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"SODIUM PERCARBONATE" (SPC) AS A HYDROGEN PEROXIDE SOURCE FOR ORGANIC SYNTHESIS

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"Sodium percarbonate" (SPC) is an inexpensive, stable, safe and commercially available material which may be used as a hydrogen peroxide source for organic synthesis. Epoxidation, amine and sulfide oxidation reactions were simply performed with the solid reagent in moderate to excellent yield.

Hydrogen peroxide is a most useful reagent in organic chemistry, with wide application for epoxidation and other important oxidations.[1] However, it is sometimes necessary to employ highly concentrated or anhydrous H_2O_2, with the accompanying instability and danger.[2] In this paper we present our initial results which show that "sodium percarbonate" (SPC) may be used as a safe hydrogen peroxide and/or hydroperoxide source, with a long shelf life. SPC, a commercial bleaching agent, is a convenient, easy-to-handle, inexpensive and powerful oxidant with a wide range of application. The molecular formula is generally written as the crystallization adduct of Na_2CO_3 and H_2O_2, $Na_2CO_3 \cdot 3/2\ H_2O_2$.

H_2O_2 may be liberated from SPC, with the aid of a small amount of water, and used for such reactions as epoxidation of conjugated double bonds. Thus Vitamin K_3 (0.5 g) stirred with SPC (0.93 g) and H_2O (3 ml) for 10 min in ethanol (10 ml), gave a white crystalline product after addition of water (50 ml), filtration and drying in vacuo, (0.46 g, 84% Vitamin K_3 oxide), (Table 1, run 1, method A).

The activated alkene, benzalacetophenone, was epoxidized in good yield under similar conditions (run 3, method C) but improvement was found with the addition of acetonitrile to the system (run 2, method B). There are several reports of nitriles acting as coreactants for epoxidations in alkaline media,[3-5] the increased activity being attributed to the generation of peroxycarboximidic acids, which behave as reactive intermediates. Non-activated alkenes, such as cyclohexene, were also oxidized, although only in the presence of acetonitrile and at a slower rate. Sulfides were quantitatively converted to sulfones, and phenylamines, without strong electron withdrawing sustituents, to nitrobenzenes.

A typical procedure for an oxidation, (method B), involved adding SPC (0.54 g, 4 mmol H_2O_2), diphenylsulfide (0.37 g, 2 mmol), H_2O (0.2 ml) and CH_3CN (1.5 ml) to MeOH (5 ml) in a screw-capped test tube and sonicating in a ultrasound bath. The organic fraction was isolated by addition of water (25 ml) and extraction into CH_2Cl_2 (5 ml, 3x), followed by drying ($MgSO_4$) and solvent removal to give spectroscopically pure diphenylsulfone (89%). Although mechanical agitation was

effective for straightforward oxidations, such as those of sulfides, it gave somewhat lower yields for more difficult ones (e.g. styrene and cyclohexene).

The wet alcoholic solvents appear to be essential for successful liberation of H_2O_2. Cyclohexene gave virtually no epoxide in dry CH_3CN or CCl_4, and THF was ineffective as a solvent for the oxidation of phenylamine. Thus the oxidising activity of the reagent seems to be due to H_2O_2 arising from dissolution of SPC, rather than from solid-liquid two-phase activation. The alkaline medium allows the generation of hydroperoxide anion, and the peroxycarboximidic intermediate in the presence of CH_3CN. We are currently studying other applications of SPC, in systems such as acidic methanol, and trifluoroacetic acid-anhydride.

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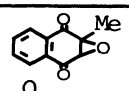
Table 1. Oxidations using SPC

Run	Substrate	Method[a]	SPC[b]	Time/h	Temp/°C	Product	Yield/%[c]
1	2-methylnaphthoquinone	A	2.0	0.25	25		- (84)
2	benzalacetophenone	B	2.0	3.5	38	PhCOCH$\overset{O}{\frown}$CHPh	80 (75)[d]
3		C	2.0	3.5	38		68 (58)
4	benzalacetone	B	2.0	23.5	38	MeCOCH$\overset{O}{\frown}$CHPh	64 (53)
5	phenylallylalcohol	B	1.3	24	45	PhCH$\overset{O}{\frown}$CHCH$_2$OH	75 (55)
6	styrene	B	2.0	48	38	styrene oxide	73[e]
7	cyclohexene	B	1.3	24	30	cyclohexene oxide	- (74)
8		B	3.0	120	38		61[f]
9	diphenylsulfide	B	2.0	6	42	diphenylsulfone	100 (89)[g]
10	dibenzylsulfide	B	2.0	6.5	55	dibenzylsulfone	100 (77)
11	diethylsulfide	B	2.0	6.5	55	diethylsulfone	100 (74)
12	phenylamine[h]	B	1.5	23	42	nitrobenzene	84 (71)
13		C	2.0	24	42	nitrobenzene	0
14	4-chlorophenylamine[j]	B	2.0	24	42	4-chloronitrobenzene	65 (53)

a) Methods A and B in text, C same as B but no CH_3CN. b) Molar equivalent as H_2O_2. c) GLC or NMR yields, (isolated). d) Similar result when SPC replaced by 30% aq. H_2O_2 + Na_2CO_3 (method D) or sonication replaced by shaking (method E), but lower yield (60% GLC) when both replaced (method F). e) (48h, GLC) 69, 62, and 15% by methods D, E, and F respectively; (72h, GLC) 87, 68, 79 and 15% by methods B, D, E, and F respectively. f) Addition of SeO_2 gave a similar result, but MoO_3 caused rapid H_2O_2 decomposition and little epoxidation. g) 43% sulfone + 14% sulfoxide (GLC) when using 1 equiv. H_2O_2 (similarly by methods D, E and F). h) No oxidation in THF as solvent, with or without CH_3CN. j) Substituted phenylamines, 4-$EtCO_2$-, 4-NO_2-, 2-NO_2- gave <5 % oxidation.

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