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Reactions of Alkenes with Sodium Perborate and Sodium Chloride

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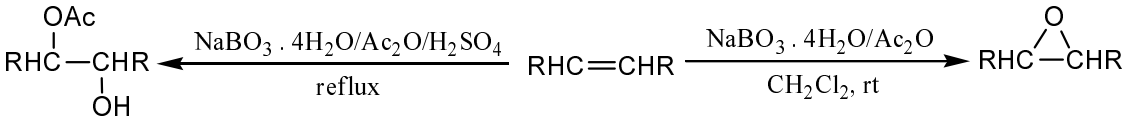
Sodium perborate oxidatively chlorinates a variety of alkenes with sodium chloride to form the corresponding chloro derivatives under mild conditions.

Key Words: Alkenes, acetoxy alcohols, chlorohydrins, sodium perborate, sodium chloride.

Introduction

Sodium perborate ($NaBO_3$. nH_2O, n=1-4) has been found to be an excellent reagent for the oxidation of a wide class of organic compounds. It is an inexpensive, stable and easily handled oxidant and is often used in acetic acid or other carboxylic acids in synthesis.[1] Sodium perborate and acetic anhydride oxidize alkenes into oxiranes or vicinal acetoxy alcohols under different reaction conditions (Scheme 1). A wide range of acyclic and cyclic alkenes have been converted to the corresponding epoxides and acetoxy alcohols by sodium perborate oxidations.[2]



Scheme 1

Kabalka et al.[3] have used a combination of sodium perborate and sodium bromide in acetic acid for the bromination of alkenes[3a] and alkynes[3b] and obtained the corresponding vicinal dibromo alkanes and *trans*-dibromo alkenes in good yields (Scheme 2). At high temperatures, bromination of alkenes results predominantly in the formation of solvolytic bromo derivatives, such as bromohydrines, bromo acetates, and acetoxy alcohols, by using this new bromination agent.[4]

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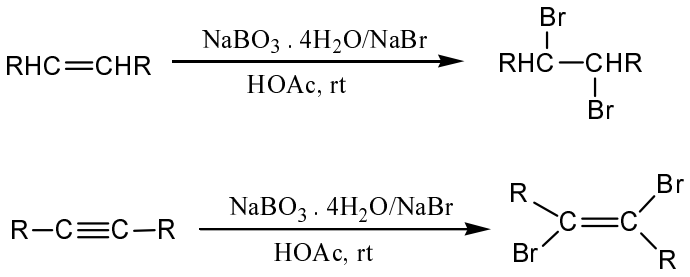
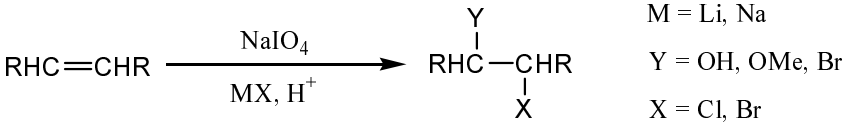


Scheme 2

Sudalai and co-workers[5] have reported similar results with sodium periodate oxidations. Sodium periodate oxidatively halogenates a variety of olefins with alkali metal halides as the halogen source. This method provides the 1,2-functionalization of olefins by the addition of 2 different functional groups, such as water or alcohols and halogens (halohydroxylation or haloalkoxylation) (Scheme 3).



Scheme 3

In the present work, we report that sodium perborate oxidatively chlorinates a variety of alkenes with sodium chloride as the chlorine source to form the chloro derivatives under mild conditions.

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. ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)-MHz spectrometers. Column chromatography was performed on silica gel 60 (70-230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. NaCl was purchased commercially from Merck. Benzonorbornadiene **4**[8] was prepared as reported.

