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INDIRECT ELECTROCHEMICAL METHODS OF NITRATION: NOVEL NITROACETAMIDATION OF DIENES

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Solutions of nitronium tetrafluoroborate in acetonitrile prepared by anodic oxidation of nitrogen dioxide, efficiently nitrate aromatics, enolsilyethers, alkenes and conjugated dienes to afford respectively nitroaromatics, α-nitroketones, vicinal nitroamides and mixtures of nitroacetamides by 1,2- and 1,4-addition.

Indirect electrochemical procedures based on inorganic transition metals are presently used both in laboratory and industrial preparations. The potential of other electrogenerated reagents in organic synthesis has been indicated by the nitroxyl-mediated electrooxidation of amines[1] and of alcohols[2], and in a recent review[3]. Although nitroaromatics have been obtained by co-electrolysis of aromatic compounds with nitrites or nitrates[4] the use of electrogenerated nitronium salts in organic nitration procedures has been limited. The nitration of some aromatics has been followed[5] by g.l.c. analysis. In this paper we describe the electrochemical generation of nitronium tetrafluoroborate (NO_2BF_4) in acetontrile, and the use of this reagent in a number of nitration procedures. The known nitration of aromatics, the nitration of enolsilylethers[6] and the nitroacetamidation of alkenes[7] are readily achieved in very high yield without resort to the commercially available salt NO_2BF_4 which is expensive and very moisture sensitive. We further describe the nitroacetamidation of conjugated dienes a novel procedure affording readily separable unsaturated 1,2- and 1,4-nitroacetamides.

Anodic oxidation of an acetonitrile solution of nitrogen dioxide at constant current ($50mA/cm^2$) using a divided H-cell (platinum mesh electrodes, $LiBF_4$ as electrolyte) afforded solutions of NO_2BF_4 (∿0.25M with 80% current efficiency and 80% yield based on nitrogen dioxide). Solutions were assayed for NO_2BF_4 by withdrawal of aliquots, which were reacted with benzene, and then analysed by g.l.c. for nitrobenzene.

In Table 1 we report the results of reactions of the electrogenerated reagent with a variety of substrates. On a preparative scale we confirm the earlier analytical report[5] of the efficient nitration of aromatic compounds. Nitration of benzene and 2-cyanotoluene gives nitrobenzene (1) and 2-cyano-4-nitrotoluene (2) respectively. Nitration of trimethylsilyloxycyclopentene and of trimethyl-silyloxycyclohexene gives the nitroketones (3) and (4) in 95% and 80% yield respectively. We attribute the much inferior yields in use of non-electrogenerated nitronium tetrafluoroborate[6] to the presence of acid impurities. Significantly the generation of such impurities in the electrochemical procedure is not important.

Table 1

Reaction[a] of Nitronium Tetrafluoroborate

Organic Substrate	Product	Yield[b] using electrogenerated NO_2BF_4(%)	Literature yield with non-electrogenerated NO_2BF_4(%)
Benzene	(1)	80	93 [c]
2-Cyanotoluene	(2)	79	90 [c]
Trimethylsilyloxy-cyclopentene	(3)	95	41 [d]
Trimethylsilyloxy-cyclohexene	(4)	80	37 [e]
Styrene	(5)	50	63 [f]
4-Bromostyrene	(6)	50	84 [f]
Trans-β-methylstyrene	(7)	81	61 [f]
α-Methylstyrene	(8)	69	28 [f]
Trans-stilbene	(9)	82	72 [f]
Cyclopentene	(10)	20	13 [f]

a) Reactions were carried out at -70°C in $MeCN/CH_2Cl_2$ with addition of the organic substrate to the solution of NO_2BF_4 with the exception of preparation of (1) and (2) at 0°C in MeCN.

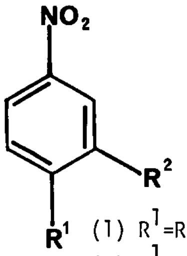
b) Yields refer to products isolated after crystallisation or distillation, or in the case of nitroamide (10) after flash chromatography.

c) S J Kuhn and G A Olah, J.Am.Chem.Soc., 1961, 83, 4564.

