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Insecticidal Benzoylphenylurea-S-Carbamate: A New Propesticide with Two Effects of Both Benzoylphenylureas and Carbamates

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New propesticides with two effects of both benzoylphenylureas and carbamates were designed and synthesized by the key intermediate N-chlorosulfenyl-N-methylcarbamate, which was prepared for the first time. These benzoylphenylurea-S-carbamates were identified by ^{1}H NMR spectroscopy and elemental analyses. The bioactivities of the new compounds were evaluated. These benzoylphenylurea-S-carbamates exhibited excellent larvicidal activities against Oriental armyworm, some of which were good as compared to the parent benzoylphenylureas. Toxicity assays indicated that these benzoylphenylurea-S-carbamates had knockdown activities of carbamates at higher concentrations and insect growth regulator activities of benzoylphenylureas at lower concentrations. We found that the title compounds exhibited good systemic larvicidal activities against Oriental armyworm, which were especially advantageous when combating sucking pests. Some of these title compounds can kill aphids and mosquitoes as well.

KEYWORDS: Benzoylphenylurea-S-carbamate; carbamate; benzoylphenylurea; larvividal activity; propesticide; armyworm; aphid

INTRODUCTION

Benzoylphenylureas (BPUs), discovered in the 1970s, are known well as commercial chitin formation inhibitors. In contrast to traditional pesticides, BPU and its derivatives mainly control the growth and development process of insects by interfering with chitin biosynthesis and breeding (*1*−*3*). Consequently, the toxicity of BPUs to vertebrates and environmental impact is very low and a high insecticidal selectivity is achieved. However, BPUs do not have systemic properties (*4*). As a consequence, BPUs cannot effectively control sucking pests such as aphids and hidden feeders such as bollworms, budworms, and stem borers.

Carbamates have excellent insecticidal activities against a broad spectrum of insects. They possess knocking-down, fast-killing, and systemic effects. However, they are toxic to mammals. Eya has reported that formamidine-S-carbamates possess improved ovicidal and acarcidal activities and are less toxic to mice than the methylcarbamates (*5*). Many biscarbamoyl sulfide derivatives of methylcarbamate insecticides have also been reported to retain the good insecticidal activity of the parent methylcarbamate but were substantially less toxic to the white mouse (*6*). We have also reported that the BPUs substituted by N-alkyl carbamylosulfenyl could retain the insecticidal activity of the parent BPUs and that the solubility and hydrophobicity of these BPU derivatives were improved at the same time (*7*). It would be desirable to combine the insecticidal activity of BPU and carbamate into a single pesticidal compound and suffer shortcomings in their ancillary properties.

This paper is concerned with the synthesis and toxicological properties of a series of BPU-S-carbamates of general structures **II**, which are a novel class of compounds having the pesticidal properties of both the BPU and the carbamate.

EXPERIMENTAL PROCEDURES

Instruments. The title compounds were synthesized under a nitrogen atmosphere. Proton NMR spectra were obtained at 300 MHz using a Bruker AC-P300 spectrometer in $CDCl_3$ solution with tetramethylsilane as the internal standard. Chemical shift values (δ) were given in ppm. Elemental analyses were determined on a Yanaca CHN Corder MT-3 elemental analyzer. MS were recorded with VG ZAB-HS spectrometer using the EI method. The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co., Beijing, China) and were uncorrected. Yields were not optimized.

General Synthesis. Solvents were dried by standard methods and distilled prior to use. 2-Chlorobenzoyl, 2,6-dichlorobenzoyl, and 2,6-diflurobenzoyl isocyanates were synthesized by the method of the literature (*8*). Sulfur dichloride was prepared by the reaction of sulfur monochloride with chlorine (*9*). Pyridine was distilled over sodium hydroxide pellets and kept dry by storing over the same reagent.

