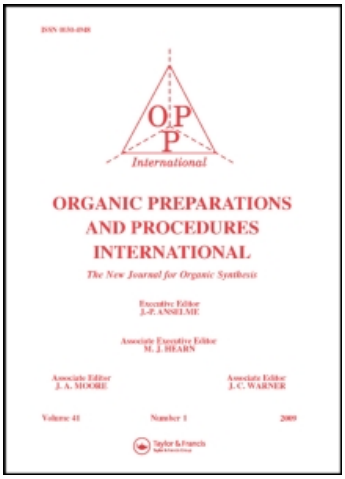

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NEW EFFICIENT SYNTHESIS OF 2-ALKYLTHIO-5-BENZYLJDENE-4H-IMIDAZOLIN-4-ONES

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NEW EFFICIENT SYNTHESIS OF 2-ALKYLTHIO-5-BENZYLIDENE-4H-IMIDAZOLIN-4-ONES

Submitted by (10/25/02)

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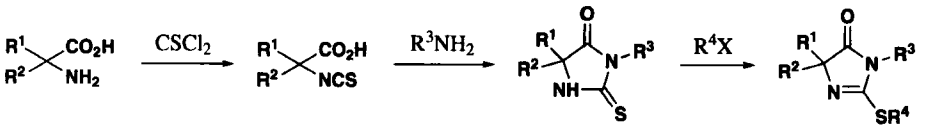
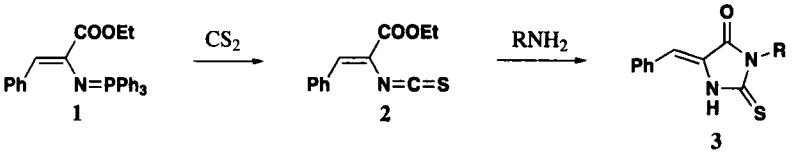
4H-Imidazolin-4-ones are important heterocycles having biological and pharmaceutical activities,[1-6] and some 2-alkylthioimidazolinones show significant fungicidal activities.[7-9] However, most of the 2-alkylthioimidazolinones reported are of the 5,5-disubstituted type and were generally synthesized from corresponding α-aminoacetic acid[9,10] (*Eq. 1*). Unfortunately, 5-benzylidene-2-alkylthioimidazolinones cannot be prepared by this general method for the



(1)

corresponding starting material would be unstable vinyl amino acetic acids. Recently, we became interested in the synthesis of biologically active imidazolinones *via* tandem aza-Wittig reaction[11-13] and now report a new efficient preparation of 5-benzylidene-2-alkylthioimidazolinones from the stable vinyliminophosphorane **1**.

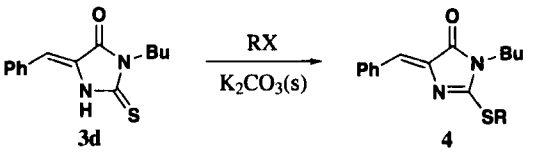
The easily accessible vinyliminophosphorane **1**[14] reacted with carbon disulfide to give vinyl isothiocyanate **2**. While the reaction of **2** with aliphatic primary amines took place smoothly at room temperature to give 2-thioxo-4-imidazolidinones **3** in 65-95% yields, aromatic primary amines required reflux in acetonitrile in the presence of potassium carbonate (*Eq. 2*).



(2)

The results are listed in *Table 1*. Some of 2-thioxo-4-imidazolidinones **3** were also compared with authentic samples prepared previously by condensation of 2-thiohydantoin with aromatic aldehyde,[15] or by reaction of 4-benzylidene-2-benzylthio-2-thiazolin-5-ones with various primary aromatic amines in the presence of sodium acetate in acetic acid.[16]

S-Alkylation of **3d** with alkyl halides in the presence of potassium carbonate provided 2-alkylthio-5-benzylidene-4H-imidazolin-4-ones **4** in 63-87% yields. While activated alkylating agents (RI, $BrCH_2COR$) reacted at room temperature, the other alkylating reagents required heating at 50~60°C (*Table 2*).



