

An Unusual Zinc-Promoted Reductive Retro-Wagner-Meerwein Rearrangement

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Received 10.6.1996

Bromination and dehydrobromination of exocyclic olefin **8** resulted in the formation of bromomethylene compound **9** and Wagner-Meerwein rearrangement product **10**. The dehydrobromination of **10** with potassium *tert*-butoxide provided the corresponding bromomethyl compound **11** in high yield. Reaction of **11** with Zn-Cu couple in methanol afforded the methyl derivative **12** and the parent olefin **8**. The unusual formation mechanism of **8** has been discussed in term of a reductive retro-Wagner-Meerwein rearrangement.

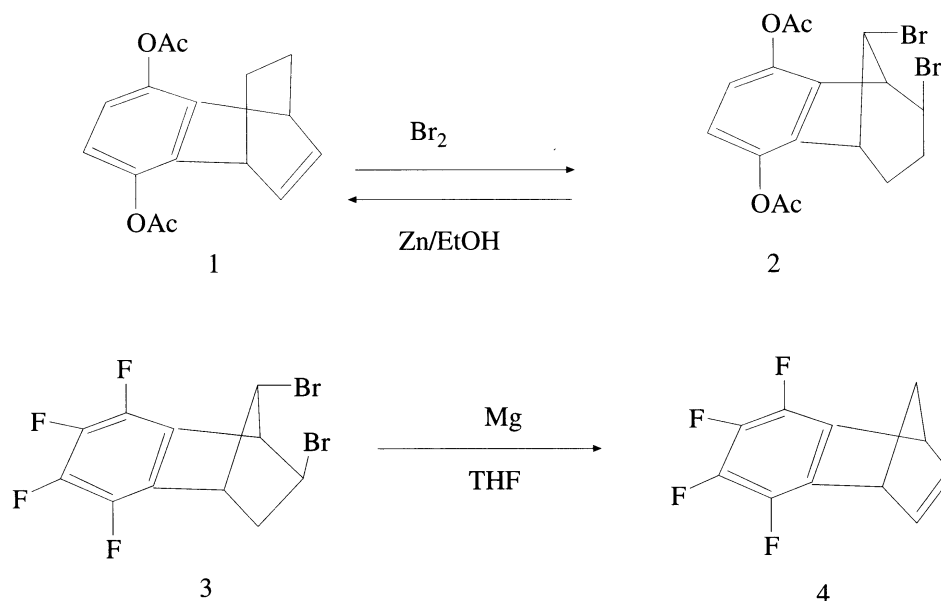
Introduction

The addition of bromine to unsaturated bicyclic systems may lead to a multiplicity of products. In the course of studying the bromination reactions of the unsaturated bicyclic systems, we noticed that the reaction temperature has a dramatic influence on product distribution¹. Bromination at room and lower temperatures give rearranged products via Wagner-Meerwein rearrangement with accompanying aryl and alky migration. However, the bromination of these hydrocarbons at higher temperatures (80-150 °C) resulted in the formation of non-rearranged products.

Smith et al.² have reported that the bromination of 5,8-diacetoxy-1,4-ethanonaphthalene **1** gives only one product, dibromide **2** produced via a Wagner-Meerwein rearrangement with accompanying aryl migration. Surprisingly, treatment of dibromide **2**, in which the bromines are not vicinally located, with zinc in ethanol provides a significant amount of returned starting olefin **1** (Scheme 1).

A similar result was obtained by Barkhash et al.³. Who observed that the rearranged dibromide, 2-*exo*-7-*anti*-dibromotetrafluorobenzonorborn-5-ene (**3**), when treated with magnesium in tetrahydrofuran gave back tetrafluorobenzonorbornadiene **4**, from which the dibromide had originated (Scheme 1).

In this paper, we describe a new system where similar rearrangements have been observed.



Scheme 1.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1 mm cells or KBr pellets for solids on a regular instrument. The ¹H and ¹³C NMR spectra were recorded on 60, 200, and 250 MHz spectrometers. Preparative thin-layer chromatography (TLC) was performed on silica gel 60₂₅₄ plates. Column chromatography was done on silica gel (60-200 mesh) from Merck Company. Benzonorbornadiene **5**⁷, and 2-methylenebenzonorbornene **8**^{4d} were prepared as reported.

