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Bromination of Benzonorbornadiene Using a Mixture of Sodium Bromide and Sodium Perborate at High Temperatures

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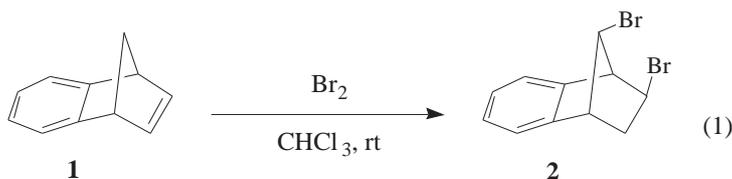
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Bromination of benzonorbornadiene (**1**) with sodium bromide in the presence of sodium perborate at room temperature gave only one product, the dibromide **2** produced via Wagner-Meerwein rearrangement. However, at high temperatures, bromination resulted predominantly in the formation of rearranged solvolytic products whose formation mechanisms are discussed.

Key Words: Bromination, benzonorbornadiene, high temperature bromination, sodium perborate

Introduction

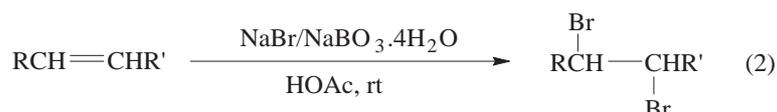
The addition of bromine to a carbon-carbon double bond is formally one of the simplest reactions typical of unsaturated compounds. The nature of the intermediates of the addition depends on the structure of the substrate and on the reaction medium. The intermediates, strongly bridged bromonium ions, are involved in the bromination of nonconjugated olefins which give *anti*-adducts.¹ However, bromination of unsaturated bicyclic systems leads to rearrangements of the molecular skeleton. For example, the electrophilic addition of bromine to benzonorbornadiene **1** leads to the formation of rearranged product **2** in almost quantitative yield (Eq. 1).^{2,3d} This compound is formed as a result of Wagner-Meerwein rearrangement.



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Balci et al.³ have observed that the reaction temperature has a dramatic influence on product distribution in the course of studying the bromination reactions of the unsaturated bicyclic systems. Bromination at room and lower temperatures give rearranged products via Wagner-Meerwein rearrangement with accompanying alkyl and aryl (in the case of benzannelated systems) migration. However, the bromination of these hydrocarbons at higher temperatures (80-150°C) resulted partly or completely in the formation of non-rearranged products.³ High temperature bromination prevents skeletal rearrangement.

Recently, Kabalka et al.⁴ reported that a mixture of sodium bromide and sodium perborate in glacial acetic acid can be utilized to convert alkenes to dibromoalkanes in excellent yields (Eq. 2).



In the present work, we studied the bromination reaction of benzonorbornadiene **1** with this new bromination agent at high temperatures and obtained totally different results with respect to the bromination carried out at room temperature.

Experimental Section

General. Melting points were determined on a Büchi model 530 apparatus and are uncorrected. Infrared spectra were recorded on a Mattson model 1000 FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on 200 (50)-MHz spectrometers. Column chromatography was performed on silica gel (60-200 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F₂₅₄ analytical aluminum plates. Benzonorbornadiene **1**⁵ was prepared as reported.

Bromination of Benzonorbornadiene 1 at Room Temperature. 3.0 g (29.1 mmol) of sodium bromide was added to a mixture of sodium perborate (2.30 g, 14.9 mmol) and benzonorbornadiene **1** (2.0 g, 14.0 mmol) in glacial acetic acid (25 mL) and stirred at room temperature for 2 h. The mixture was then diluted with water and the aqueous solution was extracted with ether, washed successively with saturated NaHCO₃ solution and water and dried over Na₂SO₄. After removal of the solvent, the residue was filtered on a short silica gel column eluted with hexane. After evaporation of the solvent the oily residue was crystallized from ethanol to give 3.40 g (80%) of *exo, anti*-9,11-dibromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (**2**).^{3d} Comparison of the spectral data of **2** with those reported in the literature^{3d} showed that they were in full agreement.

