One-Step Hydroamidation of 2-Aza-1,3-pentadienes

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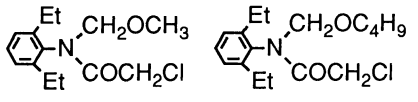
Various *N*-(1-aryl-1-alkenyl)-2-chloroacetamides bearing alkoxymethyl or alkylthiomethyl group on amide nitrogen were synthesized by a one-step hydroamidation of 2-aza-1,3-pentadienes. Some *N*-(1-aryl-1-alkenyl)-2-chloroacetamides were found to have high herbicidal activities against upland farm weeds.

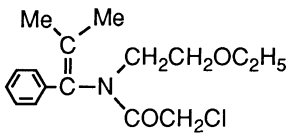
In our previous study, it is found that certain *N*-(1-aryl-1-alkenyl)-2-chloroacetamides such as 2-chloro-*N*-(2-ethoxyethyl)-*N*-(2-methyl-1-phenyl-1-propenyl)acetamide (NSK-68) showed a high herbicidal activity against upland farm weeds.[1] In order to develop highly active compounds, we have been interested in the synthesis of *N*-(1-aryl-1-alkenyl)-2-chloroacetamides bearing an alkoxymethyl group on amide nitrogen, because some well-known 2-chloroacetamide herbicides such as Alachlor and Butachlor have an alkoxymethyl group on amide nitrogen (Fig. 1). These 2-chloroacetamide herbicides were prepared by the reaction of 2,6-diethyl-*N*-methylideneaniline with chloroacetyl chloride followed by the reaction with alcohol.[2] Previously, little research had been carried out on this process, synthetic method of *N*-alkenyl-*N*-alkoxymethyl amides.

Recently, we have reported a new one-step hydroamidation of Schiff bases in the presence of trichlorosilane.[3] This reaction provides a convenient method for the preparation of amides from Schiff bases. In a previous paper, we have described a facile synthesis of 2-aza-1,3-butadienes.[4] 2-Aza-1,3-dienes have become useful intermediates for the construction of heterocyclic compounds and many reactions were investigated.[5] For instance, Georg and co-worker[6] described the synthesis of *N*-vinyl-*β*-lactams by the reaction of 2-aza-1,3-dienes with acid chlorides. On the other hand, Alper and Amaratunga[7] reported the reductive acylation of 1-aza-1,3-dienes using cobalt carbonyl, carbon monoxide, and methyl iodide under phase transfer catalysis conditions.



Alachlor

Butachlor



NSK-68

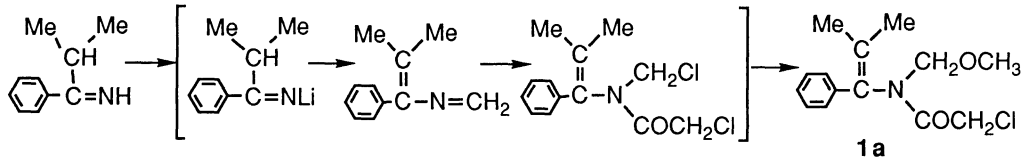
Fig. 1. Chloroacetamide herbicides.

In this study, we have tried to apply the hydroamidation to 2-aza-1,3-pentadienes to prepare herbicidally active *N*-(1-aryl-1-alkenyl)-2-chloroacetamides bearing alkoxymethyl or alkylthiomethyl group.

Results and Discussion

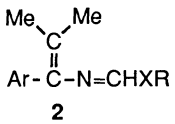
Synthesis of 2-Chloro-*N*-methoxymethyl-*N*-(2-methyl-1-phenyl-1-propenyl)acetamide (1a). At first, we aimed at the synthesis of 2-chloro-*N*-methoxymethyl-*N*-(2-methyl-1-phenyl-1-propenyl)acetamide (**1a**) referring to the structure of Alachlor. We have previously synthesized a number of *N*-(1-aryl-1-alkenyl)-2-chloroacetamides according to the reaction of Schiff bases with chloroacetyl chloride. So we tried to prepare *N*-methoxymethyl-2-methyl-1-phenyl-1-propanimine as a starting Schiff base. However, we were unable to obtain a satisfactory compound, probably due to its instability. Then we planned to synthesize **1a** via methanimine compound, similar to the synthesis of Alachlor. 2-Methyl-1-phenyl-1-propanimine was allowed to react with *n*-BuLi, followed by the treatment with bromomethyl methy ether. After that, the reaction with chloroacetyl chloride and methanol was carried out successively to give **1a** in 5% yield. The reaction might proceed via methanimine compound as shown in Scheme 1. However, this method does not seem to be suitable for the preparation of *N*-(1-aryl-1-alkenyl)-2-chloroacetamides bearing alkoxyalkyl moiety, because the yield of **1a** was considered low. Although many similar experiments were carried out, the reproducibility of yield was poor. This may be attributed to the instability of intermediary methanimine, caused by the difficulties of controling temperature during the reactions. To explore a general preparative method, we attempted the hydroamidation of 2-aza-1,3-pentadienes.

