Easy Access to (*E,Z*)-*β*-Nitro-α,*β*-olefinated Hydrazones, 6-Oxo-1,6-dihydropyridazines, and 4-Chloro-1-aminopyrroles by Domino Reactions of 1,2-Diaza-1,3-butadienes with Halogen-Coactivated Methylene or Methine Compounds

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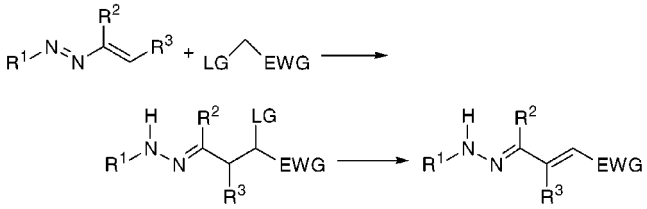
In the presence of a catalytic amount of sodium methoxide, 1-aminocarbonyl-1,2-diaza-1,3-butadienes react with bromonitromethane to give stereoselectively *β*-nitro-α,*β*-olefinated hydrazones as *E,Z* stereoisomers. In the presence of a stoichiometric amount of sodium hydride, the same substrates with dialkyl halomalonates furnish the expected α,*β*-olefinated hydrazones, and in the presence of a stoichiometric amount of sodium hydroxide, the unexpected dialkyl 3-methyl-6-oxo-1,6-dihydropyridazine-4,5-dicarboxylates are obtained in one pot by a domino process concluding in a [4 + 2] cyclization. α,*β*-Olefinated hydrazones have been shown to be the possible intermediates in the formation of 1,6-dihydropyridazine derivatives. The domino reaction of 1-aminocarbonyl-1,2-diaza-1,3-butadienes with α,α-dichloroacetophenone produces directly alkyl 4-chloro-2(chloromethyl)-5-phenyl- or alkyl 4-chloro-2(methoxymethyl)-5-phenyl-1*H*-aminopyrrole-3-carboxylates as a consequence of [3 + 2] cyclization and chlorine transfer.

Introduction

The reaction between 1,2-diaza-1,3-butadienes and activated methylene compounds bearing a leaving group is a convenient entry to *β*-functionalized-α,*β*-olefinated hydrazones.[1] These compounds derive from the preliminary 1,4-addition (Michael-type) of activated methylene compounds to the azo-ene system of 1,2-diaza-1,3-butadienes to give α-substituted hydrazones by formation of a new carbon−carbon single bond. The often spontaneous subsequent elimination of the leaving group produces *β*-functionalized-α,*β*-olefinated hydrazones (see Scheme 1).

These compounds are of interest as both products and intermediates in organic chemistry thanks to the conjugated heterodiene system suitable for Michael-type additions[2] or hetero [4 + 2] cycloadditions of Diels−Alder-type.[3] It is also worth highlighting the ability of 1,2-diaza-1,3-butadienes to readily undergo nucleophilic attacks. That capacity represents a valuable alternative route for

Scheme 1



different functionalizations of the carbon atom in the α-position to the carbonyl group that is especially inclined toward electrophilic agents.[4,5] Therefore, new *β*-functionalized-α,*β*-olefinated carbonyl compounds can be obtained from these hydrazone derivatives by one of the methods reported in the literature for the regeneration of the parent carbonyl compounds from hydrazones.[6] These facts prompted us to extend our previous investigations[1] to the reactions of 1,2-diaza-1,3-butadienes with various halogen-coactivated methylene or methine compounds. Surprisingly, some significant differences in the behavior of these reactions were observed.

