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Quaternary Ammonium Periodate as a New Oxidizing Agent

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Synopsis. Quaternary ammonium periodate has been found to be a useful oxidizing agent to convert a 1,2-diol and an olefin to the corresponding carbonyl compound in anhydrous aprotic solvents. The resulting carbonyl compounds have been reacted with alkyllithium to prepare alcohols in one-pot from a 1,2-diol or an olefin.

Sodium and potassium periodate are useful oxidants to convert sulfides and 1,2-diols to the corresponding sulfoxides and carbonyl compounds. The necessity of employing water as a solvent or as a cosolvent mixed with an organic solvent such as methanol, however, places some restrictions on the use of periodates.1)

In order to overcome the restrictions, the alkali salt has been converted to the quaternary ammonium salt. The quaternary ammonium periodate does not require water to oxidize a 1,2-diol and an olefin to the corresponding carbonyl compounds in aprotic solvents.

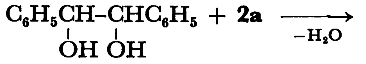
Three quaternary ammonium periodates (**2a**—**c**) were readily prepared from equimolar quantities of sodium periodate and the corresponding quaternary ammonium halides (**1a**—**c**) in aqueous solutions at 0 °C.

$$\mathrm{NaIO_4} + [\mathrm{R^1R^2R^3R^4N}]^+\mathrm{X^-} \xrightarrow{-\mathrm{NaX}} [\mathrm{R^1R^2R^3R^4N}]^+\mathrm{IO_4}^-$$

1a; $R^1 = CH_3(CH_2)_{15}$, $R^2 = C_6H_5CH_2$ **2a**; 90%
R^3, $R^4 = CH_3$, X = Cl
1b; $R^1 = C_6H_5CH_2$, R^2, R^3, $R^4 = CH_3CH_2$ **2b**; 84%
X = Br
1c; R^1, R^2, R^3, $R^4 = CH_3(CH_2)_3$, X = Br **2c**; 94%

Each compound has similar oxidizing ability,2) but benzylhexadecyldimethylammonium periodate (**2a**) was used in the following experiments since **2c** changed color yellow on storage at room temperature and **2b**, although readily soluble in dichloromethane, is sparingly soluble in ethereal solvents such as THF and dioxane.

2a was allowed to react with an equimolar amount of *dl*-1,2-diphenyl-1,2-ethanediol (**3dl**) in refluxing THF for 6 h, and almost all the **3dl** disappeared on TLC and a new spot of benzaldehyde appeared. The resulting benzaldehyde was isolated as a semicarbazone (81% yield).



$$\underset{\mathrm{OH}}{\mathrm{C_6H_5CH}}\text{-}\underset{\mathrm{OH}}{\mathrm{CHC_6H_5}} + \mathbf{2a} \xrightarrow[-\mathrm{H_2O}]{}$$

3dl

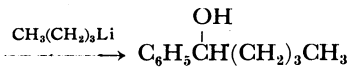
$$2\mathrm{C_6H_5CHO} + [\mathrm{CH_3(CH_2)_{15}N(CH_3)_2CH_2C_6H_5}]^+\mathrm{IO_3}^-$$

81% **4**
(as semicarbazone)

The above reaction produces one equivalent of water, and so the oxidation was conducted in the presence of molecular sieves to remove the water. The resulting benzaldehyde (**5**) was subsequently allowed to react with an alkyllithium to give the corresponding alcohol in one-pot. For example, a mixed solution of **3dl** and **2a** in dioxane was refluxed in the presence of molecular sieves3) for 2 h and the resulting benzaldehyde

$$\mathbf{3dl} + \mathbf{2a} \longrightarrow [\mathrm{C_6H_5CHO}]$$

5

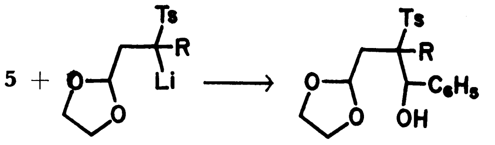


$$\xrightarrow{\mathrm{CH_3(CH_2)_3Li}} \overset{\mathrm{OH}}{\mathrm{C_6H_5CH}}\mathrm{(CH_2)_3CH_3}$$

6, 71%

was treated with butyllithium without isolation to give 1-phenyl-1-pentanol (**6**) (71% yield).