Synthesis of 2-Aza-1,3-pentadienes. Some 2-aza-1,3-pentadienes were prepared according to the method described previously.[4] Namely, the reaction of 1-aryl-2-methyl-1-propanimines with orthoesters were carried out to give 3-aryl-4-methyl-2-aza-1,3-pentadienes (**2**) bearing an alkoxyl group at 1-position. The structures and yields of compounds are described in Table 1. The yields of 2-aza-1,3-pentadienes were dependent on the substituents. In general, the 2-aza-1,3-pentadienes having isopropoxyl group were obtained in good yields, compared with the compounds having other alkoxyl



Scheme 1.

Table 1. 3-Aryl-4-methyl-2-aza-1,3-pentadienes (**2**)



2

No.	Ar	X	R	Yield/%	Bp/°C/mmHg
2b	C_6H_5	O	Et	33	104/3
2f	2-Naphthyl	O	Et	31	133—136/0.12
2g	2-Furyl	O	Et	19	55—57/0.4
2h	2-Thienyl	O	Et	58	72—74/0.25
2i	C_6H_5	O	*n*-Pr	10	110—115/0.7
2k	3-Me-C_6H_4	O	*i*-Pr	41	90—92/0.2
2l	4-Me-C_6H_4	O	*i*-Pr	62	92—95/0.2
2p	3-Thienyl	O	*i*-Pr	69	78—80/0.1
2q	5-Me-2-thienyl	O	*i*-Pr	75	80/0.1
2s	5-MeO-2-thienyl	O	*i*-Pr	45	100—105/0.1
2u	C_6H_5	O	*i*-Bu	22	85—88/0.12

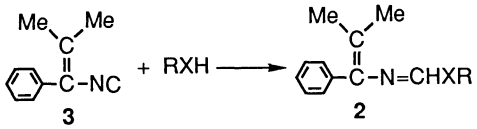
groups. This is probably due to the steric protection around the carbon-nitrogen double bond. However, this method is not applicable to all of 2-aza-1,3-pentadienes.

It is well known that the reaction of isocyanides with alcohols affords the corresponding 1-alkoxy-2-aza-1,3-butadienes.[8] Secondly, we attempted to prepare 4-methyl-3-phenyl-2-aza-1,3-pentadienes by use of 2-methyl-1-phenyl-1-propenyl isocyanide (**3**) as a starting material. At first, **3** was prepared from the formylation of 2-methyl-1-phenyl-1-propanimine using formic acetic anhydride, followed by dehydration.[9] Though D. H. Barton and co-workers proved that 1,4-diazabicyclo[2.2.2]octane is the most effective base in the dehydration process, we obtained **3** in good yield using pyridine/$POCl_3$ in hexane.

The reaction of **3** with alcohols or thiols was carried out to give 4-methyl-3-phenyl-2-aza-1,3-pentadienes (**2t, w—z**) in moderate yields, as shown in Table 2. The reaction with thiols took place more rapidly than those with alcohols, because of their high nucleophilicity. We failed in the similar reaction of **3** with phenol in place of alcohol. It was already known to us that the reaction of isocyanide with phenol was complicated.[10]

Hydroamidation of 2-Aza-1,3-pentadienes. 2-Aza-1,3-pentadienes (**2**) were treated with chloroacetyl chloride in the presence of trichlorosilane in benzene (Scheme 2). The results were summarized in Table 3.