Results and Discussion

gem-Halo-nitro derivatives are important starting materials in organic chemistry, in particular as precursors of nitroalkanes and nitroalkenes that in turn are

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Scheme 2

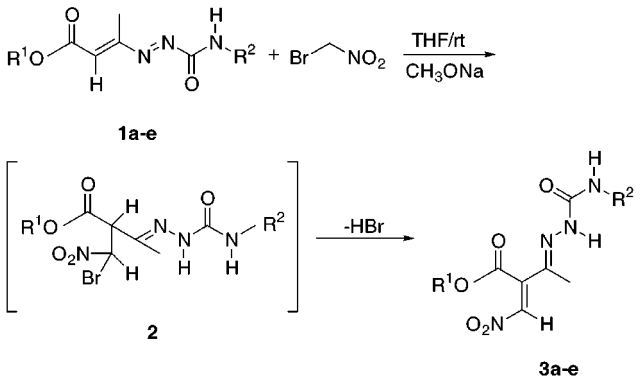

Table 1. Yields and Reaction Times of α,β-Olefinated Hydrazones 3a−k

1	R^1	R^2	3	yield[a] (%)	reaction time (h)
1a	Me	H	**3a**	78	6.0
1b	Et	H	**3b**	67	6.0
1c	*i*-Pr	H	**3c**	65	5.0
1d	Me	Ph	**3d**	75	5.0
1e	Et	Ph	**3e**	73	3.0

[a] Yield of pure isolated products.

useful tools in organic synthesis.[7] 1-Aminocarbonyl-1,2-diaza-1,3-butadienes **1a**−**e** easily react in tetrahydrofuran at room temperature with bromonitromethane in the presence of a catalytic amount of sodium methoxide to give β-nitro-α,β-olefinated hydrazones **3a**−**e** in good to excellent yields (Scheme 2 and Table 1). The reaction likely proceeds by formation of 1,4-adduct intermediates **2** (monitored by TLC) that is concomitant with their transformation into α,β-olefinated hydrazones as a consequence of hydrogen bromide elimination. Nitroalkenes and α,β-olefinated hydrazones containing the nitro group in the β-position are valuable tools in organic synthesis.[2,3,6,7] Moreover, the nitro group showed good leaving ability in previous analogous circumstances in which 1,2-diaza-1,3-butadienes were reacted with β-nitroketones, β-nitroesters, or β-nitrosulfones, not allowing the isolation of any nitro derivative.[1] As a result of the presence of two stereogenic centers, compounds **3a**−**e** can theoretically exist as four different stereoisomers, *E,E*-, *E,Z*-, *Z,E*-, and *Z,Z*-, where the first letter refers to the C=N configuration and the second letter to the C=C configuration, respectively (Figure 1). However, NOE experiments demonstrated that these compounds are exclusively *E,Z* stereoisomers because irradiation of CH_3 produced NOE enhancement of NH and CH and vice versa. This evidence suggests the proximity of these three groups, in accordance with the *E* configuration of the C=N center and *Z* configuration of the C=C center. Therefore, the behavior of this reaction is highly stereospecific.

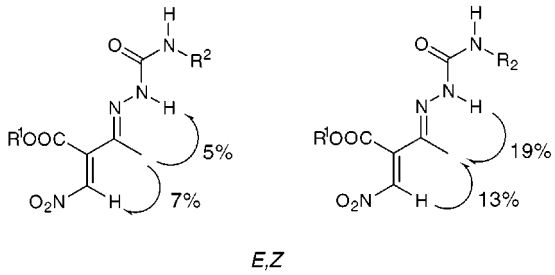

Figure 1. NOE effects observed during NMR investigations.

