9 H), 3.18 (m, 2 H), 3.21 (m, 2 H), 7.35 (d, 2 H, J = 8.08 Hz), 7.82 (d, 2 H, J = 8.08 Hz), 8.76 (s, 1 H), 11.48 (br, 2 H); HRMS calcd for $C_{20}H_{21}N_5O_4$ m/z 395.1593, found m/z 395.1576.

Acknowledgment. We are deeply indebted to Dr. George S. K. Wong, who pioneered the palladium coupling procedure in our group for the attachment of carbon side chains to related heterocycles and who also provided us with the above procedure for the preparation of *tert*-butyl 4-ethynylbenzoate.

Registry No. **2**, 52454-37-2; **4**, 33963-89-2; **5**, 33047-42-6; **6**, 111323-82-1; **7**, 111292-00-3; **8**, 111292-02-5; **10**, 59247-47-1; **11**, 111291-96-4; **12**, 111291-97-5; **13**, 17231-51-5; **14**, 111291-98-6; **15**, 111291-99-7; **16**, 111292-01-4; **17**, 108473-08-1; 4-bromobenzoyl chloride, 586-75-4; (trimethylsilyl)acetylene, 1066-54-2; guanidine hydrochloride, 50-01-1.

3-Allyl-4-aryl-1,3,4-oxa(and thia)diazolidine-2,5-diones and Thio Analogues via a Facile Polyhetero-Claisen Rearrangement

Kurt H. Pilgram, Richard D. Skiles, and Daniel A. Kleier*

Biological Sciences Research Center, Shell Agricultural Chemical Company, Modesto, California 95352

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The attempted preparation of 2-(allyloxy)-4-aryl-1,3,4-oxa(and thia)diazolin-5(4*H*)-ones and thio analogues **4** by treatment of allyl 2-aryl-2-(chlorocarbonyl)hydrazinecarboxylates and thio analogues **3** with base at 15–25 °C gave instead 3-allyl-4-aryl-1,3,4-oxa(and thia)diazolidine-2,5-diones and thio analogues **5**. The inability to detect **4** indicates that these compounds undergo Claisen rearrangement in an extremely facile fashion.

Introduction

Prior to this investigation, disubstituted-1,3,4-oxadiazolidine-2,5-diones have been prepared by two methods. Hurd and Cesark[1] found that pyrolysis of 2-carbethoxy-1,2-dialkylhydrazinecarbonyl chlorides, at 140–180 °C, provides disubstituted diazasuccinic anhydrides in quantitative yields.

Henderson and Zweig[2] reported that diphenyldiazasuccinic anhydride could be prepared in 35% yield by the copper(II)-catalyzed pyrolysis of the corresponding hydrazinecarbonyl chloride.

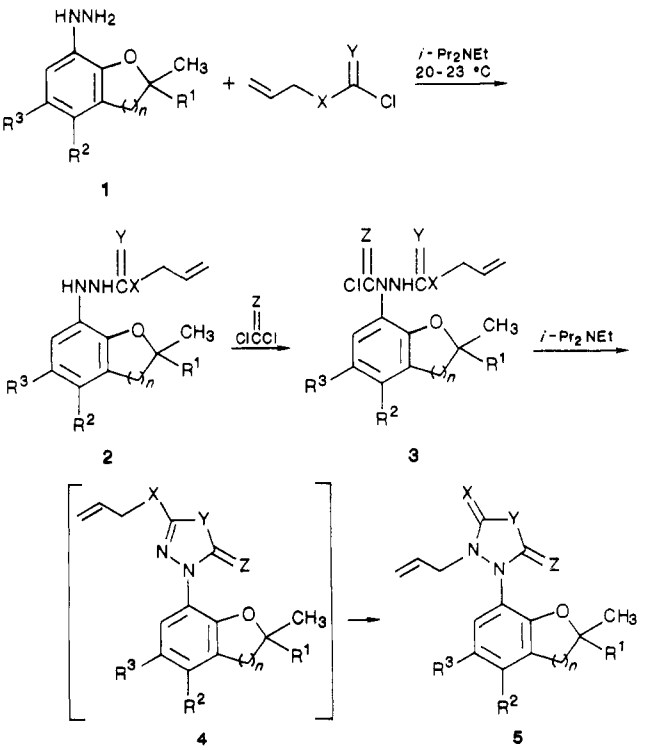
In an attempt to prepare 2-allyloxy analogues and thio derivatives of the broad-spectrum insecticide 4-(2,3-dihydro-2,2,4-trimethylbenzofuran-7-yl)-2-methoxy-1,3,4-oxadiazol-5(4*H*)-one,[3] several arylhydrazines **1** were converted into allyl 2-aryl-2-(chlorocarbonyl)hydrazinecarboxylates and thio analogues **3** (Scheme I). However, when the **3** compounds were subjected to dehydrochlorination conditions, e.g., diisopropylethylamine, 15–25 °C, the desired **4** compounds were not isolated as they readily underwent Claisen rearrangement to give 3-allyl-4-aryl-1,3,4-oxa(and thia)diazolidine-2,5-diones ("diazasuccinic anhydrides") **5** and thiono analogues. These results are discussed in the present paper.