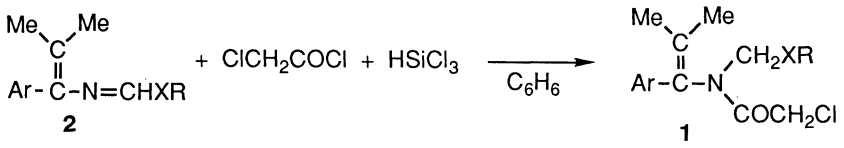
Table 2. 4-Methyl-3-phenyl-2-aza-1,3-pentadienes (**2**)



3 **2**

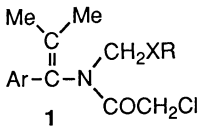
No.	X	R	Yield/%	Bp/°C/mmHg
2t	O	*n*-Bu	78	90/0.1
2w	S	*n*-Pr	48	100—103/0.15
2x	S	*i*-Pr	63	92—94/0.15
2y	O	$CH_2CH{=}CH_2$	68	76/0.1
2z	O	$CH_2C_6H_5$	66	135—137/0.12

As shown in the table, the hydroamidation of 2-aza-1,3-pentadienes proceeded smoothly to afford *N*-(1-aryl-1-alkenyl)-2-chloroacetamides (**1**) bearing both alkenyl moiety and alkoxymethyl moiety in one group, or bearing alkylthiomethyl moiety in another group. Both on amide nitrogen. The mechanism of this reaction seems to be identical to that described before. Namely, **3** and chloroacetyl chloride react to form iminium salt-type compound, or its chlorine adduct as a intermediate, which further reacts with trichlorosilane to afford **1**. In the ^1H NMR spectra of **1**, the signal of methylene protons between nitrogen atom and oxygen atom were split into two doublets (J=10 Hz). This suggests that the rotation



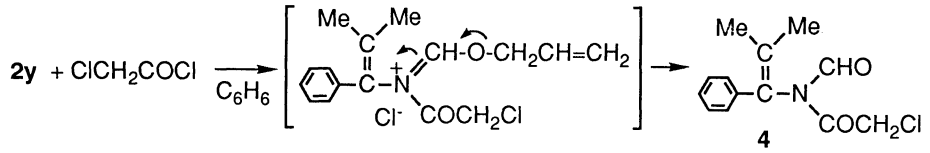
Scheme 2.

Table 3. *N*-(1-Aryl-1-alkenyl)-2-chloroacetamides (**1**)



No.	Ar	X	R	Yield/%	Bp/°C/mmHg
1b	C_6H_5	O	Et	42	123—124/0.1
1c	3-Me-C_6H_4	O	Et	56	137/0.25
1d	4-F-C_6H_4	O	Et	44	143/0.5
1e	3-CF_3-C_6H_4	O	Et	38	136/0.25
1f	2-Naphtyl	O	Et	46	97—98[a]
1g	2-Furyl	O	Et	44	120/0.2
1h	2-Thienyl	O	Et	39	133/0.2
1i	C_6H_5	O	*n*-Pr	51	142—143/0.25
1j	C_6H_5	O	*i*-Pr	63	140/0.1
1k	3-Me-C_6H_4	O	*i*-Pr	88	135—136/0.1
1l	4-Me-C_6H_4	O	*i*-Pr	70	137/0.1
1m	4-F-C_6H_4	O	*i*-Pr	61	128—130/0.1
1n	2-Furyl	O	*i*-Pr	61	118—120/0.1
1o	2-Thienyl	O	*i*-Pr	59	135/0.1
1p	3-Thienyl	O	*i*-Pr	63	147—148/0.3
1q	5-Me-2-thienyl	O	*i*-Pr	64	156—157/0.45
1r	3-MeO-2-thienyl	O	*i*-Pr	76	155—157/0.7
1s	5-MeO-2-thienyl	O	*i*-Pr	68	162—163/0.4
1t	C_6H_5	O	*n*-Bu	36	157—158/0.45
1u	C_6H_5	O	*i*-Bu	67	138/0.1
1v	C_6H_5	O	*s*-Bu	15	123/1/0.1
1w	C_6H_5	S	*n*-Pr	60	155/0.1
1x	C_6H_5	S	*i*-Pr	54	154/0.15

a) Melting point (uncorrected).