3d 4 (3)

Table 1. Preparation of 3-Substituted 2-Thioxo-4-imidazolidinones (**3**) from Vinyl Isothiocyanate (**2**)

Compounds	R	Condition	Yield (%)[a]	mp. (*lit.*) (°C)
3a	Et	r.t./30 min	65	167-168
3b	*n*-Pr	r.t./20 min	95	120-121
3c	*i*-Pr	r.t./30 min	88	122-124
3d	*n*-Bu	r.t./50 min	72	107-108
3e	Cyclohexyl	r.t./10 min	95	160-162 (162-164[15])
3f	4-MeC_6H_4	80°C/2 hr	61	187-188 (185[16])
3g	2-MeC_6H_4	80°C /2 hr	64	165-166 (164[16])
3h	4-ClC_6H_4	80°C /2 hr	95	259-261 (257[16])
3i	4-BrC_6H_4	80°C /3 hr	85	245-246 (244[16])

a) Yields based on vinyliminophosphorane **1**.

Table 2. Alkylation of **3d** to 2-Alkylthio-4H-imidazolin-4-ones (**4**)

Compounds	RX	Condition	Yield (%)[a]	mp (°C)
4a	MeI	r.t./2 hr	70	113-114
4b	*n*-$C_6H_{13}Br$	60°C /3 hr	63	35-36
4c	$PhCH_2Cl$	50°C /4 hr	77	82-83
4d	$ClCH_2CN$	50°C /2 hr	67	98-100
4e	$BrCH_2COPh$	r.t./1 hr	76	161-162
4f	$ClCH_2CONH_2$	50°C /4 hr	64	163-165
4g	$BrCH_2COOMe$	r.t./2 hr	87	82-83
4h	$ClCH_2COOEt$	50°C /2 hr	78	84-85
4i	BrCH(Me)COOEt	50°C /2 hr	82	75-76

a) Yields based on 2-thioxo-4-imidazolidinone **3d**.

EXPERIMENTAL SECTION

Melting points are uncorrected. MS were measured on a HP5988A spectrometer. IR were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. NMR were recorded in $CDCl_3$ on a Varian XL-200 spectrometer and resonances are given in ppm (δ) relative to TMS. Elemental analyses were taken on a Perkin-Elmer 2400 CHN Elemental Analysis Instrument. CS_2 is poisonous and an efficient hood should be used.

Preparation of 3-Alkyl-2-thioxo-4-imidazolidinones (3a-e). General Procedure.- To a solution of vinyliminophosphorane **1**[14] (2.25 g, 5 mmol) in dry methylene chloride (15 mL) was added excess carbon disufide (5 mL). After the reaction mixture was refluxed for 28 hours, the solvent was removed under reduced pressure and ether/petroleum ether (1:2, 20 mL) was added to precipitate triphenylphosphine sulfide which was removed by filtration. The filtrate was evaporated to give isothiocyanate **2**, which was used directly without further purification. To a solution of the crude **2** in CH_3CN (15 mL) was added RNH_2 (5 mmol) and the mixture was allowed to stand for 10~50 min at room temperature. The precipitated solid was collected and washed with water and ethanol, crystallized from methylene chloride/petroleum ether to give 3-alkyl-2-thioxo-4-imidazolidinone **3a-e**.

Compound **3a**: yield 65%, yellow crystals, mp. 167-168°C. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.82 (s, 1H, N-H), 7.41~7.22 (m, 5H, Ar-H), 6.70 (s, 1H, =CH), 3.95 (q, 2H, J = 7.8Hz, NCH_2), 1.29 (t, 3H, J = 7.8Hz, CH_3). IR (KBr, cm^{-1}): 3255 (N-H), 1708 (C=O), 1648 (C=C). MS (m/z, %): 232 (M^+, 93), 203 (18), 189 (7), 117 (100).

Anal. Calcd for $C_{12}H_{12}N_2OS$: C, 62.05; H, 5.21; N, 12.06. Found: C, 62.13; H, 5.39; N, 11.94

Compound **3b**: yield 95%, yellow crystals, mp. 120-121°C, ^1H NMR ($CDCl_3$, 200 MHz): δ 8.82 (s, 1H, N-H), 7.48~7.24 (m, 5H, Ar-H), 6.67 (s, 1H, =CH), 3.84 (t, 2H, J = 7.3Hz, NCH_2), 1.75~0.89 (m, 5H, CH_2CH_3). IR (KBr, cm^{-1}): 3252 (N-H), 1706 (C=O), 1646 (C=C). MS (m/z, %): 246 (M^+, 100), 231 (10), 213 (88), 203 (97), 160 (72), 117 (92).

