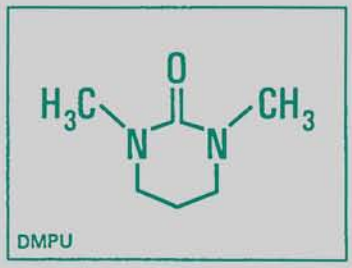
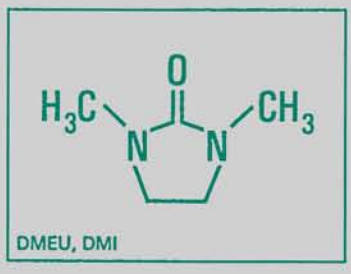
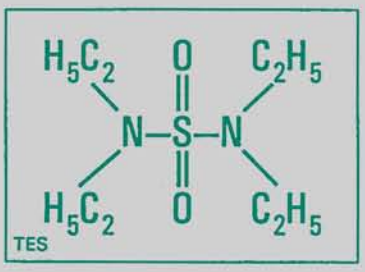
N,N'-DIMETHYLPROPYLENEUREA
1,2-DIMETHYL-2-IMIDAZOLIDINONE
N,N,N',N'-TETRAETHYLSULFAMIDE



DMPU



DMEU, DMI



TES

New Dipolar Aprotic Solvents

FLUKA offers the three new dipolar aprotic solvents **41664 1,3-Dimethyltetrahydro-2(1H)-pyrimidinone (N,N'-Dimethylpropyleneurea) DMPU, 40727 1,3-Dimethyl-2-imidazolidinone (N,N'-Dimethylethyleneurea) DMEU** or **DMI,** and **86718 N,N,N',N'-Tetraethylsulfamide, TES.** These novel solvents for organometallic reactions have been shown in several cases to be favorable substitutes for the carcinogenic HMPA.

DMPU and DMEU are new N-alkylated ureas with high dipole moments and dielectric constants[1]. **DMPU** recently was shown by Seebach et al.[2] to be an excellent replacement of HMPA as cosolvent in oxirane opening with lithium acetylide, in a Wittig olefination, in the double deprotonation of nitroalkanes, in the Michael addition of lithium dithianide to 2-cyclohexenone, and in the selective generation of certain enolates. Some of the attractive properties of DMPU are: a 33% solution in THF is stable to LDA up to at least -35°, DPMU solidifies below -20° and a 50% solution in THF remains clear and homogenous down to at least -78°[2].

DMEU (DMI) was used as solvent for the preparation of trimethylsilyl sodium, one of the strongest bases known[3], and was shown to be more stable than HMPA in the reaction of trimethylchlorosilane with lithium[4]. DMEU was found by T. Mukaiyama et al.[5] to be the solvent of choice for the transformation of allylic iodides into homoallylic alcohols. It may also be used as solvent for dehydrations and dehydrohalogenations with methyltriphenoxyphosphonium iodide[6].

N,N,N',N'-Tetraethylsulfamide, TES, recently was proposed by H. Richey et al.[7] as advantageous solvent for Grignard reagents. TES shows a greater stability towards these strongly basic and nucleophilic reagents than HMPA. Even organolithium compounds have a limited stability at ambient temperatur in TES[7].