Results

7-Hydrazino-2,3-dihydro-2,2-dimethylbenzofuran[3] (**1a**), 8-hydrazino-3,4-dihydro-2,5-dimethylbenzopyran[4] (**1c**), 7-hydrazino-2,3-dihydro-2,2,4-trimethylbenzofuran[3] (**1b**), and 8-hydrazino-5-chloro-3,4-dihydro-2,6-dimethylbenzopyran[4] (**1d**) reacted readily with allyl chloro(and thiol and dithio)-formate in the presence of diisopropylethylamine (Hünig's base) as acceptor for hydrogen chloride to give the respective allyl hydrazinecarboxylates ("carbazates"), thio and dithio derivatives **2** in good yields (Table I).

All **2** compounds reacted readily with phosgene at 0–20 °C in solution (THF, toluene, ethyl acetate) to give chlorocarbonylated allyl carbazates **3a–c** in essentially quantitative yields. Thiophosgene reacted analogously with **2d** to give **3e**. With the exception of **3a**, which melted at

Scheme I[a]



[a] (**a**) $R^1 = CH_3$, $R^2 = R^3 = H$, X = Y = Z = O, n = 1; (**b**) $R^1 = R^2 = CH_3$, $R^3 = H$, X = S, Y = Z = O, n = 1; (**c**) $R^1 = R^3 = H$, $R^2 = CH_3$, X = Y = Z = O, n = 2; (**d**) $R^1 = H$, $R^2 = Cl$, $R^3 = CH_3$, X = Y = S, Z = O, n = 2; (**e**) $R^1 = H$, $R^2 = Cl$, $R^3 = CH_3$, X = Y = Z = S, n = 2.

* Current address: Agricultural Products Dept., E. I. du Pont de Nemours and Company, Inc., Wilmington, DE 19898.

(1) Hurd, C. D.; Cesark, F. F. *J. Am. Chem. Soc.* **1967**, *89*, 1417.
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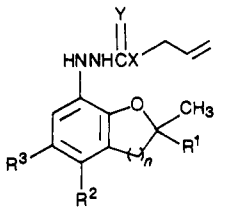
0022-3263/88/1953-0038$01.50/0

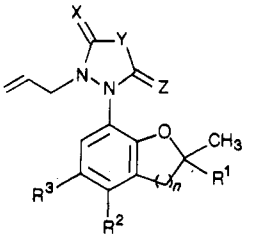
Table I. Allyl 2-Arylhydrazinecarboxylates and Thio Analogues



no.	R^1	R^2	R^3	n	X	Y	% yield	mp, °C[a]
2a	CH_3	H	H	1	O	O	67	90–91
2b	CH_3	CH_3	H	1	S	O	62	86–87
2c	H	CH_3	H	2	O	O	65	72–74
2d	H	Cl	CH_3	2	S	S	27	135–136

[a] See footnote to Table II.

