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Catalysis by ionic liquid: a simple, green and efficient procedure for the Michael addition of thiols and thiophosphate to conjugated alkenes in ionic liquid, [pmIm]Br

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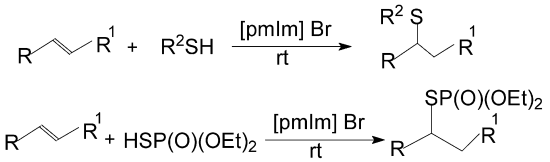
Abstract—A room temperature ionic liquid, 1-pentyl-3-methylimidazolium bromide, [pmIm]Br efficiently catalyzes Michael addition of thiols and diethyl dithiophosphate to a variety of conjugated alkenes such as α,β-unsaturated carbonyl compounds, carboxylic esters, nitriles and chalcones without requiring any other organic solvent and catalyst. The ionic liquid can be recycled for subsequent reactions without any appreciable loss of efficiency.

1. Introduction

Ionic liquids have been the subject of considerable current interest as environmentally benign reaction media in organic synthesis because of their unique properties of non-volatility, non-flammability, recyclability and ability to dissolve a wide range of materials, among others.[1] During the past few years a variety of ionic liquids have been demonstrated as efficient and practical alternatives to organic solvents for many important organic transformations.[1,2] However, the ability of ionic liquids as a clean catalyst has not been explored to any great extent[3] although it is of much importance in the context of green synthesis. As a part of our drive[4] to avoid organic solvent and toxic catalysts in reactions we have initiated a program to explore the use of benign molten salts[4e–g] and room temperature ionic liquids as efficient catalysts as well as reaction media for useful organic transformations.

The Michael reaction, since its discovery in 1889[5] has been used as one of the most useful methods for effecting carbon–carbon bond formation and later has also been efficiently manipulated for carbon–sulfur and carbon–nitrogen bond forming processes.[6] This reaction is usually carried out under acid or base catalysis. However, to avoid side reactions occasionally encountered in presence of a strong acid or a base, several inorganic salts such as alumina,[7a] zeolite,[7b] bismuth nitrate[7c] among others have been introduced. Recently, conjugate addition of mercaptans to enones has attracted considerable interest[8] as it leads to the synthesis of biologically active compounds such as the calcium antagonist diltiazem.[9] Thus, a number of procedures either based on the activation of thiol by a base or activation of the acceptor olefins with Lewis acids have been developed.[8,10] We report here the novel application of an inexpensive room temperature ionic liquid, 1-pentyl-3-methylimidazolium bromide,[11] [pmIm]Br as an efficient catalyst as well as reaction medium for the Michael addition of thiol and thiophosphate to conjugated alkenes without any conventional solvent and catalyst for the first time (Scheme 1).



R = alkyl/aryl; R^1 = COMe, COPh, CO_2Et etc.; R^2 = *n*-Bu, Ph

Scheme 1.

2. Results and discussion

The experimental procedure is very simple. A mixture of conjugated alkene, thiol (or dithiophosphate) and ionic liquid, [pmIm]Br was stirred at room temperature for a period of time. The reaction mixture was extracted with ether and the crude product was purified by column chromatography. The residual ionic liquid after being dried under vacuum was reused for subsequent reactions.

Keywords: Michael addition; Thiol; Thiophosphate; Ionic liquid; Green catalysis.
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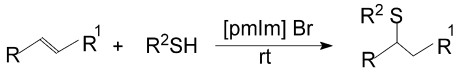
Table 1. Michael addition of thiols to conjugated alkenes



