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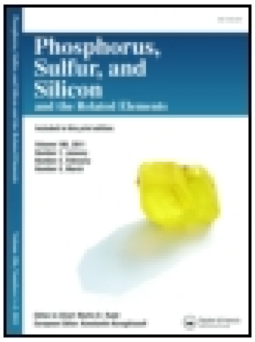

Phosphorus, Sulfur, and Silicon and the Related Elements

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PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
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A novel approach toward thioester bond formation mediated by *N,N′*-diisopropylcarbodiimide in water

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ABSTRACT

A simple and efficient method has been developed for the synthesis of thioesters from carboxylic acids and thiols using *N,N′*-diisopropylcarbodiimide (DIC). The reactions were carried out in water as an environmentally friendly and green solvent. The developed procedure presents an economic, efficient, mild, and very simple protocol for thioesterification reaction in aqueous media.

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KEYWORDS
Thioesterification; *N,N′*-diisopropylcarbodiimide; aqueous reactions

GRAPHICAL ABSTRACT

Introduction

Thioesters are valuable building blocks in chemical biology and useful intermediates in organic synthesis that are applied for acyl transfer,[1,2] peptide coupling,[3] coupling partners in organometallic reactions[4,5] and also as protecting groups for thiols.[6] Thioesters are also significant intermediates in a variety of biological systems,[7–9] and are broadly exist in many medicinal agents and biologically active compounds.[10] Therefore, in the past few years, considering the biological and chemical importance of thioesters, numerous methods for their synthesis have been developed, such as condensation of thiol and carboxylic acid by dehydrating reagents,[11] *trans*-thioesterification of active carboxylic acid derivatives with thiol,[12] thioesterification of carboxylic acids with thiol in the presence of trifluoroacetic acid,[13] thiocarbonylation of aryl halides and thiols with carbon monoxide in the presence of palladium catalyst,[14] the cross-dehydrogenative coupling of aldehydes with disulfides or thiols in the presence of a radical initiator, with the combination of *N*-Heterocyclic carbene catalyst, Dess–Martin periodinane, as well as metal catalysts such as $FeBr_2$ and CuCl.[15–20]

Recently, the utilization of water as an environmentally benign solvent has received remarkable interest in organic synthesis, owing to its very favorable qualities such as safety, nontoxicity, availability, environmental friendliness, and greater chemo-selectivity compared to organic solvents.[21–24] Moreover, it is unnecessary to dry reagents, solvents, and substrates before utilization in aqueous media. Thus, time, drying agents, and energy can be saved.

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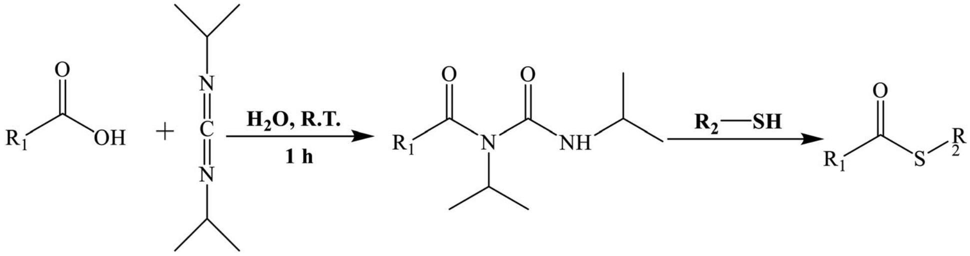


Scheme 1. Thioesterification of carboxylic acids in water.

In connection with our studies on the evaluation and development of various types of organic reactions in aqueous media,[25–37] we recently presented the preparation of two abundant and important functional groups "ester and amide" in the presence of DIC in water as a safe and easily available solvent.[38] In a continuation of this work, we wish to report herein a new strategy for thioester bond formation in water. This procedure presents simple and efficient access to highly functionalized thioesters under mild and environmentally friendly conditions (Scheme 1).

