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Synthesis of 2-R-2,2-dinitroethanol orthoesters in ionic liquids

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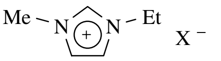
The syntheses of tris(2-R-2,2-dinitroethyl)ortoformates and tetrakis(2-R-2,2-dinitroethyl)orthocarbonates in ionic liquids are described.

2,2,2-Trinitroethyl and 2-fluoro-2,2-dinitroethyl compounds are important energetic materials, which are used as the ingredients of explosive compositions,[1] propellant formulations[2] and gas-generating compositions.[3] 2,2,2-Trinitroethanol **1a** and 2-fluoro-2,2-dinitroethanol **1b** are strategic precursors in the synthesis of these compounds.[4] The reactivity of electronegatively substituted alcohols is much lower than that of usual alcohols. Moreover, under basic conditions, alcohols **1a** and **1b** decompose.

Hill[5] reported the synthesis of trinitroethanol orthoesters by refluxing a solution of dry alcohol **1a** with trichloromethyl compounds in the presence of anhydrous ferric chloride.[5] A similar approach was used for the synthesis of 2-fluoro-2,2-dinitroethanol orthoesters.[6] Because this method was long and potential explosion hazard, an alternate route was required.

Room temperature ionic liquids are promising reaction media for a variety of chemical processes.[7,8] Ethylmethylimidazolium salts (Figure 1) can be advantageous reaction media because they are most widely available, fire-resistant, recyclable and have a limited vapour pressure, allowing efficient recovery of organic products.



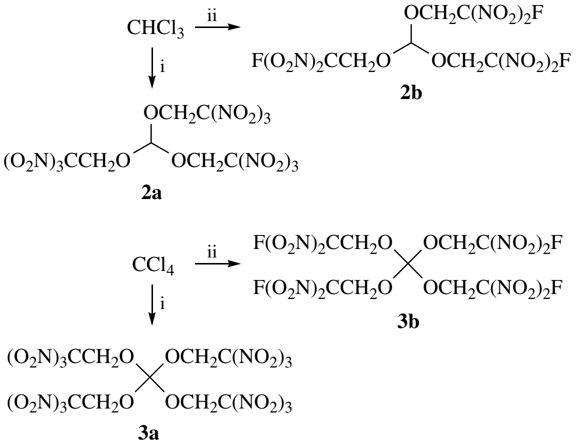
[emim] = ethylmethylimidazolium
X = Cl, BF_4, PF_6, $AlCl_4$

Figure 1 Structures of room temperature ionic liquids.

Previously,[9] we described the reaction of CCl_4 with poor nucleophiles such as aminofurazans[10] using [emim][$AlCl_4$] as the solvent and the catalyst. Two chlorine atoms of CCl_4 were displaced under these conditions and corresponding (3-R-furazan-4-yl)dichloroimines were prepared in good yields.

Here, we report the synthesis of trinitroethanol and 2-fluoro-2,2-dinitroethanol orthoformates **2** and orthocarbonates **3** (Scheme 1) using the ionic liquids as both solvents and Lewis acid catalysts.

We studied [emim][X] as a solvent for chlorine displacement in CCl_4 by trinitroethanol **1a** as a model electronegatively substituted alcohol. Table 1 summarises the results of these experiments. In all of the reactions, both alcohol **1a** and CCl_4 were thoroughly dried before use. These reactants were converted into desired orthocarbonates **3a** in ionic liquids on heating with stirring for ~3 h.[†] Gaseous HCl evolved during the reaction. Table 1 indicates that the anion played an important role in this transformation. Thus, we found that [emim][$AlCl_4$] was a more effective medium than other ionic liquids in terms of yield (Table 1, entry 7). The reaction was unsuccessful when [emim][Cl] was used (Table 1, entry 1). The treatment of trinitroethanol **1a** with CCl_4 in the presence of $FeCl_3$ in ionic liquids afforded desired orthocarbonates **3a** in high yields.[‡] The recycling/re-use of the solvent in several syntheses of compound **3a** were performed without regeneration of the ionic liquid with no drop in yields.