General Synthetic Procedure for I_{1-10}. To a stirred solution of sulfur dichloride (0.01 mol) in dichloromethane (15 mL) was added dropwise a solution of N-methylcarbamate (0.01 mol) and pyridine

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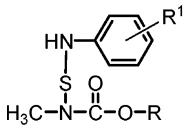
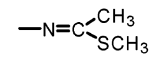
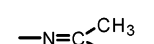
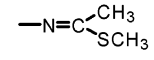
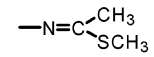
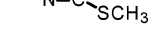
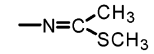
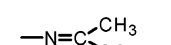
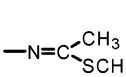
Table 1. Melting Points and Yields of Compounds $\mathbf{I}_{1-10}$



$\mathbf{I}_{1\text{-}10}$

compd.	R	R^1	m.p. (°C)	yield (%)
$\mathbf{I}_1$		4-CF_3	133-134	31.0
$\mathbf{I}_2$		4-Cl	136-138	47.9
$\mathbf{I}_3$		4-F	117-118	23.8
$\mathbf{I}_4$		4-CN	165-168	29.1
$\mathbf{I}_5$		3-CF_3-4-Cl	131-133	29.7
$\mathbf{I}_6$		4-OCF_3	80-82	51.3
$\mathbf{I}_7$		4-Br	121-122	36.2
$\mathbf{I}_8$		3-Br-4-CF_3	143-145	43.1
$\mathbf{I}_9$		4-OCF_3	66-68	31.2
$\mathbf{I}_{10}$		4-CF_3		

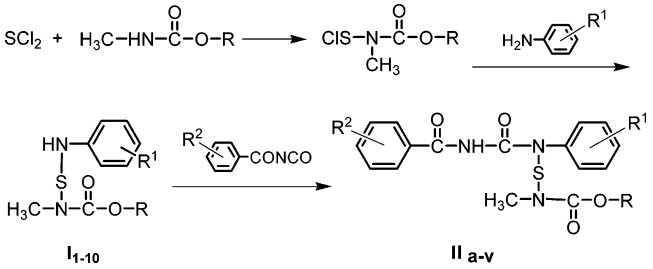
(0.011 mol) in dichloromethane (5 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min. Then, the reaction mixture was added dropwise to a solution of substituted aniline (10 mmol) and pyridine in dichloromethane (20 mL). Then, the resulting mixture was concentrated under reduced pressure and extracted with ethyl ether. The organic phase was washed with saturated brine, dried over anhydrous sodium sulfate, and filtered. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on a silica gel using a mixture of petroleum ether (60−90 °C) and ethyl acetate as the eluent to give $\mathbf{I}_{1-9}$ as white crystals. The melting points and yields of compounds $\mathbf{I}_{1-9}$ are listed in **Table 1**. Compound $\mathbf{I}_{10}$ was not purified and used for further operations.

General Synthetic Procedure for IIa−v. A solution of substitutedbenzoyl isocyanate (2 mmol) in dichloromethane (10 mL) was added dropwise to a solution of $\mathbf{I}_{1-10}$ (2 mmol) in dichloromethane (5 mL) at room temperature. The reaction was monitored by thin-layer chromatography. After the reaction was completed, the solvent was evaporated off under reduced pressure, and the residue was recrystallized from ethyl ether. The melting points, yields, and elemental analyses of compounds **IIa−v** are listed in **Table 2**. The ^{1}H NMR analyses of compounds **IIa−v** are listed in **Table 3**.

Biological Assay. All bioassays were performed on representative test organisms reared in the laboratory. The bioassay was repeated at 25 ± 1 °C according to statistical requirements. Assessments were made on a dead/alive basis, and mortality rates were corrected using Abbott's formula (*10*). Evaluations are based on a percentage scale of 0−100 in which 0 = no activity and 100 = total kill.