Results and discussion

Using water as a green reaction medium has received remarkable interest, from the environmental and economical point of view. It is clear that, in a water solvent, a hydrogen ion of carboxylic acid is transported to a water molecule. Therefore, in aqueous media reactivity of carboxylic acids is increased, thus, carboxylate ion can react easily and quickly with DIC. Giving this fact, in the previous work, we selected DIC as a suitable coupling reagent and water as a green and efficient solvent, for the synthesis of two valuable, abundant and basic functional moieties in nature.[38] In the present study, we aimed to investigate thioester bond formation, in connection with our previous study.[38] In this regard, the reaction of thiol (1 mmol), carboxylic acid (1 mmol), and DIC (1 mmol) in water leads to the formation of corresponding thioester in high yield. The structures of the products were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectra (see experimental section). For example, the IR spectrum of entry 1 showed strong absorption at 1671 cm^{-1} which is attributed to the carbonyl group of thioester (O = C–S). The ^{1}H-NMR spectrum of entry 1 showed signals at $\delta = 7.54$-8.38 ppm for aromatic protons of phenyl and naphthyl groups. The ^{1}H-decoupled ^{13}C NMR spectrum of entry 1 is in agreement with the proposed structure.

In view of the success of the above-mentioned reaction, we explored the scope of this promising reaction by varying the structure of the carboxylic acid and thiol component. As presented in Table 1, both aromatic and aliphatic carboxylic acids reacted easily with DIC to give the corresponding *N*-acylurea derivatives B,[37] and then in the presence of thiol functionality, aromatic and aliphatic samples, derivatives B can be easily converted to the related thioesters at room temperature in high yields. As shown in Table 1, benzoic acids containing electron-donating groups such as methyl and tert-butyl provided corresponding thioesters in high yields (entry 3 and entry 8). *N*-acylurea derivatives B, bearing halogen substituents such as –Br and –Cl at the para and meta positions also reacted smoothly with thiol samples to form the corresponding thioesters in excellent yields.

In the present work, we also used benzoic acids bearing $-NO_2$ and –CN moieties, but the yields were poor (10–20%) in these cases.

The important role of water in the progress of reaction, was also demonstrated by additional experiments in the presence of dichloromethane as an example of an organic solvent. In this regard, the obtained product from the reaction of DIC with benzoic acid as an acid moiety was lower as compared to in a water solvent. Because, acid cannot ionize in organic solvents, thus, its activity is low, and some amount of acid remains in the reaction mixture. As a result, the yield of thioester was reduced. In addition, it is necessary to mention that thiol cannot be ionized in the organic solvents, thus, its nucleophilic reactivity was lower in organic solvents, compared to water.

In addition, in order to prove the importance of DIC as an efficient coupling reagent in the present work, we used DCC instead of DIC. However, the reaction time was higher and further purification was needed.

Based on our experiments and previous studies,[37,38] a possible mechanism for thioester bond formation in the water solvent was proposed (Scheme 2). Firstly, carboxylic acid A in water ionizes to give hydronium ion and carboxylate ion. Then, intermediate B is formed from the reaction of carboxylate ion with DIC D. Finally, the nucleophilic attack of thiol to intermediate B provides thioester C.

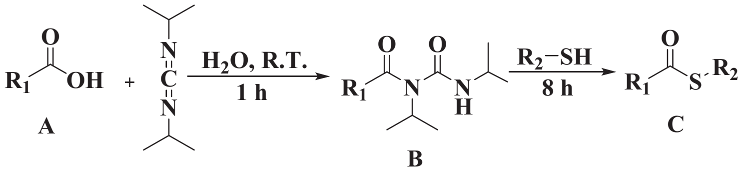
Moreover, we compared the performance of our procedure with some other previous methods in thioester bond formation (Table 2). It can be clearly seen that our procedure is superior to most of the other procedures in terms of yield and reaction conditions.