Table II. 3-Allyl-4-aryl-1,3,4-oxa(and thia)diazolidine-2,5-diones and Thio Analogues



										EI/MS IR absorptn	
no.	R^1	R^2	R^3	*an*	X	Y	Z	% yield	mp, °C[b]	M^+	$\nu_{C=O}$ (in cm^{-1})
5a	CH_3	H	H	1	O	O	O	78	*a*	288	1850, 1780
5b	CH_3	CH_3	H	1	S	O	O	97	47–49	318	1794
5c	H	CH_3	H	2	O	O	O	62	52–54	302	1842, 1769
5d	H	Cl	CH_3	2	S	S	O	55	*a*	368	1692
5e	H	Cl	CH_3	2	S	S	S	55	*a*	384	

[a] Highly viscous liquid at room temperature. [b] Satisfactory analyses (±0.1 for C, H, N) were obtained.

78–80 °C, none of the highly viscous *N*-(chlorocarbonyl)-carbazates **3b–e** showed any tendency to crystallize.[5] Characteristic lines in the ^1H NMR spectra of **3** near 4.6 ppm ($-OCH_2-$) and absorption bands in the infrared near 3300 (–NH) and 1200 cm^{-1} (C–OC) are in support of structure **3** and do not indicate O–N migration of the allyl group prior to cyclization.

Treatment of **3a–e** with Hünig's base (1–3 molar equiv) in methanol–THF at 20–23 °C resulted in the formation and isolation of the 3-allyl-4-aryl-1,3,4-oxadiazolidine-2,5-diones **5a** and **5c**, the corresponding 2-thione **5b**, and the 5-oxo-1,3,4-thiadiazolidine-2-thione, **5d**, as well as the corresponding 2,5-dithione **5e** (Table II). None of the **4** compounds could be detected in the reaction mixtures (Scheme I).

Discussion

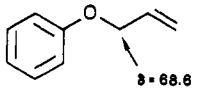
^{13}C NMR and infrared spectroscopy proved to be decisive in assigning structures.

In the ^{13}C NMR spectra of all cyclized **5** compounds, the chemical shift between δ 36 and 47 found for these materials suggested CH_2N isomers. There are no lines in the 60-ppm region indicative of CH_2O isomers. The chemical shift values for the CH_2 carbon atoms of allyl phenyl ether[7]

Table III. ^{13}C NMR Positions for NCH_2 of 5a–e

no.	CH_2N (in ppm) (solvent $CDCl_3$)	no.	CH_2N (in ppm) (solvent $CDCl_3$)
5a	42.69	**5d**	35.9
5b	41.99	**5e**	36.4
5c	47.2		

(**6**) (δ 68.6) and *N*-allylaniline[8] (**7**) (δ 46.4) support these assignments (Table III). The lines near 150–160 ppm are consistent with an anhydride structure.



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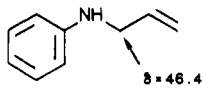

7

Infrared spectra in methylene chloride of the two disubstituted diazasuccinic anhydrides in which both X and Z equal oxygen, **5a** and **5c**, show carbonyl frequencies typical of diazasuccinic anhydrides.[2] A strong band appears at 1840–1850 cm^{-1}, with a stronger band about 70 wavelengths lower, near 1770–1780 cm^{-1}. In **5c**, these occur at 1842 and 1769 cm^{-1}, while in **5a** they appear at 1850 and 1780 cm^{-1} (Table II).

The 2-propargyloxy compound **8**, which does not undergo Claisen rearrangement under these mild conditions (15–25 °C), exhibits a single carbonyl band at 1802 cm^{-1} and a stronger band at 1659 cm^{-1}; the latter can be attributed to the endocyclic C=N stretch. The enhanced intensity of this band is most likely due to coupling or

(4) Pilgram, K. H.; Skiles, R. D. U.S. Pat. 4558040, 1985 (to Shell Oil Company).

(5) A variety of alkyl 2-(chlorocarbonyl)-2-(substituted phenyl)-hydrazinecarboxylates analogous to **3** are crystalline solids that are relatively stable and can be isolated in high yield in form of crystalline solids (from methanol or ether–hexane).[6]

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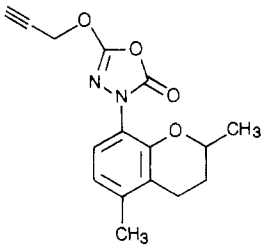
(8) *Sadtler Standard Carbon-13 NMR Spectra*, #6700; *Carbon-13 NMR Spectral Data*, #1452; Bremser, et al., Verlag Chemie.