Larvicidal Activity against Oriental Armyworm. The larvicidal activities of the title compounds **IIa−v** and the parent compounds were evaluated using a previously reported procedure (*7*, *11*). 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. Each treatment was replicated three times. Percentage mortalities were evaluated 4 days after treatment. For comparative purposes, the parent compounds, penfluron, diflubenzuron, triflumuron, N-2,6-diflurobenzoyl-N′-4-trifluromethoxylphenylurea (diftrifmeouron), N-2-chlorobenzoyl-N′-4-trifluromethylphenylurea (chlotrifmeuron), and methomyl, were tested under the same conditions. Penfluron, diflubenzuron, triflumuron, and methomyl are commercial insecticides.

Scheme 1



$\mathbf{I}_{1\text{-}10}$ $\mathbf{II}_{a\text{-}v}$

Systemic Larvicidal Activities against Oriental Armyworm. The systemic larvicidal activities of the title compounds **IIb**, **IIf**, **IIi**, and **III** and the parent compounds were evaluated using a previously reported procedure (*12*). The systemic larvicidal activity was tested against Oriental armyworm [*M.* (=*Pseudaletia*) *separata* (Walker)] by plant-irrigating application. Each test compound was prepared to terminal concentrations of 100, 25, 10, and 5 mg L^{-1} by adding distilled water with a little emulsifier 2201. For each dose, 100 mL of the test solution was irrigated at the root of a corn plant in a pot. After irrigation for 24 h, individual corn leaves were cut and placed on Petri dishes. The dishes were infested with 10 fourth-instar armyworm larvae. After feeding for 24 h, fresh corn leaves were added to the dishes. Each treatment was replicated four times. Percentage mortalities were evaluated 4 days after treatment. For comparative purposes, the parent compounds, diflubenzuron, diftrifmeouron, chlotrifmeuron, and methomyl, were tested under the same conditions.

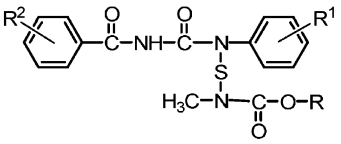
Insecticidal Activity against Aphis. The insecticidal activities of the title compounds **IIb** and **IIf** and the parent compounds methomyl were tested against *Aphis laburni* Kaltenbach by foliar application. About 60 aphids were transferred to the shoot with 3−5 fresh leaves of horsebean. The shoot with aphids was cut and dipped into the solution of 200 μg/mL of test compound for 2 s, after removing extra solutions on the leaf; the aphids were raised in the shoot at 25 ± 1 °C and 85% relative humidity for 16 h. Each experiment for one compound was triplicated. The revised death rate was calculated by Abbott's formula.

Larvicidal Activity against Mosquito. The larvicidal activity of the title compound **IIf** against mosquito was tested. The title compound **IIf** was prepared to a terminal concentration of 5 mg L^{-1} by dissolving **IIf** in acetone and adding distilled water. Ten fourth-instar mosquito larvae were put into the 10 mL of the test solution and raised for 8 days; the results were expressed by death percentage.

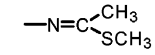
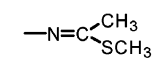
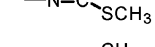
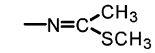
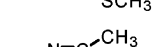
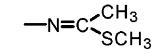
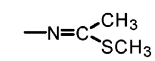
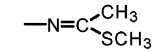
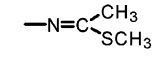
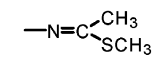
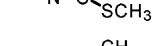
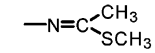
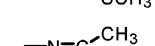
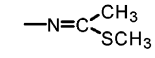
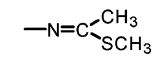
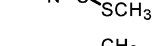
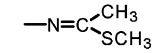
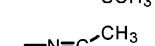
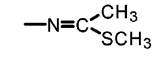
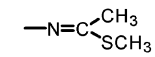
RESULTS AND DISCUSSION