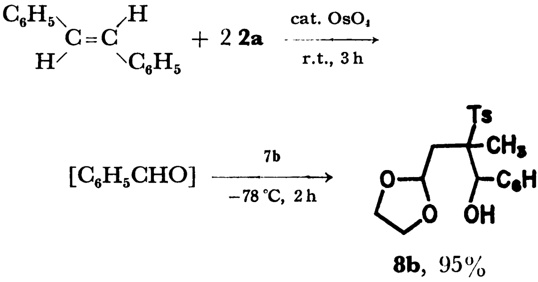
Similarly the alcohol **8a**, **b**,4) precursors of furan derivatives, were prepared from **3** and the corresponding alkyllithiums **7a**, **b**5,6) in good yields.



7a, R = H **8a**, 82% from **3meso**
7b, R = CH_3 **8b**, 87% from **3meso**
84% from **3dl**

Pappo *et al.* have reported a procedure for the cleavage of olefinic bonds with sodium periodate and a catalytic amount of osmium tetraoxide. It was noted that water was required in all the reactions to effect hydrolysis of the intermediary osmate ester.7) Consequently **2a** was used in the place of sodium periodate in this procedure in anhydrous aprotic solvents.

To a mixture of *trans*-stilbene and two molar quantities of **2a** in dioxane was added a catalytic amount of osmium tetraoxide at room temperature under nitrogen. The clear solution became green and then yellow and accompanied by the precipitation of **4**. After stirring for 3 h at room temperature and subsequent addition of THF, the reaction mixture was cooled to −78 °C and allowed to react with alkyllithium **7b** to give the expected alcohol **8b** (95% yield from stilbene).



8b, 95%

This oxidation reaction was also conducted with equimolar quantities of *trans*-stilbene and **2a** and 36% of the stilbene was recovered and 51% of benzaldehyde (as semicarbazone) was obtained. The diol **3** was not detected on TLC.

From the above results, it is evident that water is not required in the oxidative cleavage of a diol or an olefin with quaternary ammonium periodate in aprotic solvents. Work is now in progress to determine the scope and limitation of this oxidation reaction.

Experimental

All melting points are uncorrected. The NMR and IR spectra were recorded on JEOL JNM/MH-60 and JASCO IRA-1 spectrometers, respectively.

Materials. All the solvents were distilled according to the standard methods and stored over a drying agent. Thin-layer chromatography (TLC) was performed on Merck's Kieselgel 60 PF_{254} (Art. 7749).

*Benzylhexadecyldimethylammonium Periodate (**2a**).* Benzylhexadecyldimethylammonium chloride (**1a**, 2.407 g, 6 mmol) and sodium periodate (1.070 g, 6 mmol) were dissolved in a minimal amount of water, respectively, and mixed at 0 °C. Whereby a white precipitate separated out immediately. After vigorous stirring for 30 min, the precipitated **2a** was filtered and dried under vacuum (3.168 g, 96%, mp 74—77 °C). Recrystallization from benzene–hexane gave pure **2a** (90% yield; 2.963 g). Mp 76—77 °C. Found: C, 54.15; H, 8.46; N, 2.54%. Calcd for $C_{25}H_{46}INO_4$: C, 54.44; H, 8.41; N, 2.54%.

In a similar manner, **2b** and **2c** were prepared from the corresponding quaternary ammonium halides and sodium periodate in excellent yields.

2b: Mp 149—150 °C. Found: C, 40.66; H, 5.79; N, 3.71%. Calcd for $C_{13}H_{22}INO_4$: C, 40.73, H, 5.74; N, 3.66%.

2c: Mp 193 °C (dec). Found: C, 44.18; H, 8.58; N, 3.30%. Calcd for $C_{16}H_{36}INO_4$: C, 44.34; H, 8.37; N, 3.23%.