Bromination of Benzonorbornadiene 1 at 90°C. To a mixture of sodium perborate (2.30 g, 14.9 mmol) and benzonorbornadiene (2.0 g, 14.0 mmol) in glacial acetic acid (25 mL) heated at 90°C was added 3.0 g (29.1 mmol) of sodium bromide. Stirring was continued at 90°C for 20 min after the addition of sodium bromide. The reaction mixture was cooled to room temperature and worked up in the same way as described above. After removal of the solvent, the oily residue (3.10 g) was chromatographed over silica gel (110 g). Elution with hexane gave **2** as the first fraction (1.16 g, 27.3%).

Continued elution with hexane-ethyl acetate (95:5) afforded the *exo, anti*-11-bromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-9-yl acetate (**4**) as the second fraction (0.36 g, 9.1%): colorless crystals, mp 65-66°C from ether; ¹H NMR (200 MHz, CDCl₃) δ 7.25 (m, 1H, ArH), 7.13 (br s, 3H, ArH), 4.67 (dd, J = 7.0, 2.9 Hz,

1H, H₉), 4.10 (m, 1H, H₁₁), 3.65 (br s, 1H, H₈), 3.47 (m, 1H, H₁), 2.44 (dt, A part of AB system, J = 13.1, 3.6 Hz, 1H, H_{10*exo*}), 2.10 (s, 3H, CH₃), 2.05 (b dd, B part of AB system, J = 13.1, 8.3 Hz, 1H, H_{10*endo*}); ¹³C NMR (50 MHz, CDCl₃) δ 172.42, 147.15, 143.39, 129.50, 129.08, 124.13, 123.26, 77.29, 57.44, 56.15, 51.68, 35.12, 23.13; IR (CHCl₃) 3004, 2851, 1753, 1509, 1454, 1344, 1250, 1166, 1040, 1009, 978, 822, 744 cm⁻¹. MS (EI) *m/z* (% rel. intensity) 282/280 (M⁺, 8), 222/220 (22), 158.1 (73), 141.1 (46), 129.1 (62), 116.1 (100). HRMS (EI) calcd for C₁₃H₁₃O₂⁸¹Br (*m/z*) 282.007845, found 282.007841.

Continued elution with the hexane-ethyl acetate (85:15) afforded the *exo*, *anti*-11-bromotricyclo [6.2.1.0^{2,7}]undeca-2,4,6-trien-9-ol (**3**)⁶ as the third fraction (0.07 g, 2%): colorless crystals, mp 96-97°C (Lit⁶. 97-99.5°C) from ether-hexane; ¹H NMR (200 MHz, CDCl₃) δ 7.22-7.07 (m, 4H, ArH), 4.18 (m, 1H, H₁₁), 3.89 (m, 1H, H₉), 3.56 (br s, 1H, H₈), 3.51 (m, 1H, H₁), 2.62 (br s, 1H, OH), 2.31 (dt, A part of AB system, J = 13.2, 3.6 Hz, 1H, H_{10*exo*}), 2.13 (b dd, B part of AB system, J = 13.2, 7.3 Hz, 1H, H_{10*endo*}); ¹³C NMR (50 MHz, CDCl₃) δ 146.57, 144.21, 129.27, 129.04, 123.67, 123.27, 77.14, 59.42, 58.53, 51.81, 38.53.

Further elution with the same solvent mixture yielded the *exo*, *anti*-11-hydroxytricyclo [6.2.1.0^{2,7}]undeca-2,4,6-trien-9-yl acetate (**5**) as the last fraction (0.90 g, 29.3%): colorless crystals, mp 69.5-70°C from ether hexane; ¹H NMR (200 MHz, CDCl₃) δ 7.22 (m, 1H, ArH), 7.10 (br s, 3H, ArH), 4.79 (dd, J = 7.0, 2.9 Hz, 1H, H₉), 3.96 (m, 1H, H₁₁), 3.35 (br s, 1H, H₈), 3.28 (m, 1H, H₁), 2.94 (br s, 1H, OH), 2.18-1.99 (m, 2H, H₁₀), 2.10 (s, 1H, CH₃); ¹³C NMR (50 MHz, CDCl₃) δ 171.53, 147.04, 141.73, 129.19, 128.53, 124.91, 123.73, 86.60, 78.44, 54.61, 50.24, 35.35, 23.14; IR (CHCl₃) 3463, 3004, 1704, 1639, 1456, 1352, 1248, 1194, 1148, 1074, 1037, 1006, 975, 913, 763 cm⁻¹. MS (EI) *m/z* (% rel. intensity) 218.1 (M⁺, 3), 158.1 (37), 129.1 (100), 116.1 (43), 83.9 (55). HRMS (EI) calcd for C₁₃H₁₄O₃ *m/z* 218.094294, found 218.094229.

