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Synthesis and Insecticidal Evaluation of *N-tert*-Butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N,N′*-diacylhydrazines

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ABSTRACT: *A series of novel N-tert-butyl-N′-thio[O-(1-methylthioethylimino)-N″-methylcarbamate]-N,N′-diacylhydrazines were synthesized by the reaction of chlorosulfenyl[O-(1-methylthioethylimino)-N-methylcarbamate] with N-tert-butyl-N,N′-diacylhydrazine in the presence of sodium hydride. The reaction of sulfur dichloride with O-(1-methylthioethylimino)-N-methylcarbamate (Methomyl) in the presence of pyridine to yield chlorosulfenyl[O-(1-methylthioethylimino)-N-methylcarbamate] was reported for the first time. X-ray single crystal diffraction of N-tert-butyl-N′-thio[O-(1-methylthioethylimino)-N″-methylcarbamate]-N,N′-dibenzoylhydrazine demonstrated that the parent compounds N-tert-butyl-N,N′-dibenzoylhydrazine and O-(1-methylthioethylimino)-N-methylcarbamate were combined by N—S—N band to give the product. Their larvicidal activities against Oriental armyworm and Aphis laburni were evaluated. All of them exhibited excellent larvicidal activities against Oriental armyworm, with some of them showing higher larvicidal activities than the parent diacylhydrazines. Toxicity assays indicated that the products show knockdown activity for O-(1-methylthioethylimino)-N-methylcarbamate at higher concentration and insect growth regulators' activities of diacylhydrazines at lower concentrations. At the same time, the products possess insecticidal activities against the aphids.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:631–636, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20360

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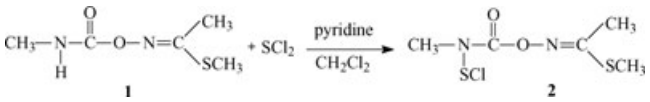
INTRODUCTION

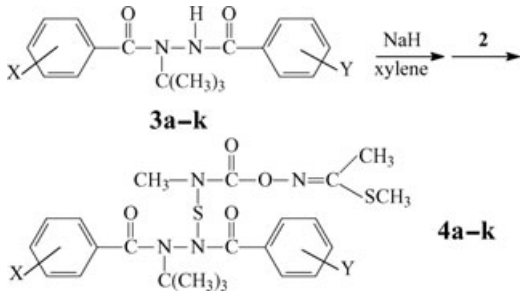
N-tert-Butyl-*N,N′*-diacylhydrazines, a new class of insect growth regulators, have been found to mimic the action of 20-hydroxyecdysone to activate the ecdysone receptor, leading to lethal premature molting [1]. Among nonsteroidal ecdysone agonists, *N-tert*-butyl-*N′*-(4-ethylbenzoyl)-*N*-3,5-dimethylbenzoylhydrazine (RH-5992) has been the first to be commercialized as a lepidopteran-specific insecticide with a low-toxicity profile toward mammals, birds, and fishes, as well as non-target arthropods such as insect pollinators, predators, and parasitoids [2]. At present, another three new structural analogues, methloxyfenozide (RH-2485),



SCHEME 1

halofenozide (RH-0345), and chromafenozide (ANS-118), have already been brought to the market [3].

It has been reported that biscarbamoyl sulfide derivatives of methylcarbamate insecticides retained the good insecticidal activity of the parent methylcarbamate but were substantially less toxic to the white mouse [4]. Encouraged by the reports, we built on the idea that the introduction of carbamate into *N-tert*-butyl-*N*,*N*′-diacylhydrazine would retain the insecticidal activity of the parent methylcarbamate and *N-tert*-butyl-*N*,*N*′-diacylhydrazine. Therefore, in a search for new insect growth regulators with improved biological properties and with a different activity spectrum, we designed and synthesized a series of novel *N-tert*-butyl-*N*′-thio-[*O*-(1-methylthioethylimino)-*N*″-methylcarbamate]-*N*,*N*′-diacylhydrazines. In the previous papers from our laboratory, we described the favorable toxicological of two series of N-sulfenylated derivatives of diacylhydrazines [5]. The results of bioassay showed that these compounds exhibit excellent larvicidal activity. This paper deals with the synthesis and biological activity of *N-tert*-butyl-*N*′-thio[*O*-(1-methylthioethylimino)-*N*″-methylcarbamate]-*N*,*N*′-diacylhydrazines of the general structure **4** as shown in Scheme 2.



