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Use of Benzotrifluoride as Solvent for Chromium-catalysed Oxidations with Sodium Percarbonate†[1]

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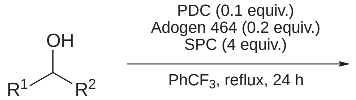
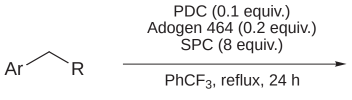
Chromium(VI)-catalysed oxidations of alcohols and benzylic methylene groups by sodium percarbonate have been carried out in refluxing benzotrifluoride; comparisons with previous studies showed that this solvent is a valuable alternative to 1,2-dichloroethane for such reactions.

In recent years, we have been much involved in chromium-catalysed oxidations using peroxides.[2] Recently, our interest has been mainly focused on the use of sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$; SPC)[2c] which is best considered as a "dry basic carrier of H_2O_2".[3] Thus, we have described oxidations of alcohols[4] and benzylic methylene groups[5] using SPC and catalytic amounts of both pyridinium dichromate (PDC)[6] and Adogen 464[7] in refluxing 1,2-dichloroethane (DCE). In this context, we were very interested in the valuable report by Ogawa and Curran who have proposed that benzotrifluoride (BTF) gives an alternative to chlorocarbon solvents for various reactions.[8] Other successes using BTF have already been documented by the same laboratory;[9] however, the new report has placed the wide scope of the use of BTF for organic synthesis in a prominent position.[10] This prompted us to examine the potential of BTF as a solvent for the above-mentioned Cr-catalysed oxidations with SPC. Effectively, the toxicity of BTF would be relatively low compared with that of DCE and the compatibility of BTF with H_2O_2 at room temperature has already been demonstrated.[8] Recent communications regarding metal-catalysed aerobic oxidations in BTF,[11–13] particularly the Ru-catalysed oxidation of primary alcohols, where the superiority of BTF over various solvents, including DCE, has been exemplified,[13] urges us to report our results.

The main results are assembled in Table 1. They were obtained under the following experimental conditions (previously documented using DCE as solvent): excess of SPC, catalytic amounts of both PDC and Adogen 464 boiled at reflux for 24 h under an air atmosphere [reactions (1) and (2)].[4,5,14] Since it is revealing to compare the new results with those obtained in DCE, the latter have been added in Table 1.



(1)



(2)

Table 1 Cr(VI)-catalysed oxidation of alcohols and benzylic methylene groups by SPC[a]

		Conversion(%)			Yield(%)	
Entry	Substrate	BTF	DCE	Isolated product	BTF	DCE
1	Indan-1-ol	100	86[4]	Indan-1-one	96	83[4]
2	Fluoren-9-ol	100	91[4]	Fluorenone	99	83[4]
3	1-Phenylpropan-1-ol	66	61[4]	1-Phenylpropan-1-one	63	60[4]
4	Benzyl alcohol	97	90[4]	Benzaldehyde	91	88[4]
5	2-Naphthalenemethanol	100	92[4]	2-Naphthaldehyde	93	87[4]
6	Methyl mandelate	94	92[16]	$PhCOCO_2Me$	14[b]	15[16,b]
7	Isophorol	86	79[4]	Isophorone	69	60[4]
8	Geraniol	80	75[4]	Citral	56	63[4]
9	Nerol	89	80[4]	Citral	75	76[4]
10	3-Methylcyclohexanol[c]	18	16[4]	3-Methylcyclohexanone	10	9[4]
11	Menthol	20	29[17]	Menthone	19	28[17]
12	Hexadecan-1-ol	46	23[4]	Hexadecanal	45	22
13[d]	Indan-1-ol	86	70[15]	Indan-1-one	76	67[15]
14	Indane	60	58[5]	Indan-1-one	38	30[5]
				Indan-1-ol	0	7[5]
				Indan-1,3-dione	18	6[5]
15	Tetraline	85	[e]	Tetral-1-one	41	
				Tetral-1-ol	19	
				1,4-Naphthoquinone	16	
16	Fluorene	74	[e]	Fluorenone	59	
17	Diphenylmethane	11	[e]	Benzophenone	11	

[a]See text and experimental section for the oxidation procedure. [b]Formation also of cleavage compounds. [c]Mixture of *cis* and *trans* isomers. [d]Using Bu^n_4NBr instead of Adogen 464. [e]Reaction not carried out under these conditions.[5,17]

We previously observed that (i) the solubilization of PDC in DCE requires the presence of lipophilic ammonium salts such as Adogen 464, and (ii) the main role of Adogen 464 is to interact with PDC; an exchange of the ammonium

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groups forms a new chromium complex which is soluble in DCE.[15] Similarly, PDC is insoluble in BTF, even at 100 °C, but is dissolved by the addition of 2 equiv. of Adogen 464.