Preparations. The title compounds **IIa−v** were prepared as shown in **Scheme 1**. The N-chlorosulfenyl-N-methylcarbamate was prepared by the reaction of sulfur dichloride with N-methylcarbamate in dichloromethane using pyridine as the acid acceptor. It has been reported that the sulfide derivatives of N-methylcarbamate were prepared by the reaction of the appropriate N-chlorosulfenyl aliphatic carbamates or N-(chlorothio)phosphinic acid amides with N-methylcarbamate (*6*, *13*−*16*). The key intermediate N-chlorosulfenyl-N-methylcarbamate was prepared for the first time. The N-chlorosulfenyl-N-methylcarbamate without further purification was reacted with substituted aniline in the presence of pyridine to give $\mathbf{I}_{1-10}$ as

Table 2. Melting Points, Yields, and Elemental Analyses of Compounds **IIa**–**v**



II a-v

	R	R^2	R^1	yield (%)	m.p. (°C)	elemental analysis (%, calc.)		
						C	H	N
II a		2,6-F_2	4-CF_3	60.0	122(dec)	44.58 (44.77)	3.19 (3.19)	10.66 (10.44)
II b		2,6-F_2	4-Cl	77.1	162-164	45.30 (45.37)	3.41 (3.41)	10.98 (11.14)
II c		2,6-F_2	4-F	78.8	123-126	46.84 (46.91)	3.38 (3.52)	11.68 (11.52)
II d		2,6-F_2	4-CN	25.0	158(dec)	48.69 (48.67)	3.50 (3.47)	14.10 (14.19)
II e		2,6-F_2	3-CF_3-4-Cl	68.6	122-124	41.98 (42.07)	2.84 (2.82)	10.10 (9.81)
II f		2,6-F_2	4-OCF_3	50.7	128-130	43.59 (43.48)	3.17 (3.10)	10.20 (10.14)
II g		2,6-F_2	4-Br	78.9	132-134	41.46 (41.69)	3.23 (3.13)	10.17 (10.24)
II h		2,6-F_2	3-Br-4-CF_3	74.4	120-122	38.93 (39.03)	2.78 (2.62)	9.27 (9.10)
II i		2-Cl	4-CF_3	65.9	116-118	44.80 (44.90)	3.49 (3.39)	10.28 (10.47)
II j		2-Cl	4-Cl	80.0	140-142	45.41 (45.51)	3.68 (3.62)	11.26 (11.17)
II k		2-Cl	4-F	88.2	129-131	46.96 (47.06)	3.80 (3.74)	11.71 (11.55)
II l		2-Cl	4-OCF_3	62.8	120-122	43.57 (43.60)	3.34 (3.29)	10.23 (10.17)
II m		2-Cl	4-Br	78.9	118-120	41.58 (41.81)	3.48 (3.32)	10.05 (10.26)
II n		2-Cl	3-Br-4-CF_3	77.3	112(dec)	39.17 (39.13)	2.57 (2.79)	9.13 (9.13)
II o		2,6-Cl_2	4-CF_3	47.1	126-129	41.97 (42.19)	3.11 (3.01)	10.02 (9.84)
II p		2,6-Cl_2	4-Cl	40.6	131-133	42.63 (42.59)	3.29 (3.20)	10.50 (10.46)
II q		2,6-Cl_2	4-F	76.9	96-98	43.83 (43.94)	3.20 (3.30)	10.99 (10.79)
II r		2,6-Cl_2	4-OCF_3	28.6	118-120	40.98 (41.03)	2.82 (2.93)	9.69 (9.57)
II s		2,6-Cl_2	4-Br	85.7	132-134	39.38 (39.03)	2.78 (2.62)	9.27 (9.10)
II t		2,6-Cl_2	3-Br-4-CF_3	80.8	134-136	37.23 (37.05)	2.61 (2.49)	8.45 (8.64)
II u		2,6-F_2	4-OCF_3	20.3	Amorphous	45.48 (45.51)	3.68 (3.65)	9.49 (9.65)
II v		2,6-F_2	4-CF_3	9.3	152-154	53.27 (43.43)	3.46 (3.36)	7.97 (7.79)

shown in **Scheme 1** and **Table 1**. We found that the BPU-S-carbamates **IIa**−**v** crystallized well; hence, the title compounds **IIa**−**v** could be purified by recrystallization from ethyl ether.

