signments require that the carbon–silver bond cleavage reactions proceeded stereospecifically with retention of configuration and are in agreement with Whitesides and Casey's finding that *cis*-1-propenyl(tri-*n*-butylphosphine)silver was converted by iodine cleanly into *cis*-1-iodopropene.[1] It was also shown that *trans*-$\mathrm{CF_3CF{=}CHCF_3}$ was formed by treating the AgF–$\mathrm{CF_3C{\equiv}CCF_3}$ reaction mixture directly with HCl in $\mathrm{CH_3CN}$. Thus the configuration of the silver compound appeared to be unchanged by sublimation and the AgF addition reaction stereospecific.[11] In aprotic solvents the *trans* addition of AgF would be expected to take place most easily by a two-step mechanism with initial addition of fluoride ion.

Preliminary experiments with $\mathrm{CF_3CF{=}C(CF_3)Ag}$ and a variety of metallic and nonmetallic halides suggest wide application of the perfluorovinylsilver compounds for syntheses in which AgX is eliminated and a perfluorovinyl group introduced in place of halogen.[13] The addition of $\mathrm{CF_3CF{=}C(CF_3)Ag}$ to excess cupric bromide in $\mathrm{CH_3CN}$ yielded $\mathrm{CF_3CF{=}C(CF_3)C(CF_3){=}CFCF_3}$[14] and *trans*-$\mathrm{CF_3CF{=}CBrCF_3}$, and analogous coupling reactions can be anticipated.[15] The high degree of thermal stability found for $\mathrm{CF_3CF{=}C(CF_3)Ag}$ and implied for other perfluorosilver compounds with silver attached to sp^2 carbon[16] will permit the use of a wide range of synthesis conditions including relatively high temperatures. Stereospecific reactions will permit the preparation of pure isomers. Our results also suggest that the preparation of useful silver compounds with other electronegative organic radicals can be accomplished.

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served for the *trans* isomers of $\mathrm{CF_3CF{=}CBrCF_3}$ and $\mathrm{CF_3CF{=}C(CH_3)CF_3}$.

[11] The chemical evidence for the configuration of the silver compound is consistent with the nmr data but does not constitute independent proof. It rests upon the assumption that both *cis*- and *trans*-$\mathrm{CF_3CF{=}C(CF_3)Ag}$ do not yield only *trans* products. Other vinyl organometallic compounds such as those of lithium and mercury characteristically react with retention of configuration.[12]

[12] G. E. Coates and K. Wade, "Organometallic Compounds," Vol. I, 3rd ed, Methuen and Co., Ltd., London, 1967.

[13] For example, *trans*-$\mathrm{CF_3CF{=}C(CF_3)HgCl}$ and [*trans*-$\mathrm{CF_3CF{=}C(CF_3)]_2Hg}$ are readily prepared from $\mathrm{HgCl_2}$: unpublished work with R. W. Ashcraft.

[14] First prepared by $\mathrm{CF_3C{\equiv}CCF_3 + F_2 \rightarrow CF_3CF{=}C(CF_3)C(CF_3){=}CFCF_3}$, bp 74.1°, $n^{20}\mathrm{D}$ 1.2849, $d^{20}{}_4$ 1.6377: unpublished work with J. O. Stoffer.

[15] A. Cairncross and W. A. Sheppard have reported that perfluorophenylcopper yields perfluorobiphenyl with cupric bromide (*J. Am. Chem. Soc.*, 90, 2186 (1968)).

[16] The thermal stability of perfluorophenylsilver has been found to be comparable to that of *trans*-$\mathrm{CF_3CF{=}C(CF_3)Ag}$: unpublished work with K. K. Sun.

William T. Miller, Richard H. Snider
Robert J. Hummel
Department of Chemistry
Cornell University, Ithaca, New York

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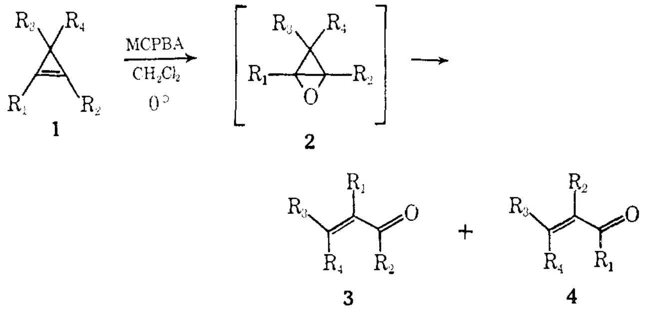
The Peracid Oxidation of Cyclopropenes. Evidence for 2-Oxabicyclo[1.1.0]butane Intermediates

Sir:

The 1-azabicyclo[1.1.0]butane system constitutes the only heterosubstituted bicyclo[1.1.0]butane to have been characterized to date.[1–4] However, the 2-oxa- and 2,4-dioxabicyclo[1.1.0]butane systems have been proposed as possible intermediates in the photoisomerization of α,β-unsaturated keto derivatives[5,6] and in the peracid oxidation of diphenylacetylene,[7,8] respectively.

