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Effective Chromium-Mediated Oxidation of Allylic and Benzylic Alcohols by Sodium Percarbonate.

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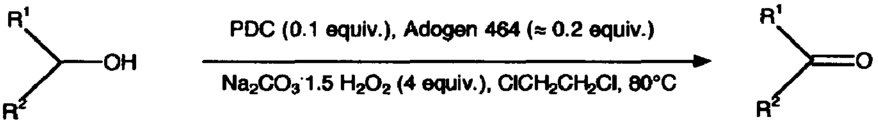
Abstract: High selectivity to the corresponding ketones and aldehydes has been observed for the title reaction when performed in 1,2-dichloroethane at 80°C in the presence of catalytic amounts of pyridinium dichromate and Adogen 464. The oxidation of unactivated alcohols was less efficient under these conditions.

The oxidation of the hydroxy group is commonly carried out using large amounts of heavy metals.[1] These procedures are usually very effective but they can cause problems with regard to product isolation and lead to quantities of poisonous residues. Environmental and economical constraints are incentives to develop catalytic alternatives using clean oxidants. The oxidation of alcohols by *t*-BuOOH in the presence of small amounts of various chromium compounds has been previously described.[2-4] Such Cr-catalyzed oxidations were much less effective when using 30% H_2O_2[5] or sodium perborate[6] as a cheaper peroxide. Although sodium percarbonate (SPC) can display similar reactivity to sodium perborate,[7] we have now investigated the properties of this inexpensive and stable crystalline compound as a substitut for *t*-BuOOH. Note that SPC is a perhydrate "$Na_2CO_3 \cdot 1.5\ H_2O_2$" and not a peroxy salt.[8] SPC is extensively used in the detergent industry as a bleaching agent and begins to emerge as a useful reagent in organic synthesis, but not yet for alcohol oxidations.[7,9-12]

Here, we are pleased to record that SPC used in conjunction with suitable Cr^{VI}- and phase-transfer-catalysts oxidizes efficiently various alcohols. A number of catalysts and solvents have been tested. Presently, the best conditions are the use of catalytic amounts of both pyridinium dichromate (PDC) and Adogen 464[13] in 1,2-dichloroethane at 80°C. As exemplified by the runs compiled in the Table, high conversions have been thus achieved from allylic and benzylic alcohols leading to carbonyl compounds with fair to high selectivities (runs 1, 2, 5-11) even with a primary alcohol (runs 12-15). As shown from 1-indanol, the presence of both catalysts is clearly required to achieve an efficient oxidation (runs 3, 4). In contrast to the preceding results, a lower conversion was obtained from saturated alcohols (runs 16, 17).



Comparisons with literature data reveal unexpected features. Under our present conditions, i) benzil has been isolated from benzoin in 67% yield (run 9) although this α-diketone was cleaved to benzoic acid when heated at 65°C for 5 min. with SPC (2 equiv.) in acetone/water,[12] ii) benzylic alcohol led selectively to benzaldehyde (run 12) while a large amount of benzoic acid was obtained in using CrO_3/*t*-BuOOH,[3] iii) eicos-1-en-3-ol afforded eicos-1-en-3-one with 98% selectivity (run 10) rather than mixtures of eicos-1-en-3-one and 3-eicosenal provided when using CrO_3 in conjunction with *t*-butyl or cumyl hydroperoxide,[2,14] iv) no epoxidation of double bonds has been noted (runs 10, 11, 13, 14) while either SPC under various other conditions[9] or Cr/*t*-BuOOH[2,14,15] can produce it, v) the Baeyer-Villiger oxidation of ketones previously achieved with SPC in an acidic medium[10] has not been observed.

In conclusion, this note affords a valuable extension of the use of PDC as catalyst and SPC as oxidant. Further studies of the Cr/SPC systems are in progress.

General oxidation procedure:

To a round-bottom flask containing a stirred mixture of PDC (0.1 mmol) in $ClCH_2CH_2Cl$ (10 ml) was added sequentially Adogen 464 (≈ 0.2 mmol), alcohol (1 mmol), and SPC (4 mmol). Then, the mixture was heated at 80°C under an air atmosphere for the specified period of time (Table).

Filtration, removal of solvents and subsequent flash-chromatography eluting with EtOAc/petroleum ether led to the pure products. Benzoic acid has been isolated from the precipitate by acid hydrolysis.

<u>Caution</u>: *SPC is a hydrogen peroxide source and usual precautions are required during the work-up to eliminate residual peroxides particularly for large scale experiments.*

Table: Oxidation of various alcohols with PDC/Adogen 464/SPC.

Run	Substrate	Time h	Conversion %	Product	Sel. %^{a}
1	1-indanol	24	86	1-indanone	97
2	"	72	93	"	96
$3^{b,c}$	"	24	12	"	83
$4^{b,d}$	"	"	10	"	80
5	1-tetralol	"	80	1-tetralone	98
6	9-hydroxyfluorene	"	91	9-fluorenone	91
7	1-phenyl-1-propanol	"	61	1-phenyl-1-propanone	98
8	"	53	75	"	98
9	benzoin	24	94	benzil	71
				+ benzaldehyde	10
				+ benzoic acid	7
10	eicos-1-en-3-ol	"	75	eicos-1-en-3-one	90
11	isophorol	"	79	isophorone	76
12	benzyl alcohol	"	90	benzaldehyde	98
13	2-naphthalenemethanol	"	92	2-naphthaldehyde	94
14	geraniol	"	75	citral (E/Z = 65/35)	84
15	nerol	"	80	citral (E/Z = 37/63)	95
16	3-methylcyclohexanol	"	16	3-methylcyclohexanone	56
17	1-hexadecanol	"	23	hexadecanal	98

[a] Selectivity (Sel.) corresponds to the yield of the isolated product calculated on the amount of substrate consumed. [b] In using 7 equiv. of SPC instead of 4 equiv. [c] In the absence of PDC and in using Aliquat 336[13] instead of Adogen 464. [d] In the absence of Adogen 464.

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