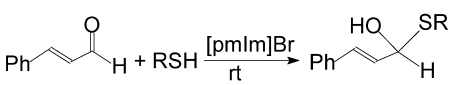
Entry	R	R^1	R^2	Time (h)	Yield (%)[a]	Reference
1	Me	COPh	*n*-Bu	1.25	85	
2	Me	COPh	Ph	0.75	88	10c
3	Me	COPh	(*p*-Cl)C_6H_4	0.75	83	
4	H	COMe	*n*-Bu	0.75	72	4g
5	H	COMe	Ph	0.75	75	4g
6	$(PhCH{=}CH)_2CO$		*n*-Bu	1.25	78[b]	8i
7	Cyclohexenone		Ph	0.5	90	4g
8	Cyclohexenone		*n*-Bu	0.75	91	7c
9	3-Methylcyclohexenone		Ph	No reaction		
10	Me	CHO	*n*-Bu	1.50	90	4g
11	Me	CHO	Ph	1.50	88	4g
12	H	CO_2Me	Ph	1.0[c]	89	4g
13	H	CO_2Me	*n*-Bu	2.0[c]	85	4g
14	CO_2Et	CO_2Et	Ph	0.75	91	4g
15	Ph	CO_2Et	Ph	No reaction		
16	H	CN	Ph	1.0[c]	90	4g
17	H	CN	*n*-Bu	1.50	88	4g
18	Ph	CN	Ph	No reaction		

[a] The yields refer to those of pure isolated products characterized by spectroscopic (IR, ^1H and ^{13}C NMR) data.
[b] The product corresponds to bis-addition.
[c] The reaction was carried out at 65 °C.

No loss of efficiency with regard to reaction time and yield was observed after three uses; however it can be mixed with fresh ionic liquid after three uses for comparable results in subsequent runs.

Both aliphatic and aromatic thiols react with a variety of acyclic and cyclic conjugated alkenes by this procedure to produce the corresponding adducts in high yields. The results are summarized in Table 1. As evident from the results, thiophenol and *n*-butanethiol underwent facile reactions with α,β-unsaturated ketones, aldehydes, esters and nitriles under this procedure. However, the reactions of α,β-unsaturated aldehydes are interesting. Crotonaldehyde undergoes the expected 1,4-addition with butanethiol (entry 10) and thiophenol (entry 11), whereas cinnamaldehyde does not combine with thiophenol even at elevated temperature. Interestingly, the reactions of butanethiol and ethanethiol proceed for 1,2-addition to the carbonyl functionality of cinnamaldehyde producing the corresponding allylic alcohols (Scheme 2) in high yields under identical reaction conditions. A diconjugated acyclic enone, 1,5-diphenylpent-1,4-dien-3-one (entry 8) undergoes bis-additions with two equivalent of thiols to provide the corresponding bis-adduct.

The conjugate addition of thiols to chalcones is considered



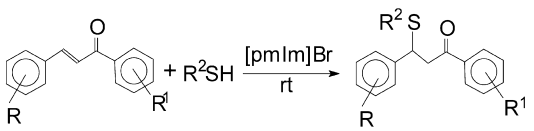
Entry	R	Time(h)	Yield(%)
1	*n*-Bu	2.5	93
2	Et	2.5	86

Scheme 2.

less facile compared to the addition to aliphatic acyclic enones and thus it is not always satisfactory with the reagents used for aliphatic enones. In our own experience, molten tetrabutylammonium bromide[4g] that efficiently catalyzes the addition of thiols to acyclic enones, esters and nitriles fails to effect reaction with chalcones. However, using the present procedure, the ionic liquid [pmIm]Br is successful for addition of aromatic as well as non-aromatic thiols to chalcones without any difficulty. The results are reported in Table 2. As evident from the results in Table 2, both electron withdrawing and electron donating substituents on aromatic ring of the chalcones are compatible with this procedure.

The addition of diethyl dithiophosphate to conjugated

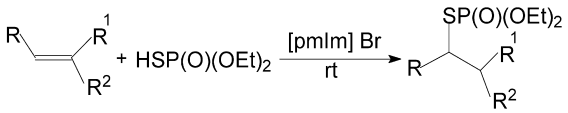
Table 2. Michael addition of thiols of chalcones



