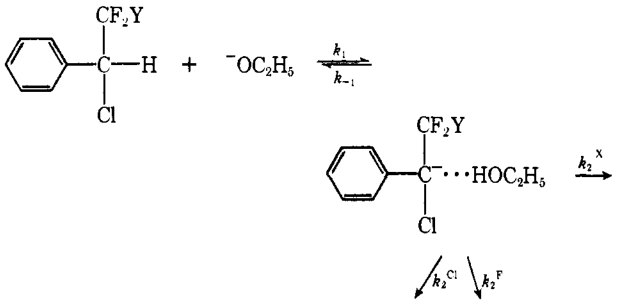
seems reasonable since the C–F bond becomes stronger with an increasing number of fluorines bonded to the same carbon atom and could therefore readily account for a switch in the mechanism of dehydrofluorination when going from IV to III.

A mechanism which involves a carbanion intermediate for the elimination of HCl from I, however, cannot be excluded, and we therefore studied both primary isotope effects and isotopic exchange reactions of benzylic hydrogens for both I and III. When I was subjected to ethoxide in EtOD, unreacted starting material was found to contain no deuterium. A similar result has been reported for β-phenylethyl bromide.[2] Since exchange of the benzylic hydrogen does not occur, the primary isotope effect for dehydrochlorination was determined directly by running $C_6H_5CDClCF_3$ in EtOH and comparing it to I. The effect at 0°, k_H/k_D = 2.8, was only 30–35% of that calculated by extrapolating Saunders' data for $C_6H_5CD_2CH_2Br$ and $C_6H_5CH_2CH_2Br$.[7] This low k_H/k_D value suggests that the reaction is either proceeding through a highly unsymmetrical transition state or that an intermediate carbanion, which has internal return to starting material, is being formed prior to chloride ion ejection. Since exchange of the benzylic proton of III is faster than the elimination reaction, it was necessary to measure elimination from $C_6H_5CDClCF_3$ in EtOD and make an appropriate correction for the solvent isotope effect. Detritiation kinetics were carried out in both EtOH and EtOD and a solvent isotope effect of 2.3 was calculated. This value is consistent with the literature.[8] Applying this correction resulted in a negligible primary kinetic isotope effect for dehydrofluorination at 25° and this is consistent with the formation of a carbanion that has substantial internal return prior to loss of fluoride.[8] Table I contains ρ values from five point Hammett σ–ρ plots for the elimination of HCl and HF and the detritiation reaction. A similar plot for the reaction of ethoxide with $C_6H_5CCl{=}CF_2$ in ethanol gave a ρ of 3.94. These high positive values point to a large development of negative charge in the transition state of all four reactions.[9] This fact coupled with the small primary isotope effects lead us to the conclusion that all four reactions are proceeding through carbanion intermediates.

The differences in the effects of a $-CF_3$ *vs.* a $-CF_2Cl$ group on either the acidity of the hydrogen or on the stabilization of a carbanion intermediate should be small.[10,11] We therefore propose a single mechanism (Scheme I) for the various reactions of our system. The initial reaction of ethoxide with the benzylic hydrogen would lead to the formation of a strong hydrogen bonded species between the carbanion and the solvent molecule formed during the reaction. It has been experimentally demonstrated that neutral carbon is a good hydrogen bonding base and suggested that carbanions should be excellent in that capacity.[13] The loss of chloride can come directly from this intermediate (k_2^{Cl}), while the hydrogen bond must be broken to allow exchange with bulk solvent (k_2^X). The activation energy for exchange of III-*t* is about 28 kcal/mol, and we see no reason why it should be less for I. Since the activation energy for dehydrochlorination is only 20 kcal/mol, the exchange process cannot compete favorably with the loss of chloride. The same type of argument can be made to support the postulated intermediate for reactions of III, since the benzylic proton should have the same order of reactivity as in I and much greater than in IV. In the ethoxide-catalyzed reaction of III, k_{-1} is apparently much larger than k_2^X, which is greater than loss of fluoride (k_2^F), and the kinetic results thus clearly show that in this case the effects of internal return can be quite substantial. Still unanswered is whether or not internal return from the postulated intermediate in the reaction of I is favored over loss of chloride. Further work is being carried out to attempt to answer this by making use of a method recently published by Streitwieser[14] and by looking at the chlorine isotope effect.[15]

Scheme I



$$k_2^{Cl}(Y = Cl) >>> k_2^x > k_2^F(Y = F)$$

Acknowledgment. This work was supported by a grant (2904-B) from the Petroleum Research Fund, administered by the American Chemical Society. One of us (H. F. K.) also thanks the National Science Foundation for a Science Faculty Fellowship to spend a year at the University of California, Berkeley, in Professor Streitwieser's group where many discussions helped in the interpretation of our experimental results.

