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Ionic liquid-assisted synthesis of trinitroethyl esters

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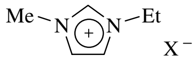
The first, highly efficient esterification of 2,2,2-trinitroethanol with alkanoyl, cycloalkanoyl, aroyl and hetaroyl chloride promoted by simple ionic liquids is described; trinitroethyl esters were characterised by X-ray crystallography.

Polynitro compounds are of significant interest as oxygen-rich energetic materials for propulsion and explosive applications.[1–3] 2,2,2-Trinitroethanol has long been recognised as a useful building block for such materials. Progress in the synthesis and chemistry of the electronegatively substituted alcohol and its analogues has been the subject matter of monographs[4,5] and reviews.[6–8]

Trinitroethyl esters of carboxylic acids are of particular interest as the ingredients of gas-generating compositions.[9,10] Some synthetic strategies used to form these esters have been reported.[4–8] The low reactivity of the alcohol requires the use of a strong condensing agent or a reactive carboxylic acid derivative to effect reaction. The esterification *via* the Lewis acid catalysed reaction of the acid chloride at reflux temperature is the most preferable procedure. The yields of trinitroethyl esters obtained in a number of the cited transformations were curiously substrate dependent and the sequence with which the reactions were carried out played a significant role in their successful execution. Because reported methods were not amenable to reproducible yields and potential explosion hazard, an alternate route was required.

Room-temperature ionic liquids (RTILs) (Figure 1), may be advantageous reaction media. The general utility and advantages of RTILs are well documented.[11–14]

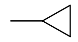
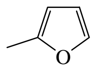
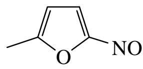
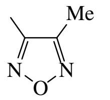
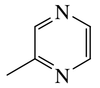


[emim] = ethylmethylimidazolium
X = $AlCl_4$, BF_4, PF_6

Figure 1 Structure of [emim][X].

Recently, we described the straightforward use of RTILs as inert reaction media for poor nucleophiles,[15,16] in particular, 2,2,2-trinitroethanol. Our attention, therefore, was focused upon

Table 1 Yields and characteristics of compounds **2a–d** from ionic liquid esterifications.

Product	R	Yield (%)	Mp/°C (Lit.)	^{1}H NMR (CDCl$_3$)		^{13}C NMR (CDCl$_3$)				^{14}N NMR
				CH$_2$	R	C(NO$_2$)$_3$	CH$_2$	CO$_2$	R	
2a	Ph	93	76–76.5 (76–77)[17]	5.63	7.49, 7.64, 7.97	123.3	61.1	163.7	126.9, 128.6, 130.2, 134.5	–34.6
2b	p-ClC$_6$H$_4$	95	84–85	5.61	7.46, 7.90	125.4	61.1	163.1	125.4, 129.2, 131.3, 141.3	–34.8
2c	(O$_2$N)$_3$CCH$_2$CH$_2$	92	92–93 (92–93)[18]	5.47	2.91, 3.45	122.6	61.3	167.3	28.0, 29.3, 128.1	–35.5 –31.2 (from R)
2d		85	3–5	5.29	0.94, 1.59	123.3	60.5	172.2	9.7, 12.3	–34.5
2e		79	48–49	5.58	6.58, 7.26, 7.67	123.2	60.6	155.3	112.5, 121.1, 141.7, 148.4	–34.8
2f		92	123–124	5.64	7.37	122.6	61.3	153.9	111.1, 121.3, 141.6, 153.4	–35.9 –33.5 (from R)
2g		95	59–60	5.73	2.54	122.4	61.4	152.0	8.6, 145.3, 155.9	–35.7
2h		74	70–72	5.72	8.72, 8.83, 9.19	122.8	61.5	161.3	141.0, 145.0, 146.3, 148.7	–35.3
4	CH$_2$[CO$_2$CH$_2$C(NO$_2$)$_3$]$_2$	95	56–57 (56–57)[19]	5.46	3.63	122.2	61.2	162.5	39.5	–35.4

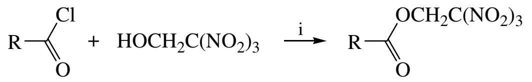
the synthesis of 2,2,2-trinitroethanol derivatives in RTILs, and we describe here the result of the application of the media to the esterification of the unusual alcohol.

The addition of 2,2,2-trinitroethanol to a solution of benzoyl chloride **1a** in [emim][AlCl$_4$] at room temperature leads to rapid gas evolution with concurrent formation of a light yellow colour. As found by ^{1}H and ^{13}C NMR spectroscopy and TLC, the major aromatic product was 2,2,2-trinitroethyl benzoate **2a** (Scheme 1) even after 0.5 h. With [emim][PF$_6$] or [emim][BF$_4$], the reaction was slower but led to a vary similar result. Ester **2a** was generally formed in a nearly quantitative yield. The recycling/reuse of the solvent in several syntheses of compound **2a** were performed without regeneration of the ionic liquid with no drop in yields. Other aromatic acid chlorides reacted similarly. Moreover, alkanoyl, cycloalkanoyl and hetaroyl chlorides reacted immediately with 2,2,2-trinitroethanol under the same conditions[†] to give corresponding products in good yields (Table 1). In all of the reactions, the solvent and reactants were thoroughly dried before use.