Entry	R	R^1	R^2	Time (h)	Yield (%)[a]	Reference
1	H	H	*n*-Bu	1.0	95	
2	H	H	Ph	0.5	94	8b
3	*p*-OMe	H	(*p*-Cl)C_6H_4	0.5	90	
4	*p*-OMe	H	*n*-Bu	1.75	86	
5	*p*-Cl	H	*n*-Bu	1.0	92	
6	*p*-Cl	H	(*p*-Cl)C_6H_4	0.5	90	
7	*p*-NO_2	H	*n*-Bu	1.5	93	
8	*p*-NO_2	H	(*p*-Cl)C_6H_4	0.75	87	
9	H	*p*-Me	Ph	0.5	91	13
10	H	*p*-Me	*n*-Bu	1.5	90	
11	*m*-OAc	H	*n*-Bu	1.5	82	
12	*m*-OAc	H	Ph	1.0	86	

[a] The Yields refer to those of pure isolated products characterized by spectroscopic (IR, ^1H and ^{13}C NMR) data.

Table 3. Michael addition of diethyl dithiophosphate to conjugated alkenes



Entry	R	R^1	R^2	Time (h)	Yield (%)[a]	Reference
1	H	COMe	H	0.05	88	
2	Me_2	COMe	H	0.75	89	12d
3	Cyclohexenone			0.75	71	
4	3-Methylcyclohexenone			No reaction		
5	Ph	COPh	H	0.75	93	12a
6	(*p*-Cl)C_6H_4	COPh	H	1	92	12a
7	(*p*-OMe)C_6H_4	COPh	H	1	90	12a
8	Ph	CO(*p*-Me)-C_6H_4	H	1	91	
9	Me	CHO	H	1.5	87	
10	Ph	CHO	H	No reaction		
11	H	CO_2Me	H	1	82	12b
12	H	CO_2Me	Me	1	89	
13	Me	CO_2Et	H	1	91	12c
14	Ph	CO_2Et	H	No reaction		
15	H	CN	H	0.75	86	
16	H	CN	Me	1	88	
17	Ph	CN	H	No reaction		

[a] The yields refer to those of pure isolated products characterized by spectroscopic (IR, ^1H and ^{13}C NMR) data.

carbonyl compounds, esters and nitriles is also found to proceed efficiently by the catalysis of this ionic liquid. The detailed results are presented in Table 3. The synthesis of these thiophosphate adducts are of considerable recent interest because of their various newer applications in industry and as useful synthetic intermediates in organic synthesis.[12]

These Michael additions are in general, very fast and clean. The crude products obtained are sufficiently pure, and purification by short column chromatography gave analytically pure samples. It has also been observed that these ionic liquid catalyzed additions are greatly influenced by the β-substitutions on the conjugated alkene. Thus, while cyclohex-2-en-1-one underwent facile addition, 3-methyl cyclohex-2-en-1-one remained inert (entry 9 in Table 1 and entry 4 in Table 3). Similarly phenyl substitutions at the β-positions of conjugated esters and nitriles made them inactive (entries 15, 18 in Table 1 and entries 14, 17 in Table 3). These inhibitions may be due to steric factors. The catalytic activity of [pmIm]Br for these Michael additions is established by the observation that no reaction was observed in the absence of ionic liquid. The optimum amount of ionic liquid has been determined to be the quantity required just to solubilize the reacting materials. Although the mechanism of action of this ionic liquid is yet to be established with further experiments it may be postulated that the bromide ion is hydrogen bonding to the thiol increasing the nucleophilicity of sulfur atom. This makes the thiolate anion a better nucleophile towards efficient addition to conjugated alkenes.

Very recently, a procedure using a [BmIm]PF_6/H_2O system has been reported for the conjugate addition of thiols to α,β-unsaturated ketones.[14] However, the present procedure using [pmIm]Br is a better alternative being more general in its application and requiring no water as an additive.

3. Conclusion

The present procedure catalyzed by a simple ionic liquid, [pmIm]Br provides an efficient and general methodology for Michael addition of thiols and diethyl thiophosphate to conjugated acyclic and cyclic enones, chalcones, aldehydes, esters and nitriles. The significant improvements offered by this procedure are: (a) fast reaction (0.5–2.0 h); (b) simple operation and mild conditions (room temperature), (c) high yields (72–95%); (d) cost efficiency providing recyclability of the catalyst, and (e) green aspects avoiding hazardous organic solvents, toxic catalysts and waste (atom efficiency). More significantly, this work clearly demonstrates the potential of a room temperature ionic liquid to act as an efficient and recyclable catalyst and shows much promise for further applications.