SCHEME 2

RESULTS AND DISCUSSION

Synthesis

Chlorosulfenyl[*O*-(1-methylthioethylimino)-*N*-methylcarbamate] **2** was prepared from the reaction of sulfur dichloride with *O*-(1-methylthioethylimino)-*N*-methylcarbamate **1** in dichloromethane using pyridine as the acid acceptor (Scheme 1). Sulfide derivatives of *O*-(1-methylthioethylimino)-*N*-methylcarbamate **1** were prepared by the reaction of the appropriate *N*-chlorosulfenyl aliphatic carbamates [4] or *N*-(chlorothio)phosphinic acid amides [6] with **1**. The key intermediate chlorosulfenyl[*O*-(1-methylthioethylimino)-*N*-methylcarbamate] **2** was prepared for the first time. Chlorosulfenyl[*O*-(1-methylthioethylimino)-*N*-methylcarbamate] **2** without further purification was reacted with *N-tert*-butyl-*N*,*N*′-diacylhydrazine **3** in the presence of sodium hydride to give products **4a–k** as shown in Scheme 2 and Table 1. *N-tert*-Butyl-*N*′-thio[*O*-(1-methylthioethylimino)-*N*″-methylcarbamate]-*N*,*N*′-diacylhydrazines **4a–k** were found to be sensitive to acid and decomposed to the starting materials when they were separated by column chromatography on silica gel; hence, yields for products **4a–k** were low.

Structure

We determined structure of the product **4a** using the X-ray crystallography data [7]. The results demonstrated that the parent compound *N-tert*-butyl-*N*,*N*′-dibenzoylhydrazine **3a** and *O*-(1-methylthioethylimino)-*N*-methylcarbamate **1** were

TABLE 1 Physical Properties of Compounds **4a–k**

Compound	*X*	*Y*	*MP (°C)*	*Yield (%)*	*States*
4a	H	H	162–164	31.5	Colorless crystal
4b	3,5-Me_2	4-Et	98–100	52.0	Colorless crystal
4c	3,5-Me_2	H	183–185	11.3	Buff crystal
4d	4-Cl	H	168–171	22.5	Buff crystal
4e	4-Cl	4-Cl	155–157	15.3	Buff crystal
4f	2,4-Cl_2	H	–	11.9	Yellow semisolid
4g	2-OMe	H	–	16.1	Colorless semisolid
4h	2-Cl	H	–	41.9	Colorless semisolid
4i	3-Cl	H	159–161	10.9	Colorless crystal
4j	4-OMe	H	140–142	22.5	Colorless crystal
4k	2-OMe	2-OMe	–	45.5	Colorless semisolid

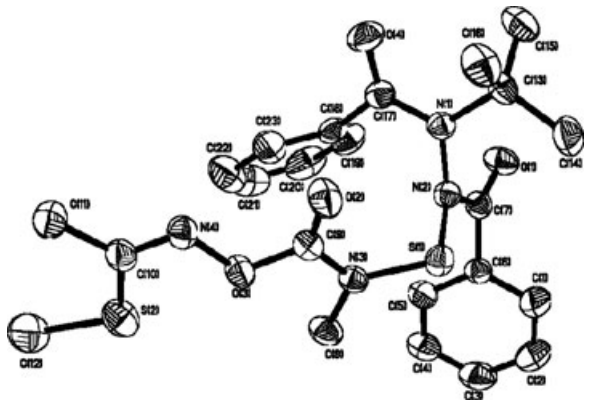


FIGURE 1 Molecular structure of *N-tert*-butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N*,*N′*-dibenzoylhydrazine **4a**.

combined by N—S—N band to give the desired structure **4a** as shown in Fig. 1.

Bioassay

We combined the bioactive units of diacylhydrazine **3** and *O*-(1-methylthioethylimino)-*N*-methylcarbamate **1** to design and synthesize novel compounds **4a–k**. The results of larvicidal activity against Oriental armyworm given in Table 2 show that the title compounds **4a–k** exhibit excellent larvicidal activities, with some of them exhibiting higher larvicidal activities than the parent diacylhydrazines **3**. For example, the larvicidal activity of the title compound (**4j**) was markedly superior to the parent compound (**3j**), and the larvicidal activity of **4k** was distinctly superior to the parent compound **3k**.