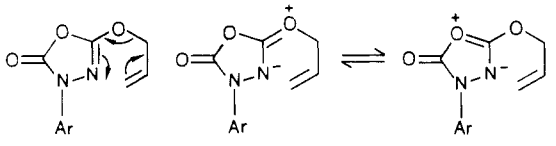
Fermi resonance with the carbonyl mode, borrowing intensity from it. In general, the 2-alkoxy- and 2-(benzyloxy)-1,3,4-oxadiazolin-5(4*H*)-ones show a carbonyl band in the 1810–1785-cm^{-1} range and a stronger band due to the enhanced C=N stretch near 1660–1680 cm^{-1}.



8

Traditionally, the Claisen rearrangement has involved the sigmatropic reorganization of an allyl vinyl ether into a homoallylic carbonyl compound by a concerted intramolecular process. Of the many polyhetero-Claisen rearrangements possible, to date relatively few have been performed involving Claisen rearrangements within heterocyclic ring systems. Studies that have been reported were carried out with allyloxy-substituted pyridines,[9,10] pyrimidines,[11-13] quinolines,[14] γ-pyrones,[15] and flavones.[16] A high-boiling tertiary amine (*N,N*-dimethylaniline) and temperatures of around 220–255 °C have normally been required to effect Claisen rearrangement. 2-(Allyloxy)-benzoxazole[17] and -benzothiazole[17] require a temperature of 200 °C for Claisen rearrangement to proceed. 5-(Allyloxy)-1-phenyltetrazole[17] rearranges already at 100–150 °C. These temperature ranges (100–255 °C) contrast dramatically with the ease with which 2-(allyloxy)-1,3,4-oxa(and thia)diazol-5(4*H*)-ones **5** undergo Claisen rearrangement (15–25 °C, present work).

Based upon differences such as these, it has been suggested[17] that the rates of rearrangement of the ethers should correlate roughly with the degree of positive character of the ether oxygen together with the degree of nucleophilicity of the nitrogen to which the rearrangement occurs. Thus, the rearrangement might be viewed as nucleophilic attack by the imino nitrogen on the terminal carbon of the allyl group of **4**. Enhanced π nucleophilicity due to the following resonance in the oxadiazolone, **9a** ⇌ **9b**, might then explain the facility of rearrangement.



4 **9a** **9b**

Alternatively, the Claisen rearrangement proceeds through a transition state that may be more or less biradical-like depending upon the nature of the substituents.[18,19] A 2-(allyloxy)-1,3,4-oxadiazol-5(4*H*)-one would pass through a transition state consisting of an allyl radical and 2-oxy-1,3,4-oxadizol-5(4*H*)-one radical for which a plethora of additional resonance structures can be proposed.

In order to better understand the factors influencing polyhetero-Claisen rearrangements, reaction energies were calculated for the Claisen rearrangement of 2-(allyloxy)-1,3,4-oxadiazolin-5(4*H*)-one, (allyloxy)formaldimine ($HN{=}CHOCH_2CH{=}CH_2 \rightarrow O{=}CNHCH_2CH{=}CH_2$) and (allyloxy)ethylene ($CH_2{=}CHOCH_2CH{=}CH_2 \rightarrow O{=}CCH_2CH_2CH{=}CH_2$). Reaction energies were calculated by using the PRDDO approximation.[21] The rearrangement of the (allyloxy)formaldimine serves as a simplified model for the rearrangement of 2-(allyloxy)-1,3,4-oxadiazolin-5(4*H*)-one in which the influence of the heterocycle has been eliminated. Calculations on the (allyloxy)ethylene were performed for reference purposes since this reaction has been well characterized experimentally.

