\%) \quad (4)$$

The nature of this remarkable fluorination reaction is not yet understood. The reaction conditions exclude a carbene insertion into the Hg–F bond, and thus some sort of a direct fluorination of the C–Br and C–Cl bonds must be involved. Mercuric fluoride is known to be a fluorinating agent,[10] but, to the best of our knowledge, phenylmercuric fluoride has never served such a purpose.[11] There is a good possibility that we are dealing in these new reactions with a metal-activated process; an indication that this may be so is given by the observation that bromoform, bromodichloromethane, carbon tetrabromide, and 7,7-dibromonorcarane are not fluorinated by phenylmercuric fluoride under these conditions. Extension of this new reaction to the fluorination or partial fluorination of other halomethylmercurials and of halomethyl derivatives of other metals or metalloids is under investigation in these laboratories, and studies aimed at a better understanding of this novel fluorination reaction are also in progress.

Phenyl(trifluoromethyl)mercury serves excellently as a CF_2 precursor. While this mercurial is very stable thermally (surviving unchanged a 10-day reflux period in cyclooctene), the sodium iodide procedure[3] can be applied to good advantage to give a useful CF_2 transfer chemistry. Unexpected, and of preparative advantage, was the finding that a solvent for the sodium iodide (such as 1,2-dimethoxyethane[3]) was not required; the reactions could be carried out using benzene or excess olefin as diluent (eq 5). Thus in a typical reaction, a mixture of 5.5 mmol of $PhHgCF_3$, 12.5 mmol of well-dried[3] NaI, and 16.5 mmol of cyclohexene in 15 ml of dry benzene was stirred and heated at reflux under nitrogen for 19 hr. Filtration from 3.6 g of white solid (from which PhHgI was recovered by Soxhlet extraction) was followed by vacuum trap-to-trap distillation of the filtrate. Gas–liquid partition chromatography showed that 7,7-difluoronorcarane[3] was present in 83% yield. Prepared in similar manner were 1,1-difluoro-2-*n*-amylcyclopropane (70%) and 1,1-difluoro-2-trimethylsilylmethylcyclopropane (99%) from 1-heptene and allyltrimethylsilane, respectively.



(5)

The phenyl(fluorodichloromethyl)mercury prepared by the PhHgF fluorination procedure reacted with sodium iodide (1:1 molar ratio) in DME in the presence of cyclohexene (1 hr at room temperature, 3 hr at reflux) to give 7-fluoro-7-chloronorcarane in 89% yield.

The available evidence indicates that the trihalomethyl-substituted metal–NaI reactions proceed *via* nucleophilic displacement of CX_3^- by iodide ion, followed by decomposition of the trihalomethyl anion to the dihalocarbene.[1,3] In the case of $PhHgCCl_3$ such reactions appear to require the use of DME as solvent. The fact that this solvent is not required in the case of phenyl(trifluoromethyl)mercury may find an explanation in the enhanced Lewis acidity of the mercury atom in this mercurial (as compared with phenyl(trichloromethyl)mercury) due to the powerful electron-attracting effect of the CF_3 substituent. This point also is under investigation.

The relative ease of preparation of $PhHgCF_3$ and its release of CF_2 under mild, neutral conditions, uncomplicated by major side reactions, suggest that this mercurial will find extensive application in CF_2 transfer chemistry.

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[7] The added HF, for reasons as yet undiscerned, acts as a reaction moderator. In its absence, induction periods followed by very vigorous frothing often are observed. At −65° no reaction occurs; at 0° a slow reaction commences. Operationally, however, it is advantageous to start out at the lower temperature.

[8] These solids are not pure phenylmercuric bromide. In one case in which they were examined more closely, soxhlet extraction with benzene gave phenylmercuric bromide in 70% yield.

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[11] In the laboratory, the use of mercuric fluoride is of limited practicality: anhydrous HF must be used for the *in situ* generation of HgF_2 from mercuric oxide, and this necessitates the use of metal equipment (silver-lined steel being recommended). In any case, mercuric fluoride and mercuric bromide (produced in a fluorination reaction) would undergo secondary reactions with the $PhHgCX_3$ compound used, and so mercuric fluoride would not be applicable in the present purpose.