---

(7) W. H. Saunders, Jr., and D. H. Edison, *J. Amer. Chem. Soc.*, **82**, 138 (1960).

(8) A. Streitwieser, Jr., J. A. Hudson, and F. Mares, *ibid.*, **90**, 648 (1968).

(9) A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

(10) W. A. Sheppard, *Tetrahedron*, **27**, 945 (1971).

(11) Kinetic evidence for this is given in ref 5. Further confirmation comes from kinetic studies on reactions of ethoxide with $C_6H_5CR{=}CFCl$ in ethanol, where rates are the same for R = $-CF_3$ or $-CF_2Cl$.[12]

(12) H. F. Koch and R. L. Decker, Jr., unpublished results.

(13) L. L. Ferstandig, *J. Amer. Chem. Soc.*, **84**, 3553 (1962).

(14) A. Streitwieser, Jr., W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmake, C. J. Chang, and T. L. Kruger, *ibid.*, **93**, 5096 (1971).

(15) A review of using various isotope effect studies in elimination reactions has just appeared: A. Fry, *Chem. Soc. Rev.*, 1, 163 (1972).

(16) (a) Supported by NSF-URP Grant GY-7413 during the summer of 1970. (b) Supported by NSF-URP Grant GY-9839 during the summer of 1972.

H. F. Koch,* D. B. Dahlberg, A. G. Toczko,[16a] R. L. Solsky[16b]
Department of Chemistry, Ithaca College
Ithaca, New York 14850

Received August 31, 1972

Bridgehead Halogen Exchanges

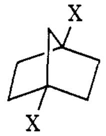
Sir:

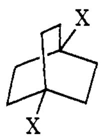
Nucleophilic substitutions at bridgehead positions of small bicyclic ring systems are well known to require vigorous reaction conditions.[1] Classical results with 1-halobicyclo[2.2.1]heptane derivatives established that

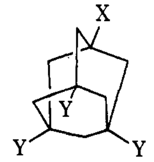
---

(1) (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, 1, 283 (1966); (b) V. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960); (c) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).

substitutions occur very slowly even in the presence of halophilic reagents such as silver ion[2] or aluminum chloride[3] at high temperatures. A more recent example[4a] illustrating the conditions used for such reactions is the two-step conversion of 1,4-dichlorobicyclo[2.2.2]octane (**2**), *via* the diol, to 1,4-dibromo or 1,4-diodo derivatives. The metal-promoted hydrolysis was carried out over 17 hr at 215° in a sealed reactor, while subsequent conversion of diol to dibromide occurred in 8 hr at 150° in 48% hydrobromic acid.[4b] The presence of two halogens decreases their individual reactivity;[1a] however, even with the more reactive 1-adamantyl ring system (**3**, X = halogen; Y = H) direct halogen exchanges require several hours near 150° in concentrated hydrohalic acids.[5]


1


2


3

We have found a simple, fast, and efficient method for halogen (Cl, Br, I) exchanges at the bridgeheads of ring systems **1**, **2**, and **3**. The procedure involves the generation and use of aluminum halide catalysts *in situ* by reaction of excess aluminum with bromine in a halogenated solvent. When a bridgehead halide of systems **1**, **2**, or **3** is added, the exchange with solvent halogen readily occurs. Solvents, chosen so far by their availability and ease of isolation of product, may be CH_3I or CH_2I_2 for iodine transfer, CH_2Br_2 or $CHBr_3$ for bromine transfer, and $CHCl_3$ or CCl_4 for chlorine transfer. Generation of catalyst is most convenient using aluminum foil with bromine, but iodine has also been used. More specific conditions and yields of products are presented in Table I.