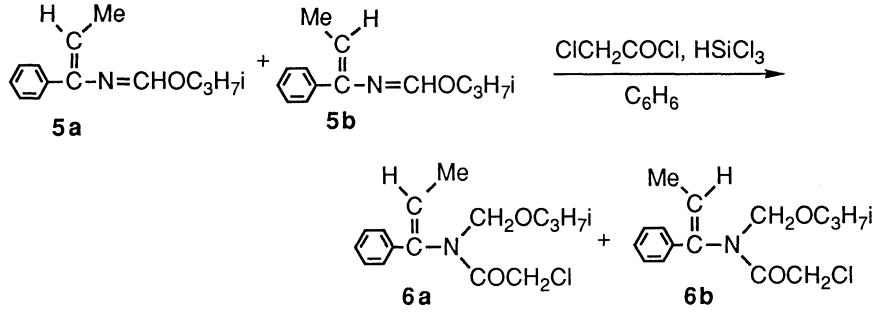


Scheme 3.

around N–C–O bond was hindered sterically by the bulky structure around the methylene protons.

When compound **2y** which is a 2-aza-1,3-pentadiene bearing allyloxy group was used in this reaction at room temperature, 2-chloro-*N*-formyl-*N*-(1-methyl-1-phenyl-1-propenyl)acetamide (**4**) was obtained in good yield (Scheme 3). A similar result was observed in the reaction of **2z** which is a 2-aza-1,3-pentadiene bearing benzyloxy substituent. This could be explained by the easy release of allyl cation or benzyl cation from the intermediate as shown in Scheme 3.

When a mixture of two isomers (**5a**:**5b**=2:1) was employed as a starting material, two 2-chloroacetamide isomers (**6a** and **6b**) were obtained in yields of 53 and 33%, respectively (Scheme 4). The structure of the major isomer **6a** was assigned on the basis of NOE spectrum. It is not obvious that the isomers ratio was altered during the reaction. The ^{1}H NMR signal of



Scheme 4.

Table 4. Herbicidal Activities against Upland Farm Weeds

Compound	Dosage (ga.i./a)	Herbicidal activity			
		A	B	C	D[a]
1d	10	5	5	2	4
	2.5	3	4	0	1
1h	10	5	5	0	5
	2.5	4	4	0	2
1j	10	5	5	1	4
	2.5	5	4	0	3
NSK-68	10	5	5	5	5
	2.5	4	4	0	3
Alachlor	10	5	5	3	5
	2.5	4	5	2	4

a) A, *Echinochloa utilis*; B, *Setaria vilidis*; C, *Bidens pilosa*; D, *Amaranthus viridis*.

methylene protons between nitrogen atom and oxygen atom of **6a** appeared two doublets similar to those of other compounds. However, that of **6b** was observed as a singlet.

Herbicidal Activity. The herbicidal activity of the compounds synthesized here against upland farm weeds was examined. The results of some highly active compounds are shown in Table 4 together with that of Alachlor which is one of the well-known herbicides. Among the tested compounds, **1j** exhibited the highest activity against upland farm weeds, especially against gramineous weeds. The activity of **1j** was almost equal to that of Alachlor.

In conclusion, we have succeeded in developing highly active herbicidal compounds using a one-step hydroamidation of 2-aza-1,3-dienes.

Experimental

The IR spectra were measured with a Hitachi I-2000 spectrometer. The ^{1}H NMR spectra were measured in a $CDCl_3$ solution with a Hitachi R-1500 spectrometer and in an acetone-d_6 with JEOL GSX-270 spectrometer using tetramethylsilane as an internal standard. The mass spectra were obtained on a Hitachi M-80 spectrometer. Elemental analysis data (C, H, and N) agreed within ±0.3% for the calculated values.

Synthesis of 2-Chloro-*N*-methoxymethyl-*N*-(2-methyl-1-phenyl-1-propenyl)acetamide (1a). To a flask equipped with thermometer were added 2-methyl-1-phenyl-1-propanimine (5.04 g, 0.034 mol) and anhydrous ether (20 ml). The solution was treated with *n*-BuLi in hexane (19.6 g, 0.046 mol) at −15 °C for 3 h. Bromomethyl methyl ether (6.25 g, 0.050 mol) in anhydrous ether (10 ml) was added to the solution at −15 °C and stirred for 20 h. Chloroacetyl chloride (7.33 g, 0.069 mol) in anhydrous ether (10 ml) was added to the solution at −15 °C and the mixture was stirred overnight at 0 °C. After it was warmed to room temperature, the mixture of methanol (20 ml) and triethylamine (7.03 g, 0.070 mol) was added and stirred overnight at room temperature. The reaction mixture was washed with water and the organic portion was extracted with ether and dried over magnesium sulfate. The low boiling components were evaporated. The resulting pale yellow viscous liquid was purified by column chromatography with silica gel to give colorless solid (0.45 g, 5% yield) of **1a**. Mp 44—45 °C; ^{1}H NMR ($CDCl_3$) δ=1.89 (6H, s, CH_3×2), 3.38 (3H, s, CH_3), 4.13 (2H, s, $COCH_2Cl$), 4.48 and 5.00 (2H, 2d, *J*=10 Hz, NCH_2O), and 7.30 (5H, s, aromatic H); IR (KBr) 1675 cm^{-1} (CO); MS *m*/*z* 267 (M^+, 9), 222 (8), 147 (56), 45 (100). Found: C, 62.72; H, 6.71; N, 5.21%. Calcd for $C_{14}H_{18}NClO_2$: C, 62.80; H, 6.78; N, 5.23%.

