Stereochemistry of Halogenation of Nitronate Adducts from 4-Methoxy-1-nitronaphthalene and RMgX to 1-Halogeno-2-alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalenes and of Subsequent Elimination to Alkylhalogenonaphthalenes. Crystal Structure of a Tetrahydronaphthalenone Derivative

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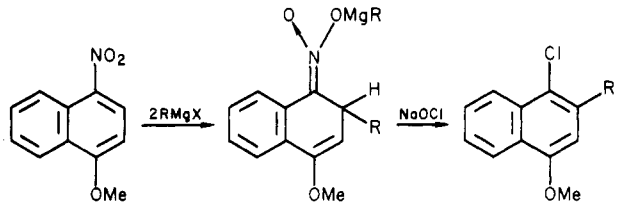
Studies on the stereochemical aspects of the reactivity of nitronate adducts from RMgX and nitroarenic systems have been extended to their reaction with electrophilic reagents other than H_3O^+. The reaction of C-bromination of the 1,4-adducts from 4-methoxy-1-nitronaphthalene and RMgX (R = CH_3, $PhCH_2CH_2$, $PhCH_2$) and the subsequent base-catalyzed elimination reaction have been investigated and compared with the results from the corresponding reaction of C-chlorination previously reported. The formation of alkylhalogenonaphthalenes prevails with respect to the formation of the corresponding alkylnitro derivatives; this has been interpreted in terms of a bimolecular antiperiplanar elimination of *r*-1-halogeno-*t*-2-alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalenes derived from the attack of halogens upon the nitronate function of the naphthalenic adducts. Factors concurring in determining the high observed stereoselectivity of the C-halogenation reaction have been investigated and interpreted. The geometry of the above-mentioned intermediates has been established through an X-ray diffraction analysis of the 1-bromo-1-nitro-2-methyl-1,2,3,4-tetrahydronaphthalen-4-one obtained from the corresponding 1-bromo-4-methoxy-2-methyl-1-nitro-1,2-dihydronaphthalene by hydrolysis in acidic medium.

Formation of nitronate adducts from conjugate addition[2] of RMgX to mononitroarenic systems as well as a number of aspects of their reactivity have been previously reported.[3]

Recently we have found that treatment of a THF solution of 1,4-addition compounds like **2** with sodium hypochlorite in strong basic medium leads to aromatic chloroalkyl derivatives of general formula **5**[4] (eq 1).



1 2 5

An analogous formation of chloro derivatives was reported in the literature,[5] resulting from the reaction of NaOCl with σ-anionic adducts derived from the nucleophilic attack of MeO^- on nitrobenzofurazans and related systems. Differently from the rather complex mechanism there suggested,[6] we proposed that the action of the hypochlorite ion could be explained in terms of an initial chlorination[7] at the carbon atom bearing the nitronate function. An immediate elimination of HNO_2 from the resulting compound **4** (see Scheme I) was promoted by the strongly basic medium leading to products **5**.

The main question arising from this interpretation was how to explain why HNO_2 elimination is highly preferred over HCl elimination.

On pursuing our investigations on the stereochemical aspects[8] of the reactivity of nitronate adducts from RMgX and nitroarenic systems, we studied their decomposition with electrophilic reagents other than Cl^+ and H^+.

In this paper we report the results obtained in the C-bromination reactions of **2**, which prove the validity of the previously proposed mechanism and, in addition, indicate that the elimination pathway in products of types **4** and **6** is closely related to the stereochemistry of their formation.

Results

Interaction between 1 and 2 mol of RMgX (**a**, R = CH_3; **b**, R = $PhCH_2CH_2$; **c**, R = $PhCH_2$) at 0 °C in tetrahydrofuran (THF) gives almost exclusively the 1,4-addition products[9] **2**. Treatment of this solution with an excess of sodium hypobromite and sodium hydroxide in water at 0 °C immediately leads most likely to the formation of *r*-1-bromo-4-methoxy-1-nitro-*t*-2-substituted-1,2-dihydronaphthalene[10] (**6**) through a highly stereoselective C-bromination at the nitronate function of **3**; compound **6** is almost the only product obtained. Subsequent base-promoted elimination reactions to give 1-bromo-4-methoxy-2-substituted (**8**) and 4-methoxy-1-nitro-2-substituted naphthalene (**9**) were sufficiently slow as to allow removal of **6** from the basic medium before its decomposition proceeded to an appreciable extent. Formation of **8a** and

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(2) (a) Bartoli, G.; Leardini, R.; Medici, A.; Rosini, G. *J. Chem. Soc., Perkin Trans. 1* **1978**, 692. (b) Bartoli, G.; Bosco, M.; Melandri, A.; Boicelli, A. C. *J. Org. Chem.*, **1979**, *44*, 2087.