4. Experimental

4.1. General

The ionic liquid, [pmIm]Br was prepared following a reported procedure.[11] IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 300 and 75 MHz, respectively.

4.1.1. General experimental procedure for Michael additions. Representative one (entry 1, Table 2). A mixture of chalcone (253 mg, 1 mmol), butanethiol (117 mg, 1.3 mmol) and [pmIm]Br (300 mg) was stirred at room temperature for a period of time as required to complete the reaction (TLC). The reaction mixture was washed with ether (3×10 mL) and the combined ether extract was evaporated to leave the crude product which was purified by column chromatography over silica gel (hexane/ether 96:4) to give pure adduct,

1,3-diphenyl-3-(thiobutyl)propan-1-one (315 mg, 92%) as a colorless oil; IR 3028, 2952, 1675, 1603 cm^{-1}; ^1H NMR δ 0.82 (t, J=7.2 Hz, 3H), 1.26–1.34 (m, 2H), 1.39–1.56 (m, 2H), 2.27–2.37 (m, 2H), 3.52 (d, J=7.0 Hz, 2H), 4.55 (t, J=7.0 Hz, 1H), 7.17–7.54 (m, 8H), 7.88–7.91 (m, 2H); ^{13}C NMR δ 14.0, 22.4, 31.5, 31.7, 44.7, 45.9, 127.6, 128.3 (2C), 128.5 (2C), 128.8 (2C), 128.9, 129.0, 133.6, 137.3, 142.7, 197.4. Anal. calcd for $C_{19}H_{22}OS$: C, 76.47; H, 7.43. Found: C, 76.31; H, 7.28.

The residual ionic liquid was further washed with ether and after being dried under vacuum was reused for subsequent reactions. This procedure was followed for all the conjugate additions listed in Tables 1–3. The known compounds were identified by comparison of their spectral data with those reported,[4g,7c,8b,i,10c,12a–d,13] and the new compounds were properly characterized by their IR, ^1H NMR and ^{13}C NMR spectroscopic data and elemental analyses. These data are presented below in order of their entries in the Tables 1–3.

4.1.2. 1-Phenyl-3-(thiobutyl)butan-1-one (entry 1, Table 1). Colorless oil; IR (neat) 3032, 2929, 1685, 1596 cm^{-1}; ^1H NMR δ 0.91 (t, J=7.4 Hz, 3H), 1.35 (d, J=6.7 Hz, 3H), 1.36–1.46 (m, 2H), 1.53–1.64 (m, 2H), 2.57 (t, J=7.3 Hz, 2H), 3.05–3.33 (m, 2H), 3.42–3.52 (m, 1H), 7.26–7.59 (m, 3H), 7.90–7.97 (m, 2H); ^{13}C NMR δ 14.1, 22.2, 22.5, 31.0, 32.2, 35.9, 46.6, 128.5 (2C), 129.1 (2C), 133.3, 137.4, 198.7. Anal. calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53. Found: C, 70.96; H, 8.45.

4.1.3. 1-Phenyl-3-(4-chlorothiophenyl)butan-1-one (entry 3, Table 1). Colorless oil; IR (neat) 3062, 1681, 1475 cm^{-1}; ^1H NMR δ 1.37 (d, J=6.7 Hz, 3H), 3.07–3.31 (m, 2H), 3.85–3.92 (m, 1H), 7.20–7.57 (m, 7H), 7.89–7.91 (m, 2H); ^{13}C NMR δ 21.3, 39.5, 45.7, 128.2 (2C), 128.8 (2C), 129.3 (2C), 133.5, 133.8 (2C), 134.1, 137.8, 147.5, 198.2. Anal. calcd for $C_{16}H_{15}OSCl$: C, 66.08; H, 5.20. Found: C, 65.92; H, 5.03.