41664	**1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, DMPU purum** >99% (GC); B.P.$_{.25}$230°; d_4^{25} 1.0596 (N,N'-Dimethylpropyleneurea; 1,3-Dimethyl-2-oxo-hexahydropyrimidine) $CH_2CH_2CH_2N(CH_3)CONCH_3$ $C_6H_{12}N_2O$ M_r 126.17 [7226-23-5]		50 ml sFr. 20.—	US$ 13.30
			250 ml sFr. 85.—	US$ 56.70
40727	**1,3-Dimethyl-2-imidazolidinone, DMEU, DMI purum** 99% (GC); B.P. 221-223° (N,N'-Dimethylethyleneurea) $CH_2CH_2N(CH_3)CONCH_3$ $C_6H_{10}N_2O$ M_r 114.10 [80-73-9]	1 lt ≈ 1.06 kg	25 ml sFr. 18.—	US$ 12.00
			100 ml sFr. 65.—	US$ 43.30
86718	**N,N,N',N'-Tetraethylsulfamide, TES purum** >99% (GC); B.P.$_{.0.02}$70°; d_4^{28} 1.0441 lt ≈ 1.04 kg $(C_2H_5)_2NSO_2N(C_2H_5)_2$ $C_8H_{20}N_2O_2S$ M_r 208.32 [2832-49-7]		100 ml sFr. 25.—	US$ 16.70
			500 ml sFr. 105.—	US$ 70.00

References:

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[4] H. Sakurai, F. Kondo, ibid. *117,* 149 (1976)
[5] T. Mukaiyama et al., Chem. Lett. 1507 (1980)
[6] C.W. Spangler et al., J. Chem. Soc. Perkin I 2287 (1981)
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Besides the three new solvents shown above FLUKA offers a large number of other aprotic dipolar compounds useful as solvents or cosolvents. For specifications and prices see the Catalogue 13, 1982/83.

29545 **1-Cyclohexylpyrrolidone**
34700 **N,N-Dibutylformamide**
32330 **N,N-Diethylformamide**
38401 **N,N-Diisopropylformamide**
38840 **N,N-Dimethylacetamide**
40250 **N,N-Dimethylformamide**
41640 **Dimethyl sulfoxide, DMSO**
04810 **1-Ethylpyrrolidone**
47721 **4-Formylmorpholine**
47725 **1-Formylpiperidine**
47728 **1-Formylpyrrolidine**
52730 **Hexamethylphosphoramide, HMPA**
66179 **N-Methylcaprolactame**
69118 **1-Methylpyrrolidone**
86148 **Sulfolane**
86892 **Tetrabutylurea**
86705 **Tetraethylurea**
87850 **Tetramethylurea**
93230 **Tripiperidinophosphine oxide**
93404 **Tripyrrolidinophosphine oxide**

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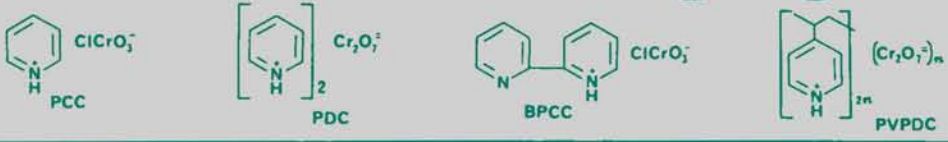
8203

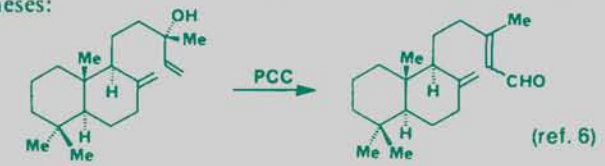
Chromium Oxidizing Agents



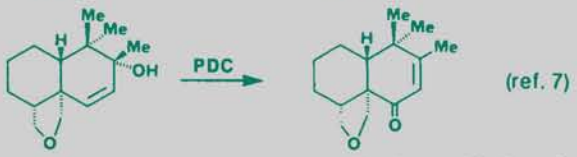
Pyridinium chlorochromate (PCC)
Pyridinium dichromate (PDC)

Since their introduction, **pyridinium chlorochromate (PCC)**[1] and **pyridinium dichromate (PDC)**[2,3] have become widely used reagents for the selective oxidation of alcohols to carbonyl compounds. Considerable literature has accumulated regarding the effects of solvents and acidities on **PCC** and **PDC** oxidations.[1,3-5]

The concomitant oxidation and [1,3]-rearrangement of allylic alcohols has been exploited in natural-product syntheses:

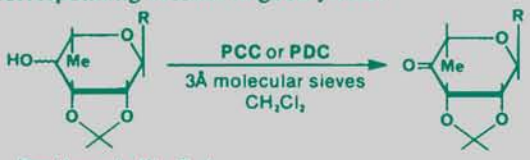


(ref. 6)



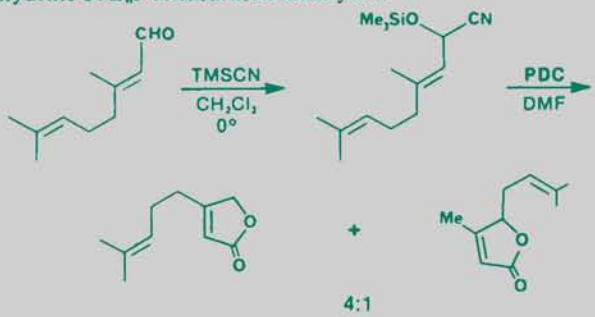
(ref. 7)

Molecular sieves catalyze the normally slow oxidation of suitably protected nucleosides and sugars, affording the corresponding ketones in good yields:[8]

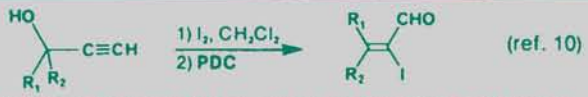


R = theophyllin-7-yl

Recently, a number of **PCC** and **PDC** oxidations involving substrates other than alcohols have appeared, effectively broadening the scope of these reagents. Corey and Schmidt[9] have developed a new Δ^2-butenolide synthesis involving the **PDC** oxidation of *O*-trimethylsilyl cyanohydrins of α,β-unsaturated aldehydes:

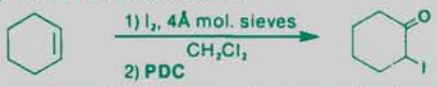


PDC oxidation of α-ynol-I_2 complexes provides a route to α-iodo-α,β-unsaturated aldehydes:

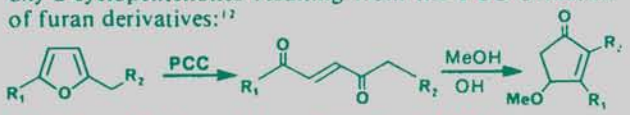


(ref. 10)

Under similar conditions, cyclic olefins give moderate to good yields of α-iodoketones:[11]



Piancatelli and co-workers have described a synthesis of conjugated ene-dione compounds and the derived 4-methoxy-2-cyclopentenones resulting from the **PCC** oxidation of furan derivatives:[12]



2,2′-Bipyridinium chlorochromate (BPCC)

BPCC was recently introduced[13] as a reagent which alleviates some of the difficulties inherent in the use of **PCC**. With **BPCC**, the chromium byproducts associated with Cr(VI) oxidations are easily removed by filtration through Celite. In addition, the internal buffering action of the 2,2′-bipyridyl moiety may make **BPCC** especially useful in the oxidation of substrates containing acid-sensitive protecting groups.

Poly(4-vinylpyridinium dichromate) (PVPDC)

PVPDC is a polymer-supported pyridinium dichromate which effects the oxidation of primary alcohols to aldehydes. Good to excellent yields were obtained using the wet reagent in nonpolar solvents such as cyclohexane. Chromium-containing byproducts are retained by the resin, and are removed by simple filtration.[14]

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19,014-4	**Pyridinium chlorochromate**	**100g $16.75** **500g $52.00**
21,469-8	**Pyridinium dichromate**	**100g $14.10** **500g $46.75**
23,674-8	**2,2′-Bipyridinium chlorochromate**	**25g $20.00** **100g $58.00; 500g $175.00**
23,746-9	**Poly(4-vinylpyridinium dichromate),** cross-linked	**5g $9.50; 25g $30.00**