The mode of action of the title compounds **4a–k** is very interesting. Toxicity assays indicated that at higher concentrations, the title compounds could rapidly kill armyworms as the parent compounds **1** in 2 h, whereas at the lower concentration, the title compounds could induce a premature, abnormal, and lethal larval molt after 4 days of treatment, similar to the parent compounds **3**. For example, product **4b** possess knockdown activity against the armyworm, whereby the insects were knocked down in 1 h and a percentage mortality of 100% in 24 h at 25 mg kg^{-1} was realized, but it has no knockdown activity against the armyworm and the percentage mortality is found to be 70% in 96 h at 10 mg kg^{-1}.

As for the toxicity of the metabolite, we suggest that in vivo release of the toxic parent compound *O*-(1-methylthioethylimino)-*N*-methylcarbamate **1** and diacylhydrazines **3** after treatment is responsible for the toxicity of the title compounds **4a–k**. Hence, these compounds have knockdown activities due to *O*-(1-methylthioethylimino)-*N*-methylcarbamate

TABLE 2 Larvicidal Activities of Products **4a–k** and Their Parent Compounds **3a–k** and **1** Against Oriental Armyworm

	Larvicidal Activity (%) at Concentration (mg kg^{-1})						
Compound	500	200	50	25	10	5	2.5
4a	–	–	100	55	0	–	–
3a (RH-5849)	–	–	100	45	0	–	0
4b	–	–	100	100	70	20	10
3b (RH-5992)	–	–	–	–	100	75	55
4c	–	–	100	40	0	0	–
3c	–	–	100	90	25	10	–
4d	–	–	100	50	0	–	–
3d	–	–	100	100	50	0	–
4e	–	–	100	40	0	–	–
3e	–	–	100	90	10	10	0
4f	–	–	90	20	10	–	–
3f	–	–	100	60	10	0	–
4g	–	–	100	100	10	–	–
3g	–	–	100	90	75	0	–
4h	–	–	90	30	0	–	–
3h	–	–	100	90	0	–	–
4i	–	–	100	60	0	–	–
3i	–	–	95	45	–	–	–
4j	–	–	100	100	–	–	–
3j	60	0	–	–	–	–	–
4k	–	–	–	100	–	–	–
3k	10	0		–	–	–	–
1 (Methomyl)	–	–		–	100	60	0

(Methomyl) and insect growth regulators' activities of diacylhydrazines.

Moreover, we have found that the title compounds possess insecticidal activities against the aphids. For example, at 200 mg kg^{-1}, percentage mortalities of compounds **4a–e**, **4h–k**, and **1** (Methomyl) for the aphids are 18%, 75%, 95%, 84%, 29%, 92%, 48%, 21%, 23%, and 100%, respectively. However, their parent diacylhydrazine compounds have no activities against aphids.

In conclusion, a series of novel *N-tert*-butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N*,*N′*-diacylhydrazines were synthesized by the reaction of chlorosulfenyl[*O*-(1-methylthioethylimino)-*N*-methylcarbamate] with *N-tert*-butyl-*N*, *N′*-diacylhydrazine in the presence of sodium hydride. The reaction of sulfur dichloride with *O*-(1-methylthioethylimino)-*N*-methylcarbamate (Methomyl) in the presence of pyridine to yield chlorosulfenyl[*O*-(1-methylthioethylimino)-*N*-methylcarbamate] was reported for the first time. X-ray single crystal diffraction of *N-tert*-butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N*,*N′*-dibenzoylhydrazine demonstrated that the parent compounds *N-tert*-butyl-*N*,*N′*-dibenzoylhydrazine and *O*-(1-methylthioethylimino)-*N*-methylcarbamate were combined by N—S—N band to give the product. We have demonstrated that all of the products exhibited excellent larvicidal activities against Oriental armyworm, with some of them showing higher larvicidal activities than the parent diacylhydrazines. Toxicity assays indicated that the products have knockdown activity due to *O*-(1-methylthioethylimino)-*N*-methylcarbamate at higher concentration and insect growth regulators' activities of diacylhydrazines at lower concentrations. At the same time, it was found that the products possess insecticidal activities against the aphids.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen with exclusion of moisture. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer in $CDCl_3$, with tetramethylsilane as internal standard. Chemical shift values (δ) are given in parts per million (ppm). Elemental analyses were determined on an MT-3 elemental analyzer. IR spectra were recorded with a Shimadzu-435 spectrometer. Melting points were taken on a Thomas-Hoover melting point apparatus and were uncorrected. Column chromatographic purification was carried out by using silica gel.