Our first experiments, carried out on secondary benzylic alcohols, were encouraging (runs 1–3 in Table 1); using BTF rather than DCE, conversions and yields were indeed increased, and high selectivities[18] were preserved. Similar observations were made in the oxidation of primary benzylic alcohols: the corresponding aldehydes were cleanly obtained and the overoxidation to acids was negligible (runs 4 and 5). As previously noted,[16] the oxidation of an α-functionalized benzylic alcohol such as methyl mandelate led mainly to cleavage compounds (run 6). The oxidation of primary and secondary allylic alcohols yielded aldehydes and ketones, respectively, with good selectivities (runs 7–9).

As in DCE,[4] saturated secondary alcohols were resistant to oxidation in BTF (runs 10 and 11). In contrast, the oxidation of hexadecan-1-ol was much more effective under these new conditions and, furthermore, highly selective (run 12).

When a smaller ammonium salt such as tetrabutylammonium bromide was used instead of Adogen 464, the oxidation of indan-1-ol was less effective (run 13). The presence of a long alkyl substituent on the nitrogen atom of the ammonium salt was already required for good efficiency of the procedure in DCE.[15]

When indane, tetraline and fluorene were subjected to similar experimental conditions, we observed the ready oxidation of their benzylic methylene groups, affording the corresponding ketones with fair yields (runs 14 to 16). However, the same procedure induced only a low conversion of diphenylmethane (run 17). Surprisingly, the oxidation of ethylbenzene led to many compounds.

In conclusion, the use of BTF is compatible with that of SPC and chromium oxides, even at its reflux temperature. Furthermore, we can state that BTF is not only a replacement for 1,2-dichloroethane but it can also improve the efficiency of the chromium-catalyzed oxidations by sodium percarbonate.

Experimental

Reagents and commercial substrates were used as received. Some alcohols were obtained by reduction of the corresponding ketones by $NaBH_4$ in MeOH. Home-made plates (silica gel 60 $PF_{254+366}$ from Merck) were used for preparative thin-layer chromatography.

Typical Oxidation Procedure.—In a 25 ml round-bottomed flask containing PDC (38 mg, 0.1 mmol) and Adogen 464 (81 mg, ~0.2 mmol) was added BTF (10 ml). After complete dissolution of the chromium complex at reflux temperature were added SPC [either 628 or 1256 mg, 4 or 8 mmol, see reactions (1) and (2)] and the substrate (1 mmol). The mixture was stirred and boiled under reflux in an atmosphere of air for 24 h, then cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure.[19] The residue was taken up with a small amount of CH_2Cl_2 and then subjected to preparative thin-layer chromatography, eluting with EtOAc–light petroleum (bp 30–60 °C) (10/90). The oxidized compounds were identified by comparison with commercial samples (TLC, IR, ^1H NMR).

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Reference and notes

1 Part of this work was presented as a poster at XIth International Symposium on Homogeneous Catalysis; 12–17 July, 1998; St Andrews, Scotland.

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14 The boiling point of BTF is 102 °C while DCE boils at 83 °C. Preliminary experiments using BTF as solvent have shown that reactions carried out at 83 or 102 °C lead to similar results.

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18 Selectivity represents the yield based on the amount of substrate consumed.

19 Following a referee's remark regarding the recoverability of the solvent, preparative experiments were carried out using 8 mmol of indan-1-ol in 80 ml of BTF. Some BTF (55–60 ml) was thus recovered by distillation of the filtrate under atmospheric pressure. After complete evaporation of the solvent under reduced pressure, the residue was subjected to flash chromatography, eluting with EtOAc–light petroleum (bp 30–60 °C) (20/80).