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(4) Bartoli, G.; Bosco, M. *Synthesis* **1980**, *8*, 616.

(5) Mallory, F. B.; Varimbi, S. P. *J. Org. Chem.* **1963**, *28*, 1656.

(6) In that case a mechanism was suggested which involved a synchronous attack of the chlorine of the hypochlorite ion to the carbon of the Meisenheimer like adduct, bearing the nitrogroup and of the oxygen to the hydrogen attached to the vicinal sp^3 carbon atom in a five-membered cyclic transition state; the chloro derivative was formed by expulsion of nitrite ion and hydroxide ion with concomitant aromatization of the six-membered ring.[5]

(7) Neilsen, A. T.; "The Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Wiley-Interscience: New York, 1969; Vol. I, Chapter 7 and references cited therein.

(8) Bartoli, G.; Bosco, M.; Baccolini, G. *J. Org. Chem.* **1980**, *45*, 2649.

(9) The product of 1,6-addition was observed in a maximum of 5% yield only when R was the bulky benzyl group.[8]

(10) Nomenclature according to IUPAC rules: *J. Org. Chem.* **1970**, *35*, 2849.

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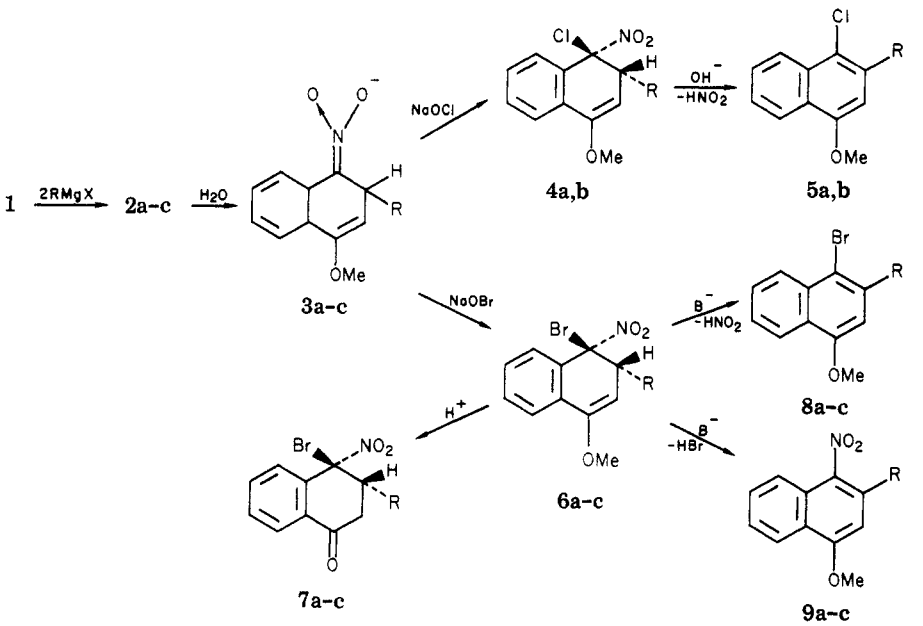
Scheme I[a]



[a] a, R = CH_3; b, R = $PhCH_2CH_2$; c, R = $PhCH_2$. B^- = MeO^-, OH^-.

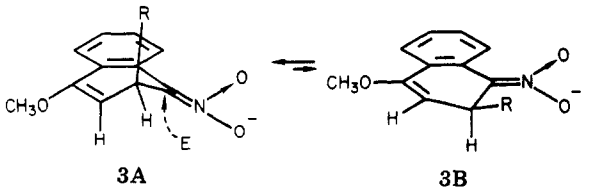
9a, for instance, went to completion after ~48 h.