Table I. Yields and Conditions of Reaction for Production of Bridgehead Halides

Initial halide (mmol)	Solvent (ml)	Br_2, mmol[a]	Conditions	Product (% yield)
1-Adamantyl bromide (6.97)	CH_2I_2 (25)	1.95	20°, 30 sec	1-Adamantyl iodide (47)
(9.30)	$CHCl_3$ (25)	1.95	65°, 90 min	1-Adamantyl chloride (89)
3, X = Y = Br (1.11)	CH_2I_2 (6)	0.58	80°, 15 min	**3**, X = Y = I (83)
	$CHCl_3$ (25)	0.58	20°, 20 hr	**3**, X = Y = Cl (88)
2, X = Cl (5.86)	CH_3I (75)	3.90	20°, 8 min	**2**, X = I (79)
(2.31)	$CHBr_3$ (25)	0.98	20°, 2 hr	**2**, X = Br (80)
2, X = Cl (0.084)	$CHBr_3$ (3)	0.098	80°, 20 hr	*b*
1, X = Cl (6.06)	CH_2I_2 (25)	2.53	100°, 1 hr	**1**, X = I (30, 85 crude)
	CH_2Br_2 (120)	3.90	100°, 1 hr	**1**, X = Br (75)

[a] Catalyst prepared by heating bromine in the given solvent at reflux for $CHCl_3$ or CH_3I or at 80° for others with a strip of common aluminum foil, 3–7 mmol of Al per mmol of Br_2. Aluminum dust seemed generally less reactive toward bromine. [b] Initially formed [2.2.2] compound is isomerized to a 2:1 ratio of [3.2.1] and [2.2.2] compounds.

1-Adamantyl bromide is readily exchanged with halogen from solvent (using CH_3I, CH_2I_2, $CHCl_3$, or CCl_4) in a few minutes at room temperature. However, in the preparation of adamantyl iodide major side reactions give rise to adamantane (*ca.* 30%) and to polyhalogenated products, especially over longer reaction times. The reaction in chloroform gives 1-adamantyl chloride in excellent yield (89%) without significant competition from the known[6] aluminum chloride promoted halogenation reaction. In $CHCl_3$-$AlBr_3$ at room temperature 1,3,5,7-tetrabromoadamantane[7] (**3**, X = Y = Br) gives rise to three products (by glpc analysis), which all transform in sequence to a fourth product which is 1,3,5,7-tetrachloroadamantane, mp 194°, nmr ($CDCl_3$) δ 2.35. These products correspond to mono-, di-, tri-, and tetrasubstitution of bromine by chloride. Similarily, in diiodomethane as solvent, tetrabromoadamantane produces the nicely symmetrical and remarkably high melting 1,3,5,7-tetraiodo compound **3** (X = Y = I), mp 370° dec, nmr ($CDCl_3$) δ 3.22.

The bridgehead dichloride in the bicyclo[2.2.2]octyl system **2** may be converted at room temperature to the diiodide, mp 240°, nmr ($CDCl_3$) δ 2.60, using iodomethane as the source of iodine. In bromoform, the initially formed [2.2.2] dibromide (**2**, X = Br) is isomerized at 80° over a few hours to a 2:1 ratio of 1,5-dibromobicyclo[3.2.1]octane and 1,4-dibromobicyclo[2.2.2]octane. However, the unrearranged [2.2.2]octyl compound, mp 251°, nmr ($CDCl_3$) δ 2.40, is easily isolated in 80% yield from a reaction at room temperature.

The reaction is applicable to normally very unreactive bridgehead bicyclo[2.2.1]heptyl halides. Moderate temperatures are necessary, however; the 1,4-dichloride[8] of structure **1** is readily converted to the diiodide (mp 101°; nmr (benzene) singlet δ 2.0, AB quartet δ 1.78 and 1.40, J_{AB} = 8 Hz) in methylene diiodide at 100° or to the dibromide (mp 73°; nmr (benzene) singlet δ 1.98, AB quartet δ 1.80 and 1.50, J_{AB} = 8 Hz) in methylene dibromide at 100°.

While the exchange of halogen between aluminum halides and methyl halides proceeds only in the order

$$CH_3Cl \xrightarrow{AlBr_3} CH_3Br \xrightarrow{AlI_3} CH_3I^{9}$$

the aluminum halide promoted exchanges reported here are not similarly restricted. However, like the methyl halides, in the bicyclic systems there is a structural impossibility of forming stable elimination products, and the desired bridgehead halogen compounds are

---

[2] P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, **61**, 3184 (1939); W. v. E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *ibid.*, **75**, 1008 (1953).