Synthesis of 2-Aza-1,3-butadienes. Synthesis of 2q: To a 100 ml flask equipped with a distillation head were added 2-methyl-1-(5-methy-2-thienyl)-1-propanimine (6.08 g, 37 mmol), triisopropyl orthoformate (7.00 g, 37 mmol), and a small amount of *p*-toluenesulfonic acid. The mixture was heated in an oil bath (150 °C) for about 10 min until the 2-propanol, which was formed during the reaction, was distilled out. The resulting mixture afforded a yellow liquid (6.42 g, 75%) of 1-isopropoxy-4-methyl-3-(5-methy-2-thienyl)-2-aza-1,3-pentadiene which boiled at 80 °C/0.1 mmHg (Table 1, **2q**). (1mmHg=133.322 Pa). ^{1}H NMR ($CDCl_3$) δ=1.30 (6H, d, *J*=6 Hz, CH_3×2), 1.77 (3H, s, CH_3), 1.90 (3H, s, CH_3), 2.43 (3H, s, CH_3), 5.07 (1H, quint., *J*=6 Hz, OCH), 6.58 (2H, s, thienyl H), 7.31 (1H, s, N=CHO); IR (KBr) 1630 cm^{-1} (N=CHO); MS *m*/*z* 237 (M^+, 100), 194(38), 124(50). Found: C, 65.57; H, 8.15; N, 6.01%. Calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90%.

Synthesis of 2-Methyl-1-phenyl-1-propenyl Isocyanide (3). 2-Methyl-1-phenyl-1-propanimine (17.6 g, 0.11 mol) and acetonitrile (200 ml) were combined in a flask. A formic acetic anhydride (35.7 g, 0.41 mol) was added with stirring at 0 °C. The mixture was stirred at room temperature overnight and then heated in an oil bath (50 °C) for 4 h. The reaction mixture was added to an excess of potassium carbonate solution. The organic portion was extracted with ethyl acetate and dried over anhydrous sodium sulfate. The ethyl acetate was then distilled to give a yellow liquid (18.1 g, 87%) of *N*-

formyl-2-methyl-1-phenyl-1-propenylamine which boiled at 115—117 °C/0.15 mmHg. *N*-Formyl-2-methyl-1-phenyl-1-propenylamine (31.03 g, 0.18 mol), pyridine (150 ml), and hexane (100 ml) were combined in a flask. Phosphoryl chloride (17.60 g, 0.12 mol) was added with stirring at −6 °C to the mixture. The mixture was stirred at room temperature overnight and then poured onto ice-water. The organic portion was extracted with hexane and dried over anhydrous sodium sulfate. The hexane was then distilled to give a pale yellow liquid (10.40 g, 37% yield) of **3**, which boiled at 60 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s, CH_3), 2.04 (3H, s, CH_3), 7.30 (5H, s, aromatic H); IR (KBr) 2104 cm^{-1} (NC); MS *m/z* 157 (M^+, 100), 115 (73).