Product **6** is stable, though poorly, only in dilute solutions of dried apolar organic solvents, so that it was impossible to isolate and purify it. Nevertheless its characterization was attempted by means of spectroscopic investigations: in particular, the ^1H NMR spectrum of the crude **6a** was recorded immediately after its formation (see Experimental Section).

In the presence of traces of water a slow decomposition to the stable *r*-1-bromo-1-nitro-*t*-2-substituted-1,2,3,4-tetrahydronaphthalen-4-one[10] (**7**), as the main product, was observed. Very likely, traces of mineral acids, arising from the spontaneous decomposition to **8** and/or to **9**, catalyzed the hydrolysis of the vinyl ether to the carbonilic function. In fact, when a dichloromethane solution of **6** was treated with dilute hydrochloric acid, compound **7** was obtained in high yields (60–80%, after 6 h) free from elimination products. On the other hand, treatment of a methanolic solution of **6** with methoxide ion gave compounds **8** and **9** free from the ketone with analogously high yields. Moreover, for all alkyl substituents the yields from this method were much higher than those from the direct decomposition in the reaction medium, whereas no appreciable variation was found in the **8** to **9** ratios. Although ketone **7** can exist in two diastereomeric forms, ^1H and ^{13}C NMR spectra always indicated the presence of only one (almost pure) isomer in every compound we obtained. None of the spectroscopic techniques mentioned above could allow us to assign either the cis or trans configuration to this isomer; the structure of **7**, as depicted in Scheme I, was unambiguously assigned on the evidence resulting from the X-ray diffraction analysis of compound **7a** (see Figure 1). Hence, because the acid-promoted hydrolysis of the vinyl ether function of **6** cannot affect the relative configurations at the C_1 and C_2 sp^3 carbons, it follows that the C-bromination is a highly stereoselective process leading almost exclusively to the isomer having the bromine atom and the alkyl group trans.

Discussion

Two strictly connected factors[8] converge to determine the stereoselectivity of the C-bromination on **3**. (1) The presence of an alkyl group on the sp^3 carbon vicinal to the nitronate function causes **3** to assume the configuration **3A** since in configuration **3B** a strong steric strain arises



3A **3B**

E = H_3O^+, NaOCl, NaOBr

from interactions between the alkyl group and the oxygen atoms of the nitronate function.[11] (2) In conformer **3A** the axial alkyl group causes the electrophilic reagent to preferentially approach the reaction center from the opposite, less hindered, axial direction.[12]

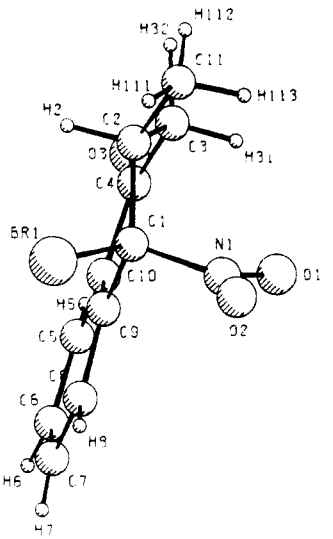


Figure 1. Structure of **7a** from X-ray diffraction analysis.

(11) Johnson, F. J.; Malhotra, S. K. *J. Am. Chem. Soc.* **1965**, *87*, 5492.
(12) Johnson, F. J.; Malhotra, S. K. *J. Am. Chem. Soc.* **1965**, *87*, 5493.

Table I. Selected Dihedral Angles

atoms (I-J-K-L)	angle,[a] deg
H(2)-C(2)-C(1)-Br	-52.3
H(2)-C(2)-C(1)-NO_2	-168.7
CH_3-C(2)-C(1)-Br	68.7
CH_3-C(2)-C(1)-NO_2	-47.8
C(2)-C(1)-C(9)-C(10)	15.9
Br-C(1)-C(9)-C(8)	-43.7
H(31)-C(3)-C(2)-H(2)	-177.9
H(32)-C(3)-C(2)-H(2)	66.6
O(3)-C(4)-C(3)-H(31)	-94.5
O(3)-C(4)-C(3)-C(9)	-176.3

[a] The dihedral angle has a positive sign if the vector is clockwise from vector J-I when viewed down vector J-K and a negative sign if counterclockwise.