Reaction of Cyclohexene with Sodium Perborate and Sodium Chloride. 1.75 g (30.0 mmol) of sodium chloride was added to a mixture of sodium perborate (2.30 g, 15.0 mmol) and cyclohexene (1.10 g, 13.4 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 $NaHCO_3$ solution and water and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed over silica gel. Elution with hexane-ethyl acetate (90:10) gave as the first fraction *trans*-2-chlorocyclohexanol (**2**)[6] (0.40 g, 22%, pale yellow oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.73 (ddd, J = 11.4, 9.2, 4.4 Hz, 1H, H_2), 3.51 (dt, J = 5.6, 9.2 Hz, 1H, H_1), 2.68 (br s, 1H, OH), 2.26-2.01 (m, 2H), 1.76-1.52 (m, 3H), 1.45-1.18 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 77.12, 69.14, 37.04, 34.94, 27.64, 25.98.

Continued elution with the same solvent mixture afforded *trans*-2-hydroxycyclohexyl acetate (**3**)[6,7] (0.52 g, 25%, pale yellow oil) as the second fraction. Comparison of the spectral data of **3** (partly ^{1}H NMR and IR) with those reported in the literature[7] showed that they were in agreement. ^{1}H NMR (200 MHz,

$CDCl_3$) δ 4.52 (m, 1H, H_1), 3.50 (m, 1H, H_2), 2.56 (br s, 1H, OH), 2.04 (s, 3H, CH_3), 1.97 (m, 2H), 1.65 (m, 2H), 1.41-1.15 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.22, 80.08, 74.54, 35.05, 31.94, 25.84, 25.74, 23.23.

Reaction of Benzonorbornadiene 4 with Sodium Perborate and Sodium Chloride. The reaction was carried out at room temperature for 3 h as described above using 2.0 g (14.1 mmol) of benzonorbornadiene (**4**), 2.30 g (15.0 mmol) of sodium perborate, 1.75 g (30.0 mmol) of sodium chloride 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-ethyl acetate (90:10) gave as the first fraction *exo*, *anti*-11-chlorotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-9-ol (**5**) (0.13 g, 5%): colorless crystals, mp 100-101 ^{o}C from ether; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21-7.08 (m, 4H, ArH), 4.01 (m, 1H, H_{11}), 3.91 (bdd, J = 8.3, 3.7 Hz, 1H, H_9), 3.47 (m, 1H, H_8), 3.36 (m, 1H, H_1), 2.88 (m, 1H, OH), 2.50 (dt, A part of AB system, J = 13.5, 3.7 Hz, 1H, H_{10exo}), 2.18 (bdd, B part of AB system, J = 13.5, 7.7 Hz, 1H, H_{10endo}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.27, 143.30, 129.47, 128.67, 124.38, 124.07, 86.67, 60.29, 57.58, 51.19, 39.11; IR ($CHCl_3$) 3460, 3024, 2401, 1522, 1432, 1220, 1085, 790, 752, 674 cm^{-1}.

Continued elution with the same solvent mixture afforded *exo*, *anti*-11-hydroxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-9-yl acetate (**6**)[4] as the second fraction (1.125 g, 41%): colorless crystals, mp 69-70 ^{o}C (Lit.[4] 69.5-70 ^{o}C) from ether-hexane. The ^{1}H NMR, ^{13}C NMR, and IR spectral data for **6** are identical with those reported in the literature.[4]

Reaction of Styrene with Sodium Perborate and Sodium Chloride. The reaction was carried out at room temperature for 24 h as described above using 1.46 g (14.0 mmol) of styrene, 2.30 g (14.9 mmol) of sodium perborate, 1.75 g (29.9 mmol) of sodium chloride and 25 mL of glacial acetic acid and after work-up the residue (1.50 g) was chromatographed over silica gel (110 g). Elution with hexane-ethyl acetate (97:3) gave [(E)-2-chloroethenyl]benzene (**8**)[10] as the first fraction (0.27 g, 14%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15 (br s, 5H, ArH), 6.67 (d, A part of AB system, J = 13.6 Hz, 1H, olefinic), 6.46 (d, B part of AB system, J = 13.6 Hz, 1H, olefinic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.26, 130.72 (2C), 130.06, 128.07 (3C), 120.70.