exo-2-Benzonorborneol 6. Boron trifluoride etherate (22.7 g, 0.16 mol) was slowly added to a solution of benzonorbornadiene **5** (32.0 g, 0.16 mol) and sodium borohydride (4.56 g, 0.12 mol) in 150 mL of dry THF over the course of twenty minutes under nitrogen. The resulting suspension was stirred for 3 hours at 0 °C. The reaction mixture was subsequently treated with 3N NaOH (70 mL) and 30% H₂O₂ (80 mL) at 0 °C and then heated for 20 minutes at 30-50 °C. A major part of the THF was removed under reduced pressure and the residue extracted with ether. The ether extracts were washed with 2% sodium sulfite solution and water, and the organic layer was dried over MgSO₄. Evaporation of the ether gave 18.0 g (69%) of **6**, which crystallized on standing (mp 73-74 °C (Lit⁶ 74.5-75.5 °C). The NMR spectrum was identical to that reported⁶.

2-Benzonorbornenon 7. A solution of *exo*-2-benzonorborneol **6** (15 g, 93 mmol) in CH₂Cl₂ (50 mL) was added dropwise over 15-20 minutes to a stirred solution of PCC (22 g) in CH₂Cl₂ (100 mL) at 0 °C. After stirring at room temperature for 48 hours, the resulting brown solution was filtrated. The filtrate was extracted with CH₂Cl₂, washed with water, and dried over Na₂SO₄. After the solvent was removed, the residue was purified on a short silica gel column eluted with CH₂Cl₂ to give **7** (7.2 g, 48%) as an oily colorless liquid. The NMR spectrum was identical to that reported⁶.

Bromination and Dehydrobromination of 2-Methylenebenzonorbornene 8^{4d}. To a solution of **8** (700 mg, 4.48 mmol) in 20 mL of CCl₄, bromine (718 mg, 4.48 mmol) was added dropwise in 6 mL of CCl₄ at room temperature until the color persisted. Stirring was continued at room temperature for 15 minutes following the addition of bromine. The reaction mixture was washed with aqueous NaHSO₃ and

water. The organic layer was dried over MgSO_4 , and after filtration, the solvent was removed to give crude dibromide (1.23 g, 86%).

The crude dibromide was dissolved in a solution of 0.7 g of KOH in 20 ml of 95% ethanol, and the resulting solution was refluxed for 3 hours. Water was added, and the aqueous mixture was extracted with ether. The ether extracts were washed with water and dried over MgSO_4 . The ether was removed, and the residue (0.89 g) was subjected to preparative thin-layer chromatography (silica gel-petroleum ether) to give 230 mg (21%) of a 70/30 mixture of cis/trans isomer of **9**^{4d} and 280 mg (19%) of the Wagner-Meerwein rearranged product **10**. Following are data for the Wagner-Meerwein rearranged product **10**: ^1H NMR (250 MHz, CDCl_3) δ 7.51 (m, 1H, aromatic H), 7.14 (m, 3H, aromatic H), 4.16 (d, $J=10.7$ Hz, 1H), 4.04 (d, $J=10.7$ Hz, 1H), 4.01 (ddd, $J=7.3, 2.9, 2.0$ Hz, 1H), 3.34 (m, 1H), 2.53 (ddd, $J=13.5, 4.0, 3.0$ Hz, 1H), 2.28 (ddd, $J=13.5, 7.3, 2.2$ Hz, 1H), 2.23 (dd, $J=9.2, 1.4$ Hz, 1H), 2.04 (ddd, $J=9.2, 4.0, 1.9$ Hz, 1H); ^{13}C NMR (63 MHz, CDCl_3) δ 149.52, 142.97, 127.78, 126.55, 122.36, 121.00, 58.55, 54.95, 49.99, 44.85, 43.61, 34.54; IR (neat, cm^{-1}) 3065, 3020, 2940, 2865, 1470, 1460, 1245, 1215, 1105, 990, 940, 760.

Reaction of 1-Bromomethyl-2-*exo*-bromobenzonorbornene **10** with Potassium *tert*-Butoxide.