Table II. Interatomic Bond Lengths (Å) with Estimated Standard Deviations[a] in Parentheses

C(4)-C(10)	1.451 (10)	C(1)-N(1)	1.554 (8)
C(4)-O(3)	1.232 (12)	N(1)-O(1)	1.215 (9)
C(4)-C(3)	1.502 (13)	N(1)-O(2)	1.193 (10)
C(3)-C(2)	1.513 (14)	C(8)-C(9)	1.376 (10)
C(2)-C(11)	1.543 (13)	C(8)-C(7)	1.408 (12)
C(2)-C(1)	1.502 (10)	C(7)-C(6)	1.358 (14)
C(1)-C(9)	1.537 (10)	C(6)-C(5)	1.337 (12)
C(1)-Br(1)	1.954 (8)	C(5)-C(10)	1.402 (12)
C(10)-C(9)	1.388 (11)		

[a] The estimated standard deviations do not contain cell constant errors, and the bond lengths have not been corrected for thermal motion.

On this ground we interpreted, in our previous report on the C-protonation reaction,[8] the increasing stereoselectivity when the steric hindrance of the alkyl substituent increases in terms of a gradual shift to the left of the equilibrium between **3A** and **3B** as well as of a higher preferentiality of the proton toward an axial approach to conformer **3A**. The present results indicate that the C-bromination reaction practically follows an almost complete stereoselective pathway even in the case of the small methyl group; these findings afford a more punctual evaluation of the factors involved. In particular, in nitronate **3**, the equilibrium between the two conformers must be almost completely shifted to the left for all alkyl substituents; as a consequence, the observed stereoselectivity essentially depends upon the concomitant effects of the bulkiness of the axial group and of the entering electrophile that is responsible for directing the attack at **3A** from the less hindered side.

Conclusions drawn from the results of the C-bromination also suit the analogous chlorination reaction so that we might assume that the action of NaOCl on the intermediate **3** leads to a preferential formation of the isomer *r*-1-chloro-*t*-2-methyl-4-methoxy-1-nitro-1,2-dihydronaphthalene (**4a**). Hence the base-promoted formation of the chloro derivative **5** from **4** can be accounted for in terms of a preferred bimolecular antiperiplanar elimination over syn elimination,[13,14] in nonplanar compound **4**.[15]

From the microwave spectral data of Butcher,[16] Katritzky estimated that the dihedral angle between diaxial hydrogens of the methylene groups in 1,3-cyclohexadienic systems and that between axial and equatorial ones are close to 164° and 45°, respectively.[17] In compound **4a**, as well as in **6a–c**, even higher values for dihedral angles of diaxial and axial–equatorial groups are to be expected, owing to the greater distortion due to the bulky substituents. On the other hand the values measured from X-ray data for H–C(3)–C(4)–NO_2 and H–C(3)–C(4)–Br in compound **7a** are 168° and 52°, respectively (see Table I).

In systems **4** as well as in **6** a synchronous elimination will easily occur between the trans, diaxial groups (NO_2 and H; dihedral angle close to the ideal value of 180° for antiperiplanar elimination), whereas the cis groups (Cl or Br and H) will eliminate with greater difficulty; their dihedral angle, in fact, does not fulfill the ideal geometry (0°) for a syn elimination, and this would bring about a strain in a transition state where the bulky substituents (nitro and methyl group) should have an almost eclipsed configuration.

In addition in *cis*-2-alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalene[8] as well as in other 1-substituted dihydronaphthalenes,[18] ^{1}H NMR data provide unambiguous evidence for an axial preference of nitro and hydrogen groups.

