Novel Applications of Sodium Perborate to the Oxidation of Aromatic Aldehydes, α-Hydroxycarboxylic Acids, 1,2-Diketones, α-Hydroxyketones, 1,2-Diols and Some Unsaturated Compounds

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Sodium perborate in acetic acid at 95 °C oxidizes aromatic aldehydes, α-hydroxycarboxylic acids, 1,2-diketones, benzoin, 1,2-diols, and some unsaturated compounds.

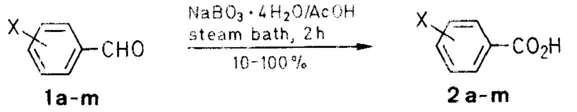
The application of sodium perborate tetrahydrate [$NaBO_3 \cdot 4H_2O$], a stable, non-toxic, and inexpensive chemical, as oxidant in organic chemistry has not yet been fully explored. Recently arylamines, sulfides, ketones, and hydroquinones have been oxidized by this reagent,[3] and olefins have been oxidized to oxiranes and vicinal acetoxyalcohols.[4,5] We now report some new uses of sodium perborate for the following reactions:

- oxidation of aromatic aldehydes;
- oxidative decarboxylation of α-hydroxycarboxylic acids;
- oxidative cleavage of 1,2-diketones, benzoin, and 1,2-diols;
- two-step oxidative cleavage of unsaturated compounds.

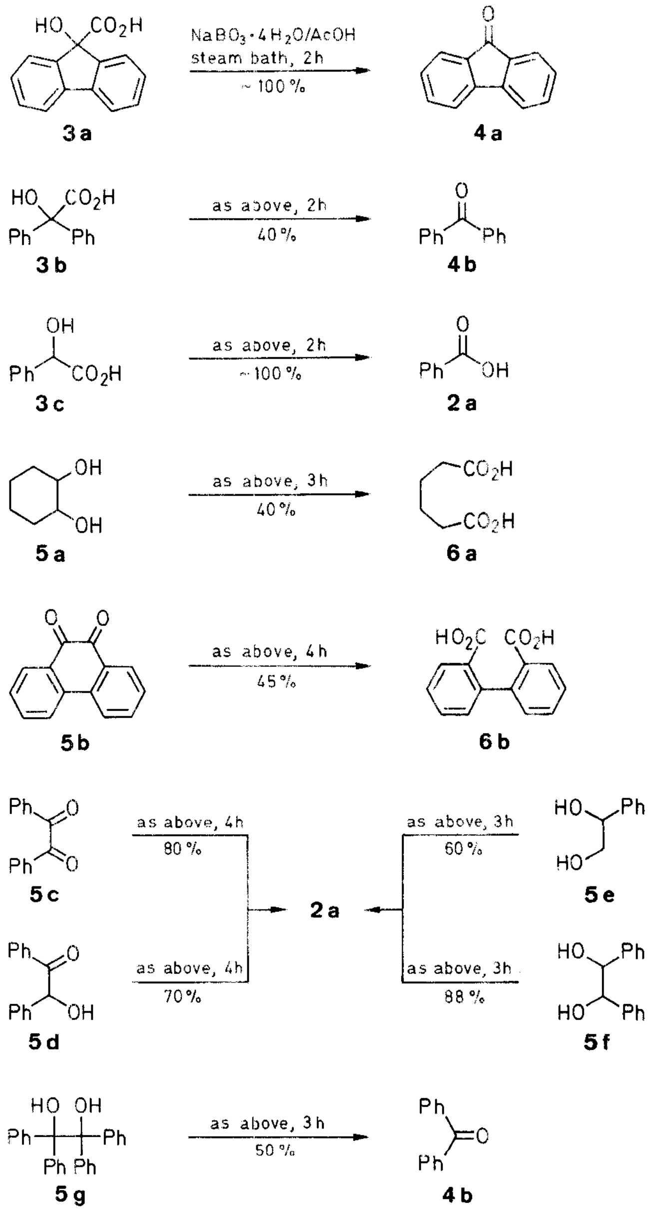
A unique feature of the perborate reagent is that alcohols having carbonyl or hydroxy groups in the α-position readily undergo oxidative cleavage, although it has previously been reported[3] that alcohols remain unaffected by this reagent. This simple procedure can also be used for the cleavage of C–C multiple bonds and may provide an alternative to ozonolysis or more traditional methods of oxidation that often involve harsh or expensive reagents.[6]