Continued elution with the same solvent mixture afforded (1,2-dichloroethyl)benzene (**9**)[10] as the second fraction (0.25 g, 10%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (br s, 5H, ArH), 4.83 (dd, J = 8.1, 6.5 Hz, 1H, benzylic), 3.85 (dd, A part of AB system, J = 11.5, 6.5 Hz, 1H, methylenic), 3.76 (dd, B part of AB system, J = 11.5, 8.1 Hz, 1H, methylenic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.10, 131.02, 130.71 (2C), 129.42 (2C), 63.58, 50.19.

Continued elution with the same solvent mixture afforded 2-chloro-1-phenylethyl acetate (**10**) as the third fraction (0.42 g, 15%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37 (m, 5H, ArH), 5.96 (dd, J = 7.7, 4.8 Hz, benzylic), 3.90-3.62 (m, 2H, methylenic), 2.16 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.19, 139.32, 130.71, 130.62 (2C), 128.65 (2C), 76.99, 48.30, 22.78; IR ($CHCl_3$) 3063, 3024, 2966, 1965, 1894, 1740, 1496, 1464, 1375, 1240, 1027 cm^{-1}.

Continued elution with hexane-ethyl acetate (95:5) afforded 2-chloro-1-phenylethanol (**11**)[11] as the fourth fraction (80 mg, 4%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38 (m, 5H, ArH), 4.88 (dd, J = 8.4, 3.7 Hz, 1H, benzylic), 3.74 (dd, A part of AB system, J = 11.1, 3.8 Hz, 1H, methylenic), 3.63 (dd, B part of AB system, J = 11.1, 8.4 Hz, 1H, methylenic), 2.81 (m, 1H, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ

142.04, 130.56 (2C), 130.32, 128.02 (2C), 76.05, 52.75.

Continued elution with the same solvent mixture afforded 2-chloro-2-phenylethanol (**12**)[12] as the fifth fraction (50 mg, 2%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52-7.24 (m, 5H, ArH), 4.97 (t, J = 6.6 Hz, 1H, benzylic), 4.09-3.78 (m, 2H, methylenic), 2.32 (m, 1H, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.01, 130.69 (2C), 130.55, 129.45 (2C), 69.86, 66.66.

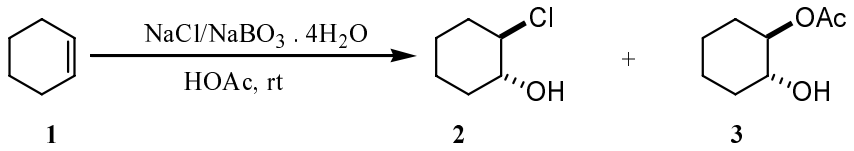
Continued elution with the same solvent mixture afforded 2-hydroxy-2-phenylethyl acetate (**13**)[13] as the sixth fraction (0.12 g, 5%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31 (m, 5H, ArH), 4.86 (dd, J = 8.1, 3.7 Hz, 1H, benzylic), 4.18 (dd, A part of AB system, J = 11.5, 3.7 Hz, 1H, methylenic), 4.09 (dd, B part of AB system, J = 11.5, 8.1 Hz, 1H, methylenic), 3.65 (m, 1H, OH), 2.03 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.90, 142.08, 130.44 (2C), 130.02, 128.13 (2C), 74.12, 71.23, 22.74.

Further elution with the same solvent mixture yielded 2-hydroxy-1-phenylethyl acetate (**14**)[13] as the last fraction (0.10 g, 4%, colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33 (m, 5H, ArH), 5.83 (dd, J = 7.1, 4.6 Hz, 1H, benzylic), 3.88-3.71 (m, 2H, methylenic), 3.24 (m, 1H, OH), 2.12 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.31, 139.23, 130.48 (2C), 130.24, 128.65 (2C), 78.78, 67.72, 22.99.