*Reaction of **2a** with **3dl**.* A mixed solution of **3dl** (107 mg, 1/2 mmol) and **2a** (304 mg, 1.1/2 mmol) in THF (7 ml) was refluxed for 6 h under nitrogen. After evaporation of the solvent, the residue was partitioned between ether and water. To the ethereal layer was added a solution of semicarbazide hydrochloride (112 mg, 1 mmol) in water–methanol followed by the addition of several drops of pyridine and the mixture worked up in the usual way to give benzaldehyde semicarbazone (81% yield, 131 mg). Mp 223—224 °C (lit, 224—225 °C).

*1-Phenyl-1-pentanol (**6**).* A mixed solution of **3dl** (107 mg, 1/2 mmol) and **2a** (304 mg, 1.1/2 mmol) in dioxane (4 ml) was refluxed for 2 h in the presence of molecular sieves[3] under nitrogen. After the addition of THF (10 ml) at room temperature (the precipitated benzylhexadecyldimethylammonium iodate (**4**) was dissolved), the reaction mixture was cooled to −78 °C followed by the addition of butyllithium (1.1 mmol) and allowed to warm to room temperature and kept overnight. After the addition of buffer solution (pH 7) and filtration, the filtrate was evaporated to remove the organic solvent and saturated with sodium chloride followed by extraction with ether. The crude residue obtained by evaporation of the extract was subjected to preparative TLC (ethyl acetate/hexane=1/5) to give the expected alcohol **6** (116 mg, 71% yield). The compound exhibited IR and NMR spectral data in accordance with assigned structure.

Oxidative Cleavage of trans-*Stilbene with **2a**.* To a mixed solution of *trans*-stilbene (90 mg, 1/2 mmol) and **2a** (606 mg, 2.2/2 mmol) in dioxane (2 ml) was added a catalytic amount of osmium tetraoxide (*ca.* 1.5 mg) dissolved in dioxane (2 ml) at room temperature under nitrogen. The clear solution became green and then yellow accompanied by the precipitation of **4**. After stirring for 3 h at room temperature followed by the addition of THF (10 ml), the reaction mixture was cooled to −78 °C and the lithium salt **7b** (1.1 mmol, THF solution) added. The pale yellow mixture was stirred for 2 h at −78 °C and treated with pH 7 buffer solution at −78 °C. After the similar work-up as described above, the expected alcohol **8b** (345 mg)[4] was obtained in a 95% yield from stilbene.

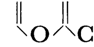
References

1) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Inc., Calfornia (1972), p. 353.

2) For example, when **2b** was reacted with an equimolar amount of **3** in dichloromethane at room temperature for 24 h under nitrogen, benzaldehyde was obtained in good yield (85% from **3dl** and 88% from **3meso** as semicarbazone, respectively).

3) Molecular Sieves 4A 1/16 from Wako Pure Chem. Ind. Ltd.

4) **8a** and **8b** consist of two diastereoisomers, respectively. The corresponding furan derivatives **9a** and **9b** were obtained by refluxing in dry benzene containing a trace of *p*-toluenesulfonic acid (see also Refs. 5 and 6). **9a** (R=H): 58% (from **8a**), oil, IR 1595, 1570, 1160, 1010, 900, 760 cm^{-1}; NMR (CCl_4) δ 6.51 (q, 1H), 6.69 (d, 1H), 7.2—7.9 (m, 6H). **9b** (R=CH_3): 63% (from **8b**), oil, IR 1600, 1590, 1160, 1060, 885, 760 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 3H), 6.20 (d, 1H, J=2 Hz), 7.05—7.70 (m, 6H).



9a, b

5) K. Inomata, S. Aoyama, and H. Kotake, *Bull. Chem. Soc. Jpn.*, **51**, 930 (1978).

6) H. Kotake, K. Inomata, H. Kinoshita, S. Aoyama, and Y. Sakamoto, *Heterocycles*, **10**, 105 (1978).

7) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Jonson, *J. Org. Chem.*, **21**, 478 (1956).