Synthesis of 2-Aza-1,3-pentadienes. Synthesis of 2t: A mixture of **3** (3.00 g, 0.019 mol), *n*-butyl alcohol (3.00 g, 0.040 mol) and Cu_2O (0.50 g, 0.003 mol) was heated at 120 °C for 2 h with stirring. The reaction mixture was distilled under a reduced pressure to afford a colorless liquid (3.46 g, 78% yield) of 1-butoxy-4-methyl-3-phenyl-2-aza-1,3-pentadiene which boiled at 90 °C/0.1 mmHg (Table 2, **2t**). ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, m, CH_3), 1.53 (4H, m, CH_2×2), 1.57 (3H, s, CH_3), 1.96 (3H, s, CH_3), 4.16 (2H, m, OCH_2), 7.16 (6H, m, N=CHO and aromatic H); IR (KBr) 1632 cm^{-1} (N=CHO); MS *m/z* 231 (M^+, 100), 175 (41), 158 (53), 104 (51). Found: C, 77.96; H, 9.20; N, 6.03%. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.06%.

The other 2-aza-1,3-pentadienes (**2**) were prepared by the methods similar to those described above.

One-Step Hydroamidation of 2-Aza-1,3-pentadienes. A typical procedure is as follows. To a solution of 1-isopropoxy-4-methyl-3-phenyl-2-aza-1,3-pentadiene (3.50 g, 0.016 mol) in benzene (40 ml) was added slowly a mixture of chloroacetyl chloride (2.49 g, 0.022 mol) and trichlorosilane (3.00 g, 0.022 mol). The reaction mixture was stirred for several hours at room temperature, and then heated in an oil bath (50 °C) for 2 h. The mixture was cooled to room temperature and neutralized with aqueous potassium carbonate under ice-cooling. The organic portion was extracted with ether and dried over magnesium sulfate. The low boiling components were evaporated. The resulting yellow liquid was purified by column chromatography with silica gel to give a pale yellow viscous liquid (3.00 g, 63% yield) of 2-chloro-*N*-isopropoxymethyl-*N*-(2-methyl-1-phenyl-1-propenyl)acetamide (Table 3, **1j**). ^{1}H NMR ($CDCl_3$) δ=1.14 (6H, d, *J*=6 Hz, CH_3×2), 1.88(6H, s, CH_3×2), 3.88(1H, quint., *J*=6 Hz, OCH), 4.16 (2H, s, $COCH_2Cl$), 4.50 and 5.15 (2H, 2d, *J*=10 Hz, NCH_2O), and 7.34 (5H, s, aromatic H); IR (KBr) 1665 cm^{-1} (CO); MS *m/z* 295 (M^+, 1), 222 (19), 187 (24), 147 (33), 43 (100). Found: C, 65.02; H, 7.49; N, 4.51%. Calcd for $C_{16}H_{22}NClO_2$: C, 64.97; H, 7.50; N, 4.51%.

The other 2-chloroacetamides **1** were prepared by the similar method described above.

Synthesis of 4. To a solution of 1-allyloxy-4-methyl-3-phenyl-2-aza-1,3-pentadiene (2.67 g, 0.012 mol) in benzene (30 ml) was added slowly a solution of chloroacetyl chloride (1.15 g, 0.013 mol) and trichlorosilane (2.06 g, 0.015 mol) in benzene (10 ml). The reaction mixture was stirred for one day at room temperature. The mixture was neutralized with aqueous potassium carbonate under ice-cooling. The organic portion was extracted with ether and dried over magnesium sulfate. The low boiling components were evaporated. The resulting solid was dried under a reduced pressure to give a pale orange solid (2.50 g, 80% yield) of **4**. ^{1}H NMR ($CDCl_3$) δ=1.74 (3H, s, CH_3), 1.93 (3H, s, CH_3), 4.13 and 4.19 (2H, 2s, $COCH_2Cl$), 7.24 (5H, s, aromatic H), and 9.35 (1H, s, CHO); IR (KBr) 1732 and 1712 cm^{-1} (CO); MS *m/z* 251 (M^+, 39), 222 (20), 174 (100), 147 (78). Found: C, 62.08; H, 5.56; N, 5.61%. Calcd for $C_{13}H_{14}NClO_2$: C, 62.03; H, 5.61; N, 5.57%.

One-Step Hydroamidation of 5. To a solution of 1-isopropoxy-3-phenyl-2-aza-1,3-pentadiene (3.00 g, 0.015 mol) in benzene (30 ml) was added slowly a solution of chloroacetyl chloride (1.89 g, 0.017 mol) and trichlorosilane (2.20 g, 0.016 mol) in benzene (10 ml) in an ice bath. The reaction mixture was stirred for several hours at room temperature, and then heated in an oil bath (50 °C) for 1 h. The mixture was cooled to room temperature and neutralized with aqueous potassium carbonate under ice-cooling. The organic portion was extracted with ether and dried over magnesium sulfate. The low boiling components were evaporated. The resulting yellow viscous liquid was purified by column chromatography with silica gel to give a white solid (1.45 g, 53% yield) of **6a** and a white solid (0.45 g 33% yield) of **6b**.

