

Green Sonochemical Synthesis of Technical Fenitrothion Using Protic Ionic Liquid

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ABSTRACT: In this study, a new environmentally-friendly method for the synthesis of technical Fenitrothion is offered. Apart from using ionic liquid as the innocuous and recoverable solvent, this methodology offers sonochemical-assisted synthesis. Technical Fenitrothion has been obtained from the reaction of 3-methyl-4-nitrophenol as a critical intermediate in this green method. According to this methodology, *m*-cresol is nitrated by ferric nitrate as the nitrating agent in the presence of triethyl ammonium nitrate ionic liquid as a recoverable protic solvent under ultrasonic irradiation, in short reaction time and high yield. Ionic liquid caused more para selectivity of nitration by steric hindrance through hydrogen bond formation with phenolic oxygen, which inhibited ortho substitution of the aromatic ring, and 4-isomer obtained as the major product. The developed process provided task-specific ionic liquid preparation from by-products and the possibility of recycling the ionic liquid for five consecutive runs, which has the benefit of eliminating waste products generated out of this procedure following green chemistry principles.

KEYWORDS: Green synthesis; Technical Fenitrothion; Triethylammonium nitrate; Sonochemical; Nitration, Ionic liquid.

INTRODUCTION

Global population growth has led to the consumption of a wide range of products related to food and also increased the demand for the production of agricultural products, which has resulted in an increase in the consumption of pesticides [1]. Fenitrothion was one of the most commonly used pesticides from the late 50's, and it was used against pests such as flies, mosquitoes, cockroaches, and locusts [2]. Fenitrothion is a non-systemic

compound of the organophosphate insecticide, which like other organophosphate compounds, exerts its effect by inhibiting acetylcholinesterase enzymes. When acetylcholinesterase is inactivated, acetylcholine accumulates in the nervous system, leading to continued nervous stimulation [2].

Due to the environmental crises and the pollution caused by the production process, synthetic chemists

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have decided to find a green alternative methodology of technical pesticides green chemistry's role in the development of processes [3], has led to less pollution and more effective synthesis than classic pathways [4]. In this regard, the current investigation involves synthesizing *O*, *O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate as technical fenitrothion via environmentally friendly procedure from 3-methyl-4-nitrophenol as a critical intermediate[5]. The process of synthesizing the technical fenitrothion in a green method mainly focuses on preparing 3-methyl-4-nitrophenol from *m*-cresol. The nitration of phenolic compounds has significant industrial attention, and recent research shows the importance of pollutants derived from these processes. Considering the classical nitration methods, which have a series of functional defects such as the use of hazardous chemicals [6-8], high costs [9, 1]), lengthy processes, and disposal issues [7, 11], the invention of novel green methodologies are highly required.

In the proposed green access to 3-methyl-4-nitrophenol, *m*-cresol was nitrated in the presence of ferric nitrate as nitrating agents and protic ionic liquid TEAN under sonochemical conditions. In this regard, utilizing harmful acidic solvents was eliminated by replacing ferric nitrate. As well, using ionic liquid has received much attention in green chemistry in recent years. Ionic liquids have been considered promising alternative to many environmentally friendly applications, catalysts and reagents in organic reactions. Confirmed characteristics and excellent usefulness is rooted in the unique properties of these materials [12]. The presence of ionic liquid made it possible to react in a safer condition with higher para-selectivity. The main point of the process mentioned above is that the ionic liquid utilized in nitration will be reproduced in the production process. It is also worthy of mentioning that the reusability of the ionic liquid several times can be considered as a cost-effective strategy following green chemistry [13-16]. As a result, in addition to being safer, material waste would considerably decrease. Also, data obtained in previous reports of *m*-cresol nitration via general nitration methods resulted in producing by-products, including ortho isomers [5]. Ionic liquids facilitate para selectivity of nitration reaction

by making hydrogen bonds between protic ionic liquid and phenolic group [13, 14, 17-19]. Accordingly due to, steric hindrance, which inhibits ortho substitution of the aromatic ring and plays a significant role in this synthetic process.