Although substitution of chlorine or bromine for hydrogen can reduce the stability of an axial nitro group, the energy required to restore this conformation must nevertheless be low. Besides, a preferential axial arrangement of the nitro group in **6a–c**, may be stated on the basis of the ^{1}H NMR spectrum of **6a**. The value of 3.3 Hz found for the coupling constant between H-2 an H-3 is comparable with the *J* value of 2.2 Hz reported for the coupling between the vinylic H-3 hydrogen and the vicinal axial H-2 in dihydronaphthalenic systems;[18] on the other hand, this value is too far from the 6-Hz value assigned to the corresponding $J_{H(2)eq-H(3)}$, so that it is conceivable to suppose that in intemediates **4** and **6** the nitro group and the hydrogen atom are arranged in such a way as to assume a preferential diaxial conformation. Therefore, it is not surprising to find in **4** a great preference for HNO_2 over HCl elimination despite the difference in the heterolytic bond-breaking energies between C–Cl and C–NO_2 linkages. On the contrary, in the case of **6a–c** the great leaving group ability of bromine counterbalances in part the tendency toward antiperiplanar elimination, so that the HBr loss may become competitive with the HNO_2 loss.

Experimental Section

^{1}H NMR spectra were recorded at 100 MHz on a Varian XL-100 instrument operating in the CW mode. Proton-noise-decoupled ^{13}C NMR spectra were recorded at 25.16 MHz with a Varian XL-100 by the FT technique; resonance assignments were made with the aid of the off-resonance technique. Proton and ^{13}C shifts are given in parts per million from Me_4Si in $CDCl_3$ solvent. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer. THF, dried over sodium and distilled, was redistilled from $LiAlH_4$ immediately before use. 4-Methoxy-1-nitronaphthalene (**1**) was a commerical product (EGA Chemie).

Sodium hypobromite solutions were prepared immediately before use, as follows: 0.04 mol of bromine was added dropwise under a nitrogen flow to a stirred solution of 10% aqueous sodium hydroxide (60 mL) cooled in a ice bath.

Preparation and Attempted Purification and Characterization of *r*-1-Bromo-4-methoxy-1-nitro-*t*-2-substituted-1,2-dihydronaphthalenes 6a–c. A solution of alkylmagnesium halide (0.04 mol) in THF (50 mL) was added dropwise at 0 °C under nitrogen to a solution of **1** (0.02 mol) in the same solvent. The mixture was stirred for a few minutes (~3) and then poured into a freshly prepared aqueous alkaline solution of NaOBr

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(15) Mislow, K.; Glass, H. A. W.; Hopps, H. B.; Simon, E.; Wahl, G. H. *J. Am. Chem. Soc.* **1964**, *86*, 1710.
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(17) Cohen, D.; Miller, J. T.; Heaney, H.; Constantine, P. R.; Katritzky, A. R.; Semple, B. M.; Sewell, M. J. *J. Chem. Soc. B* **1967**, 1248.
(18) Cook, M. J.; Katritzky, A. H.; Pennington, F. C.; Semple, B. M. *J. Chem. Soc. B* **1969**, 523.

(0.04 mol) under vigorous stirring at 0 °C. After a few minutes the reaction mixture was added to of ~200 mL of dichloromethane and the inorganic material immediately filtered out. The organic layer was washed several times with water and dried over magnesium sulfate. Any attempt to isolate **6a–c** from this solution by chromatography or recrystallization was unsuccessful, on account of its tendency to decompose.

A rough characterization of the product was possible by means of a ^1H NMR analysis carried out before appreciable decomposition.

To this end, a portion of the dichloromethane solution of crude **6a** was evaporated under vacuum at room temperature and dissolved in $CDCl_3$, and its spectrum was immediately recorded. Besides minor signals relative to decomposition products **8a** and **9a** and to other byproducts, resonances consistent with the hypothesized structure of **6a** were singled out at δ 1.4 (3 H, d, J = 7 Hz, CH_3), 3.58 (1 H, m, J = 3.2 Hz, H(2)), 3.72 (3 H, s, OCH_3), 4.87 (1 H, d, H(3)). No clear evidence was found of the presence, even in traces, of the cis isomer of **6a**.

A more precise characterization of **6** and the undoubted assignment of its stereochemical configuration could be effected by conversion of compounds **6a–c** into the stable compounds **7a–c**.