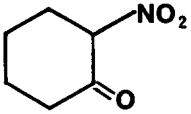
d) P Elfehail, P Dampawan and W Rajac, Synth.Comm., 1980, 10, 929.

e) See reference 6.

f) See reference 8.



(1) $R^1=R^2=H$
(2) $R^1=CH_3$; $R^2=CN$



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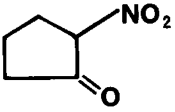
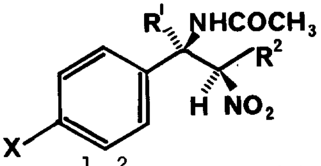
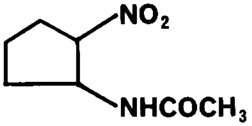


(3)

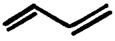
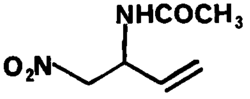
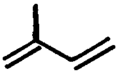
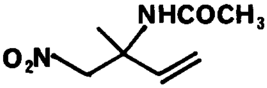
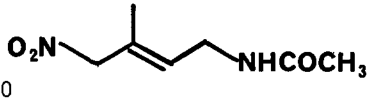
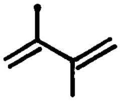
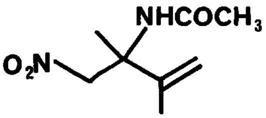
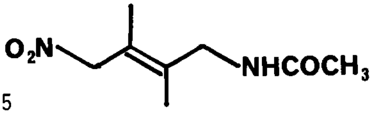
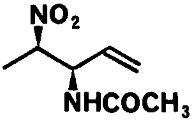
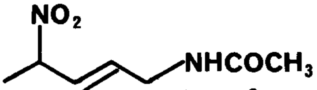
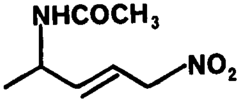
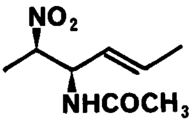
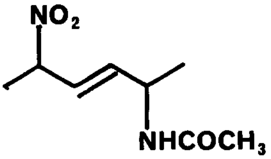


(5) $R^1=R^2=X=H$
(6) $R^1=R^2=H$; X=Br
(7) $R^2=CH_3$; $R^1=X=H$
(8) $R^1=CH_3$; $R^2=X=H$
(9) $R^1=X=H$; $R^2=Ph$



(10)

Table 2 : Reaction[a] of Nitronium Tetrafluoroborate with Dienes.

Diene	Products[b] and Yields (%)			
		48	51	
		39	50	
		35	35	
		26	64	 3 ratio 2 
		6	78	

a) Conditions as described in Table 1.

b) All the products are previously undescribed. Structures are supported by satisfactory i.r., ^1H and ^{13}C n.m.r. spectra and satisfactory analytical and/or high resolution mass spectrometric data. Yields refer to products isolated after crystallisation or after flash chromatography.

We[8] have recently extended the known[7] nitroacetamidation of aliphatic alkenes to the preparation of vicinal nitroamides from styrenes using non-electrogenerated nitronium tetrafluoroborate. In Table 1 we report the synthesis of the nitroamides (5-10) using electrogenerated NO_2BF_4. The presence of high concentrations of the electrolyte $LiBF_4$ influences neither the observed regioselectivity nor the stereoselectivity of addition. The observed selectivity closely parallels results obtained[9] with other nitronium salts. In the case of all entries in Table 1 the use of a cheap electrogenerated reagent can replace efficiently an expensive commercial reagent.

In Table 2 we report the first study of the nitroacetamidation of conjugated dienes. Reaction of electrogenerated NO_2BF_4 affords in each case a readily separable (chromatography on silica gel) mixture of the less polar stable crystalline 1,2-nitroacetamides and the more polar but less stable crystalline 1,4-nitroacetamides.

This easy preparation from dienes of a variety of polyfunctional products susceptible to further synthetic transformation emphasizes the potential utility of electrogenerated NO_2BF_4 in organic synthesis.

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