On the other hand, to solve the nitration problems, low reaction rate, and yield, this reaction is carried out under ultrasound irradiation instead of ordinary multi-hour refluxes, which enhancing the yield and reaction rate because of acoustic cavitation characteristics. According to this, generation and collapsing transient bubbles in non-volatile ionic liquid release driving energy in a short time [20-22]. Another purpose of designed method in nitration step of technical fenitrothion synthesis was as follows:

Recyclability of task-specific ionic liquid as both solvent and catalyst

Application of ultrasound conditions instead of multi-hour refluxes

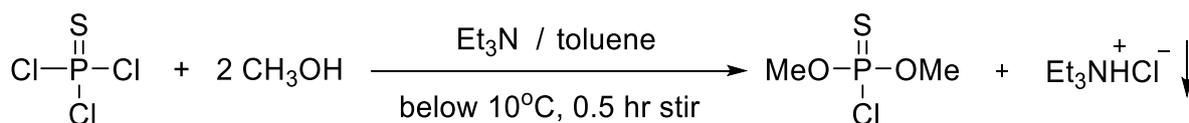
EXPERIMENTAL SECTION

Materials and methods

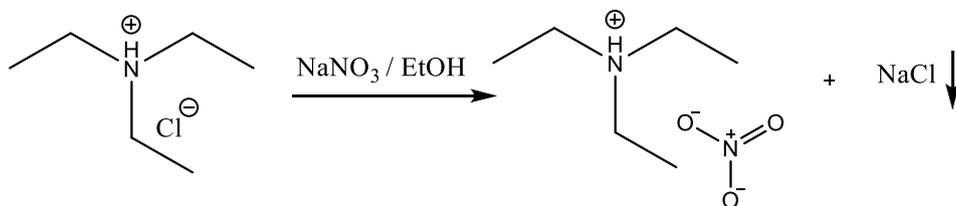
All chemicals obtained from Merck and Aldrich Chemical Company were the best available purity and used without further purification unless otherwise indicated. Melting points were measured by an Electrothermal 9100. The progress of reactions was monitored by TLC using silica gel 60 F254 plates. IR spectra recorded on Bruker FT-IR spectrometer. ¹H-NMR spectra were recorded on Bruker 250 MHz spectrometers in CDCl₃ in TMS as internal standard.

Preparation of dimethyl chlorothiophosphate

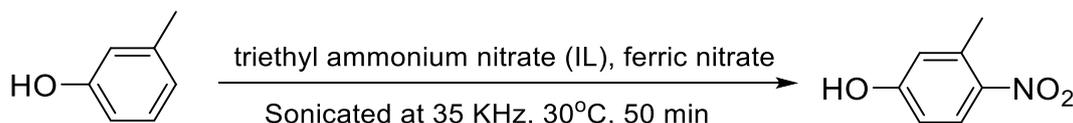
To a mixture of methanol (6.9 mmol, 0.28 mL) and triethylamine (5.8 mmol, 0.81 mL) in toluene (4 mL), thiophosphoryl chloride (3.1 mmol, 0.315 mL) was added as long as it was in the ice bath and stirred for 30 minutes. This reaction produced triethylammonium chloride as a by-product by adding thiophosphoryl chloride. The resulting mixture was filtrated, and the resulting precipitate was stored to synthesis ionic liquid. The colorless filtrate used for the technical Fenitrothion synthesis is *O*, *O*-Dimethyl phosphorochloridothioate in toluene [23] (Scheme 1).



Scheme 1: Dimethyl chlorothiophosphate synthesis.



Scheme 2: Preparation of triethylammonium nitrate.



Scheme 3: Synthesis of 3-methyl-4-nitrophenol using ultrasonic and ionic liquid.

Preparation of triethylammonium nitrate

To synthesize protic ionic liquid triethylammonium nitrate, triethylammonium chloride from the previous step dissolved in ethanol and heated up to 55 °C. Then, the sodium nitrate was added portion-wise to the mixture.