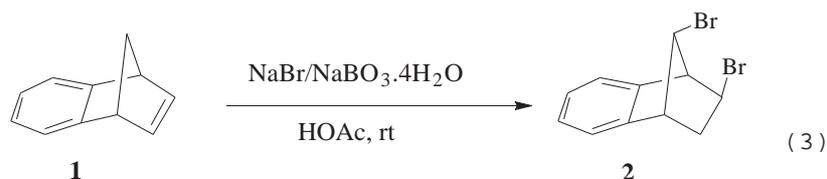
Bromination of Benzonorbornadiene 1 at 120°C. The reaction was carried out as described above using 2.0 g (14.0 mmol) of benzonorbornadiene, 2.30 g (14.9 mmol) of sodium perborate, 3.0 g (29.1 mmol) of sodium bromide and 25 mL of glacial acetic acid and after work-up, the residue (2.20 g) was chromatographed over silica gel (110 g). Elution with hexane-ethyl acetate (90:10) gave as the first fraction the *exo*, *anti*-11-(acetyloxy)tricyclo [6.2.1.0^{2,7}]undeca-2,4,6-trien-9-yl acetate (**12**)^{3d} (0.10 g, 2.7%): colorless crystals, mp 77-78°C (Lit.^{3d} 80.5-81°C) from ether-hexane. The ¹H NMR, ¹³C NMR, and IR spectral data for **12** are identical with those reported in the literature.^{3d}

Continued elution with the same solvent mixture afforded **5** as the second fraction (1.80 g, 59%).

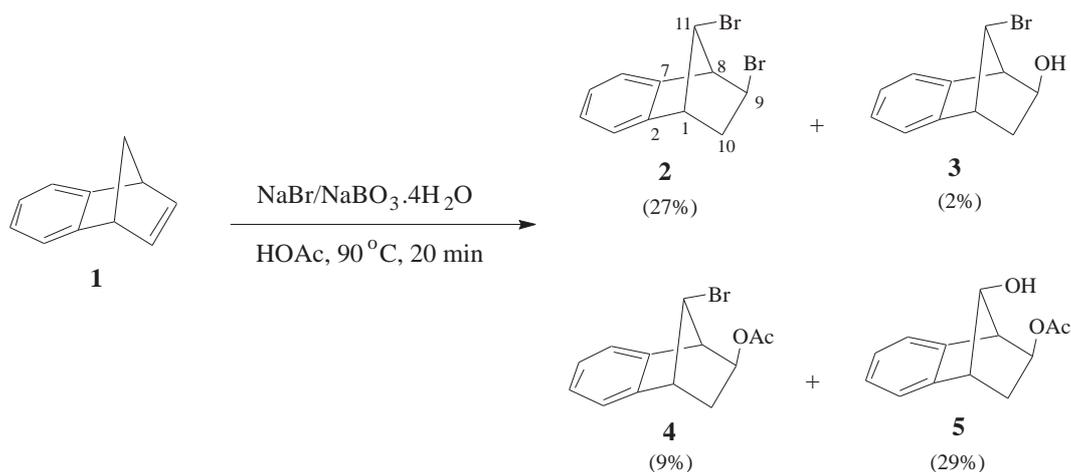
Bromination of Cyclohexene at 70°C. The reaction was carried out at 70°C as described above using 1.11 g (13.4 mmol) of cyclohexene, 2.30 g (14.9 mmol) of sodium perborate, 3.0 g (29.1 mmol) of sodium bromide and 25 mL of glacial acetic acid and after work-up, the residue (1.90 g) was chromatographed over silica gel (110 g). Elution with hexane gave 1.0 g (31%) of *trans*-1,2-dibromocyclohexane (**14**)⁴ as the first fraction. Continued elution with hexane-chloroform (80:20) afforded the *trans*-2-bromocyclohexyl acetate (**15**)¹¹ (0.60 g, 20%, pale yellow liquid) as the second fraction: ¹H NMR (200 MHz, CDCl₃) δ 4.84 (m, 1H), 3.90 (ddd, J = 10.6, 9.1, 4.4 Hz, 1H), 2.30 (m, 1H), 2.11 (m, 1H), 2.04 (s, 3H, CH₃), 1.72 (m, 2H), 1.35 (m, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 171.60, 77.70, 54.58, 37.60, 33.18, 27.52, 25.32, 22.98.