Bioassay. *Larvicidal Activity against Oriental Armyworm.* The results of larvicidal activity tests given in **Table 4** show that the title compounds **IIa**−**v** exhibit excellent larvicidal

Table 3. ^{1}H NMR of Compounds **IIa**–**v**

	δ (ppm)
IIa	2.32 (s, 3H, CH_3), 2.42 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 6.92 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.35 (m, 1H, Ph), 7.42 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.67 (d, 2H, $^3J_{HH}$ = 8.1 Hz, Ph), 11.19 (s, 1H, NH)
IIb	2.30 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 3.20 (s, 3H, NCH_3), 6.89 (t, 2H, $^3J_{HH}$ = 8.1 Hz, Ph), 7.28–7.38 (m, 3H, Ph), 7.35 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 11.07 (s, 1H, NH)
IIc	2.30 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 6.89 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.06 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 7.19–7.38 (m, 3H, Ph), 11.05 (s, 1H, NH)
IId	2.31 (s, 3H, CH_3), 2.41 (s, 3H, SCH_3), 3.17 (s, 3H, NCH_3), 6.91 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.35 (m, 1H, Ph), 7.42 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.69 (d, 2H, $^3J_{HH}$ = 8.1 Hz, Ph), 11.25 (s, 1H, NH)
IIe	2.30 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 3.23 (s, 3H, NCH_3), 6.91 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.31–7.40 (m, 2H, Ph), 7.52 (d, 1H, $^3J_{HH}$ = 9.0 Hz, Ph), 7.61 (d, 1H, $^4J_{HH}$ = 2.1 Hz, Ph), 11.12 (s, 1H, NH)
IIf	2.30 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 6.90 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.20–7.38 (m, 5H, Ph), 11.12 (s, 1H, NH)
IIg	2.30 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 6.89 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.13 (d, 1H, $^3J_{HH}$ = 9.0 Hz, Ph), 7.28–7.38 (m, 1H, Ph), 7.50 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 11.07 (s, 1H, NH)
IIh	2.30 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 3.23 (s, 3H, NCH_3), 6.91 (t, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.28–7.40 (m, 2H, Ph), 7.60 (d, 1H, $^4J_{HH}$ = 2.4 Hz, Ph), 7.72 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ph), 11.15 (s, 1H, NH)
IIi	2.29 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 3.19 (s, 3H, NCH_3), 7.28–7.42 (m, 5H, Ph), 7.52–7.55 (m, 1H, Ph), 7.65 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 11.04 (s, 1H, NH)
IIj	2.29 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 3.20 (s, 3H, NCH_3), 7.39 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 7.30–7.38 (m, 5H, Ph), 7.52–7.54 (m, 1H, Ph), 10.96 (s, 1H, NH)
IIk	2.29 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 7.06 (t, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 7.20–7.36 (m, 5H, Ph), 7.52–7.55 (m, 1H, Ph), 10.99 (s, 1H, NH)
IIl	2.29 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 7.21–7.36 (m, 7H, Ph), 7.51–7.54 (m, 1H, Ph), 10.99 (s, 1H, NH)
IIm	2.29 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 7.14 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.30–7.54 (m, 6H, Ph), 10.99 (s, 1H, NH)
IIn	2.29 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 3.23 (s, 3H, NCH_3), 7.28–7.38 (m, 4H, Ph), 7.53–7.55 (m, 1H, Ph), 7.60 (d, 1H, $^4J_{HH}$ = 2.1 Hz, Ph), 7.72 (d, 1H, $^3J_{HH}$ = 8.1 Hz, Ph), 11.04 (s, 1H, NH)
IIo	2.32 (s, 3H, CH_3), 2.41 (s, 3H, SCH_3), 3.21 (s, 3H, NCH_3), 7.17–7.28 (m, 3H, Ph), 7.38 (d, 2H, $^3J_{HH}$ = 8.1 Hz, Ph), 7.63 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 11.12 (s, 1H, NH)
IIp	2.32 (s, 3H, CH_3), 2.41 (s, 3H, SCH_3), 3.22 (s, 3H, NCH_3), 7.16–7.26 (m, 5H, Ph), 7.33 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 11.02 (s, 1H, NH)
IIq	2.32 (s, 3H, CH_3), 2.42 (s, 3H, SCH_3), 3.22 (s, 3H, NCH_3), 7.05 (t, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 7.16–7.26 (m, 5H, Ph), 11.02 (s, 1H, NH)
IIr	2.32 (s, 3H, CH_3), 2.41 (s, 3H, SCH_3), 3.23 (s, 3H, NCH_3), 7.17–7.32 (m, 7H, Ph), 11.02 (s, 1H, NH)
IIs	2.32 (s, 3H, CH_3), 2.41 (s, 3H, SCH_3), 3.22 (s, 3H, NCH_3), 7.12 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.16–7.24 (m, 3H, Ph), 7.49 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 11.02 (s, 1H, NH)
IIt	2.31 (s, 3H, CH_3), 2.41 (s, 3H, SCH_3), 3.25 (s, 3H, NCH_3), 7.19–7.29 (m, 4H, Ph), 7.58 (d, 1H, $^4J_{HH}$ = 3.0 Hz, Ph), 7.70 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ph), 11.07 (s, 1H, NH)
IIu	1.50 [s, 6H, $(CH_3)_2$], 2.17 (s, 3H, SCH_3), 3.19 (s, 3H, NCH_3), 6.90 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ph), 7.21–7.39 (m, 5H, Ph), 7.64 (s, 1H, =CH), 10.90 (s, 1H, NH)
IIv	2.39 (s, 3H, CH_3), 3.32 (s, 3H, NCH_3), 6.83–6.92 (m, 4H, Ph), 7.09 (d, 1H, $^3J_{HH}$ = 7.5 Hz, Ph), 7.25–7.37 (m, 2H, Ph), 7.47 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.70 (d, 2H, $^3J_{HH}$ = 9.0 Hz, Ph), 11.34 (s, 1H, NH)

