*m*-chloroperbenzoic acid (MCPBA)[12,13] in methylene chloride at 0°. The reactions were exothermic and accompanied by the precipitation of *m*-chlorobenzoic acid. Intermittent analysis for oxidant with starch–iodide revealed that the reactions were complete within 15 min. Extraction with aqueous potassium carbonate followed by the removal of solvent afforded a colorless oil which in each case was analyzed by vpc[14,15] and spectral methods to give the results presented in Chart I.

Aside from the reasonable expectation of normal behavior for the $\pi$ bond of cyclopropenes toward the electrophilic oxygen of peracids, the proposed 2-oxabicyclo[1.1.0]butane intermediate is most logically consistent with the formation of *both* rearranged products **3a**, **4a**, and **3b**, **4b** from the oxidation of unsymmetrical cyclopropenes **1a** and **1b**, respectively. These products are analogous to the butadiene derivatives resulting from the thermal rearrangement of bicyclo[1.1.0]butanes[16–18] in which the central bond remains intact.

Attempts to isolate a 2-oxabicyclo[1.1.0]butane and subsequently elucidate the mechanism of the rearrangement are in progress.

**Acknowledgment.** The Varian A-60A nmr spectrometer and the Hitachi RMU-6D mass spectrometer employed in this work were purchased through a National Science Foundation grant to Brown University.

---

Böll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963); (c) G. L. Closs and L. E. Closs. *ibid.*, **83**, 1003 (1961).

(12) The *m*-chloroperbenzoic acid (80% minimum) was obtained from the FMC Corp., Inorganic Chemical Division, New York, N. Y., but is now available from the Aldrich Chemical Co., Milwaukee, Wis., and Aztec Chemicals, Elyria, Ohio.

(13) An excess of cyclopropene is desirable to minimize the formation of secondary oxidation products arising from Baeyer–Villiger and/or epoxidation reactions of **3** and **4**.

(14) In the 1-methylcyclopropene case, a stream of the gas was bubbled by means of a sintered-glass gas inlet tube through a stirred solution of MCPBA in methylene chloride at 0°. The work-up conditions involved filtration and solvent removal followed by direct vpc analysis. The solubility and polymerization tendency of the products precluded aqueous basic work-up.

(15) All analytical and preparative vpc work was accomplished satisfactorily with a 0.25 in. × 10 ft column packed with 15% SE-30–Chromosorb W DMCS acid washed 80–100 mesh.

(16) For a review of bicyclo[1.1.0]butane chemistry see K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968); see also G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

(17) For other examples of rearrangements which may proceed *via* azabicyclobutane intermediates see: (a) R. K. Armstrong, *J. Org. Chem.*, **31**, 618 (1966); (b) N. C. Castellucci, M. Kato, H. Zenda, and S. Masamune, *Chem. Commun.*, 473 (1967); (c) A. S. Monahan and S. Tang, *J. Org. Chem.*, **33**, 1445 (1968); (d) E. A. Chandross and G. Smolinsky. *Tetrahedron Lett.*, **19** (1960); (e) A. Padwa and D. Eastman, *J. Org. Chem.*, **34**, 2728 (1969).

(18) It has been proposed that formation of benzil in the peracid oxidation of diphenylacetylene arises from rearrangement of a dioxabicyclobutane intermediate. See ref 7 and 8.

**J. Ciabattoni, P. J. Kocienski**
*Metcalf Research Laboratories*
*Brown University, Providence, Rhode Island 02912*

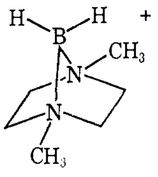
*Received July 28, 1969*

---

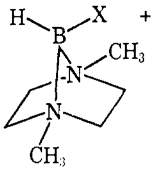
## Boron Cation Homomorphs of Norbornane

*Sir:*

We wish to report the facile synthesis of boron cations I and II where the boron atom serves as the bridging element between two nitrogen atoms and where it is the common member of two five-membered rings. This cation is a homomorph of norbornane with the bridgehead positions occupied by nitrogen atoms.