The reactant and product geometries were optimized by using the MM2 program.[22] Since reliable force constants were not available for some ring angles and bonds, the heterocyclic rings were further refined by using electronic structure theory at the INDO level of approximation.[23]

The calculated reaction energy for the Claisen rearrangement of the (allyloxy)ethylene was −13.9 kcal/mol. This compares favorably with an experimental heat of reaction of −17 kcal/mol[24] and gives confidence in the reaction energies calculated for the hetero-Claisen rearrangements. The reaction energy for the (allyloxy)formaldimine was calculated to be −12.8 kcal/mol and that for the 2-(allyloxy)-1,3,4-oxadiazolinone was calculated to be −10.7 kcal/mol. Since the calculated reaction energies vary only modestly for these three Claisen rearrangements, the explanation for the unusual facility with which the rearrangement of the 2-(allyloxy)oxadiazolinone occurs must be sought in the kinetics of these reactions.

To this purpose, reaction pathway calculations for the rearrangement of the (allyloxy)formaldimine and the (allyloxy)ethylene were performed. These calculations used the syncronous transit method with orthogonal optimization[25] and used a GVB wavefunction[26] with one split pair to describe the allyl vinyloxy biradical character expected in the transition state. Since the MM2-optimized reactant and product geometries were chair-like in nature, the transition state had a chair conformation. The calculated activation barrier was 32.1 kcal/mol for the rearrangement of the (allyloxy)ethylene. This compares reasonably with an experimental value of approximately 25 kcal/mol.[27] At the same level of approximation, the calculated activation barrier for the rearrangement of the (allyloxy)formaldimine was actually higher (44 kcal/mol). Since the experimental observations reported here suggest that the rearrangement of an (allyloxy)formaldimine is

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more facile than that of (allyloxy)ethylene when the formaldimine is incorporated within an oxadiazolinone ring system, the presence of the ring system is probably responsible for lowering the activation barrier.

To unambiguously establish the role of the heterocycle in facilitating the hetero-Claisen rearrangement would require rather sophisticated calculations using larger basis sets and including correlation effects. The use of more sophisticated wavefunctions is particularly important if one wishes to establish whether the transition state is biradical-like in nature.

Experimental Section

***S*-Allyl 2-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-hydrazinethiocarboxylate (2b).** To a chilled (0 °C) solution of 9.6 g (50 mmol) of **1b** and 6.5 g (0.05 mol) of Hünigs base in 150 mL of tetrahydrofuran was added dropwise and with stirring 6.8 g (50 mmol) of *O*-allyl chlorothioformate (addition time 5 min). After 0.5 h at 0 °C, the solvent was removed under rotary evaporation. The residue was diluted with 200 mL of cold water and 200 mL of ether. Further extraction with two 200-mL portions gave an ethereal extract which was dried and concentrated. Silica gel column chromatography (solvent 2[20] of the reaction mixture gave 9.0 g (62%) of **2b** as a tan solid, mp 86–87 °C (from ether–hexane): IR (CH_2Cl_2) ca. 3337 (NH), 3000–2800 (CH), 1678 (C=O), 1636 (C=C), 1605–1445 (Ar ring), 1250–1100 (COC); EI-MS, m/z 292 (M^+), 251 (M^+ – allyl), 231, 218, (M^+ – allyl – SH), 191 (Ar – $NHNH^+$), 174, 161, 147, 133, 105, 91, 77, 65, 41 ($allyl^+$); ^{13}C NMR ($CDCl_3$) 175.2 (s, >C=O), 145.9 (s, ≥CO), 134.2 (d, =CH-) ($J_{^1H-^{13}C}$ = 158 Hz), 128.5 (s, ≥CN), 127.6 (s, >C=), 126.1 (s, >C=), 121.2 (d ≥CH) (J = 158 Hz), 117.4 (t, $=CH_2$) (J = 158 Hz), 112.7 (d, ≥CH) (J = 158 Hz), 87.9 (s, >CO), 42.4 (t, CH_2S) (J = 132 Hz), 32.0 (t, Ar CH_2) (J = 126 Hz), 28.6 (q, $>C(CH_3)_2$) (J = 126 Hz), 18.3 ppm (q, Ar CH_3) (J = 127 Hz).