Results and Discussion

Benzenorbornadiene **1** was prepared as reported⁵ and reacted with a mixture of sodium bromide and sodium perborate in glacial acetic acid at room temperature and yielded only the corresponding rearranged dibromide **2** in 80% yield (Eq. 3). This was not a surprise because of the great tendency of benzenorbornadiene **1** to undergo Wagner-Meerwein rearrangement. The formation of only dibromide (**2**), was in accordance with the results obtained by Kabalka et al.⁴



We also reacted benzenorbornadiene (**1**) with a mixture of sodium bromide and sodium perborate in glacial acetic acid at 90°C. Surprisingly, we obtained a completely different product distribution. From the reaction at 90°C we isolated four products (**2-5**) after chromatographic separation (Scheme 1).



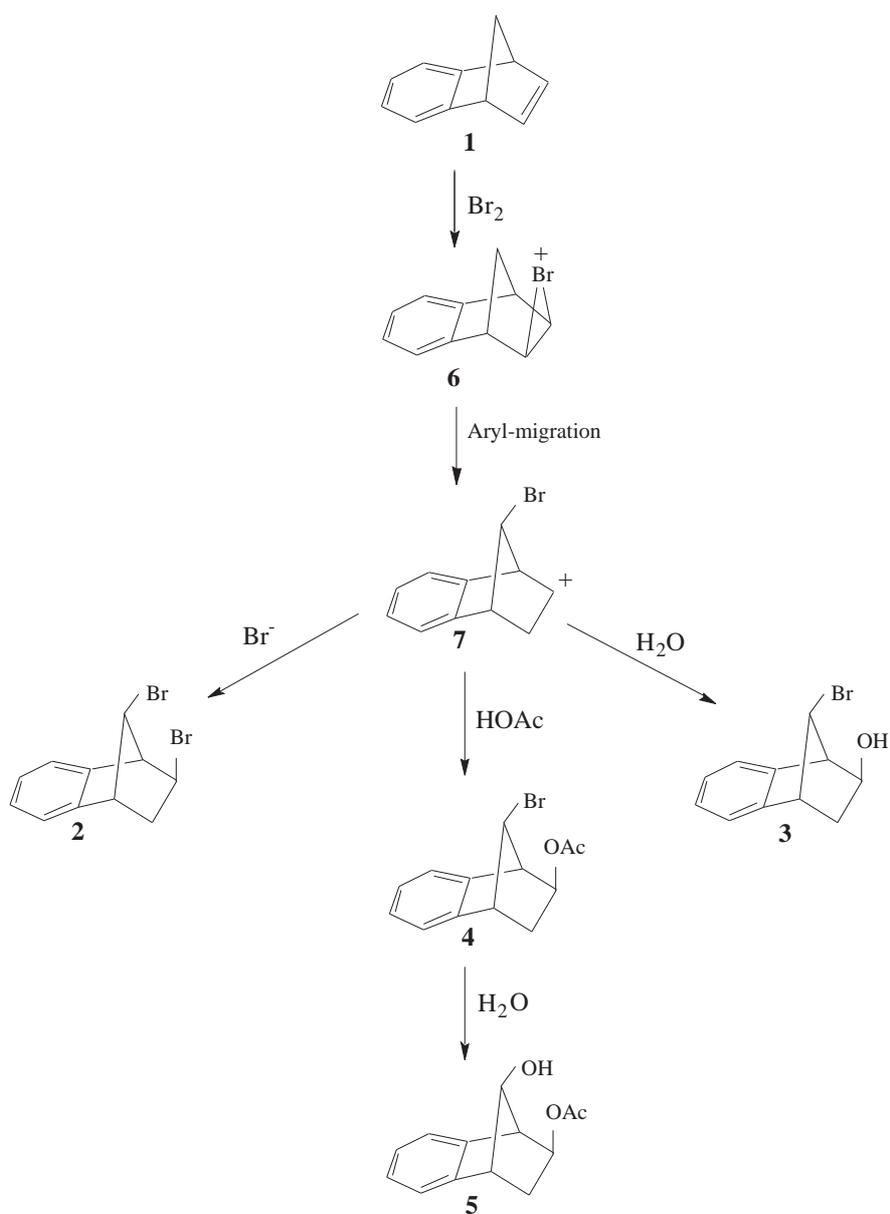
Scheme 1

The bromohydrin **3**⁶ was reported by Wilt and Chenier from **1** by treatment with bromine and water or by hydrolysis of **2** in the presence of CaCO₃. The other new products (**4** and **5**) have been fully characterized by ¹H and ¹³C NMR measurement and mass spectral data and the signal assignments were made by extensive double resonance experiments and comparison of the spectra with those of **2**.^{3d}

In order to test whether the isolated compounds **3-5** formed by bromination of **1** with sodium bromide-sodium perborate mixture in acetic acid are solvolysis products, we heated the dibromide **2** at 90°C under the given reaction conditions for 3 h and observed that the dibromide **2** is stable. Solvolysis of halogenated benzenorbornenes is well known but requires the assistance of a Lewis acid such as silver ion.^{6,7}