The reaction between 1-aminocarbonyl-1,2-diaza-1,3-butadienes and different dialkyl halomalonates in the presence of sodium hydride or sodium hydroxide was also investigated. Some interesting diversities in the pathways of these reactions have been observed. In particular, the reaction in the presence of a stoichiometric amount of sodium hydride between 1-aminocarbonyl-1,2-diaza-1,3-butadienes **1a**−**e** and dimethyl bromomalonate **4a** or diethyl bromomalonate **4b** in tetrahydrofuran at room temperature gave the expected α,β-olefinated hydrazones **6f**−**k** in good yields (Scheme 3 path a and Table 2). This reaction proceeds via preliminary fomation of 1,4-adduct intermediates **5** together with halogenidric acid elimination. This mechanism was confirmed by the occasional isolation of the 1,4-adduct **5**, in the course of a reaction between 1-aminocarbonyl-1,2-diaza-1,3-butadiene **1b** and dimethyl bromomalonate **4a**. In the presence of a stoichiometric amount of sodium hydroxide, 1-aminocarbonyl-1,2-diaza-1,3-butadienes **1a**−**c** reacted with diethyl bromomalonate **4b** or dimethyl chloromalonate **4c** in tetrahydrofuran at room temperature to afford initially the 1,4-adduct intermediates **5** (monitored by TLC). By addition of methanol, the intermediates **5** were converted under reflux into unexpected dialkyl 3-methyl-6-oxo-1,6-dihydropyridazine-4,5-dicarboxylates **7a**−**f** in good yields (Scheme 3 path b and Table 3). This conversion passes through the preliminary formation of α,β-olefinated hydrazones **6** to give 1,6-dihydropyridazines **7** by a base-catalyzed heterocyclization process ascribable to an internal NH nucleophilic attack on the ester group of the dialkyl halomalonates with consequential loss of an alcohol molecule. The loss of the carbamoyl residue also occurs. Therefore, the whole reaction is a classic example of a domino process concluded in [4 + 2] cyclization.[8] The formation of 1,6-dihydropyridazines **7a**−**f** by treatment of α,β-olefinated hydrazones **6a**−**f** with sodium hydroxide confirmed this pathway (Scheme 3 path c and Table 3). Thus, this reaction represents a new and convenient entry to both useful heterodiene systems[2,3] and polyfunctionalized dihydropyridazine rings that are extremely important for their biological and herbicidal activity.[9−11]

In the presence of a catalytic amount of sodium hydride, the reaction of 1-aminocarbonyl-1,2-diaza-1,3-

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Scheme 3

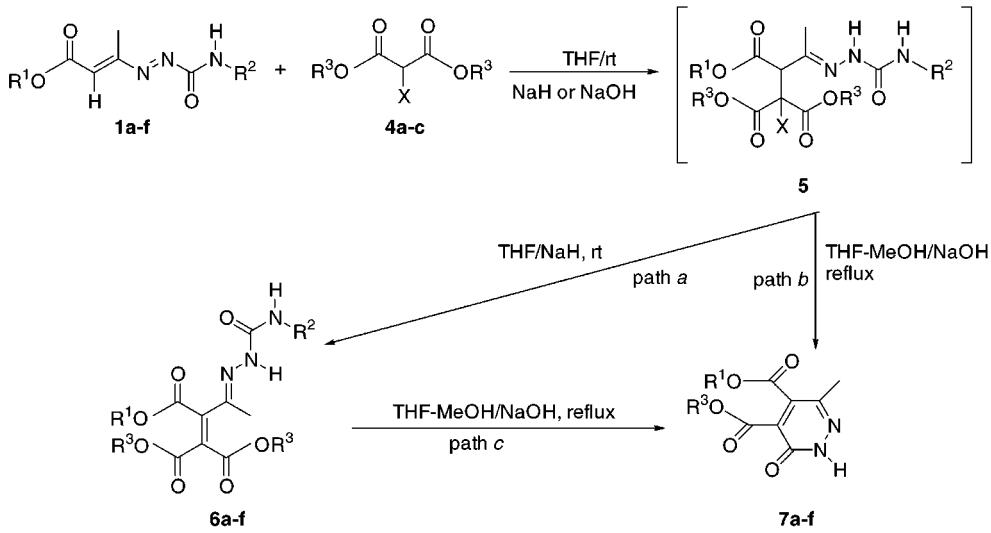

Table 2. Yields and Reaction Times of α,*β*-Olefinated Hydrazones 6a−f

1	R^1	R^2	4	R^3	X	6	yield[a] (%)	reaction time (h)
1b	Et	H	**4a**	Me	Br	**6a**	65	0.1
1c	*i*-Pr	H	**4a**	Me	Br	**6b**	51	0.1
1e	Et	Ph	**4a**	Me	Br	**6c**	67	0.1
1a	Me	H	**4b**	Et	Br	**6d**	61	0.1
1c	*i*-Pr	H	**4b**	Et	Br	**6e**	52	0.1
1d	Me	Ph	**4b**	Et	Br	**6f**	68	0.1