We wish to report the preliminary results of our investigation of the peracid oxidation of three alkyl-substituted cyclopropenes, **1a–c**. In all cases the production of the α,β-unsaturated aldehyde and/or ketone derivatives **3** and **4** in high yield is best rationalized by initial epoxidation of **1** to give an unstable intermediate, 2-oxabicyclo[1.1.0]butane (**2**), followed by rearrangement.[9] In a typical experiment, the cyclopropenes **1a–c**[10,11] were treated with <1 equiv of commercial

Chart I. Products of the Peracid Oxidation of Cyclopropenes



Cyclopropene	% yield of **3**[a]	% yield of **4**[a]
a, R_1 = Me; $R_2 = R_3 = R_4$ = H	41[b]	59[b]
b, $R_1 = R_3 = R_4$ = Me; R_2 = H	64[c]	36[d]
c, $R_1 = R_2 = R_3 = R_4$ = Me	90[e]	

[a] Represent approximate vpc yields. [b] The identity of vpc retention times with commercially available authentic samples served to establish the structures of methacrolein (**3a**) and methyl vinyl ketone (**4a**). [c] α,β-Dimethylcrotonaldehyde (**3b**) was collected by preparative vpc and identified from the following spectral data: ir ($\mathrm{CHCl_3}$, $\mathrm{cm^{-1}}$) 1670 (s), 1660 (s), 1655 (s), 1640 (s); nmr ($\mathrm{CDCl_3}$, δ) 10.1 (1 H, s), 2.20 (3 H, q, J = 1–1.5 Hz), 1.97 (3 H, s), 1.74 (3 H, q, J = 1–1.5 Hz); mass spectrum m/e 98. The epoxyformate ester derived from Baeyer–Villiger oxidation of **3b** followed by epoxidation appears as a minor product if MCPBA is in excess. [d] Mesityl oxide was identified by comparison of its vpc retention time with that of commercially available authentic material. [e] α-Methylmesityl oxide (**3c**) was collected by preparative vpc and identified from the following spectral data: ir ($\mathrm{CCl_4}$, $\mathrm{cm^{-1}}$) 1685 (s), 1625 (m); nmr ($\mathrm{CDCl_3}$, δ) 2.23 (3 H, s), 1.87 (6 H, s), 1.78 (3 H, s); mass spectrum m/e 112. The formation of **3c** was actually nearly quantitative since the only minor product was identified as the epoxy ketone derived from **3c** by further oxidation.

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[1] A. G. Hortmann and D. A. Robertson, *J. Amer. Chem. Soc.*, **89**, 5974 (1967).

[2] A. G. Hortmann and J. E. Martinelli, *Tetrahedron Lett.*, 6205 (1968).

[3] W. Funke, *Angew. Chem. Intern. Ed. Engl.*, 8, 70 (1969).

[4] Heterocyclic bicyclobutanes of doubtful validity have been described in the earlier literature. For a review see W. L. Mosby in "The Chemistry of Heterocyclic Compounds," Vol. 15, Part One, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1961, pp 7–9.

[5] H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, **91**, 887 (1969).

[6] O. L. Chapman and W. R. Adams, *ibid.*, **90**, 2333 (1968).

[7] R. N. McDonald and P. A. Schwab, *ibid.*, **86**, 4866 (1964).

[8] J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964).

[9] After completion of this work we became aware of a related study of the reaction of 1,2,3-triphenylcyclopropene with peracids in which *cis*- and *trans*-α-phenylchalcone were observed as products: L. E. Friedrich and R. A. Cormier, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7–12, 1969, ORGN-151.

[10] For a good review of cyclopropene chemistry see G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 53 (1966).

[11] The cyclopropenes **1a–c**, respectively, were prepared by reported methods in comparable yields: (a) F. Fisher and D. E. Applequist, *J. Org. Chem.*, 30, 2089 (1965); (b) G. L. Closs, L. E. Closs, and W. A.

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 π 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

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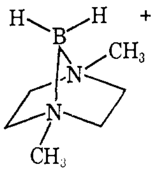
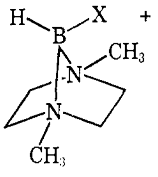
Boron Cation Homomorphs of Norbornane

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), δ (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), δ (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), δ (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 δ -3.75, -3.80 and -3.81,

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