Conversion of 6a–c into *r*-1-Bromo-1-nitro-*t*-2-substituted-1,2,3,4-tetrahydronaphthalen-4-ones 7a–c. To the dichloromethane solution obtained as described above was added a few milliliters of water, and the mixture was stirred at room temperature overnight. The organic layer was then separated, washed with water, dried, evaporated at reduced pressure, and chromatographed on a silica gel column with benzene as eluent.

The yields obtained for products **7a–c**, were 41%, 45%, and 43%, respectively.

An improved reaction procedure allowed us to increase the yields of **7a–c**.

A THF solution of **2a–c** (0.02 mol) was treated with NaOBr as described above. The reaction mixture was stirred for 2–3 min and then treated with a cold aqueous solution of SO_2 until the excess of NaOBr was completely reduced and extracted with CH_2Cl_2. The organic layer was washed with water and treated with a few milliliters of dilute hydrochloric acid (5%). This mixture was kept overnight at room temperature under vigorous stirring, washed with water, dried, and evaporated at reduced pressure. The residue was submitted to chromatographic purification on a silica gel column with benzene as eluent. Analytical data and yields of the compounds **7a–c** follow.

7a: 68% yield; mp 95–97 °C; $\nu_{C=O}$ 1680, ν_{NO_2} 1545 and 1290 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, d, J = 6.5 Hz, CH_3), 2.82–3.4 (3 H, m, H-2, H-3.1, H-3.2), 7.4–8.16 (4 H, m, H-5, H-6, H-7, H-8), ^{13}C NMR 17.1 (CH_3), 42.5 (C-3), 43.5 (C-2), 101.6 (C-1), 127.0–138.4 (aromatic carbons), 193.9 ppm (C=O).

Anal. Calcd for $C_{11}H_{10}NO_3Br$: C, 46.50; H, 3.55; N, 4.93; Br, 28.13. Found: C, 46.74; H, 3.25; N, 4.87; Br, 28.50.

7b: 72% yield; mp 100–102 °C; $\nu_{C=O}$ 1690, ν_{NO_2} 1553 and 1305 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3–3.1 (7 aliphatic H, complex band), 7.25 (5 H, m, C_6H_5), 7.5–8.2 (4 H, m, H-5, H-6, H-7, H-8); ^{13}C NMR 32.0, 32.8, and 39.7 (C-3, CH_2, CH_2, interchangeable), 46.9 (C-2), 101.6 (C-1), 126.2–139.4 (aromatic carbons), 193.3 ppm (C=O).

Anal. Calcd for $C_{18}H_{16}NO_3Br$: C, 57.77; H, 4.31; N, 3.74; Br, 21.35. Found: C, 57.71; H, 4.30; N, 3.71; Br, 21.41.

7c: 81% yield; 112–114 °C; $\nu_{C=O}$ 1685, ν_{NO_2} 1550 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2–3.7 (5 aliphatic H, complex band), 7.10–8.14 (9 aromatic H); ^{13}C NMR 37.4 and 39.2 (C-3 and CH_2 interchangeable), 50.1 (C-2), 101.4 (C-1), 127.1–136.3 (aromatic carbons), 193.6 ppm (C=O).

Anal. Calcd for $C_{17}H_{14}NO_3Br$: C, 56.68; H, 3.92; N, 3.89; Br, 22.18. Found: C, 56.78; H, 3.81; N, 3.82; Br, 22.20.

Base-Promoted Elimination Reaction of 6a–c to 1-Bromo-4-methoxy-2-substituted-naphthalenes 8a–c and to 4-Methoxy-1-nitro-2-substituted-naphthalenes 9a–c. When **6a–c** was not immediately removed from the basic reaction medium in which it formed, its decomposition to **8a–c** and **9a–c** proceeded and was accomplished in 48 h at most: so (method A), after the addition of the THF solution of **2a–c** to the hypobromite solution, the reaction mixture was vigorously stirred for several hours (from 24–48 h) at room temperature, and then treated with ~200 mL of benzene. The mixture was filtered to remove inorganic material, and the organic layer was separated, washed several times with water, and dried over $MgSO_4$. After solvent removal, the residue was submitted to chromatographic separation on a silica gel column. Elution with 1:1 benzene–petroleum ether gave the following compounds.