[a] Yield of pure isolated products.

butadienes **1a**−**d** with α,α-dichloroacetophenone in tetrahydrofuran at room temperature probably furnished 1,4-adduct intermediates **8**. The isolation of these products was difficult because of their poor stability. Hence, after disappearance of the reagents (monitored by TLC), the reaction mixture in tetrahydrofuran was heated under reflux, and in this way the 1,4-adducts **8** were converted into interesting alkyl 4-chloro-2(chloromethyl)-5-phenyl-1*H*-aminopyrrole-3-carboxylates **9a**−**c** in good yields (Scheme 4 path a and Table 4). After evaporation of tetrahydrofuran, the same reaction mixture in methanol under reflux produced interesting alkyl 4-chloro-2(methoxymethyl)-5-phenyl-1*H*-aminopyrrole-3-carboxylates **10a**−**d** in good to excellent yields (Scheme 4 path b and Table 4). In the case of the reaction between substrates **1d** and α,α-dichloroacetophenone, product **9** was obtained in very poor yield and the reaction mixture was extremely complex. The domino pyrrole ring closure is in accordance with our previous findings. In fact, the one-pot 1,4-addition and ring annulation of nucleophilic reagents bearing a ketone function in the α-position to the attacking carbon atom with 1,2-diaza-1,3-butadienes concluding in a [3 + 2] cyclization process have been previously reported.[5,8] In this case, however, an interesting chlorine transfer was also observed.[12] This mild, simple, and direct procedure for the preparation of 4-chloro-1-aminopyrrole derivatives represents a very important goal in the chemistry of the pyrrole ring that is a valuable skeleton in organic, polymeric, natural, biological, medicinal, and agricultural products.[13] In particular, 1-aminopyrrole derivatives seem to be quite difficult to prepare by Knorr and its modified procedures, mainly because of the severe reaction conditions and/or the formation of dihydropyridazine byproducts. The limited presence of 1-aminopyrroles in the literature can be ascribed to relatively few procedures existing for their preparation.[14,15]

Conclusion

The present investigation confirms that the reaction between 1,2-diaza-1,3-butadienes and nucleophiles bearing a leaving group provides straightforward access to α,*β*-difunctionalized-α,*β*-olefinated hydrazones by means of a simple one-flask 1,4-addition of the attacking nucleophiles to the azo-ene system of conjugated azoalkenes and the 1,2-elimination of the leaving groups from these adducts. Indeed, in this case unprecedented *β*-nitro-α-alkoxycarbonyl-α,*β*-olefinated hydrazones as *E*,*Z* stereoisomers were stereoselectively obtained, and new *β*,*β*′-dialkoxycarbonyl-α-alkoxycarbonyl-α,*β*-olefinated hydrazones were produced. The parent *β*-nitro- or *β*,*β*′-di-

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Table 3. Yields and Reaction Times of 4,5-Alkyl-3-methyl-6-oxo-1,6-dihydropyridazine-4,5-dicarboxylates 7a−f

1	R^1	R^2	4	R^3	X	7	yield (%)	reaction time (h)	6	R^1	R^2	R^3	7	yield (%)	reaction time (h)
1a	Me	H	**4b**	Et	Br	**7a**	60[a]	0.1[b], 4.0[c]	**6a**	Me	H	Et	**7a**	71[d]	3.5[e]
1b	Et	H	**4b**	Et	Br	**7b**	69[a]	0.5[b], 6.0[c]	**6b**	Et	H	Et	**7b**	68[d]	3.0[e]
1c	*i*-Pr	H	**4b**	Et	Br	**7c**	65[a]	0.2[b], 8.0[c]	**6c**	*i*-Pr	H	Et	**7c**	73[d]	6.0[e]
1a	Me	H	**4c**	Me	Cl	**7d**	68[a]	0.5[b], 5.5[c]	**6d**	Me	H	Me	**7d**	66[d]	4.5[e]
1b	Et	H	**4c**	Me	Cl	**7e**	61[a]	0.1[b], 14.0[c]	**6e**	Et	H	Me	**7e**	78[d]	6.0[e]
1c	*i*-Pr	H	**4c**	Me	Cl	**7f**	68[a]	0.2[b], 4.5[c]	**6f**	*i*-Pr	H	Me	**7f**	68[d]	3.5[e]