As the reaction was processed, insoluble anionic chloride precipitated. When the precipitation was terminated, the resulting solution cooled, filtered, and the solvent evaporated by distillation in vacuum [24](Scheme 2).

Preparation of 3-methyl-4-nitrophenol

The procedure was followed by R. Rajagopal's method with some modifications (17). A mixture of m-cresol (2 mmol, 0.21 mL) and ferric nitrate (1.3 mmol, 0.54 g) in triethylammonium nitrate (2 g) was sonicated at 30 °C for 50 minutes in an ultrasonic bath at 35 kHz. As the completion of the reaction confirmed by TLC, the mixture diluted with 2 mL of water, and it filtered. The product from the precipitate extracted with ethyl acetate (2*5 mL). Then the solvent evaporated under vacuum and afforded crude product. Subsequently, the product purified by Column chromatography on silica gel (n-Hexane/Ethyl acetate, 1:1) (Scheme 3).

The current reaction without ferric nitrate carried out in imidazolium, alkylammonium nitrate, and sulfate ILs

in different temperature conditions (Table 1); the desired result was not achieved.

Preparation of O, O-dimethyl-O-(3-methyl-4-nitrophenyl) phosphorothioate

The synthesized 3-methyl-4-nitrophenol (2.5 mmol, 0.382 g) was added to dimethyl chlorothiophosphate in toluene synthesized in the previous step and stirred at room temperature for 30 minutes. Subsequently, it was refluxed at 70°C for 3 h. After the completion of the reaction, monitored by TLC, the solution was washed with cold water (2*5 mL), and the organic layer was dried over anhydrous Na₂SO₄, the solvent evaporated in a rotary vacuum evaporator, and the product was purified by Column chromatography on silica gel (n-Hexane/Ethyl acetate, 1:1) [23] (Scheme 4).

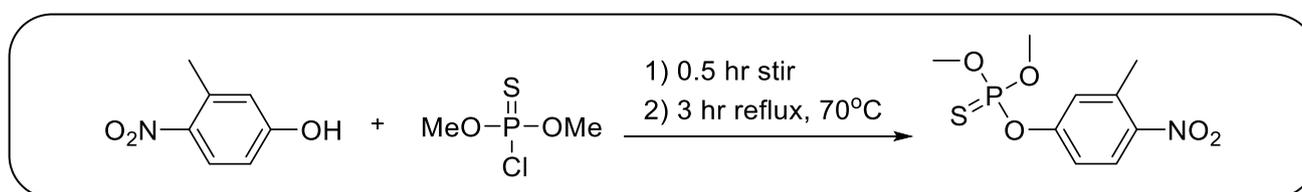
Recycling of ionic liquid

The ionic liquid from the 3-methyl-4-nitrophenol synthesis step (Scheme 3) was recovered by evaporating water in a rotary vacuum evaporator. Reusability of ionic liquid examined by nitration of m-cresol with recycled ionic liquid and added nitrating agent (Fig. 3), obtained data show that ionic liquid was recyclable for five times (Fig. 1).

Table 1: Optimization of *m*-cresol nitration with different conditions.

Entry	Condition	T (°C)	Time (min)	Yield (%)	Ref.
1	TEAN (sonication)	80	120	0	Current study
2	TEAN/EAN ^a (sonication)	80	120	0	Current study
3	TEAN/[Bmim]BF ₄ ^b (sonication)	80	120	0	Current study
4	TEAN/TEAS ^c (sonication)	80	120	0	Current study
5	[Bmim]BF ₄ /ferric nitrate (sonication)	80	120	0	Current study
6	Triethylammonium chloride/ferric nitrate (sonication)	80	120	0	Current study
7	Triethylammonium chloride/ferric nitrate (grinding)	rt	120	0	Current study
8	[Bmim]NO ₂ /ferric nitrate (sonication)	30	45	54(62/38) ^d	Current study
9	EAN/ferric nitrate (sonication)	30	45	85(74/26) ^d	(22)
10	TEAN/ferric nitrate (sonication)	30	45	87(85/15) ^d	Current study

a) Ethylammonium nitrate; b) 1-Butyl-3-methylimidazolium tetrafluoroborate; c) Triethylammonium sulfate; d) Ratio *p*/*o*- isomer



Scheme 4: Technical Fenitrothion synthesis.