To a solution of **10** (0.200 g, 0.63 mmol) in 10 ml dry and freshly distilled THF was added 0.21 g (1.87 mmol) of potassium *tert*-butoxide at room temperature. The resulting reaction mixture was stirred for 4 hours at room temperature. The mixture was diluted with water, and the aqueous phase was extracted with petroleum ether. The combined organic layers were washed with water, dried over MgSO_4 , and evaporated to give the crude product (0.18 g) which was chromatographed over silica gel with petroleum ether yielding 0.14 g (94%) of **11** as a colorless liquid: ^1H NMR (250 MHz, CDCl_3) δ 7.22 (m, 2H), 6.96 (m, 2H), 6.86 (dd, $J=5.3, 3.1$ Hz, 1H), 6.60 (d, $J=5.3$ Hz, 1H), 4.14 (d, $J=10.5$ Hz, 1H), 4.01 (d, $J=10.5$ Hz, 1H), 3.88 (m, 1H), 2.44 (dd, $J=6.9, 1.6$ Hz, 1H), 2.25 (d, $J=6.9$ Hz, 1H); ^{13}C NMR (63 MHz, CDCl_3) δ 153.31, 150.81, 145.18, 143.61, 124.99, 124.70, 122.07, 120.59, 72.86, 61.96, 50.02, 33.07; IR (neat, cm^{-1}) 3060, 2970, 2930, 2860, 1450, 1320, 1245, 1230, 760, 730, 700.

Reduction of 1-(Bromomethyl)benzonorbornadiene **11 with Zn-Cu Couple.** To a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.69 g) in water (30 mL), Zn dust (0.76 g) was added with stirring. The resultant couple was allowed to settle, the supernatant was decanted, and the residue was washed sequentially with water and MeOH. The couple was suspended in MeOH (40 mL), which had been saturated with NH_4Cl , the bromide **11** (0.16 g, 0.68 mmol) was added, and the mixture was refluxed with stirring for 3 hours. The mixture was filtered, and the filtercake washed with ether. The combined filtrate was diluted with water, extracted with ether, and dried over CaCl_2 . The ether was removed, and the residue (80 mg) was subjected to preparative thin layer chromatography (silica gel-pentane) to give 60 mg (56%) of a 90/10 mixture of **12/8**. The spectral data of **12** matched those reported in the literature⁹.

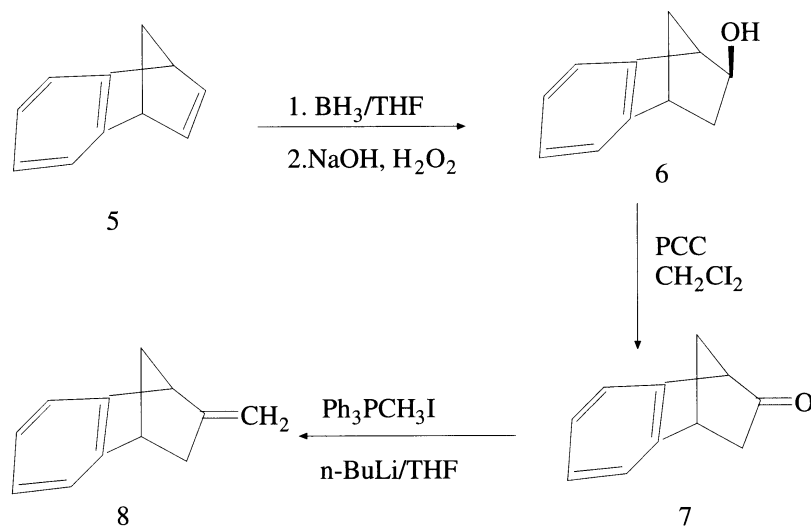
Reaction of 1-Bromomethyl-2-*exo*-bromobenzonorbornene **10 with Zn.** To a stirred solution of **10** (0.33 g, 1.04 mmol) in 15 mL of anhydrous DMSO was added 90 mg of Zn dust and a small amount of iodine. The reaction mixture was heated at a bath temperature of 90°C for 20 hours. After the mixture was cooled to room temperature, the insoluble materials were separated by filtration. The filtrate was diluted with water and extracted with ether. The combined ether extracts were washed with water and dried over MgSO_4 . The ether was removed in vacuo, and the residue was filtered over 30 g of silica gel eluting with *n*-hexane to give 78 mg (47%) of 2-methylenebenzonorbornene **8**.

Results and Discussion

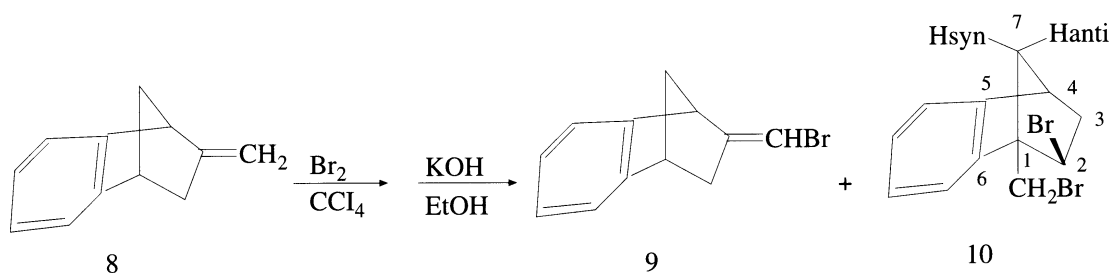
In connection with our studies on the strained bicyclic allenes and alkynes⁴, we were interested in the synthesis of exocyclic bromomethylene compound **9**. For this reason, we studied the bromination reaction of 2-methylenebenzonorbornene **8**.