8a: 29% yield; mp 63–64 °C (from hexane; lit.[19] mp 62–63.5 °C); ^1H NMR ($CDCl_3$) δ 2.60 (3 H, s, CH_3), 3.96 (3 H, s, OCH_3), 6.68 (1 H, s, H-3), 7.32–7.64 and 8.10–8.30 (2 H and 2 H, m, H-5, H-6, H-7, H-8).

8b: 33% yield; mp 68–69 °C (from *n*-hexane); ^1H NMR ($CDCl_3$) δ 2.86–3.34 (4 H, m, CH_2CH_2), 3.86 (3 H, s, OCH_3), 6.52 (1 H, s, H-3), 7.25 (5 H, s, C_6H_5), 7.30–7.66 and 8.10–8.34 (4 H, m, H-5, H-6, H-7, H-8).

Anal. Calcd for $C_{19}H_{17}BrO$: C, 66.87; H, 5.02; Br, 23.42. Found: C, 66.95; H, 4.95; Br, 23.54.

8c: 34% yield; mp 86–88 °C (from *n*-hexane); ^1H NMR ($CDCl_3$) δ 3.87 (3 H, s, OCH_3), 4.36 (2 H, s, CH_2), 6.63 (1 H, s, H-3), 7.24 (5 H, s, C_6H_5), 7.20–7.35 and 8.16–8.38 (4 H, m, H-5, H-6, H-7, H-8).

Anal. Calcd for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.12; H, 4.68; Br, 24.90.

Further elution with the same eluent mixture gave compounds **9a–c** which were identified by comparison with authentic samples.[8] Yields for these compounds follow: **9a**, 16%; **9b**, 17%; **9c**, 17%. Improved yields could be obtained by following the next alternative procedure (method B).

The dried dichloromethane solution of **6a–c** prepared as indicated above was evaporated under reduced pressure. The residue was dissolved in 50 mL of methanol and treated with a solution of potassium hydroxide (0.03 mol) in the same solvent. The mixture was allowed to stand at room temperature for 4–10 h, diluted with water, and extracted with benzene.

The benzenic solution was worked up as described above, and the title compounds were recovered in the following yields (percent): **8a**, 42; **8b**, 59; **8c**, 56; **9a**, 21; **9b**, 27; **9c**, 26.

Table III. Relevant Bond Angles (deg) with Estimated Standard Deviations in Parentheses

C(10)-C(4)-O(2)	121.4 (8)
O(3)-C(4)-C(3)	120.0 (7)
C(3)-C(4)-C(10)	118.6 (8)
C(4)-C(3)-C(2)	112.8 (7)
C(3)-C(2)-H(2)	104.5 (4.2)
C(3)-C(2)-C(11)	110.2 (7)
C(3)-C(2)-C(1)	113.7 (7)
C(11)-C(2)-H(2)	111.9 (4.1)
C(11)-C(2)-C(1)	112.9 (7)
H(2)-C(2)-C(1)	103.1 (3.6)
Br(1)-C(1)-N(1)	106.7 (5)
Br(1)-C(1)-C(9)	107.3 (6)
Br(1)-C(1)-C(2)	108.5 (5)
N(1)-C(1)-C(9)	107.3 (6)
N(1)-C(1)-C(2)	110.3 (5)
C(2)-C(1)-C(9)	114.4 (6)
C(1)-C(9)-C(10)	119.8 (6)
C(9)-C(10)-C(4)	122.5 (7)

Table IV. Summary of Crystallographic Data

molecular formula	$C_{11}H_{10}NO_3Br$
mol wt	284.1
linear abs coef. [μ(MoKα)]	35.75 cm^{-1}
ρ (calcd)	1.69 g/cm^3
space group	$P2_1/n$
cell dimensions a	10.634 (3) Å
b	13.000 (3) Å
c	8.592 (2) Å
β	110.10 (6)°
Z	4
V	1115.45 Å^3
no. of rflctns measd	1969
no. of unique rflctns	1404
final R	0.058
final R_w	0.062

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Crystal Structure Determination. Compound **7a** was recrystallized from *n*-hexane, and the sample used in the structure determination was 0.3 × 0.5 × 0.6 mm. All diffraction measurements were made on a Philips PW 1100 diffractometer using MoKα radiation and a graphite monochromator. The orientation matrix and cell dimensions were determined from 25 accurately centered reflections. Pertinent crystallographic information is summarized in Table IV.