activities against Oriental armyworm, which are parallel to those of the parent BPUs. For example, the larvicidal activity of the title compounds **IIf** was equal to the parent diftrifmeouron. The mode of action of the title compounds **IIa**−**v** is very interesting. Toxicity assays indicate that at higher concentrations (for example, 50 mg L^{-1}) the title compounds **IIa**−**v** have the knockdown activities and kill armyworm in 2 h, i.e., as fast as the parent N-methylcarbamates, whereas at lower concentrations (below 10 mg L^{-1}) the title compounds **IIa-v** can interfere with chitin biosynthesis of armyworm, like the parent BPUs, and symptoms of toxicity include discoloration, weight loss, cessation of feeding, and death.

Systemic Larvicidal Activities against Oriental Armyworm. The results of systemic larvicidal activities against Oriental armyworm of some compounds and the parent compounds are summarized in **Table 5**. The title compounds **IIb**, **IIf**, **IIi**, and **III** exhibit good systemic larvicidal activities against Oriental armyworm. Toxicity assays indicate that the title compounds **IIb**, **IIf**, **IIi**, and **III**, like the parent compound methomyl, can cause armyworm convulsion and vomit water as the main poison symptom within 20 min and kill armyworms within 1 h. Hence, we have found that the title compounds have systemic properties, being absorbed from a plant's roots and effectively transferred to other parts of the plant such as leaves. This property is especially advantageous when combating sucking pests, for a systemic insecticide can spread all through a plant and kill any targeted insects that feed on it.

The insecticidal activities of the title compounds **IIb** and **IIf** at 200 mg L^{-1} against *A. laburni* Kaltenbach were 54 and 36%, respectively, as compared with 100% mortality of methomyl at the same concentration. The larvicidal activity of the title compound **IIf** against mosquito was 100% at 5 mg L^{-1}.