The procedure for the oxidation of aldehydes **1a–m** and α-hydroxycarboxylic acids **3a, b, c** (as optimized using the oxidation of benzaldehyde) consist of heating on a steam bath for 2 h a mixture of the substrate, sodium perborate, and glacial acetic acid. Work-up with chloroform to separate the neutral and acidic fractions afforded the desired products in good yields (Table). However, the yields of acids **2h, j** from 2- and 4-methoxybenzaldehydes **1h, j** were poor, probably due to attack of the oxidant at the more reactive positions *ortho* and *para* to the methoxy groups. This assumption is supported by the extensive decomposition of anisole under identical experimental conditions. Portionwise addition of an excess of perborate is recommended since the reagent itself undergoes slow decomposition at steam-bath temperature. The yield of benzophenone (**4b**; 20 %) from benzilic acid (**3b**) could be improved (40 %) by replacing acetic acid by 6 N hydrochloric acid. Vicinal diketones **5b, c** and benzoin (**5d**) required larger amounts of reagents and longer reaction times to afford carboxylic acids **6b** or **2a**, respectively. The aliphatic aldehydes so far investigated did not react satisfactorily.

When the unsaturated compounds **7a–d** and **8** are treated with sodium perborate under the aforementioned conditions the



1, 2	X	**1, 2**	X	**1, 2**	X
a	H	**f**	3-NO_2	**j**	4-OMe
b	2-Cl	**g**	4-NO_2	**k**	2-OH
c	3-Cl	**h**	2-OMe	**l**	3-OH
d	4-Cl	**i**	3-OMe	**m**	4-OH
e	2-NO_2				



major products are vicinal acetoxyalcohols which are accompanied by small amounts of carboxylic acids. Alkaline hydrolysis of these acetoxyalcohols affords the diols which can then be oxidized by the same perborate reagent to give products **2a** or **6a** arising from cleavage of the multiple bond. Thus, this two-step procedure constitutes a suitable method for such conversions.

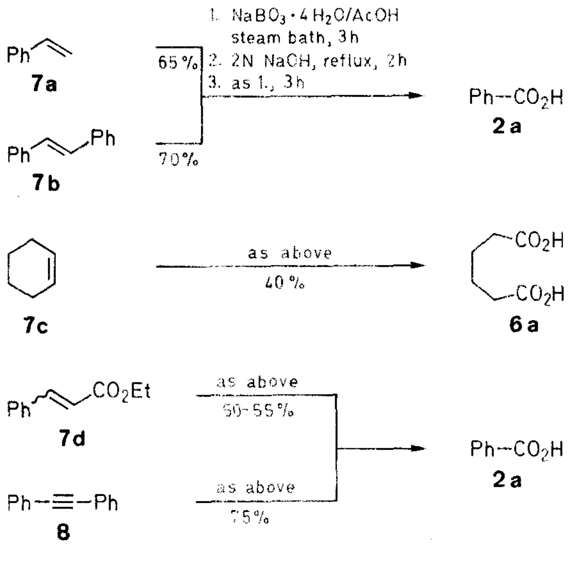


Table. Oxidations with the Sodium Perborate Reagent

Substrate	Procedure	Product[a]	Yield (%)	mp (°C)	
				found	reported[7]
1a	A	**2a**	90	121	122
1b	A	**2b**	100	136	137
1c	A	**2c**	90–95	156	158
1d	A	**2d**	100[b]	235	236
1e	A	**2e**	45	143	144
1f	A	**2f**	90–95	139	140
1g	A	**2g**	100	240	241
1h	A	**2h**	10	98–99	100
1i	A	**2i**	90	107	109
1j	A	**2j**	15	183	184
1k	A	**2k**	[c]	...	155
1l	A	**2l**	95[b]	199	200
1m	A	**2m**	[c]		213
3a	A	**4a**[d]	100	82	83
3b	A	**4b**[e]	40[f]	46	48
3c	A	**2a**	100	120	122
5a	C	**6a**	40[g]	150	151
5b	B	**6b**	45	228	229
5c	B	**2a**	80	120	122
5d	B	**2a**	70	120	122
5e	C	**2a**	60	120	122
5f	C	**2a**	88	120	122
5g	C	**4b**[e]	50	46	48
7a	D	**2a**	65	121	122
7b	D	**2a**	70	122	122
7c	D	**6a**	40[g]	149	151
7d	D	**2a**	50–55	121	122
8	D	**2a**	75	121	122

[a] Recrystallized from water (except for **4a** and **4b**) and characterized by mixture mp and comparison of the IR spectra with those of authentic samples.