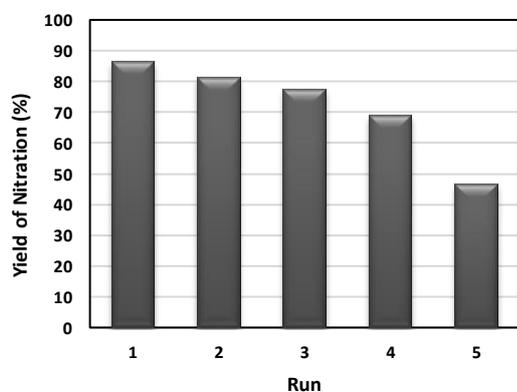


Fig. 1: Reusability of recovered ionic liquid.

RESULTS AND DISCUSSION

Green chemistry is an implication, which aims chemists to improve the safety of chemical processes [25, 26]. Based on the fundamentals of green chemistry, minimizing energy consumption is one of the essential terms in establishing new techniques that include sonochemical synthesis [27]. Thus, the application of ultrasounds has been considered as a new trend in green chemistry methods due to its

environmental protection [20, 28]. On the other hand, the cavitation effects of ultrasonic irradiation and its effect to improve the mass transfer process caused to be used widely in organic chemistry reactions and play an essential role in promoting the reaction [21, 22]. In this regard, the importance of ionic liquids should not be neglected in designing new green techniques; ionic liquids are being studied widely as eco-friendly alternatives to the use of organic solvents [28].

Synthesis of dimethyl chlorothiophosphate

The dimethoxylation of thiophosphoryl chloride was conducted in toluene solvent and obtained dimethyl chlorothiophosphate in colorless liquid; triethylammonium nitrate precipitated as a by-product of reaction as a white solid. The melting point was measured (found 260 oC, and agreed with reported data 261 °C [29]).

Green synthesis of 3-methyl-4-nitrophenol

A new selective method for the nitration of *m*-cresol under the sonochemical condition in the presence of ionic liquid triethylammonium nitrate and ferric nitrate was

Table 2: Nitration process of m-cresol in various conditions.

Entry	Condition	T (°C)	Time (h)	Yield (%)				Ref.
				Mononitrated product ^b (4:2:6-nitro)	Dinitrated product	Other	Total ^a	
1	Ferric nitrate/TEAN (sonicated)	30	0.75	87 (85:0:15)	-	-	87	Current study
2	HNO ₃ /H ₂ SO ₄	0-5	1	51 (5:11:84)	43	6	100	(30)
3	HNO ₃ /Silica gel	Rt	1	75 (64:13:23)	19	6	100	(31)
4	NaNO ₃ / NaNO ₂ / H ₂ SO ₄	Rt	12	82 (41:23:28)	-	8	90	(32)
5	HNO ₃ /Yb-Mo-HKSF	Rt	10	87 (53:9:25)	-	5	91	(33)
6	POCl ₃ / H ₂ SO ₄ / HNO ₃ /H ₂ O	<0	30	80 (88:3:9)	5	-	85	(5)
7	Ferric nitrate/ether	Rt	20	54 (67:0:33)	-	-	54	(34)

a) Total yield of reagent conversion

b) Total yield of mononitration isolate product

performed, giving yellow solid 3-methyl-4-nitrophenol; IR (KBr) spectrum, ν , cm⁻¹: 1076 (C-N), 1208 (C-O), 1317 (N-O), 1589 (N-O), 3303 (O-H); Melting points were measured in open capillaries, found 125-127 °C (reported: 125-130 °C (35))