[3] W. v. E. Doering and E. F. Schoenewaldt, *ibid.*, **73**, 2333 (1951).

[4] (a) J. C. Kauer, U. S. Patent 3,255,254; *Chem. Abstr.*, **65**, 15249 (1966). (b) The only facile halogen exchange at bridgehead positions of ring systems **1** and **2** is the conversion of 1-iodobicyclo[2.2.1]heptane and 1,4-diiodobicyclo[2.2.2]octane to the corresponding chloro derivatives using ICl in $CFCl_3$ or CCl_4 at room temperature; see J. C. Kauer, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 22-27, 1970, No. B14.

[5] F. N. Stepanov and Yu. I. Srebrodolskii, *Zh. Org. Khim.*, **2**, 1633 (1966); *Chem. Abstr.*, **66**, 115355 (1967).

[6] I. Tabushi, J. Hamuro, and R. Oda, *J. Chem. Soc. Jap.*, **89**, 794 (1968).

[7] H. Stetter and C. Wulff, *Chem. Ber.*, **93**, 1366 (1960).

[8] C. F. Wilcox, Jr., and J. G. Zajacek, *J. Org. Chem.*, **29**, 2209 (1964).

[9] H. C. Brown and W. J. Wallace, *J. Amer. Chem. Soc.*, **75**, 6279 (1953).

therefore obtained in high yields. While the mechanism of this halogen exchange is unclear, the isomerization of the bicyclo[2.2.2]octyl system[10] under longer reaction times suggests that the halophilic catalyst can promote an internal halogen exchange perhaps involving only partial carbonium ion character.

Acknowledgment. This work was supported by the National Research Council of Canada. We wish to thank Dr. J. C. Kauer (E. I. du Pont de Nemours and Co.) for a generous supply of 1,4-dichlorobicyclo-[2.2.2]octane.

---

[10] W. v. E. Doering and M. Barber, *J. Amer. Chem. Soc.*, 71, 1514 (1949); P. v. R. Schleyer, K. R. Blanchard, and C. D. Woody, *ibid.*, **85**, 1358 (1963).

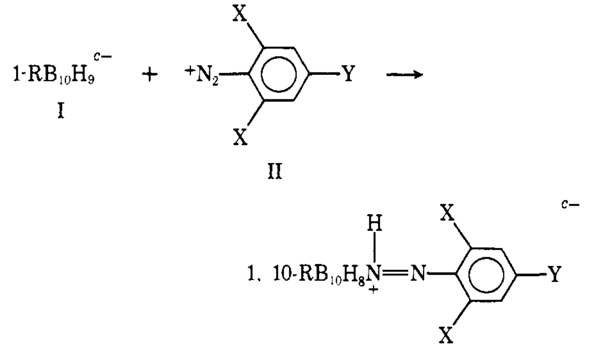
James W. McKinley, Richard E. Pincock,* W. Bruce Scott
Department of Chemistry, University of British Columbia
Vancouver 8, Canada

Received November 6, 1972

A Novel Transfer of the Diazonium Function from Carbon to Boron

Sir:

The azo coupling of aryldiazonium ions with $B_{10}H_{10}{}^{2-}$ has been shown to be a useful pathway to apically substituted $B_{10}H_{10}{}^{2-}$ derivatives[1]



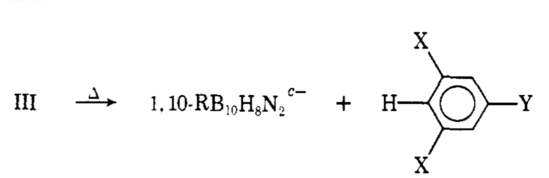
I

II

III

(1)

We wish to report a novel method of generating the diazonium function at boron by the thermal decomposition of III.