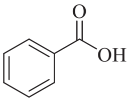
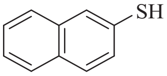
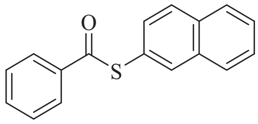
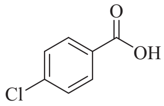
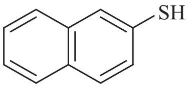
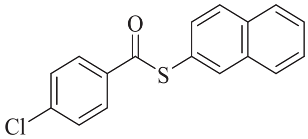
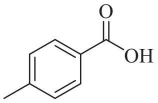
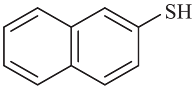
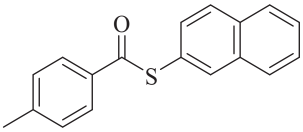
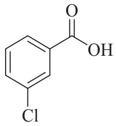
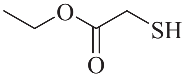
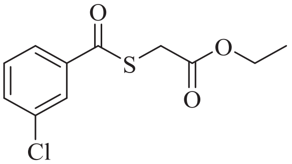
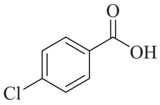
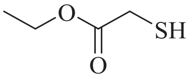
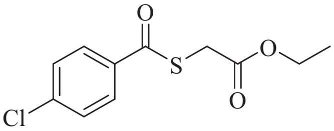
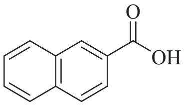
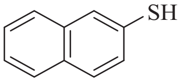
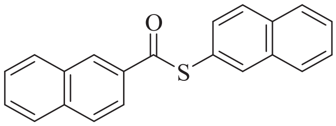
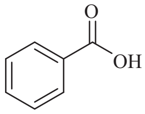
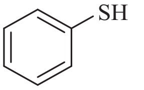
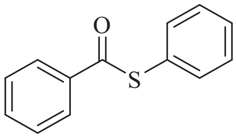
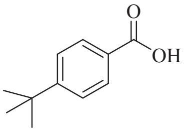
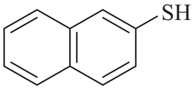
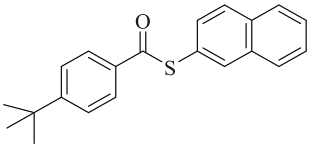
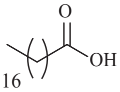
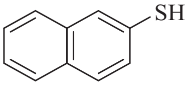
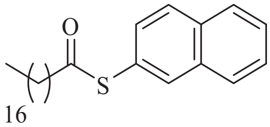
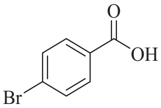
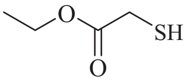
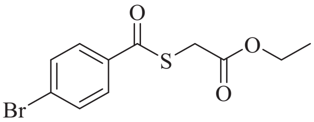
Experimental section

Materials and methods

All chemical compounds were purchased from Sigma-Aldrich (USA), Fluka (Switzerland), and Merck (Germany), and were used without additional purification. The methods used to monitor the reactions are TLC and NMR. The FTIR spectra were obtained using a Jasco 6300 FTIR spectrometer in the range of 400–4000 cm^{-1} with samples dispersed in KBr pellets at room temperature. ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ on a Bruker DRX-250 Avance

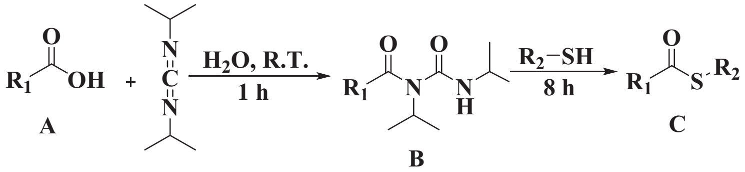
Table 1. Thioesterification reactions of carboxylic acids in water.[a]

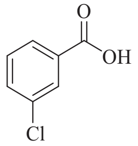
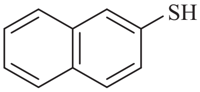
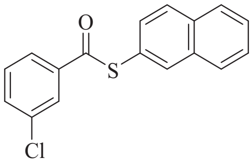


Entry	Acid	Thiol	Product	Yield[b]	Ref.
1				95	[39]
2				93	[40]
3				93	-
4				92	[41]
5				91	[42]
6				94	[43]
7				91	[40]
8				94	-
9				91	[44]
10				92	[45]

(*continued*)

Table 1. Continued.



Entry	Acid	Thiol	Product	Yield[b]	Ref.
11				93	–

[a]Reaction conditions: carboxylic acid (1 mmol), thiol (1 mmol), DIC (1 mmol), 2 mL H_2O, R.T.

[b]Isolated yield.

spectrometer at 250.13 and 62.90 MHz, respectively. The Supplemental Materials contains sample ^{1}H and ^{13}C NMR and IR spectra of the known products (Figures S1–S23).

General procedure for the synthesis of thioester in water

A typical experimental procedure is described below. To stirred solution of 1 mmol of carboxylic acid in H_2O at room temperature, was added DIC (1 mmol), and then the reaction mixture was stirred for 1 h. After this time, the 1 mmol of thiol was added and the reaction mixture was stirred for 8 h at room temperature. Then, the water was removed by filtration and the obtained solid washed with lukewarm water several times in order to eliminate the by-product diisopropyl urea (DIU).