Methylene compound **8**⁵ was synthesized as shown in Scheme 2. The ketone **7**⁶ was prepared by hydroboration of readily available benzonorbornadiene **5**⁷, followed by oxidation of *exo* alcohol **6**⁶. The ketone **7** was converted to the desired methylene compound **8** by Wittig reaction.

Bromination and dehydrobromination of **8** afforded an isomeric mixture of bromomethylene compound **9**^{4d} (21%, *cis*- and *trans*-isomer in a ratio of 7:3) and dibromide **10** in a yield of 19%, obviously formed by Wagner-Meerwein rearrangement⁸ (Scheme 3).



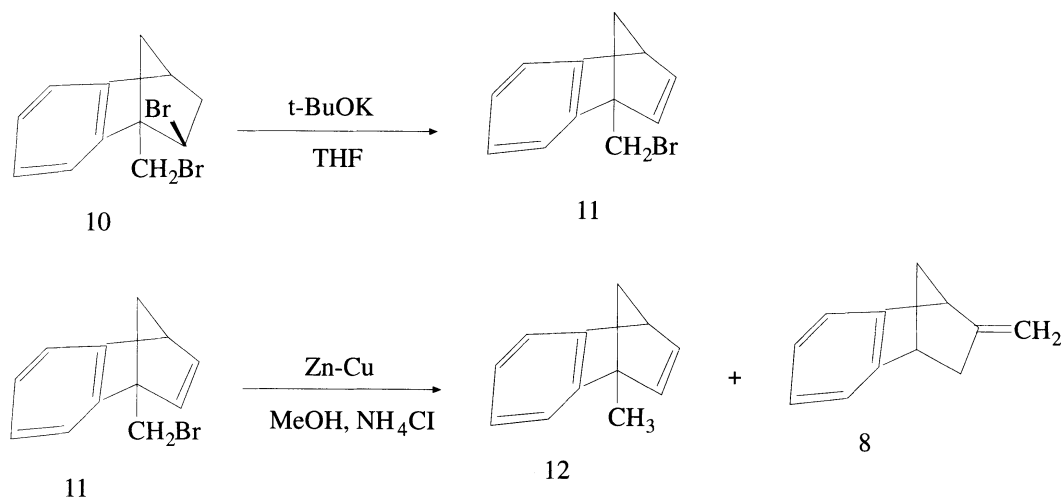
Scheme 2.



Scheme 3.

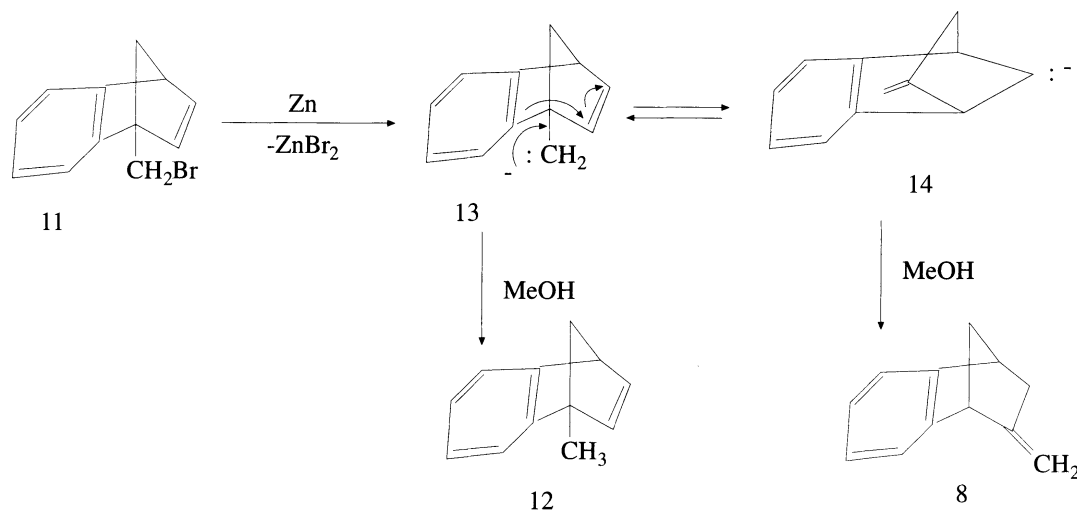
The structure of rearranged product **10** was determined by NMR spectral data. The interesting feature of its ¹H NMR spectra is the AB system arising from the bromomethyl protons (–CH₂Br) which are bonded to an asymmetric carbon atom. Both the A-part (down field resonance) and the B-part of the AB system give a doublet (*J*=10.7 Hz) at δ 4.16 and δ 4.04, respectively. The *exo* configuration of bromine at C₂ carbon atom has been established by means of long-range (⁴*J*) coupling between *H*₂ and *H*_{7syn} protons. In the case of ⁴*J* in the bicyclic systems, one speaks of the **M** or **W** arrangement. In **10** the bonding arrangement of the coupled protons *H*₂ and *H*_{7syn} meets the **M** criterion. The fact that there is any measurable coupling between *H*₂ and *H*_{7syn} (⁴*J*_{27syn} = 2.0 Hz) is an indication for the *exo* configuration of the bromine atom at C₂. ¹³C NMR data was also consistent with the proposed structure showing 6 aliphatic and 6 aromatic carbons.