General Synthetic Procedure for Chlorosulfenyl[O-(1-methylthioethylimino)-N-methylcarbamate] **2**

To a stirred solution of sulfur dichloride (0.08 mol) and dichloromethane (15 mL) was added dropwise a solution of pyridine (0.008 mol) in dichloromethane (5 mL) at −10°C. A solution of *O*-(1-methylthioethylimino)-*N*-methylcarbamic acid **1** (0.007 mol) in dichloromethane (5 mL) was then added dropwise at −10°C. The mixture was stirred at room temperature for 4 h. Then the reaction mixture was concentrated under reduced pressure, followed by the addition of hexane (10 mL). The mixture was filtered to give a yellow liquid. It was used for further operations without purification.

General Synthetic Procedure for N-tert-Butyl-N′-thio[O-(1-methylthioethylimino)-N″-methyl carbamate]-N,N′-diacylhydrazines **4a–k**

To a stirred mixture of *N-tert*-butyl-*N*,*N′*-diacylhydrazine **3** (0.006 mol) in anhydrous xylene (40 mL) was added sodium hydride (0.007 mol) over a period of 5 min. The mixture was refluxed for 2 h, and then cooled to −10°C. The above solution of crude chlorosulfenylcarbamate **2** was added dropwise. After the addition was complete, the reaction mixture was stirred for 6 h at room temperature. The solid was then filtered off and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether (60°C–90°C) and dichloromethane and ethyl acetate (5:1:1 by volume) as the eluent. *N-tert*-butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N*,*N′*-diacylhydrazines **4a–k** were obtained. Physical properties of compounds **4a–k** are listed in Table 1.

Data for **4a**: ^{1}H NMR ($CDCl_3$, ppm): δ 1.65 (br s, 10H, $C(CH_3)_3$, NCH), 2.11 (br s, 1H, NCH), 2.33 (s, 3H, $N{=}CCH_3$), 2.43 (s, 3H, SCH_3), 2.67 (br s, 1H, NCH), 7.25–7.66 (m, 10H, ArH). Anal. Found: C, 56.53; H, 5.70; N, 11.64. Calcd. for $C_{23}H_{28}N_4O_4S_2$: C, 56.54; H, 5.78; N, 11.47.

Data for **4b**: ^{1}H NMR ($CDCl_3$): δ 1.22 (t, 3H, CCH_3, J = 7.5 Hz), 1.64 (br s, 10H, $C(CH_3)_3$, NCH), 2.12 (br s, 1H, NCH), 2.29 (s, 6H, $Ar(CH_3)_2$), 2.31 (s, 3H, $N{=}CCH_3$), 2.41 (s, 3H, SCH_3), 2.64 (q, 2H, CH_2, J = 7.5 Hz), 2.67 (br s, 1H, NCH), 6.70–7.26 (m, 7H, ArH). ^{13}C NMR ($CDCl_3$, ppm): 13.6 (SCH_3), 15.2 (CH_2CH_3), 18.8 (NCH_3), 21.2 ($Ar(CH_3)_2$), 27.8 (br, $C(CH_3)_3$), 28.7 ($N{=}CCH_3$), 40.5 (CH_2CH_3), 62.1 ($C(CH_3)_3$), 123.3 (Ar—H), 123.4 (Ar—H), 123.5 (Ar—H), 123.6 (Ar—H), 123.8 (Ar—H),

127.1 (Ar—H), 128.1 (Ar—H), 130.6 (Ar—H), 137.8 (Ar—H), 146.8 (Ar—H), 153.8 (N—CO—O), 162.3 (N=C), 163.9 (—S—N—CO—), 175.2 (*t*-Bu—N—CO—). IR (cm^{-1}, KBr): 2970, 1755, 1690, 1652, 1429, 1354, 1264, 1069, 759. Anal. Found: C, 59.52; H, 6.50; N, 10.24. Calcd. for $C_{27}H_{36}N_4O_4S_2$: C, 59.53; H, 6.66; N, 10.29.