S-(naphthalen-2-yl) benzothioate (entry 1)

White solid; m.p: 105-107 °C; IR (KBr) 3062, 1671, 1447, 1204, 903, 684 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.54-8.38 (m, 12H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 125.5, 126.7, 127.2, 127.5, 127.8, 128.6, 128.8, 131.4, 133.7, 134.9, 136.5, 137.1, 190.2.

S-(naphthalen-2-yl) 4-chlorobenzothioate (entry 2)

White solid; m.p: 129-131 °C; IR (KBr) 2926, 1662, 1425, 1203, 875 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.47-8.09 (m, 11H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 126.6, 127.3, 127.8, 128.9, 129.1, 129.4, 131.2, 131.9, 135.0, 189.8.

S-(naphthalen-2-yl) 4-methylbenzothioate (entry 3)

White solid; m.p: 72-74 °C; IR (KBr) 3062, 2924, 1669, 1205, 857 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.29-8.06 (m, 11H).^{13}C NMR (62.90 MHz, $CDCl_3$): δ 21.8, 124.9, 126.5, 1271, 127.6, 127.8, 128.0, 128.8, 129.5, 131.5, 133.4, 134.1, 135.0, 144.7, 190.1.

Ethyl 2-((3-chlorobenzoyl) thio) acetate (entry 4)

White solid; m.p: 51-53 °C; IR (KBr) 2966, 1614, 1246, 1463, 1686, 668 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.15 (t, $J = 5.2$ Hz, 3H), 3.81 (s, 2 H), 4.20 (m, 2 H), 7.36-7.94 (m, 3H), 8.06 (s, 1 H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 14.1, 31.5, 61.9, 128.0, 128.7, 129.0, 129.3, 131.4, 131.8, 168.4, 189.0.

Ethyl 2-((4-chlorobenzoyl) thio) acetate (entry 5)

White solid; m.p: 53-55 °C; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.15 (t, $J = 5.5$ Hz, 3H), 3.87 (s, 2 H), 4.21 (m, 2 H), 7.44-8.03 (m, 4H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 14.1, 31.4, 61.7, 128.1, 128.7, 129.2, 129.4, 131.6, 131.8, 168.4, 189.2.

S-(naphthalen-2-yl) naphthalene-2-carbothioate (entry 6)

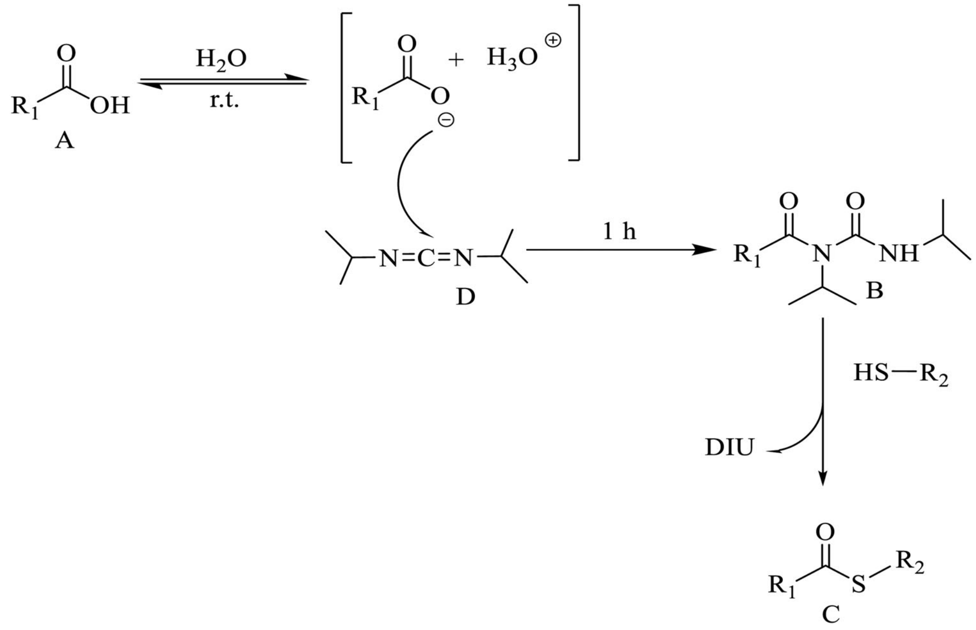
White solid; m.p: 165-167 °C; IR (KBr) 3052, 1708, 1425, 1171, 1061, 771 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.46-8.46 (m, 13 H), 9.16 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 124.5, 124.9, 125.7, 126.2, 126.5, 126.8, 127.5, 127.7, 128.1, 128.4, 128.8, 131.9, 132.1, 134.0, 135.5, 188.8.