We found that it is possible to effect a similar esterification of a diacid dichloride to a diester. Thus, when a solution of malonyl dichloride **3** in [emim][PF$_6$] was treated with 2,2,2-trinitroethanol (Scheme 2), desired ester **4** was obtained in 95% yield.

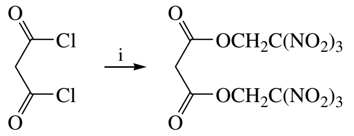
The ester structures were established by ^{1}H, ^{13}C and ^{14}N NMR spectroscopy (Table 1). The location region of chemical shifts in the ^{1}H, ^{13}C and ^{14}N NMR spectra, corresponding to the trinitroethyl moiety, are consistent between products. By this expedient these chemical shift values can be used as the diagnostics of 2,2,2-trinitroethanol esters.

Compounds **2a**, **2b** and **2g** were also characterised by single crystal X-ray crystallography[‡] for the first time. ORTEP views of the structures are shown in Figure 1. In all the compounds, the Ar–C(O)OC fragment is slightly nonplanar. The nonplanarity is more pronounced for **2g** with the exocyclic torsion angle C(5)–C(4)–C(3)–O(2) being 19.3(2)°. For the comparison of the orientations of C–C(NO$_2$)$_3$ groups, we choose the torsion angles listed in Table 2. It can be seen that the orientation of the C(NO$_2$)$_3$ group relative to the C(2)–O(2) bond is nearly the same for all the compounds, which is in an agreement with NMR data.



1a–d **2a–d**

Scheme 1 *Reagents and conditions*: i, [emim][X], ambient temperature.



3 **4**

Scheme 2 *Reagents and conditions*: i, [emim][PF$_6$], ambient temperature.

[†] *General procedure for the preparation of 2,2,2-trinitroethyl benzoate* **2a**. To a mixture of [emim][PF$_6$] (20 ml) and benzoyl chloride **1a** (1.4 g, 10 mmol), trinitroethanol (1.81 g, 10 mmol) was added under argon and anhydrous conditions. The reaction mixture was stirred at room temperature until the complete consumption of the starting reactants (0.5–3 h, according to TLC and NMR). The product was separated from the residue by extraction with a mixture of CH$_2$Cl$_2$ and diethyl ether (1:1). The combined extracts were washed with cold water and dried with MgSO$_4$. The solution was passed through a short SiO$_2$ pad and evaporated to give product **2a** (see Table 1).

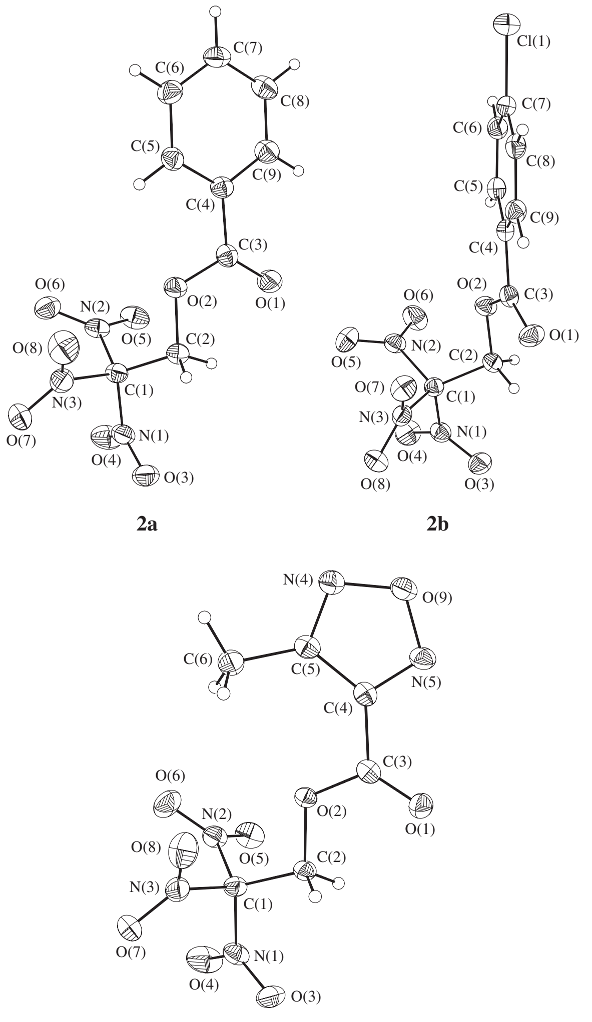
[‡] Reflections for compounds **2a**, **2b** and **2g** were collected on a SMART 1000 CCD diffractometer [λ(MoKα) = 0.71073 Å, graphite monochromator, ω-scans] at 120 K. The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in an anisotropic approximation. All the hydrogen atoms were placed in geometrically calculated positions and refined within a riding model.