Acetylation of 2-Chloro-2-phenylethanol 12. To a stirred solution of chloro alcohol **12** (30 mg, 0.19 mmol) in 10 mL of CH_2Cl_2 was added acetyl chloride (0.15 g, 1.9 mmol) and the reaction mixture was stirred at room temperature for 24 h. After evaporation of the solvent and excess acetyl chloride, the residue was filtered on a short silica gel column eluted with hexane-ethyl acetate (97:3) to give 32 mg (84%) of 2-chloro-2-phenylethyl acetate **15** (colorless oil): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37 (m, 5H, ArH), 5.04 (t, J = 6.9 Hz, 1H, benzylic), 4.42 (d, J = 6.9 Hz, 2H, methylenic), 2.07 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.75, 139.72, 130.81, 130.67 (2C), 129.36 (2C), 69.83, 61.40, 22.55; IR ($CHCl_3$) 3055, 2927, 1753, 1523, 1472, 1395, 1242, 1036, 782, 706 cm^{-1}.

Results and Discussion

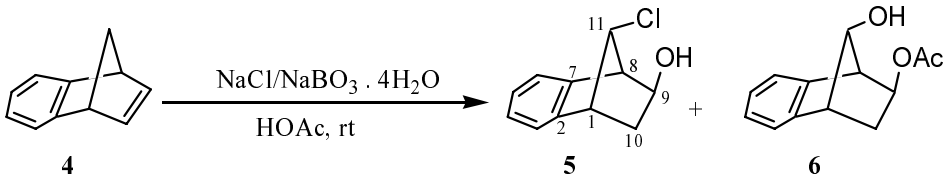
For the oxidative chlorination we chose a cyclic (cyclohexene), a bicyclic (benzonorbornadiene) and an acyclic (styrene) alkene. Reaction of cyclohexene with a mixture of sodium chloride and sodium perborate in glacial acetic acid at room temperature gave the known chlorohydrin **2**[6] and acetoxy alcohol **3**[6,7] in yields of 22% and 25%, respectively (Scheme 4). The trans-stereochemistry of **2** was determined by measuring the vicinal chloromethine-oxymethine coupling constant (J = 11.4 Hz). The spectral data (partly ^{1}H NMR and IR) of **3** matched those reported in the literature[7].



Scheme 4

A similar product distribution was observed during the oxidative chlorination of benzonorbornadiene **4**[8] as well as in the reaction of cyclohexene. Benzonorbornadiene **4** was prepared as reported[8] and reacted with a mixture of sodium chloride and sodium perborate under conditions as described for **1,** and 2 rearranged

products were isolated, **5** and **6**[4], in yields of 5% and 41%, respectively (Scheme 5). This was not a surprise because of the great tendency of benzonorbornadiene **4** to undergo Wagner-Meerwein rearrangement during electrophilic addition reactions.[9]



4 **5** **6**

Scheme 5

The structure of the chlorohydrin **5** has been elucidated on the basis of ^{1}H and ^{13}C NMR and extensive double resonance experiments and by comparison of the spectral data with those of the bromo derivative[4] of **5**. We have studied[4] the bromination of benzonorbornadiene **4** with a sodium bromide-sodium perborate mixture in acetic acid at high temperatures (90 and 120 ^{o}C) and obtained the acetoxy alcohol **6** as the major product and the formation mechanism was discussed in detail. We assume that the acetoxy alcohol **6** in the oxidative chlorination of **4** is formed by a similar mechanism discussed therein.[4]