S-phenyl benzothioate (entry 7)

White solid; m.p: 55-57 °C; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.54-8.18 (m, 10 H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 127.8, 128.1, 129.3, 129.7, 130.1, 134.2, 135.6, 137.1, 190.5.

S-(naphthalen-2-yl) 4-(tert-butyl) benzothioate (entry 8)

White solid; IR (KBr) 3082, 2926, 2857, 1668, 1215, 908, 818 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.37 (s. 9H), 7.51-8.05 (m, 11H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 31.1, 35.2, 125.7, 126.5, 127.1, 1267.4, 127.8, 128.0, 128.7, 131.5, 134.9, 157.2, 189.9.



Scheme 2. Proposed mechanism for thioesterification reaction in water.

Table 2. Comparison of the results with some other previously reported methods in thioesterification reactions.

Entry	Catalyst & Conditions	Time	Yield (%)[a]	Refs.
1	PPh_3/*N*-chlorobenzotriazole (NCBT), CH_2Cl_2, 0 °C to room temperature	40–200[b]	80–95	[46]
2	Sulfonated porous carbon, 100 °C, Solvent-free	45[b]	67–94	[47]
3	Trifluoromethanesulfonic acid, toluene, reflux	6–48[c]	76–97	[48]
4	$Pd(OAc)_2/PPh_3$, triethylamine, phosphonium salt ionic liquid, carbon monoxide, 100 °C	18[c]	43–97	[14]
5	Tert-butyl hydroperoxide, CuCl, 100 °C, N_2, H_2O	1[c]	31–94	[18]
6	$Cu(OAc)_2{\cdot}2H_2O$, tert-butyl hydroperoxide, 95 °C	6–17[c]	49–75	[49]
7	Poly(3,4-dimethyl-5-vinylthiazolium), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), phenazine, DMF, 27 °C	12[c]	51–98	[50]
8	*N,N′*-diisopropylcarbodiimide, H_2O, room temperature	8[c]	91–94	This work

[a] Isolated yield.
[b] Time (min).
[c] Time (h).

S-(naphthalen-2-yl) octadecanethioate (entry 9)

White solid; m.p: 56-58 °C; IR (KBr) 3085, 2918, 2848, 1686, 1636, 1471, 697 cm^{-1}; ^1H NMR (250.13 MHz, $CDCl_3$) δ 0.87 (t, $J = 6.7$ Hz, 3H), 1.26 (m, 26 H), 1.55 (m, 2 H), 1.73 (m, 2 H), 2.69 (m, 2 H), 7.44-7.98 (m, 7H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 14.1, 22.6, 25.6, 29.0, 29.3, 29.6, 31.9, 43.8, 125.7, 126.2, 126.5, 127.0, 127.4, 127.7, 128.7, 128.9, 130.9, 134.2, 192.0.

Ethyl 2-((4-bromobenzoyl) thio) acetate (entry 10)

Yellow solid; m.p: 40-42 °C; ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.14 (t, $J = 5.2$ Hz, 3H), 3.80 (s, 2 H), 4.20 (m, 2 H), 7.36-8.04 (m, 4H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 14.1, 31.2, 61.7, 128.0, 128.7, 129.0, 129.3, 131.2, 131.8, 168.4, 190.0.

S-(naphthalen-2-yl) 3-chlorobenzothioate (entry 11)

White solid; m.p: 129-131 °C; IR (KBr) 3082, 2960, 1668, 1418, 1195, 875 cm^{-1}; ^1H NMR (250.13 MHz, $CDCl_3$) δ 7.55-8.04 (m, 11H); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 125.6, 126.6, 127.3, 127.5, 128.0, 128.9, 130.1, 131.2, 133.6, 135.0, 189.2.

Conclusions

In summary, the reported method offers a cost-effective, easy, ecofriendly, and effective route for the preparation of thioesters from carboxylic acids and thiols in the presence of DIC in water as a green solvent. The developed method is general for a variety of carboxylic acids and thiols including aliphatic and aromatic samples, to afford the desired thioesters. Considering the importance of the thioester bond, we hope that our new approach may inspire researchers to develop alternative methods for the formation of thioester bond in the coming years.

Conflict of interest

The authors hereby declare that, there was no conflict of interest in the present study.

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