Data for **4c**: ^{1}H NMR ($CDCl_3$): δ 1.64–1.74 (m, 9H, $C(CH_3)_3$), 2.13 (br s, 1H, NCH), 2.28–2.32 (m, 9H, $N{=}CCH_3$, $Ar(CH_3)_2$), 2.41 (s, 3H, SCH_3), 2.51 (s, 1H, NCH), 2.66 (s, 1H, NCH), 6.82–7.42 (m, 8H, ArH). Anal. Found: C, 57.98; H, 6.21; N, 10.96. Calcd for $C_{25}H_{32}N_4O_4S_2$: C, 58.12; H, 6.24; N, 10.84.

Data for **4d**: ^{1}H NMR ($CDCl_3$): δ 1.22 (br s, 1H, NCH), 1.56–1.69 (m, 9H, $C(CH_3)_3$), 2.19 (br s, 1H, NCH), 2.33 (s, 3H, $N{=}CCH_3$), 2.43 (s, 3H, SCH_3), 2.71 (br s, 1H, NCH), 6.91–7.53 (m, 9H, ArH). ^{13}C NMR ($CDCl_3$, ppm): 13.6 (SCH_3), 18.8 (NCH_3), 27.8 (br, $C(CH_3)_3$), 29.7 ($N{=}CCH_3$), 62.1 ($C(CH_3)_3$), 127.2 (Ar—H), 127.5 (Ar—H), 127.8 (Ar—H), 128.3 (Ar—H), 130.3 (Ar—H), 133.5 (Ar—H), 133.7 (Ar—H), 135.2 (Ar—H), 157.1 (N—CO—O), 157.9 (—S—N—CO—), 162.3 (N=C), 174.9 (*t*-Bu—N—CO—). Anal. Found: C, 52.70; H, 5.15; N, 10.66. Calcd for $C_{23}H_{27}ClN_4O_4S_2$: C, 52.81; H, 5.20; N, 10.71.

Data for **4e**: ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 1H, NCH), 1.64 (br s, 9H, $C(CH_3)_3$), 2.23 (br s, 1H, NCH), 2.32 (s, 3H, $N{=}CCH_3$), 2.43 (s, 3H, SCH_3), 2.64 (br s, 1H, NCH), 6.83–7.48 (m, 8H, ArH). Anal. Found: C, 49.41; H, 4.70; N, 9.98. Calcd for $C_{23}H_{26}Cl_2N_4O_4S_2$: C, 49.55; H, 4.70; N, 10.05.

Data for **4f**: ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 1H, NCH), 1.62 (br s, 9H, $C(CH_3)_3$), 2.20 (br s, 1H, NCH), 2.29 (s, 3H, $N{=}CCH_3$), 2.39 (s, 3H, SCH_3), 2.64 (br s, 1H, NCH), 6.89–7.68 (m, 8H, ArH). Anal. Found: C, 49.53; H, 4.79; N, 10.17. Calcd for $C_{23}H_{26}Cl_2N_4O_4S_2$: C, 49.55; H, 4.70; N, 10.05.

Data for **4g**: ^{1}H NMR ($CDCl_3$): δ 1.38 (br s, 1H, NCH), 1.63 (s, 9H, $C(CH_3)_3$), 2.30 (s, 3H, $N{=}CCH_3$), 2.40 (s, 3H, SCH_3), 2.62 (br s, 2H, NCH_2), 3.55–3.85 (m, 3H, OCH_3), 6.78–7.69 (m, 9H, ArH). Anal. Found: C, 55.40; H, 6.02; N, 10.86. Calcd for $C_{24}H_{30}N_4O_5S_2$: C, 55.58; H, 5.83; N, 10.80.

Data for **4h**: ^{1}H NMR ($CDCl_3$): δ 1.43 (br s, 1H, NCH), 1.64 (s, 9H, $C(CH_3)_3$), 2.12 (br s, 1H, NCH), 2.29 (s, 3H, $N{=}CCH_3$), 2.39 (s, 3H, SCH_3), 2.65 (br s, 1H, NCH), 6.86–7.69 (m, 9H, ArH). ^{13}C NMR ($CDCl_3$, ppm): 13.6 (SCH_3), 18.8 (NCH_3), 27.5 ($C(CH_3)_3$), 27.9 ($N{=}CCH_3$), 125.9 (Ar—H), 126.3 (Ar—H), 126.5 (Ar—H), 127.5 (Ar—H), 127.9 (Ar—H), 128.5 (Ar—H), 128.7 (Ar—H), 129.9 (Ar—H), 130.3 (Ar—H), 130.6 (Ar—H), 153.8 (N—CO—O), 161.1 (N=C), 168.9 (—S—N—CO—), 175.0 (*t*-Bu—N—CO—). Anal. Found: C, 52.67; H, 5.29; N, 10.68. Calcd for $C_{23}H_{27}ClN_4O_4S_2$: C, 52.81; H, 5.20; N, 10.71.