Anal. Calcd for $C_{13}H_{14}N_2OS$: C, 63.39; H, 5.73; N, 11.37. Found: C, 63.28; H, 5.79; N, 11.18

Compound **3c**: yield 88%, yellow crystals, mp. 122-124°C, ^1H NMR ($CDCl_3$, 200 MHz); δ 8.81 (s, 1H, N-H), 7.47~7.24 (m, 5H, Ar-H), 6.60 (s, 1H, =CH), 4.99~4.91 (m, 1H, NCH), 1.50 (d, 6H, J = 6.8Hz, CH_3). IR (KBr, cm^{-1}): 3257 (N-H), 1709 (C=O), 1649 (C=C). MS (m/z, %), 246 (M^+, 64), 213 (5), 203 (58), 160 (8), 117 (100).

Anal. Calcd for $C_{13}H_{14}N_2OS$: C, 63.39; H, 5.73; N, 11.37. Found: C, 63.21; H, 5.64; N, 11.44

Compound **3d**: yield 72%, yellow crystals, mp. 107-108°C, ^1H NMR ($CDCl_3$, 200 MHz): δ 8.82 (s, 1H, N-H), 7.41~7.23 (m, 5H, Ar-H), 6.68 (s, 1H, =CH), 3.88 (t, 2H, J = 7.7Hz, NCH_2), 1.77~0.84 (m, 7H, $CH_2CH_2CH_3$). IR (KBr, cm^{-1}): 3248 (N-H), 1707 (C=O), 1647 (C=C). MS (m/z, %): 260 (M^+, 35), 227 (100), 203 (14), 160 (12), 117 (64).

Anal. Calcd for $C_{14}H_{16}N_2OS$: C, 64.59; H, 6.19; N, 10.76. Found: C, 64.51; H, 6.28; N, 10.56

Compound **3e**: yield 95%, yellow crystals, mp. 160-162°C, (*lit.*[15] 162-164°C), ^1H NMR ($CDCl_3$, 200 MHz): δ 8.80 (s, 1H, N-H), 7.45~7.23 (m, 5H, Ar-H), 6.60 (s, 1H, =CH), 4.59~4.47 (m, 1H, NCH), 2.38~0.94 (m, 10H, $(CH_2)_5$). IR (KBr, cm^{-1}): 3256 (N-H), 1709 (C=O), 1648 (C=C). MS (m/z, %): 286 (M^+, 98), 253 (13), 203 (99), 160 (46), 117 (100).

Anal. Calcd for $C_{16}H_{18}N_2OS$: C, 67.10; H, 6.33; N, 9.78. Found: C, 67.24; H, 6.37; N, 9.64

Preparation of 3-Aryl-2-thioxo-4-imidazolidinones (3f-i). General Procedure.- To the solution of **2** in CH_3CN (15 mL) was added $ArNH_2$ (5 mmol) and solid potassium carbonate (0.05 g).

The mixture was stirred for 2~3 hr at reflux and filtered; the filtrate was then evaporated *in vacuo* and the residue was recrystallized from methylene chloride/petroleum ether to give 3-aryl-2-thioxo-4-imidazolidinone **3f-i**.

Compound **3f**: yield 61%, yellow crystals, mp. 187-188°C, (*lit.*[16] 185°C), ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.19 (s, 1H, N-H), 7.56~7.16 (m, 9H, Ar-H), 6.78 (s, 1H, =CH), 2.39 (s, 3H, CH_3). IR (KBr, cm^{-1}): 3231 (N-H), 1746 (C=O), 1642 (C=C). MS (m/z, %): 294 (M^+, 100), 265 (38), 236 (14), 150 (48), 132 (50), 116 (99).

Anal. Calcd for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52. Found: C, 69.27; H, 4.84; N, 9.58

Compound **3g**: yield 64%, yellow crystals, mp. 165-166°C, (*lit.*[16] 164°C), ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.30 (s, 1H, N-H), 7.46~7.10 (m, 9H, Ar-H), 6.78 (s, 1H, =CH), 2.16 (s, 3H, CH_3). IR (KBr, cm^{-1}): 3234 (N-H), 1748 (C=O), 1645 (C=C). MS (m/z, %): 294 (M^+, 92), 279 (39), 261 (100), 233 (78), 148 (50), 116 (91).

Anal. Calcd for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52. Found: C, 69.45; H, 4.82; N, 9.35

Compound **3h**: yield 95%, yellow crystals, mp. 259-261°C, (*lit.*[16] 257°C), ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.74 (s, 1H, N-H), 7.53~7.17 (m, 9H, Ar-H), 6.80 (s, 1H, =CH). IR (KBr, cm^{-1}): 3220 (N-H), 1744 (C=O), 1641 (C=C). MS (m/z, %): 314 (M^+, 80), 316 (28), 285 (5), 170 (20), 125 (27), 117 (100).