Scheme 1 *Reagents and conditions*: i, $HOCH_2C(NO_2)_3$ **1a**, [emim][X], 70–100 °C; ii, $HOCH_2C(NO_2)_2F$ **1b**, [emim][X], 70–100 °C.

Encouraged by these results, we studied other trichloromethyl compounds and alcohols under optimised conditions, and Table 2 summarises the results. In all cases, electronegatively substituted alcohols reacted with trichloromethyl compounds in [emim][$AlCl_4$] in high yields when catalysed by $FeCl_3$.

In conclusion, we found that the displacement of a chlorine atom in trichloromethyl compounds with electronegatively substi-

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[†] *General procedure for the preparation of tetrakis(2,2,2-trinitroethyl)-orthocarbonate* **3a**. Trinitroethanol (1.81 g, 10 mmol) was added to a mixture of [emim][$AlCl_4$][11] (5 ml), CCl_4 (0.5 ml) and $FeCl_3$ (0.5 mmol) under an atmosphere of argon and anhydrous conditions. The reaction mixture was heated at 80 °C with stirring until the complete consumption of the starting alcohol (2–3 h, according to TLC). CCl_4 was removed under a reduced pressure. The product was separated from the residue by extraction with diethyl ether (7×10 ml). The combined extracts were washed with cold water to neutral reaction and dried with $MgSO_4$. The solution was passed through a short SiO_2 pad and evaporated to give the product **3a** as a solid, mp 161–162 °C (lit.,[5] mp 163 °C). ^1H NMR ([$^2H_6$]DMSO) δ: 5.39 (CH_2). ^{13}C NMR ([$^2H_6$]DMSO) δ: 62.3 (CH_2), 117.8 (C–O), 123.5 [$C(NO_2)_3$]. ^{14}N NMR ([$^2H_6$]DMSO) δ: –34.1 (NO_2). IR (ν/cm^{-1}): 3012, 2964, 2892, 1604, 1452, 1396, 1304, 1296, 1192, 1148, 1120, 1092, 1072. Found (%): C, 14.71; H 1.06; N, 23.00. Calc. for $C_9H_8N_{12}O_{28}$ (732.23) (%): C, 14.76; H, 1.10; N, 22.95.

[‡] In contrast, the $FeCl_3$-promoted reaction of trinitroethanol **1a** with CCl_4, which is a reagent and a solvent, afforded orthocarbonate **3a** in 80% yield at refluxing for 24 h.[5] A prolonged reaction time and violated solvent make the process dangerous.

Table 1 Synthesis of orthocarbonates **3a** in ionic liquids with FeCl$_3$ as a co-catalyst.

Entry	[emim][X]	FeCl$_3$	Yield (%)
1	[emim][Cl]	—	0
2	[emim][Cl]	5 mol%	41
3	[emim][BF$_4$]	—	35
4	[emim][BF$_4$]	5 mol%	72
5	[emim][PF$_6$]	—	43
6	[emim][PF$_6$]	5 mol%	79
7	[emim][AlCl$_4$]	—	54
8	[emim][AlCl$_4$]	5 mol%	83

tuted alcohols in ionic liquids provides a new safe and straightforward approach to the synthesis of orthoformate and orthocarbonate. The ready availability of starting materials combined with the high yields of these reactions make this approach highly appealing and very practical.

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Table 2 FeCl$_3$-promoted synthesis of orthoesthers with [emim][AlCl$_4$].

Entry	Alcohol	Trichloromethyl compound	Product	Yield (%)	Mp/°C
1	$HOCH_2C(NO_2)_3$	$HCCl_3$	**2a**	76	128–129 (lit.,[5] 127.6–128)
2	$HOCH_2C(NO_2)_2F$	$HCCl_3$	**2b**	88	111–112 (lit.,[6] 110–111.2)
3	$HOCH_2C(NO_2)_2F$	CCl_4	**3b**	91	136–137 (lit.,[5] 136)

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