Data for **4i**: ^{1}H NMR ($CDCl_3$): δ 1.59–1.70 (d, 10H, $C(CH_3)_3$, NCH), 2.11 (br s, 1H, NCH), 2.32 (s, 3H, $N{=}CCH_3$), 2.42 (s, 3H, SCH_3), 2.71 (br s, 1H, NCH), 6.85–7.61 (m, 9H, ArH). Anal. Found: C, 52.83; H, 5.23; N, 10.80. Calcd for $C_{23}H_{27}ClN_4O_4S_2$: C, 52.81; H, 5.20; N, 10.71.

Data for **4j**: ^{1}H NMR ($CDCl_3$): δ 1.64 (br s, 10H, $C(CH_3)_3$, NCH), 2.13 (br s, 1H, NCH), 2.30 (s, 3H, $N{=}CCH_3$), 2.40 (s, 3H, SCH_3), 2.66 (br s, 1H, NCH), 3.82 (s, 3H, OCH_3), 6.86–7.49 (m, 9H, ArH). Anal. Found: C, 55.48; H, 5.91; N, 11.05. Calcd for $C_{24}H_{30}N_4O_5S_2$: C, 55.58; H, 5.83; N, 10.80.

Data for **4k**: ^{1}H NMR ($CDCl_3$): δ 1.40 (br s, 1H, NCH), 1.71 (s, 9H, $C(CH_3)_3$), 1.86 (br s, 1H, NCH), 2.28 (s, 3H, $N{=}CCH_3$), 2.38 (s, 3H, SCH_3), 2.50 (br s, 1H, NCH), 3.77–3.81 (d, 6H, OCH_3), 6.80–7.64 (m, 8H, ArH). IR (cm^{-1}, KBr): 2951, 1704, 1671, 1595, 1338, 1253, 1024, 757. Anal. Found: C, 54.58; H, 6.00; N, 9.98. Calcd for $C_{25}H_{32}N_4O_6S_2$: C, 54.73; H, 5.88; N, 10.21.

BIOLOGICAL ASSAY

Screening Method for Insecticidal Activity Using Oriental Armyworm as Target Insect

Larvicidal activities of *N-tert*-butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N*,*N′*-diacylhydrazines **4a–k** were evaluated in comparison with the parent compounds **1** and **3a–k** using a previously reported procedure [8]. The larvicidal activity was tested against Oriental armyworm [*Mythimna* (=*Pseudaletia*) *separata* (Walker)] by foliar application. For the foliar armyworm tests, individual corn leaves were placed on moistened pieces of filter paper in Petri dishes. The leaves were then sprayed with the test solution and allowed to dry. The dishes were infested with 10 fourth-instar armyworm larvae. Percentage mortalities were evaluated after 4 days of treatment. Evaluations are based on a percentage scale of 0–100, with 0 indicating no activity and 100 total killed. The larvicidal activity is summarized in Table 2.

Screening Method for Insecticidal Activity Using Aphis laburni Kaltenbach as Target Insect

N-tert-Butyl-*N′*-thio[*O*-(1-methylthioethylimino)-*N″*-methylcarbamate]-*N*,*N′*-diacylhydrazines **4a–k** and the parent compounds **1** and **3a–k** were evaluated for their insecticidal activity against *Aphis laburni*. About 60 aphids were transferred to the shoot with three to five fresh leaves of horsebean. The shoot with aphids was cut and dipped into the solution of 200 μg mL^{-1} of test compound for 2 s. After removing extra solution from the leaf,

the aphids were raised on the shoot at 27°C ± 1°C and 85% of relative humidity for 16 h. Each experiment for one compound was triplicated. The revised death rate was calculated by the Abbott formula.

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