For **2a** (C$_9$H$_7$N$_3$O$_8$): triclinic, space group $P\bar{1}$, $a = 7.703(3)$, $b = 7.972(4)$, $c = 9.910(3)$ Å, $\alpha = 85.08(3)°$, $\beta = 84.90(4)°$, $\gamma = 72.88(4)°$, $V = 578.2(4)$ Å^3, $Z = 2$, $M = 285.18$, $d_{\text{calc}} = 1.638$ g cm^{-3}, $\mu = 0.148$ mm^{-1}, $F(000) = 292$, $wR_2 = 0.1163$, GOF = 0.995 for 2691 independent reflections with $2\theta < 56°$, $R_1 = 0.0504$ for 2116 reflections with $I > 2\sigma(I)$.

For **2b** (C$_9$H$_6$ClN$_3$O$_8$): triclinic, space group $P\bar{1}$, $a = 7.3983(11)$, $b = 9.3861(13)$, $c = 10.2912(15)$ Å, $\alpha = 109.731(3)°$, $\beta = 105.536(3)°$, $\gamma = 102.726(3)°$, $V = 608.87(15)$ Å^3, $Z = 2$, $M = 319.62$, $d_{\text{calc}} = 1.743$ g cm^{-3}, $\mu = 0.363$ mm^{-1}, $F(000) = 324$, $wR_2 = 0.1113$, GOF = 1.047 for 2891 independent reflections with $2\theta < 56°$, $R_1 = 0.0472$ for 2248 reflections with $I > 2\sigma(I)$.

For **2g** (C$_6$H$_5$N$_5$O$_9$): orthorhombic, space group $Pbca$, $a = 8.2018(13)$, $b = 11.506(2)$, $c = 23.245(4)$ Å, $V = 2193.6(6)$ Å^3, $Z = 8$, $M = 291.15$, $d_{\text{calc}} = 1.763$ g cm^{-3}, $\mu = 0.169$ mm^{-1}, $F(000) = 1184$, $wR_2 = 0.0748$, GOF = 1.047 for 2376 independent reflections with $2\theta < 54°$, $R_1 = 0.0361$ for 1658 reflections with $I > 2\sigma(I)$.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 613201, 613202 and 613203 for **2a**, **2b** and **2g**, respectively. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2006.



2a **2b**

2g

Figure 1 ORTEP views of esters **2a**, **2b** and **2g**.

For **2a** and **2g**, it can be attributed to the shortened O(2)···O(8) contact [2.870(3) Å for **2a** and 2.826(2) Å for **2g**] that might stabilise such an orientation while the corresponding distance in **2b** is equal to 2.945(2) Å. The structural differences arise mostly from the rotation about the single C(3)–O(2) bond. Because of a relatively small barier to rotation, different conformations can be related to different intermolecular interactions.

The compounds are characterised by relatively high density.‡ In all the structures, there are many slightly shortened O···O and O···N contacts with distances at the boundary between normal and shortened ones. Several contacts of medium strength are found in the structures of **2a** and **2b**, which allow us to describe their crystal packing as the built up of columns (for **2a**) and layers (for **2b**). In contrast, such contacts for the most dense structure **2g** are rather weak (O···O distances in the range 2.9–3.1 Å). Probably, more close binding inside columns and layers in **2a**,**b** is overcompensated by a larger number of weak contacts in **2g**.

In conclusion, we have first demonstrated that the esterification of 2,2,2-trinitroethanol with alkanoyl, cycloalkanoyl, aroyl and hetaroyl chloride promoted by simple ionic liquids opens a novel entry to the synthesis of trinitroethyl esters. The method is facile and, more importantly, safe.

Caution. All trinitroethyl compounds should be considered explosive and proper precautions should be taken in handling and storage of them.

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Table 2 Selected torsion angles for esters **2a**, **2b** and **2g**.

Torsion angle	2a	2b	2g
N(1)–C(1)–C(2)–O(2)	162.98(14)	159.32(16)	163.26(12)
N(3)–C(1)–C(2)–O(2)	42.78(19)	41.0(2)	–77.51(15)
N(2)–C(1)–C(2)–O(2)	–78.57(18)	–81.6(2)	43.46(17)
C(1)–C(2)–O(2)–C(3)	–135.83(15)	119.82(18)	–174.72(13)
C(2)–O(2)–C(3)–C(4)	–178.49(14)	173.43(16)	–179.87(12)

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