Allyl 2-(2,3-Dihydro-2,2-dimethylbenzofuran-7-yl)-2-(chlorocarbonyl)hydrazinecarboxylate (3a). To a solution of 10.1 g (100 mmol) of phosgene in 100 mL of ethyl acetate was added with stirring 12.3 g (50 mmol) of **2a**. After 0.5 h, TLC indicated completion of the conversion. Solvent and excess phosgene were removed in vacuo to give 15.5 g of a mushy solid which was recrystallized from ether–hexane to give 10.0 g (65%) of **3a**: mp 78–80 °C; IR (KBr) 3220 (NH), 3000–2800 (CH), 1760 (C=O, acid chloride), 1720 (C=O), 1638 (C=C), 1600–1431 (Ar Ring), and 1200–1000 cm^{-1} (COC, CCl); EI-MS, m/z 308 (M^+), 272 (M^+ – HCl), 245 (M^+ – COCl); ^1H NMR ($CDCl_3$) δ 1.45 (6 H) ($(CH_3)_2$), 305 (2 H) ($-CH_2-$), 4.65 (2 H) (OCH_2), 5–6 (3 H) ($(=CH)_3$), and 6.5–8.0 (4 H) ($=CH_2$, $(=CH)_2$, and NH).

Anal. Calcd: C, 58.3; H, 4.9; N, 9.1. Found: C, 57.9; H, 5.1; N, 8.9.

3-Allyl-4-(2,3-dihydro-2,2,4-trimethylbenzofuran-7-yl)-1,3,4-thiadiazolidine-2,5-dione (5b). To a solution of 8.0 g (22.6 mmol) of **3b** in 75 mL of methanol was added 3.0 g (23.3 mmol) of Hünigs base. After 15 min at 23 °C; thin-layer chromatography indicated that the reaction was complete. Most of the methanol was removed under rotary evaporation. The residue was diluted with 200 mL of water and extracted with 200 mL of ether. The ether was washed with 150 mL of diluted hydrochloric acid and water, dried, filtered, and concentrated at 25 °C. The residue crystallized from hexane–ether (5:1) to give 7.0 g (97%) of **5b** as a tan solid: mp 47–49 °C; IR (CH_2Cl_2) 3000–2800 (CH), 1794 (C=O), 1603 (C=C, C=N), 1600–1431 (Ar ring); EI-MS, m/z 318 (M^+), 303 (M^+ – CH_3), 233 (M^+ – allyl + CO_2), 217 (Ar – $NNCO^+$), 203 (Ar – NCO^+), 175 (Ar – N^+), 160 (Ar^+), 146, 132, 117, 105, 91, 77, 65, 41 ($allyl^+$); ^{13}C NMR ($CDCl_3$) 18.84 (q, CH_3 Ar), 28.31 (q, $(CH_3)_2C<$), 34.22 (t, CH_2), 41.99 (t, CH_2N), 88.62 (s, ≥CO, >CHO), 115–153 ppm (s, d, 10 C=).

4-Allyl-3-(5-chloro-3,4-dihydro-2,6-dimethyl-2*H*-1-benzopyran-8-yl)-2-oxo-1,3,4-thiadiazolidine-5-thione (5d). A solution of 1.2 g (2.9 mmol) of **3d** in 25 mL of methanol and 25 mL of tetrahydrofuran containing 1.3 g (10 mmol) of Hünigs base was allowed to stand at ambient temperature for 3 days. After the usual workup, the crude product was adsorbed on silica gel and chromatographed, using solvent 1.[20] The purified product, 0.6 g (55%) of **5d**, consisted of an amber syrup which showed no tendency to crystallize: ^1H NMR ($CDCl_3$) δ 1.34 (3 H) and 4.13 (1 H) ($OCHCH_3$), 1.7, 2.05, 3.25, 3.9 (4 H, $(=CH)_4$), 2.31 (3 H, $=CCH_3$), 3.09 (2 H, $=CCH_2$), 5.23 (2 H, $=CH_2$), 5.92 (1 H, =CH), and 7.08 (1 H, =CH, Ar); IR (CH_2Cl_2) 3000–2800 (CH), 1692 (C=O), 1638, 1607 (C=C, C=N, Ar ring): EI-MS, m/z 368 (M^+), 353 (M^+ – CH_3), 327 (M^+ – allyl), 267 (Ar – N_2CS^+), 225 (m/z 267 – CS), 195 (Ar^+), 41 ($allyl^+$); ^{13}C NMR ($CDCl_3$) 169.0 (s, >C=S), 149.5 (s, ≥C-O), 147.1 (s, C=O), 135.9 (s, ≥C), 132.0 (d, =CH) (J = 158 Hz), 127.5 (s, ≥CCl), 127.4 (d, ≥CH) (J = 162 Hz), 122.7 and 122.4 (s, ≥CN and ≥CMe), 119.3 (t, $=CH_2$) (J = 158 Hz), 72.3 (d, >CHO) (J = 146 Hz), 35.9 (t, CH_2N) (J = 136 Hz), 28.4 (t, CH_2Ar) (J = 130 Hz), 23.8 (t, $-CH_2CH_2-$) (J = 132 Hz), 20.7 (q, Ar CH_3) (J = 128 Hz), 19.7 ppm (Q, CH_3) (J = 130 Hz).