Intensity data were corrected for Lorentz–polarization effects but not for absorption. In all, 1264 unique nonzero reflections were used in the structural analysis. The structure was solved by the direct method ($E \geq 1.2$) with the SHELX crystallographic program system (Sheldrick, 1976). The first E map indicated positions for all the nonhydrogen atoms. The hydrogen atoms were geometrically positioned (assuming a C–H distance of 1.08 Å) and constrained to refine riding on their attached carbon atoms. The final agreement factor R was 0.058, with anisotropic temperature factors assigned to the Br, NO_2, and C=O groups. The weighting scheme was $w = 3.16/[\sigma(F_o)^2 + 0.0007\,F_o^2]$.

Figure 1 was made with the PLUTO program (Motherwell, 1976).

Selected dihedral angles, interatomic bond lengths, relevant bond angles, and crystallographic data are reported in Tables I–IV, respectively.

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Registry No. 1, 4900-63-4; **2a**, 77416-37-6; **2b**, 77416-38-7; **2c**, 77416-39-8; **6a**, 77416-40-1; **6b**, 77416-41-2; **6c**, 77416-42-3; **7a**, 77416-43-4; **7b**, 77416-44-5; **7c**, 77416-45-6; **8a**, 4708-86-5; **8b**, 77416-46-7; **8c**, 77429-55-1; **9a**, 72207-00-2; **9b**, 73323-60-1; **9c**, 73323-61-2.

Supplementary Material Available: Tables of positional coordinates and temperatures factors (2 pages). Ordering information is given on any current masthead page.

Facile Conversion of Alkenes into Alkyl Bromides via Reaction of Organoboranes with Bromine or Bromine Chloride

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Organoboranes react with either bromine or bromine chloride in aqueous media to yield the corresponding alkyl bromides under surprisingly mild conditions. The reaction is ideal for the synthesis of functionally substituted organic bromides. Sodium bromide may be utilized as the bromine source via its in situ conversion to bromine chloride by using mild oxidizing agents.

The use of organoborane technology to synthesize alkyl bromides is well documented and is rather complex.[1-4] In the presence of strong bases such as sodium methoxide, the organoboranes are readily converted to the corresponding alkyl bromides.[5] In the absence of strong bases,

$$R_3B \xrightarrow[NaOCH_3/CH_3OH]{Br_2} RBr$$

a free-radical reaction generally occurs which involves abstraction of an α-hydrogen followed by reaction with bromine. The resultant α-bromo organoborane may either be cleaved by the HBr byproduct (to yield a bromoalkane[6]) or rearrange to form a new organoborane.[7]

We recently developed a new, mild iodination procedure involving the reaction of organoboranes with iodine monochloride.[8] The reaction has proven to be of utility in

$$R_3B \xrightarrow[NaOAc]{ICl} RI$$

the radiopharmaceutical area due to the gentle reaction conditions (a variety of functionality is tolerated) and efficient utilization of the iodine nuclide.[9,10] The reaction presumably occurs via an electrophilic attack on one of the α-carbons in the electron-rich organoborane–acetate complex.[11]

We felt that organoboranes might also react with bromine and bromine chloride under more gentle ionic conditions. We have found this to be the case.

Results and Discussion

The available data suggest that bromine can react with organoboranes in an ionic fashion as well as via a free-radical process. Thus inversion of configuration has been observed when tri-*exo*-norbornylborane reacts with bromine in the presence of base.[12] In addition, the rearrangement of *B*-alkyl-9-borabicyclononanes (when they are subjected to bromine) has been postulated to be ionic in nature.[13] We decided to investigate the reaction of organoboranes with bromine and bromine chloride[14-16] in analogy to our earlier iodination studies.[8] Our results are presented in Table I.

The data indicate that the reaction is most useful for the conversion of terminal olefins into primary bromides and compliments the earlier free-radical bromination reactions which favor secondary alkyl groups.[3,17] The lower yields observed for boranes containing secondary alkyl

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