(2)

IV

IIIa, R = H; X = Y = Br; $c = 1$
b, R = $^{+}S(CH_3)_2$; X = Y = Br; $c = 0$
c, R = $^{+}N(CH_3)_3$; X = H; Y = Br; $c = 0$
d, R = H; X = H; Y = NO_2; $c = 1$
e, R = H; X = H; Y = Br; $c = 1$
IVa, R = H; $c = 1$
b, R = $^{+}S(CH_3)_2$; $c = 0$
c, R = $^{+}N(CH_3)_3$; $c = 0$

The usefulness of this method is enhanced by the fact that the diazonium function has been shown to be the most synthetically useful substituent on the $B_{10}H_{10}{}^{2-}$ cage since it can be displaced by a wide variety of nucleophiles.[2,3] In addition, the method presented here is the only method yet reported of obtaining the monodiazonium $1\text{-}B_{10}H_9N_2{}^{-}$. This compound should prove extremely useful as a precursor to monosubstituted $B_{10}H_{10}{}^{2-}$ derivatives. The overall reaction may be considered to be a transfer of the diazonium function from the phenyl ring to the $B_{10}H_{10}{}^{2-}$ cage. The $1\text{-}B_{10}H_9N_2{}^{-}$ ion was prepared by dissolving $(CH_3)_4N^{+}$IIIa in dry acetonitrile (~20 ml/g) and heating at reflux under N_2 for 3 hr. The acetonitrile was then removed *in vacuo*, and the solid was washed with diethyl ether to remove the 1,3,5-tribromobenzene formed (identified by infrared spectra). The solid residue was then extracted into acetone and filtered with decolorizing charcoal. Recrystallized $(CH_3)_4N^{+}$IVa (65% yield) was obtained by adding ethanol to the filtrate and slowly removing the solvent on a rotary evaporator. *Anal.* Calcd for $C_4H_{21}B_{10}N_3$: C, 21.90; H, 9.65; B, 49.28; N, 19.15. Found: C, 22.14; H, 9.82; B, 49.56; N, 19.48. In a similar manner $1,10\text{-}(CH_3)_2SB_{10}H_8N_2$ was synthesized starting with IIIb. After the solvent was removed the reaction mixture was heated to 40° under high vacuum to first remove the tribromobenzene, and then the product was separated from the residue by chromatography on silica gel and recrystallized from ethanol (yield 45%). The product was identified by comparison of the infrared and ^{11}B spectra with those of the known compound.[4]

The chlorinated ion, $1\text{-}(1\text{-}Br\text{-}4\text{-}N_2Ph)B_{10}Cl_9{}^{2-}$, was prepared by passing Cl_2 through an acetonitrile solution of IIIe in the presence of excess NaH at 0° in a manner similar to that previously reported.[5] *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Cl_9N_2C_6H_4Br$: C, 22.14; H, 3.73; B, 14.23; Br, 10.52; Cl, 42.01; N, 7.37. Found: C, 22.60; H, 3.82; B, 13.69; Br, 10.69; Cl, 41.95; N, 7.17. This compound was subsequently protonated by strong acid to form the monoanion which was found to be unreactive toward thermal decomposition in refluxing acetonitrile. All attempts to chlorinate IIIa in the absence of NaH resulted in the formation of partially chlorinated IVa, even at low temperatures. However, 1-chloro-2,4,6-tribromobenzene, in addition to $1,3,5\text{-}C_6H_3Br_3$, was isolated from the reaction mixture and identified by its mass spectrum. This suggests the existence of a second pathway for the formation of the $B\text{–}N_2{}^{+}$ function which involves electrophilic attack of Cl_2 on the phenyl carbon bonded to azo nitrogen.

The 80.5-MHz ^{11}B nmr spectrum of $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$ in acetonitrile contained a singlet and three doublets of area ratios 1:1:4:4 at +13.4, −22.0 (146), +17.2 (133), +25.8 (140) [chemical shifts, ppm relative to $BF_3 \cdot O(C_2H_5)_2$, and coupling constants (Hz)]. The singlet at 13.4 ppm is assigned to the apical boron attached to the diazonium group. This very high field chemical shift for an apical boron atom in the $B_{10}H_{10}{}^{2-}$ system is quite likely due to the strong electron-withdrawing character of the diazonium function.[3] The infrared spectrum of this salt contains a band at 2230 cm⁻¹ assigned to $-^{+}N{\equiv}N$ and the ultraviolet spectrum

---

[1] M. F. Hawthorne and F. P. Olsen, *J. Amer. Chem. Soc.*, **86**, 4219 (1964); **87**, 2366 (1965).

[2] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 115 (1964).

[3] W. H. Knoth, *J. Amer. Chem. Soc.*, **88**, 935 (1966).

[4] W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, 4, 280 (1965).

[5] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).