4.1.4. 3-(4-Chlorothiophenyl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (entry 3, Table 2). White crystal; mp 86–90 °C; IR (KBr) 2947, 1674, 1610 cm^{-1}; ^1H NMR δ 3.53–3.62 (m, 2H), 3.74 (s, 3H), 4.93 (dd, J_1=6.5 Hz, J_2=7.1 Hz, 1H), 6.79 (d, J=8.7 Hz, 2H), 7.17–7.54 (m, 9H), 7.89 (d, J=7.3 Hz, 2H); ^{13}C NMR δ 45.1, 48.4, 55.6, 114.3 (2C), 128.5 (2C), 129.0 (2C), 129.3 (2C), 129.4 (2C), 133.4 (2C), 133.8, 134.1, 134.6 (2C), 137.1, 159.3, 197.3. Anal. calcd for $C_{22}H_{19}O_2SCl$: C, 69.01; H, 5.00. Found: C, 69.24; H, 5.22.

4.1.5. 3-(4-Methoxyphenyl)-1-phenyl-3-thiobutylpropan-1-one (entry 4, Table 2). Colorless oil; IR (neat) 3057, 2835, 1683, 1608 cm^{-1}; ^1H NMR δ 0.84 (t, J=7.2 Hz, 3H), 1.26–1.35 (m, 2H), 1.43–1.54 (m, 2H), 2.24–2.38 (m, 2H), 3.50 (d, J=7.1 Hz, 2H), 3.77 (s, 3H), 4.52 (t, J=7.1 Hz, 1H), 6.84 (d, J=7.4 Hz, 2H), 7.26–7.56 (m, 5H), 7.90 (d, J=7.4 Hz, 2H); ^{13}C NMR δ 14.1, 22.4, 31.5, 31.7, 44.1, 45.9, 55.6, 114.2, 114.3, 128.5 (2C), 129.0 (2C), 129.2, 129.3, 133.6, 134.6, 137.2, 158.9, 197.6. Anal. calcd for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36. Found: C, 73.01; H, 7.21.

4.1.6. 3-(4-Chlorophenyl)-1-phenyl-3-thiobutylpropan-1-one (entry 5, Table 2). Colorless oil; IR (neat) 2956, 2869, 1687, 1596 cm^{-1}; ^1H NMR δ 0.84 (t, J=7.2 Hz, 3H), 1.20–1.57 (m, 4H), 2.26–2.40 (m, 2H), 3.49 (d, J=7.0 Hz, 2H), 4.52 (t, J=7.0 Hz, 1H), 7.24–7.57 (m, 7H), 7.89 (d, J=7.8 Hz, 2H); ^{13}C NMR δ 14.0, 22.3, 31.5, 31.6, 43.9, 45.7, 122.9 (2C), 128.9, 129.0, 129.1 (2C), 129.7 (2C), 133.8, 137.0, 141.3, 143.7, 197.1. Anal. calcd for $C_{19}H_{21}OSCl$: C, 68.55; H, 6.36. Found: C, 68.38; H, 6.30.

4.1.7. 3-(4-Chlorophenyl)-3-(4-chlorothiophenyl)-1-phenylpropan-1-one (entry 6, Table 2). White crystal; mp 84–86 °C; IR (KBr) 3061, 1685, 1473, 688 cm^{-1}; ^1H NMR δ 3.58 (d, J=7.1 Hz, 2H), 4.88 (t, J=7.1 Hz, 1H), 7.16–7.58 (m, 11H), 7.88 (d, J=7.8 Hz, 2H); ^{13}C NMR δ 44.8, 48.3, 128.4 (2C), 128.9 (2C), 129.0, 129.1 (2C), 129.4 (2C), 129.5 (2C), 130.8, 133.9, 134.5, 134.8 (2C), 137.5, 140.1, 196.8. Anal. calcd for $C_{21}H_{16}OSCl_2$: C, 65.12; H, 4.16. Found: C, 64.94; H, 4.04.