The structure of **10** was also supported by chemical transformation. When **10** was subjected to dehydrobromination by potassium *tert*-butoxide, **11** was obtained nearly in quantitative yield (94%), as shown in Scheme 4. For further characterization, we converted the bromomethyl compound **11** into the known compound **12**⁹ by reduction with Zn-Cu couple in MeOH containing NH₄Cl. Surprisingly, the reduction was accompanied by a small amount (10%) of the parent methylene hydrocarbon **8**.



Scheme 4.

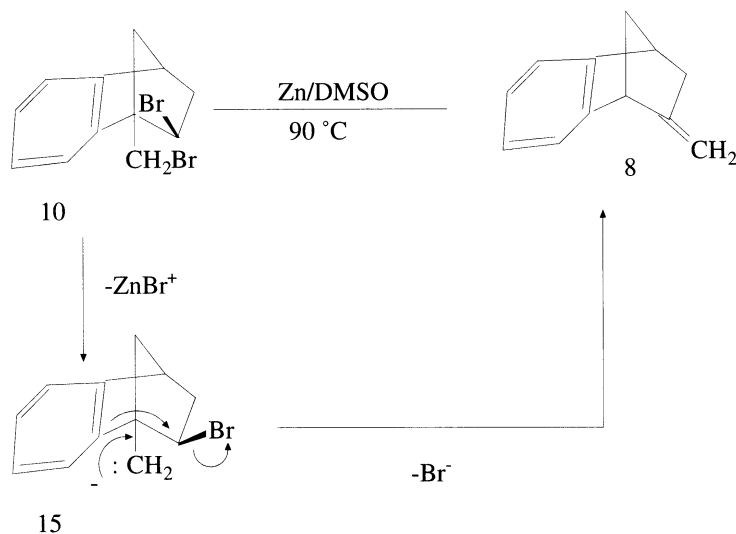
Methyl compound **12** was the expected product in this reaction, but **8** is totally unexpected and unusual and is probably formed via a carbanionic rearrangement. To the best of our knowledge, this is the first observation of a reductive retro-Wagner-Meerwein rearrangement. For this unprecedented rearrangement we suggest the following mechanism (Scheme 5). Bromomethylbenzonorbornadiene **11** is initially converted to the corresponding anion **13**, which then undergoes Wagner-Meerwein rearrangement with accompanying aryl migration to give the anion **14**. Subsequent protonation of these formed anions **13** and **14** afford the final products **12** and **8** (Scheme 5).



Scheme 5.

On the other hand, treatment of the rearranged dibromide **10** with zinc in DMSO (an aprotic solvent) at 90°C yielded the tarting olefin **8** as the sole product in a yield of 47% (Scheme 6). A similar mechanism involving the anion **15** can be considered for this rearrangement (Scheme 6). Initially formed carbanion **15**

can form the exocyclic methylene compound **8**, where electrons act as a nucleophile by substitution of the remaining bromine atom as bromide. This observation is in accordance with results obtained by Smith² and Barkhash³ (Scheme 1).



Scheme 6.

Acknowledgement

We are indebted to the Department of Chemistry (Atatürk University) for financial support of this work and the State Planning Organization of Turkey (DPT) for purchasing a 200 MHz NMR spectrometer.

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