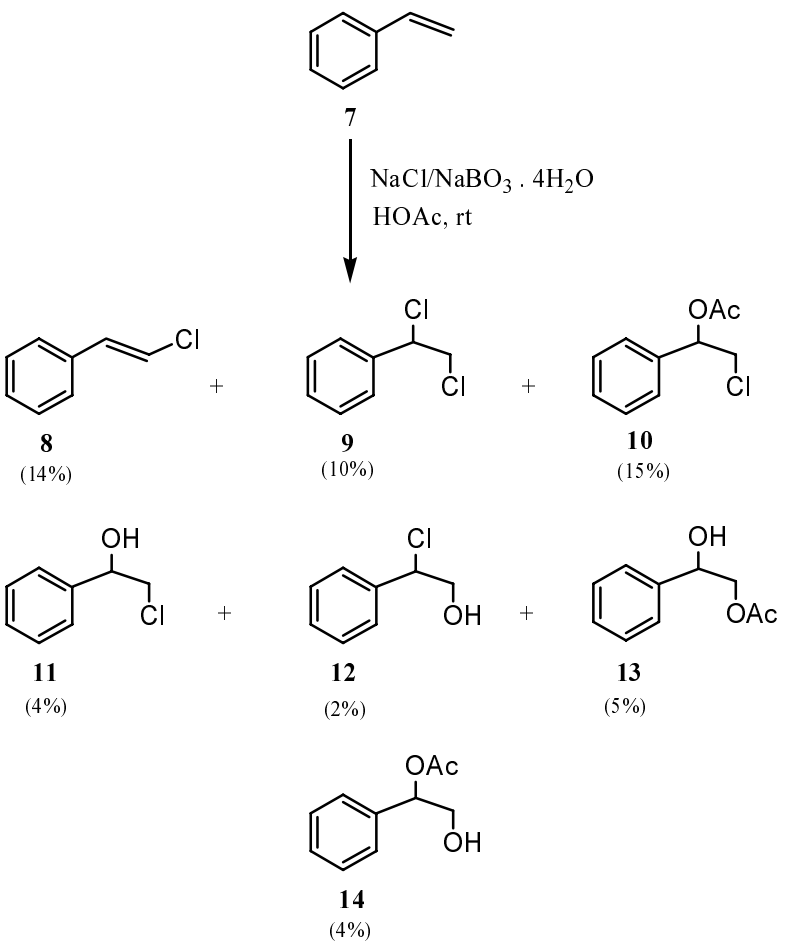
We also reacted styrene with a mixture of sodium chloride and sodium perborate in glacial acetic acid at room temperature. NMR analysis of the crude product indicated that the reaction mixture was very complex. After careful chromatographic separation we isolated 7 products, **8-14**, in a 54% total yield (Scheme 6).

The structures of the products were elucidated on the basis of ^{1}H, and ^{13}C NMR data and chemical transformations and by comparison of the spectral data with those reported in the literature.

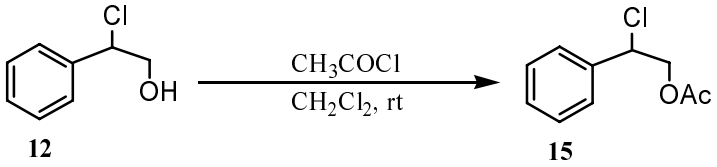
As the major products we isolated dichloride **9**[10] and vinyl chloride **8**.[10] These type products were not observed by the reaction of cyclohexene and benzonorbornadiene (**4**) in any trace. We assume that molecular chlorine, which is formed by the oxidation of sodium chloride with sodium perborate under the applied reaction conditions, adds to the double bond of styrene to produce the *vic*-dichloride **9**. Subsequent HCl elimination from the initially formed *vic*-dichloride **9** is responsible for the formation of vinyl chloride **8**. The trans-stereochemistry of vinyl chloride **8** was determined by measuring the vicinal coupling constant (J = 13.6 Hz). The structure of dichloride **9** was determined using NMR spectral data. The interesting feature of its ^{1}H NMR spectra is the AB system arising from the chloromethyl protons ($-CH_2Cl$), which are bonded to an asymmetric carbon atom. Both the A part (downfield resonance) and the B part of the AB system give a doublet of doublets at δ 3.85 (J = 11.5, 6.5 Hz) and δ 3.76 (J = 11.5, 8.1 Hz), respectively. The same characteristic AB system was also observed in the ^{1}H NMR spectra of compounds **11** and **13**.

Chloro acetate **10** was also obtained from this reaction in 15% yield and its structure was established unambiguously using ^{1}H and ^{13}C NMR spectra. ^{13}C NMR data were consistent with the proposed structure showing 3 aliphatic, 6 aromatic and 1 carbonyl carbons.

We also isolated all possible chlorohydrins (**11**[11] and **12**[12]) and acetoxy alcohols (**13**[13] and **14**[13]) from this reaction as minor products. The chlorohydrin **12** was converted to its acetate for further characterization and the other isomeric chloro acetate **15** was obtained in high yield (84%) (Scheme 7). The structure of **15** was determined on the basis of spectral data.



Scheme 6



Scheme 7

Acknowledgments

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