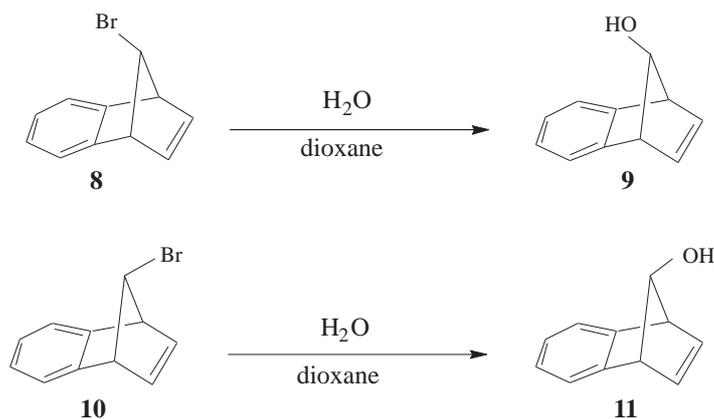
All products isolated by this reaction are Wagner-Meerwein type products and show skeleton rearrangement. Substituents are bonded in all products (**2-5**) at the C₉ carbon atom in the *exo* and at the C₁₁ carbon atom in the *anti* position. Indeed, we obtained in all cases 9-*exo*-11-*anti*-disubstituted benzenorborn-2-ene derivatives (**2-5**). On the basis of these results we think that an ionic mechanism is responsible for

the formation of **2-5** in the reaction of benzonorbornadiene (**1**) with sodium bromide-sodium perborate mixture in acetic acid at 90°C (Scheme 2). This is probably due to the polarity of the solvent used (HOAc), which stabilizes the ionic intermediates. According to this mechanism free molecular Br₂, which is formed by oxidation of sodium bromide with sodium perborate under the applied reaction conditions, adds to the double bond of **1** from the *exo*-face of the molecule to produce the *exo*-bromonium ion **6** and subsequent aryl migration gives the intermediate **7** with *anti*-brom configuration. Nucleophiles (Br⁻, HOAc and H₂O) then compete for bonding to the cationic center preferentially from the *exo*-side of the intermediate **7** to give **2-4**. Theoretical studies on the related systems revealed that electronic effects, like long-range homoconjugative stabilization and π/σ -interaction, play an important role in the determination of the origin of *exo*-selectivity.⁸