Anal. Calcd for $C_{16}H_{11}ClN_2OS$: C, 61.05; H, 3.52; N, 8.90. Found: C, 61.18; H, 3.43; N, 8.93

Compound **3i**: yield 85%, yellow crystals, mp. 245-246°C, (*lit.*[16] 244°C), ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.90 (s, 1H, N-H), 7.77~7.08 (m, 9H, Ar-H), 6.81 (s, 1H, =CH). IR (KBr, cm^{-1}): 3221 (N-H), 1741 (C=O), 1640 (C=C). MS (m/z, %): 360 (M^+, 70), 358 (75), 214 (12), 160 (22), 135 (25), 125 (39), 117 (100).

Anal. Calcd for $C_{16}H_{11}BrN_2OS$: C, 53.50; H, 3.09; N, 7.80. Found: C, 53.36; H, 3.02; N, 7.97

Preparation of 2-Alkylthio-4H-imidazolin-4-ones 4. General Procedure.- A mixture of **3d** (1.04 g, 4 mmol), alkyl halide (5 mmol) and solid potassium carbonate (1.11 g, 8 mmol) in CH_3CN (30 mL) was stirred for 1~4 hr at room temperature or 50~60°C and filtered, the filtrate was condensed and the residue was recrystallized from methylene chloride/petroleum ether to give 2-alkylthio-4H-imidazolin-4-ones **4**.

Compound **4a**: yield 70%, yellow crystals, mp. 113-114°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.12~7.32 (m, 5H, Ar-H), 6.89 (s, 1H, =CH), 3.56 (t, 2H, J = 6.8Hz, NCH_2), 2.72 (s, 3H, SCH_3), 1.67~0.90 (m, 7H, $CH_2CH_2CH_3$). IR (KBr, cm^{-1}): 1712 (C=O), 1636 (C=C). MS (m/z, %): 274 (M^+, 92), 259 (70), 245 (68), 227 (90), 185 (64), 116 (96), 74 (100).

Anal. Calcd for $C_{15}H_{18}N_2OS$: C, 65.66; H, 6.61; N, 10.21. Found: C, 65.57; H, 6.79; N, 10.24

Compound **4b**: yield 63%, yellow crystals, mp. 35-36°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.12~7.32 (m, 5H, Ar-H), 6.88 (s, 1H, =CH), 3.56 (t, 2H, J = 7.3Hz, NCH_2), 3.32 (t, 2H, J = 7.3Hz, SCH_2), 1.92~0.98 (m, 18H, $NCH_2\underline{CH_2CH_2CH_3}$ and $SCH_2\underline{(CH_2)_4CH_3}$). IR (KBr, cm^{-1}): 1712 (C=O), 1635 (C=C). MS (m/z, %): 344 (M^+, 13), 297 (18), 260 (14), 227 (100), 203 (12), 160 (13).

Anal. Calcd for $C_{20}H_{28}N_2OS$: C, 69.73; H, 8.19; N, 8.13. Found: C, 69.69; H, 8.12; N, 8.27

Compound **4c**: yield 77%, light yellow crystals, mp. 82-83°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.14~7.22 (m, 10H, Ar-H), 6.93 (s, 1H, =CH), 4.59 (s, 2H, SCH_2Ph), 3.55 (t, 2H, J = 7.3Hz, NCH_2), 1.66~0.89 (m, 7H, $NCH_2\underline{CH_2CH_2CH_3}$). IR (KBr, cm^{-1}): 1713 (C=O), 1637 (C=C). MS (m/z, %): 350 (M^+, 41), 317 (33), 259 (15), 227 (56), 160 (10), 144 (16), 91 (100).

Anal. Calcd for $C_{21}H_{22}N_2OS$: C, 71.97; H, 6.33; N, 7.99. Found: C, 71.85; H, 6.22; N, 8.04

Compound **4d**: yield 67%, light yellow crystals, mp. 98-100°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.10~7.22 (m, 5H, Ar-H), 7.01 (s, 1H, =CH), 4.12 (s, 2H, SCH_2CN), 3.56 (t, 2H, J = 6.8Hz, NCH_2), 1.67~0.92 (m, 7H, $CH_2CH_2CH_3$). IR (KBr, cm^{-1}): 2256 (CN), 1714 (C=O), 1636 (C=C). MS (m/z, %): 299 (M^+, 19), 260 (18), 227 (23), 160 (20), 144 (62), 116 (100).