I



II

a; X = Cl
b; X = Br

The synthesis of this cation was accomplished in the following manner. Trimethylamine–borane (3.78 g, 52.0 mmol) was refluxed with 52.0 mmol of N,N′-dimethylpiperazine in 35 ml of benzene for 2 hr. Iodine (9.76 g, 38.4 mmol) was then gradually added through the condenser together with an additional 10 ml of the amine, and heating was continued for 5 hr. After adding 100 ml of petroleum ether and filtering, the solid product was dissolved in water and precipitated with excess $NH_4PF_6$. The boron cation was isolated after two extractions of the precipitate with 50 ml of methylene chloride, leaving behind insoluble dimethylpiperazinium hexafluorophosphate. The crude yield of boron salt was 7.66 g, or 73% of the weight expected if 1 mol of iodine had produced 1 mol of boron cation and 1 equiv of ammonium ion. Recrystallization from 60 ml of boiling water gave I as the $PF_6^-$ salt in 80% yield: mp 265–267° dec; proton nmr ($CH_2Cl_2$ solvent), $\delta$ (ppm) *vs.* internal tetramethylsilane: $-2.93$ (6 H, $CH_3$), $-3.44$ (8 H, $CH_2$); infrared: B–H stretch at 2410 and 2510 cm$^{-1}$. *Anal.* Calcd for $C_6H_{16}BN_2{}^+PF_6{}^-$: C, 26.49; H, 5.93; N, 10.29. Found: C, 26.48; H, 6.04; N, 10.16.

This compound has been synthesized previously by the reaction of $[(CH_3)_2S]_2BH_2{}^+$ with N,N′-dimethylpiperazine.[1]

The pure B-chloro derivative, IIa, was obtained in 50% yield by bubbling chlorine gas through a 0.2 *M* solution of I in methylene chloride at room temperature. During the entire reaction period the proton nmr spectrum showed only peaks belonging to starting material or the eventually isolated product. After 20 hr 3% unreacted starting material was still present. The compound was purified after removal of solvent by recrystallization from aqueous $NH_4PF_6$ and a second recrystallization from hot water: mp 240–245° dec; proton nmr ($CH_2Cl_2$ solvent), $\delta$ (ppm): $-2.88$ (6 H), $-3.58$ (8 H); infrared: B–H stretch (singlet) at 2540 cm$^{-1}$. *Anal.* Calcd for $C_6H_{15}BClN_2{}^+PF_6{}^-$: C, 23.51; H, 4.93; N, 9.14. Found: C, 23.42; H, 4.98; N, 9.02.

Bromination was achieved by allowing I to react at room temperature for 18 hr with a large excess of elemental bromine. After removal of excess $Br_2$, the sample was recrystallized from a minimum of hot water to give a 64% yield of monobromo derivative IIb: mp 250–255° dec; proton nmr ($CH_2Cl_2$ solvent), $\delta$ (ppm): $-2.91$ (6 H), $-3.61$ (8 H); infrared: B–H stretch (singlet) at 2540 cm$^{-1}$. *Anal.* Calcd for $C_6H_{15}BBrN_2{}^+PF_6{}^-$: C, 20.53; H, 4.31; N, 7.98. Found: C, 20.79; H, 4.26; N, 7.86.

The basic norbornane structure is not only confirmed by the elemental analysis but also by the proton nmr of the halo derivatives in pyridine solution. In this solvent, both IIa and IIb give two closely spaced peaks for the $CH_2$ protons at $\delta$ $-3.75$, $-3.80$ and $-3.81$,

---

(1) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964); yield 1.3%, mp 240–250° dec.

−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 $6 \times 10^{-5}$ 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 $2 \times 10^{-9}$ 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 $3 \times 10^4$, 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]

**Acknowledgment.** This work was supported in part by the National Institutes of Health under Grant GM 13650.

---

(2) J. M. Garrett and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **90**, 7234 (1968).

(3) M. A. Mathur and G. E. Ryschkewitsch, to be submitted for publication.

(4) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967).

(5) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968).

(6) K. C. Nainan and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **91**, 330 (1969).

(7) An angle strain of 6.3 kcal/mol has been reported for norbornane: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 302.

(8) W. J. Rademaker, Ph.D. Dissertation, University of Florida, 1969.

(9) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958), report no chlorination on the 7 position in norbornane.

**G. E. Ryschkewitsch**
*Department of Chemistry, University of Florida*
*Gainesville, Florida 32601*

*Received July 3, 1969*

---

## 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

$$CF_3I + Hg \xrightarrow{\text{uv, sealed tube}} CF_3HgI \tag{1}$$

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

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-

---

(1) D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, 32, 2980 (1967).

(2) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

(3) D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *ibid.*, **89**, 959 (1967).

(4) H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2948, 2953 (1949).

(5) D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).