In summary, new propesticides with two effects of both BPUs and carbamates were designed and synthesized by the key

Table 4. Larvicidal Activities against Oriental Armyworm of Compounds **IIa**–**v** and Parent Compounds[a]

	larvicidal activity (%) at concentration (mg L^{-1})							
compounds	50	25	10	5	2.5	1.0	0.5	0.25
IIa (penfluron-S-methomyl)	100	100	100	100	100	100	95	0
IIv (penfluron-S-MTMC)	100	100	100	100	100	100	95	15
penfluron	100	100	100	100	100	100	100	95
IIb (diflubenzuron-S-methomyl)	100	100	100	100	100	90	50	20
diflubenzuron	100	100	100	100	100	100	100	45
IIc	100	100	50	10	0			
IId	100	90	78	23	0			
IIe	100	100	100	80	60	20	0	
IIf (diftrifmeouron-S-methomyl)	100	100	100	100	100	90	80	50
IIu (diftrifmeouron-S-aldicarb)	100	100	100	100	100	100	60	10
diftrifmeouron	100	100	100	100	100	100	80	40
IIg	100	100	100	100	100	90	30	0
IIh	100	95	90	85	25	0		
IIi (chlotrifmeuron-S-methomyl)	100	100	100	100	90	60	15	0
chlotrifmeuron	100	100	100	100	100	70	60	10
IIj	100	100	100	50	0			
IIk	100	95	15	5	0			
III (triflumuron-S-methomyl)	100	100	100	100	100	65	35	10
triflumuron	100	100	100	100	100	95	40	20
IIm	100	100	90	30	10	0		
IIn	100	70	10	0				
IIo	100	100	100	100	40	0		
IIp	100	50	30	10	0			
IIq	100	100	35	0				
IIr	100	90	100	100	65	0		
IIs	100	100	45	20	0			
IIt	90	40	10	0				
methomyl			100	62	0			

[a] Note that blank cells mean not tested. Penfluron is N-2,6-diflurobenzoyl-N′-4-trifluromethylphenylurea; diflubenzuron is N-2,6-diflurobenzoyl-N′-4-chlorophenylurea; triflumuron is N-2-chloro-N′-4-trifluromethoxylphenylurea; diftrifmeouron is N-2,6-diflurobenzoyl-N′-4-trifluromethoxylphenylurea; chlotrifmeuron is N-2-chlorobenzoyl-N′-4-trifluromethylphenylurea; MTMC is 3-methylphenyl methylcarbamate; methomyl is O-(1-methylthioethylimino)-N-methylcarbamate; and aldicarb is 2-methyl-2-(methylthio)propanal O-[(methylamino)carbonyl]oxime.

Table 5. Systemic Larvicidal Activities against Oriental Armyworm of Some Compounds and Methomyl

	larvicidal activity (%) at concentration (mg L^{-1})			
compound	100	25	10	5
IIb (diflubenzuron-S-methomyl)	100	95	80	25
diflubenzuron	0			
IIf (diftrifmeouron-S-methomyl)	100	100	70	5
diftrifmeouron	0			
IIi (chlotrifmeuron-S-methomyl)	100	100	85	55
chlotrifmeuron	0			
III (triflumuron-S-methomyl)	100	95	95	80
triflumuron	0			
methomyl	100	100	100	95

intermediate N-chlorosulfenyl-N-methylcarbamate, which was prepared for the first time. These BPU-S-carbamates exhibited excellent larvicidal activities against Oriental armyworm, some of which were good as compared to the parent BPUs. Toxicity assays indicated that these BPU-S-carbamates had knockdown activities of carbamates at higher concentrations (for example 50 mg L^{-1}) and insect growth regulator activities of BPUs at lower concentrations (below 10 mg L^{-1}). We found that the title compounds exhibited good systemic larvicidal activities against Oriental armyworm, which were especially advantageous when combating sucking pests. Some of these title compounds can kill aphids and mosquitoes as well.

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