4.1.8. 3-(4-Nitrophenyl)-1-phenyl-3-thiobutylpropan-1-one (entry 7, Table 2). Colorless oil; IR (neat) 2956, 2871, 1687, 1519, 1346 cm^{-1}; ^1H NMR δ 0.84 (t, J=7.2 Hz, 3H), 1.27–1.36 (m, 2H), 1.44–1.52 (m, 2H), 2.25–2.39 (m, 2H), 3.57 (d, J=7.1 Hz, 2H), 4.62 (t, J=7.1 Hz, 1H), 7.41–7.62 (m, 5H), 7.88–7.91 (m, 2H), 8.14–8.17 (m, 2H); ^{13}C NMR δ 13.9, 22.3, 31.5, 31.7, 44.1, 45.4, 123.9 (2C), 128.2 (2C), 129.1 (2C), 129.2 (2C), 133.9, 136.7, 147.3, 150.7, 196.6. Anal. calcd for $C_{19}H_{21}O_3SN$: C, 66.45; H, 6.16, N, 4.08. Found: C, 66.51; H, 6.03, N, 3.92.

4.1.9. 3-(4-Chlorothiophenyl)-3-(4-nitrophenyl)-1-phenylpropan-1-one (entry 8, Table 2). Yellow crystal; mp 95–97 °C; IR (KBr) 3058, 1681, 1519, 1346, 688 cm^{-1}; ^1H NMR δ 3.65 (d, J=7.1 Hz, 2H), 4.94 (t, J=7.1 Hz, 1H), 7.15–7.61 (m, 9H), 7.88–7.91 (m, 2H), 8.09–8.12 (m, 2H); ^{13}C NMR δ 44.3, 48.5, 124.2 (2C), 128.2 (2C), 128.4, 128.8 (2C), 128.9 (2C), 129.4 (2C), 131.6, 132.2, 134.1, 135.1 (2C), 136.6, 149.3, 196.2. Anal. calcd for $C_{21}H_{16}O_3SN$: C, 69.60; H, 4.45; N, 3.86. Found: C, 69.80; H, 4.26; N, 4.09.

4.1.10. 1-(4-Methylphenyl)-3-phenyl-3-thiobutylpropan-1-one (entry 10, Table 2). White crystal; mp 58 °C; IR (KBr) 3028, 2952, 1674, 1606 cm^{-1}; ^1H NMR δ 0.83 (t, J=7.3 Hz, 3H), 1.26–1.37 (m, 2H), 1.42–1.50 (m, 2H), 2.27–2.36 (m, 2H), 2.37 (s, 3H), 3.47 (d, J=7.1 Hz, 2H), 4.54 (t, J=7.1 Hz, 1H), 7.20–7.32 (m, 5H), 7.41 (d, J=8.2 Hz, 2H), 7.81 (d, J=8.2 Hz, 2H); ^{13}C NMR δ 14.0, 22.0, 22.3, 31.6, 31.7, 44.8, 45.7, 127.5, 128.2 (2C), 128.6 (2C), 128.9 (2C), 129.7 (2C), 134.8, 142.8, 144.4, 197.0. Anal. calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74. Found: C, 77.09; H, 7.69.

4.1.11. 3-(3-Acetoxyphenyl)-1-phenyl-3-thiobutylpropan-1-one (entry 11, Table 2). Colorless oil; IR (neat) 3024, 2952, 1764, 1675, 1604 cm^{-1}; ^1H NMR δ 0.82 (t, J=7.2 Hz, 3H), 1.26–1.34 (m, 2H), 1.39–1.56 (m, 2H), 2.15 (s, 3H), 2.27–2.37 (m, 2H), 3.52 (d, J=7.0 Hz, 2H), 4.55 (t, J=7.0 Hz, 1H), 6.89–7.54 (m, 7H), 7.89 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 14.0, 21.2, 22.4, 31.5, 31.7, 44.7, 45.9, 127.6, 128.3 (2C), 128.5, 128.8 (2C), 128.9, 129.0, 133.6, 137.3, 142.7, 157.3, 169.2, 197.4. Anal. calcd for $C_{21}H_{24}O_3S$: C, 70.76; H, 6.79. Found: C, 70.58; H, 6.89.