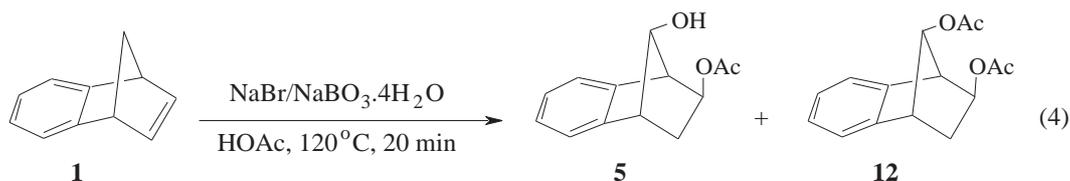
Scheme 2

The formation mechanism of the alcohol **5** is also given in Scheme 2. We assume that the primarily formed bromo acetate **4** partly hydrolyzes to the corresponding alcohol **5** with retention of configuration. Wilt and Chenier⁷ have reported that both *syn*- and *anti*-11-bromobenzonorbornadienes (**8** and **10**) hydrolyze with retention of configuration in aqueous dioxane (Scheme 3). They explained these experimental results in terms of the contrast in π -participation between aromatic and olefinic abilities to stabilize homoallylic cationic centers formed by ionization of **8** and its *anti* epimer **10**. Cristol and Nachtigall⁹ have also reported similar results in the acetolysis of chloro derivatives of **8** and **10**.

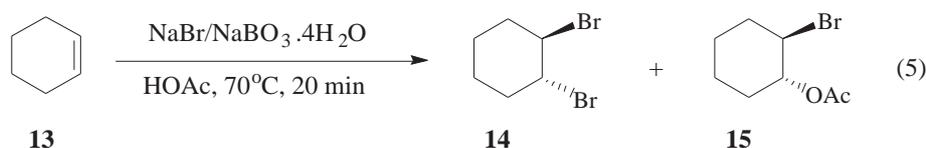


Scheme 3

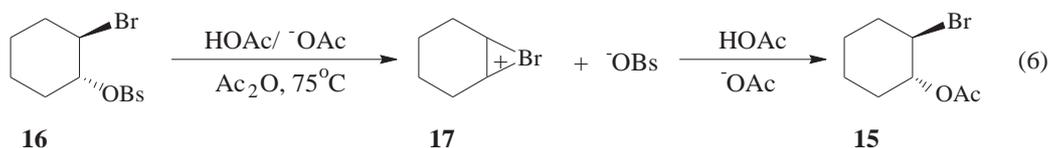
In order to see the temperature effect on product distribution at higher temperatures, benzonorbornadiene (**1**) was treated with a sodium bromide-sodium perborate mixture in glacial acetic acid at 120°C and two products were isolated, **5** and **12**, in yields of 59% and 2.7%, respectively (Eq. 4). No trace of compounds **2**, **3** or **4** was observed. We assume that the bromo acetate **4** is formed as the only product from the reaction at 120°C and then undergoes hydrolysis (as discussed above) and acetolysis to give alcohol **5** and diacetate **12**, respectively. The spectral data of **12** matched those reported in the literature.^{3d}



A similar product distribution was observed during high temperature bromination of cyclohexene as well as in the reaction of **1**. When cyclohexene (**13**) was reacted with this new bromination agent under conditions as described for **1** at 70°C, *trans*-1,2-dibromocyclohexane **14**¹⁰ and *trans* bromo acetate **15**¹¹ were isolated in 51% overall yield (Eq. 5). The *trans*-stereochemistry of **15** was determined by measuring the vicinal bromomethine-oxymethine coupling constant ($J = 10.6$ Hz).



Brown et al.¹¹ have reported that acetolysis of *trans* bromo brosylate **16** proceeds as in Eq. 6 to generate the cyclohexyl bromonium ion **17**, which captures -OAc (HOAc) to yield almost exclusively the *trans* bromo acetate **15**. This strongly supports the assumption that cyclohexyl bromonium ion **17** is formed in the reaction of cyclohexene (Eq. 5) as an intermediate that then undergoes capture by bromide ion (Br⁻) and HOAc to give **14** and **15** with *trans*-configuration, respectively.



Acknowledgments

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