[b] 10 mol of oxidant per mol of substrate is used to improve the yield.

[c] Pure products could not be isolated.

[d] Purified by evaporative distillation at 140°C/1 Torr.

[e] Purified by evaporative distillation at 135°C/2 Torr.

[f] 6N HCl is used instead of AcOH.

[g] Isolated via diethyl hexanedioate and hydrolysis thereof.

All reagents and substrates were of commercial quality and were taken from freshly opened containers. Sodium perborate tetrahydrate (L. R.) was purchased from Burgoyne burbidges and Co., Bombay. Glacial AcOH (A. R.; 1 L) was heated under reflux over $K_2Cr_2O_7$ (5 g) for 6 h and distilled before use. Reagent-quality solvents were used without further purification. Melting points are uncorrected. IR spectra were obtained using a Perkin-Elmer 297 infrared spectrophotometer.

Oxidation of Aromatic Aldehydes (1a–m) and α-Hydroxycarboxylic Acids (3a–c); General Procedure A:
A mixture of the substrate (5 mmol), $NaBO_3 \cdot 4H_2O$ (3.85 g, 25 mmol; added in 4 portions in the course of 30 min), and AcOH (2–3 mL per g of oxidant) is heated on a steam bath for 90 min, then poured into H_2O (20 mL). This mixture is extracted with $CHCl_3$ (3 × 25 mL). The organic layer is washed with H_2O (2 × 25 mL), extracted with sat. aq. $NaHCO_3$ solution (3 × 25 mL), again washed with H_2O (2 × 25 mL), dried (Na_2SO_4), and evaporated. [The residue thus obtained is identified by mp, mixed mp, IR spectrum, and the 2,4-DNP derivative]. The aq. $NaHCO_3$ extract is acidified (congo red) with concentrated HCl and extracted with $CHCl_3$ (3 × 25 mL). The organic layer is washed with H_2O (2 × 25 mL), dried (Na_2SO_4), and evaporated to give the carboxylic acid (Table) [this was characterized by mp, mixed mp, and comparison of the IR spectrum with that of an authentic sample].

Oxidation of Benzoin (5d) and 1,2-Diketones 5b, c; General Procedure B:
A mixture of the substrate (4 mmol), $NaBO_3 \cdot 4H_2O$ (9.23 g, 60 mmol; added in 8 portions in the course of 1 h), and AcOH (3–4 mL per g of oxidant) is heated on a steam bath for 3 h. The mixture is then poured into H_2O (50 mL) and then worked up as in Procedure A.

Oxidation of 1,2-Diols (5a, 5e–g); General Procedure C:
A mixture of the substrate (3 mmol), $NaBO_3 \cdot 4H_2O$ (4.61 g, 30 mmol; added in 4 portions in the course of 1 h), and AcOH (3–4 mL per g of the oxidant) is heated on a steam bath for 2 h. The mixture is then poured into H_2O (20 mL) and worked up as in Procedure A.

In the case of tetraphenylethanediol (**5f**) the product is benzophenone (**4b**) which is obtained from the neutral fraction, while in the other cases the acidic product is isolated from the $NaHCO_3$ extract.

Oxidative Cleavage of Unsaturated Compounds 7a–d and 8; General Procedure D:
A mixture of the unsaturated compound (3 mmol), $NaBO_3 \cdot 4H_2O$ (4.61 g, 30 mmol; added in 4 portions in the course of 1 h), and AcOH (2–3 mL per g of oxidant) is heated on a steam bath for 2 h. The mixture is then cooled and extracted with $CHCl_3$ (3 × 25 mL). The extract is washed with H_2O (2 × 10 mL), dried (Na_2SO_4), and evaporated. The residue containing the vicinal acetoxyalcohol is hydrolyzed with boiling 2N NaOH (20 mL) for 2 h, then cooled, and extracted with $CHCl_3$ (3 × 25 mL). The organic extract is washed with H_2O (2 × 10 mL), dried (Na_2SO_4), and evaporated to give the crude *vic*-diol. Without further purification this diol is oxidized with $NaBO_3 \cdot 4H_2O$ (4.61 g, 30 mmol; added in 4 portions in the course of 1 h) in AcOH (2–3 mL per g of oxidant) following Procedure C. The cleavage product is isolated from the $NaHCO_3$ extract as described in Procedure A.

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