4.1.12. 3-(3-Acetoxyphenyl)-1-phenyl-3-thiophenylpropan-1-one (entry 12, Table 2). Gummy mass; IR (neat) 3026, 2948, 1762, 1681, 1610 cm^{-1}; ^1H NMR δ 2.15 (s, 3H), 3.56–3.75 (m, 2H), 4.98 (dd, J_1=6.2 Hz, J_2=8.0 Hz, 1H), 6.89 (m, 12H), 7.88–7.90 (m, 2H); ^{13}C NMR δ 21.2, 45.1, 48.6, 127.8 (2C), 127.9, 128.2 (3C), 128.3, 128.5, 129.1, 129.3, 133.2 (3C), 133.7, 134.7, 137.1, 141.6, 157.3, 169.2, 197.4. Anal. calcd for $C_{23}H_{20}O_3S$: C, 73.38; H, 5.35. Found: C, 73.21; H, 5.29.

4.1.13. *O,O*-Diethyl *S*-(3-oxobutyl)phosphorodithioate (entry 1, Table 3). Colorless oil; IR (neat): 2979, 2902, 1716, 1442, 1012, 960 cm^{-1}; ^1H NMR δ 1.33 (t, J=7.1 Hz, 6H), 2.14 (s, 3H), 2.81–2.86 (m, 2H), 2.98–3.08 (m, 2H), 4.05–4.24 (m, 4H); ^{13}C NMR δ 15.7 (d, J_{CP}=8.2 Hz) (2C), 26.8 (d, J_{CP}=3.5 Hz), 29.9, 43.8 (d, J_{CP}=3.8 Hz), 63.9 (d, J_{CP}=6.2 Hz) (2C), 205.7. Anal. calcd for $C_8H_{17}S_2O_3P$: C, 37.49; H, 6.69. Found: C, 37.33; H, 6.50.

4.1.14. *O,O*-Diethyl *S*-(3-oxocyclohexyl)phosphorodithioate (entry 3, Table 3). Colorless oil; IR (neat): 2981, 2868, 1716, 1012, 960 cm^{-1}; ^1H NMR δ 1.32 (t, J=7.1 Hz, 6H), 1.72–2.52 (m, 7H), 2.78 (dd, J_1=14.4 Hz, J_2=4.8 Hz, 1H), 3.50–3.64 (m, 1H), 4.05–4.23 (m, 4H); ^{13}C NMR δ 18.2 (d, J_{CP}=8.3 Hz) (2C), 26.4, 35.1 (d, J_{CP}=5.8 Hz), 43.0, 49.2 (d, J_{CP}=3.6 Hz), 51.4 (d, J_{CP}=5.3 Hz), 66.6 (d, J_{CP}=6.2 Hz) (2C), 209.9. Anal. calcd for $C_{10}H_{19}S_2O_3P$: C, 42.54; H, 6.78. Found: C, 42.36; H, 6.61.

4.1.15. *O,O*-Diethyl *S*-[3-(4-methylphenyl)-1-phenyl-3-oxopropyl]phosphorodithioate (entry 8, Table 3). Colorless oil; IR (neat): 2979, 2900, 1601, 1606, 1440, 1015, 962 cm^{-1}; ^1H NMR δ 1.08 (t, J=7.0 Hz, 3H), 1.32 (t, J=7.0 Hz, 3H), 2.39 (s, 3H), 3.56–3.77 (m, 2H), 4.04–4.15 (m, 4H), 4.95–5.04 (m, 1H), 7.19–7.43 (m, 7H), 7.81 (d, J=8.1 Hz, 2H); ^{13}C NMR δ 15.4 (d, J_{CP}=8.8 Hz), 15.7 (d, J_{CP}=8.8 Hz), 21.5, 46.0 (d, J_{CP}=7.1 Hz), 47.8 (d, J_{CP}=3.8 Hz), 63.6 (d, J_{CP}=5.4 Hz), 63.9 (d, J_{CP}=5.4 Hz), 127.5, 128.1 (2C), 128.3 (2C), 128.6 (2C), 129.3 (2C), 133.9, 141.6, 144.2, 195.4. Anal. calcd for $C_{20}H_{25}S_2O_3P$: C, 58.80; H, 6.17. Found: C, 58.59; H, 6.03.