Anal. Calcd for $C_{16}H_{17}N_3OS$: C, 64.19; H, 5.72; N, 14.04. Found: C, 64.34; H, 5.79; N, 13.96

Compound **4e**: yield 76%, light yellow crystals, mp. 161-162°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.09~7.02 (m, 10H, Ar-H), 6.85 (s, 1H, =CH), 4.80 (s, 2H, SCH_2), 3.62 (t, 2H, J = 7.3Hz, NCH_2), 1.73~0.93 (m, 7H, $CH_2CH_2CH_3$). IR (KBr, cm^{-1}): 1714, 1695 (C=O), 1636 (C=C). MS (m/z, %): 378 (M^+, 11), 273 (21), 227 (16), 134 (16), 116 (19), 105 (100).

Anal. Calcd for $C_{22}H_{22}N_2O_2S$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.63; H, 5.78; N, 7.47

Compound **4f**: yield 64%, yellow crystals, mp. 163-165°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.02~7.23 (m, 5H, Ar-H), 6.96 (s, 1H, =CH), 5.82 (s, 2H, NH_2), 3.93 (s, 2H, SCH_2), 3.57 (t, 2H, J = 7.2Hz, NCH_2), 1.67~0.91 (m, 7H, $CH_2CH_2CH_3$). IR (KBr, cm^{-1}): 3310, 3266 (NH_2), 1714, 1675 (C=O), 1637 (C=C). MS (m/z, %): 317 (M^+, 38), 273 (14), 259 (72), 160 (20), 116 (100).

Anal. Calcd for $C_{16}H_{19}N_3O_2S$: C, 60.55; H, 6.03; N, 13.24. Found: C, 60.51; H, 6.21; N, 13.17

Compound **4g**: yield 87%, light yellow crystals, mp. 82-83°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.08~7.22 (m, 5H, Ar-H), 6.91 (s, 1H, =CH), 4.07 (s, 2H, SCH_2), 3.79 (s, 3H, OCH_3), 3.59 (t, 2H, J = 7.2Hz, NCH_2), 1.65~0.92 (m, 7H, $CH_2CH_2CH_3$). IR (KBr, cm^{-1}): 1736, 1713 (C=O), 1636 (C=C). MS (m/z, %): 332 (M^+, 100), 303 (51), 259 (88), 227 (94), 188 (73), 116 (83).

Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61.43; H, 6.06; N, 8.43. Found: C, 61.25; H, 6.11; N, 8.38

Compound **4h**: yield 78%, light yellow crystals, mp. 84-85°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.08~7.32 (m, 5H, Ar-H), 6.90 (s, 1H, =CH), 4.23 (q, 2H, J = 6.8Hz, OCH_2), 4.08 (s, 2H, SCH_2), 3.58 (t, 2H, J = 7.3Hz, NCH_2), 1.70~0.92 (m, 10H, $NCH_2\underline{CH_2CH_2CH_3}$ and $COOCH_2\underline{CH_3}$). IR (KBr, cm^{-1}): 1739, 1713 (C=O), 1633 (C=C). MS (m/z, %): 346 (M^+, 26), 259 (34), 227 (35), 144 (27), 116 (62), 31 (100).

Anal. Calcd for $C_{18}H_{22}N_2O_3S$: C, 62.41; H, 6.40; N, 8.09. Found: C, 62.32; H, 6.54; N, 8.01

Compound **4i**: yield 82%, yellow crystals, mp. 75-76°C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.08~7.24 (m, 5H, Ar-H), 6.89 (s, 1H, =CH), 4.67 (q, 1H, J = 7.6Hz, SCH), 4.23 (q, 2H, J = 6.5Hz, OCH_2), 3.56 (t, 2H, J = 7.3Hz, NCH_2), 1.76~0.91 (m, 13H, $NCH_2\underline{CH_2CH_2CH_3}$, $SCH\underline{CH_3}$ and $COOCH_2\underline{CH_3}$). IR (KBr, cm^{-1}): 1741, 1714 (C=O), 1635 (C=C). MS (m/z, %): 361 (M^++1, 26), 260 (22), 227 (34), 144 (49), 116 (100).

Anal. Calcd for $C_{19}H_{24}N_2O_3S$: C, 63.31; H, 6.71; N, 7.77. Found: C, 63.35; H, 6.64; N, 7.53

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