Our proposed mononitration methodology of m-Cresol with ferric nitrate and TEAN in sonochemical condition (Table 2, entry 1) has the benefit of eliminating the acidic nitrating agent (Table 2, entry 2-6) and also dangerous, volatile solvents (Table 2, entry 7). Another significant point of this method was that the mentioned TEAN, which has been produced as a by-product in the synthesis process as a precipitate (Scheme 1). Recyclability and reusability of the ionic liquid was another improvement achieved in this method (Fig. 1 and Fig. 3). Reusability of the TEAN was possible up to 5 times (Fig. 1)

In addition, contrary to other procedures which some drawbacks such as dinitration (Table 2, entry 2,3,6) or quinone formation (Table 2, entry 2-5) had occurred, such disadvantages were not observed in the presence of ferric nitrate (Table 2, entry 1,7).

It should note current study proceeds in a shorter reaction time (45 min, table 2, entry 1) than the traditional method without ultrasonic irradiation (Table 2, entry 2-7).

Para selectivity of the nitration reaction in the presence of triethylammonium nitrate as a recoverable Bronsted acidic ionic liquid solvent occurred via steric hindrance. The proposed structure for the interaction of TEAN and m-cresol depicted in Fig. 2. Accordingly, 4-isomer obtained as the major product with a very high ratio than other products (Table 2, entry 2-7).

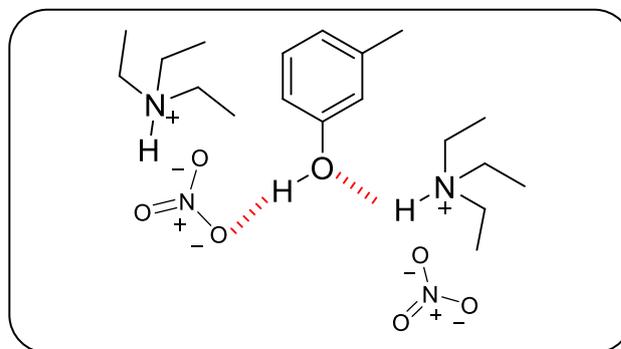


Fig. 2 Steric hindrance and Hydrogen bonding between m-cresol and ionic liquid

Furthermore, offered method considerably enhanced the yield of mono-nitrated products with the higher ratio of the desired product. However, other organic salts of alkylammonium could be used, and this reaction can be carried out in the presence of a wide range of alkylammonium salt ILs [17].

In this regard, according to data from some studies regarding ILs as nitrating agents, the current route (Scheme 3) was tried without ferric nitrate in the presence of TEAN ILs alone (Table 1, entry 1) and combination with various ILs, for instance [Bmim]BF₄, EAN, TEAS (Table 1, entry 2-4), it was found out that no result had been obtained. To clarify the key role of ferric nitrate in the reaction mechanism, the plausible mechanism described below (Fig. 3).

The mechanism of this process explained by the formation of Phenol-Fe (III) complex, which confirmed by its dark blue color. Afterward, NO₂ radicals were formed by homolytic cleavage of (O₂N)₂Fe-O-NO₂ adduct.