4.1.16. *O,O*-Diethyl *S*-(1-methyl-3-oxopropyl)phosphorodithioate (entry 9, Table 3). Colorless oil; IR (neat): 2979, 2829, 1726, 1444, 1012, 960 cm^{-1}; ^1H NMR δ 1.35 (t, J=7.1 Hz, 6H), 1.46 (d, J=6.9 Hz, 3H), 2.69–2.77 (m, 1H), 2.83–2.92 (m, 1H), 3.69–3.85 (m, 1H), 4.08–4.22 (m, 4H), 9.74 (d, J=1.4 Hz, 1H); ^{13}C NMR δ 18.2 (d, J_{CP}=8.3 Hz) (2C), 25.3 (d, J_{CP}=5.8 Hz), 41.4 (d, J_{CP}=3.7 Hz), 53.5 (d, J_{CP}=5.7 Hz), 66.6 (d, J_{CP}=6.4 Hz) (2C), 201.9. Anal. calcd for $C_8H_{17}S_2O_3P$: C, 37.49; H, 6.69. Found: C, 37.32; H, 6.49.

4.1.17. *O,O*-Diethyl *S*-(2-carbomethoxypropyl)phosphorodithioate (entry 12, Table 3). Colorless oil; IR (neat): 2981, 2875, 1737, 1440, 1014, 960 cm^{-1}; ^1H NMR δ 1.23 (d, J=7.1 Hz, 3H), 1.33 (t, J=7.1 Hz, 6H), 2.76–2.97 (m, 2H), 3.05–3.15 (m, 1H), 3.68 (s, 3H), 4.08–4.18 (m, 4H); ^{13}C NMR δ 15.7 (d, J_{CP}=8.2 Hz) (2C), 16.8, 35.9 (d, J_{CP}=3.8 Hz), 40.4 (d, J_{CP}=4.2 Hz), 51.8, 63.9 (d, J_{CP}=6.0 Hz) (2C), 174.7. Anal. calcd for $C_9H_{19}O_4S_2P$: C, 37.75; H, 6.69. Found: C, 37.58; H, 6.52.

4.1.18. *O,O*-Diethyl *S*-(2-cyanoethyl)phosphorodithioate (entry 15, Table 3). Colorless oil; IR (neat): 2983, 2902, 2250, 1442, 1010, 962 cm^{-1}; ^1H NMR δ 1.33 (t, J=7.1 Hz, 6H), 2.73–2.78 (m, 2H), 3.02–3.13 (m, 2H), 4.06–4.24 (m, 4H); ^{13}C NMR δ 18.2 (d, J_{CP}=8.2 Hz) (2C), 21.7 (d, J_{CP}=3.1 Hz), 31.4 (d, J_{CP}=3.8 Hz), 66.9 (d, J_{CP}=6.8 Hz) (2C), 119.9. Anal. calcd for $C_7H_{14}NO_2S_2P$: C, 35.14; H, 5.90; N, 5.85. Found: C, 34.98; H, 5.75; N, 5.69.

4.1.19. *O,O*-Diethyl *S*-(2-cyanopropyl)phosphorodithioate (entry 16, Table 3). Colorless oil; IR (neat) 2983, 2902, 2250, 1454, 1010, 962 cm^{-1}; ^1H NMR δ 1.33–1.47 (m, 9H), 2.98–3.12 (m, 3H), 4.10–4.25 (m, 4H); ^{13}C NMR δ 15.7 (d, J_{CP}=8.2 Hz) (2C), 17.37, 27.2 (d, J_{CP}=3.5 Hz), 36.6 (d, J_{CP}=3.5 Hz), 64.4 (d, J_{CP}=6.8 Hz) (2C), 120.9. Anal. calcd for $C_8H_{16}O_2S_2P$: C, 37.93; H, 6.37; N, 5.53. Found: C, 37.76; H, 6.29; N, 5.40.

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