6a. ^{1}H NMR ($CDCl_3$) δ=1.16(6H, d, *J*=6 Hz, CH_3×2), 1.90 (3H, d, *J*=7 Hz, CH_3), 3.94(1H, quint., *J*=6 Hz, OCH), 4.02(2H, s, $COCH_2Cl$), 4.57 and 5.27 (2H, 2d, *J*=10 Hz, NCH_2O), 6.32 (1H, q, *J*=7 Hz, CH), and 7.31 (5H, s, aromatic H); IR (KBr) 1672 cm^{-1} (CO); MS *m/z* 281 (M^+, 3), 208 (49), 173 (100), 133 (92). Found: C, 64.12; H, 7.27; N, 5.01%. Calcd for $C_{15}H_{20}NClO_2$: C, 63.94; H, 7.15; N, 4.97%.

6b. ^{1}H NMR ($CDCl_3$) δ=1.16 (6H, d, *J*=6 Hz, CH_3×2), 1.89 (3H, d, *J*=7 Hz, CH_3), 3.94(1H, quint., *J*=6 Hz, OCH), 4.14(2H, s, $COCH_2Cl$), 4.86 (2H, s, NCH_2O), 5.90 (1H, q, *J*=7 Hz, CH), and 7.31 (5H, s, aromatic H); IR (KBr) 1672 cm^{-1} (CO); MS *m/z* 281 (M^+, 2), 208 (50), 173 (100), 133 (99). Found: C, 64.03; H, 7.19; N, 5.21%. Calcd for $C_{15}H_{20}NClO_2$: C, 63.94; H, 7.15; N, 4.97%.

Herbicidal Assay against Upland Farm Weeds. Upland farm soil (clay loam) was put into porcelain pots (1/8850 a). Seeds of various plants (see Table 4) were sown in the soil at a depth of 0.5 to 1 cm. The water dilution of a wettable powder of each of the test compounds shown in Table 3 was sprayed on to the soil surface at a predetermined rate of application. After being treated, the plants were grown in a greenhouse kept at an average atmospheric temperature of 25 °C. Two weeks later, the herbicidal effect was examined. The evaluation was made on a scale of 6 (0—5), where 0 indicates normal growth, 5 indicates complete killing, and 1 to 4 indicate varying degrees of growth between normal and complete killing.

References

1) a) H. Okamoto, S. Kato, M. Ogasawara, M. Konnai, and T. Takematsu, *Agric. Biol. Chem.*, **55**, 2733 (1991); b) H. Okamoto, S. Kato, T. Kobutani, M. Ogasawara, M. Konnai, and T. Takematsu, *Agric. Biol. Chem.*, **55**, 2737 (1991).

2) a) Monsanto Co., Neth. Appl. 6602564 (1967); *Chem. Abstr.*, **67**, 99832 (1968); b) A. P. enkov, M. S. Nikolova, and N. M. Mollov, *Chem. Ind.*, **1982**, 808, and the references cited therein.

3) H. Okamoto and S. Kato, *Bull. Chem. Soc. Jpn.*, **64**, 2128 (1991).

4) H. Okamoto and S. Kato, *Bull. Chem. Soc. Jpn.*, **64**, 766 (1991).

5) J. Barluenga, J. Joglar, F. J. Gonzalez, and S. Fustero, *Synlett*, **1990**, 129.

6) G. I. Georg, P. He, J. Kant, and J. Mudd, *Tetrahedron Lett.*, **31**, 451 (1990).

7) H. Alper and S. Amaratunga, *Can. J. Chem.*, **61**, 1309 (1983).

8) T. Saegusa, I. Murase, and Y. Ito, *J. Org. Chem.*, **36**, 2876 (1971).

9) D. H. R. Barton, T. Bowles, S. Husinec, J. E. Forbes, A. Llobera, A. E. A. Porter, and S. Z. Zard, *Tetrahedron Lett.*, **29**, 3343 (1988).

10) M. Passerini, *Gazz. Chem. Ital.*, **54**, 633 (1924).