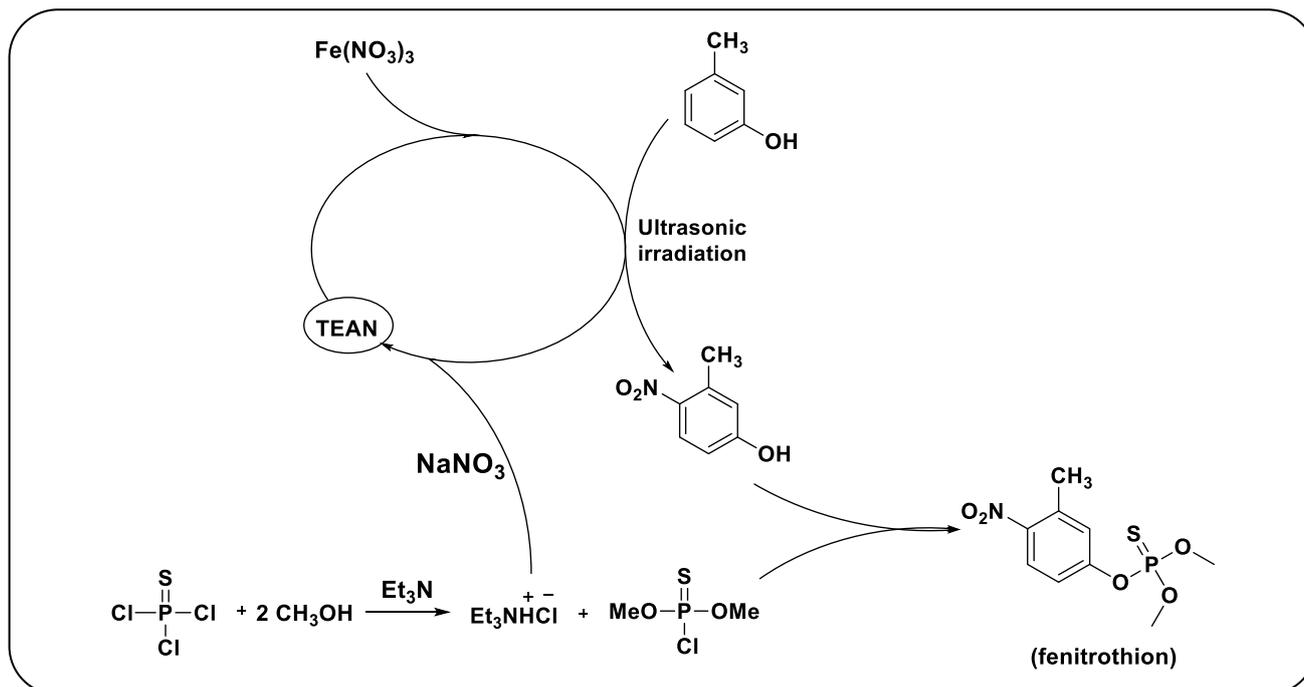


Fig. 3: Green synthesis of Technical Fenitrothion.

It's obvious that the formation and adiabatic collapse of the transient cavitation bubbles are facilitated under ultrasonic conditions [17].

Although, the reaction was conducted in the presence of ferric nitrate and organic salt [Bmim]BF₄ (Table 1, entry 5) and triethylammonium chloride under sonication and grinding conditions, respectively (Table 1, entry 6,7), still no result was obtained. As can be seen, using imidazolium nitrate (Table 1, entry 8) and alkylammonium nitrate ILs (Table 1, entry 9,10), has achieved the desired result and showed that the existence of anionic similarity and homogenization of the reaction condition would be effective. Most notably, it indicated that utilizing ILs with more substitution (TEAN) was a more regio-selective reaction and comparison results showed that more 4-isomer compound may be attributed to the alkyl substitution. Nevertheless, it can be theorized, that alkyl substitution boosts the selectivity due to steric bulk in ortho position, and it directed the reaction further to the 4-nitrated product. It is the best result that could be expected under the circumstances.

Synthesis of technical Fenitrothion

The technical fenitrothion pesticide was synthesized using the reagents produced by green reported pathway and brownish yellow liquid was achieved; Reflective

index n_D^{20} : 1.5512 (reported: 1.5528 (36)); IR(KBr) spectrum, ν , cm^{-1} : 819 (P-O-C aliphatic), 982 (P-O-C aromatic), 1043 (C-O), 1317 (N-O), 1516 (C=C), 1589 (N-O), 2964 (C-H); ¹H NMR(CDCl₃, 250 MHz, TMS): δ (ppm) 2.34 (s,3H), 3.75 (s,6H), 6.77(d,1H), 6.93(s,1H), 7.9(d,1H)

CONCLUSIONS

To summarize, we reported a simple and environmentally benign method for synthesizing technical Fenitrothion. We have developed a green, beneficial and practical procedure, which provides several ascendancies, including enhancement in the rates of reaction and para selectivity. Using sonochemical conditions instead of multi-hour refluxes, avoiding the use of harmful acids, and hazardous solvents are some other advantages of this methodology.

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