3-Allyl-4-(5-chloro-3,4-dihydro-2,6-dimethyl-2*H*-1-benzopyran-8-yl)-1,3,4-thiadiazolidine-2,5-dithione (5e). To a solution of 1.2 g (2.9 mmol) of **3e** in 20 mL of methanol and 30 mL of tetrahydrofuran was added 1.3 g (0.01 mol) of Hünigs base. After 3 days at ambient temperature, the solvents were removed under reduced pressure. The residue was washed with water, extracted into ether, and purified by silica gel column chromatography (solvent 1[20]) to give 0.6 g (55%) of amber syrup **5e**: IR (CH_2Cl_2) 3000–2800 (CH), ca. 1700 (C=N, C=C), ca. 1250–1000 (C=S, COC); EI-MS, m/z 384 (M^+), 369 (M^+ – CH_3), 343 (M^+ – allyl), 267 (Ar – N_2CS^+), 153, 41, ($allyl^+$).

2-(Propargyloxy)-4-(3,4-dihydro-2,5-dimethyl-2*H*-1-benzopyran-8-yl)-1,3,4-oxadiazolin-5(4*H*)-one (8). A solution of 3.5 g (10.4 mmol) of 2-(chlorocarbonyl)-2-(3,4-dihydro-2,5-dimethyl-2*H*-1-benzopyran-8-yl)hydrazinecarboxylic acid propargyl ester and 2.6 g (20 mmol) of Hünigs base in 50 mL of methanol was stirred at room temperature for 18 h. The solvent was removed under rotary evaporation. The residual oil was dissolved in 50 mL of ether, washed with 50 mL of 1% hydrochloric acid, dried ($MgSO_4$), filtered, and concentrated. Recrystallization from ether gave 1.5 g (48%) of **8**: mp 127–130 °C; IR (CH_2Cl_2) 3302 (CH), 3000–2800 (CH), 1807 (C=O), 1653 (C=N), 1600–1500 (Ar ring), 1200–1000 cm^{-1} (COC); ^1H NMR ($CDCl_3$) δ 1.36 (3 H) and 4.15 (1 H) (CH_3CH), 1.75, 2.1, and 2.63 (4 H, $(CH_2)_2$), 2.63 (1 H, CH), 2.21 (3 H, $=CCH_3$), 4.91 (2 H, OCH_2), 6.75 and 7.10 (2 H, $(=CH)_2$).

Anal. Calcd: C, 64.0; H, 5.4; N, 9.3. Found: C, 64.4; H, 5.5; N, 9.3.

Registry No. **1b**, 85418-54-8; **2a**, 111268-79-2; **2b**, 111268-78-1; **2c**, 111268-89-4; **2d**, 111268-90-7; **3a**, 111268-80-5; **3b**, 111268-81-6; **3d**, 111268-83-8; **3e**, 111268-85-0; **5a**, 111268-91-8; **5b**, 111268-82-7; **5c**, 111268-92-9; **5d**, 111268-84-9; **5e**, 111268-86-1; **8**, 111268-88-3; $CH_2=CHCH_2OC(=S)Cl$, 111268-77-0; 2-(chlorocarbonyl)-2-(3,4-dihydro-2,5-dimethyl-2*H*-1-benzopyran-8-yl)hydrazinecarboxylic acid propargyl ester, 111268-87-2.