[a] Yield of pure isolated products based on **1**. [b] Time of disappearance of reagent **1**. [c] Reflux time to obtain products **7a**−**f** from **5**. [d] Yield of pure isolated products based on **6**. [e] Reflux time to obtain products **7a**−**f** from **6**.

Scheme 4

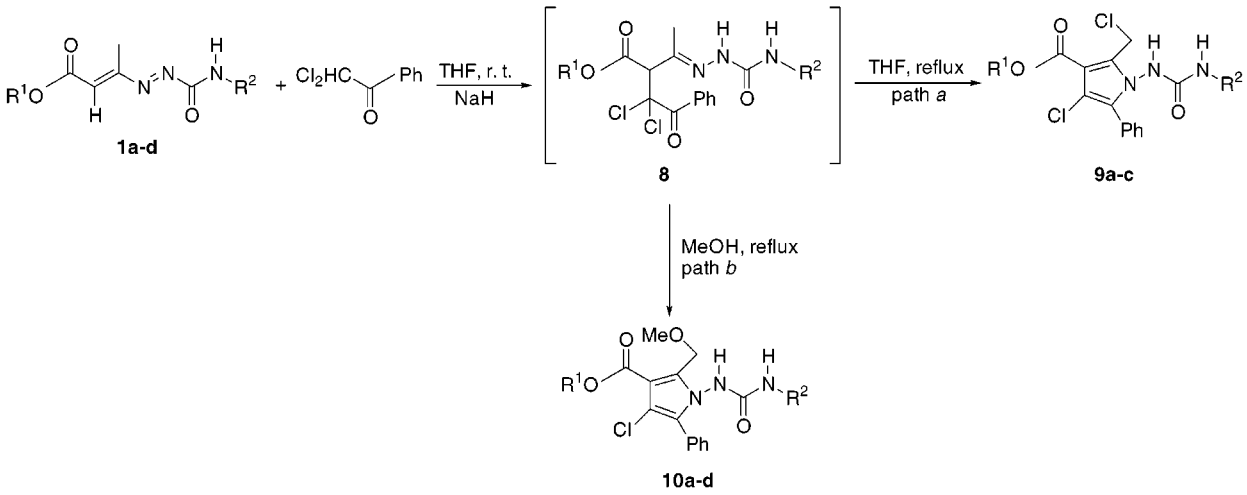

Table 4. Yields and Reaction Times of Alkyl 4-Chloro-2(chloromethyl)-5-phenyl-1*H*-pyrrole-3-carboxylates 9a−c and Alkyl 4-Chloro-2(methoxymethyl)-5-phenyl-1*H*-pyrrole-3-carboxylates 10a−d

1	R^1	R^2	9	yield[a] (%)	teaction time (h)		10	yield[a] (%)	reaction time (h)
1a	Me	H	**9a**	54	0.1[b]	2.5[c]	**10a**	84	0.1[b], 2.0[c]
1b	Et	H	**9b**	41	0.1[b]	2.0[c]	**10b**	67	0.1[b], 0.5[c]
1c	*i*-Pr	H	**9c**	40	0.1[b]	1.0[c]	**10c**	71	0.1[b], 2.0[c]
1a	Me	Ph					**10d**	57	0.1[b], 0.5[c]

[a] Yield of pure isolated products. [b] Time of disappearance of reagent **1**. [c] Reflux time to obtain products **9a**−**c** and **10a**−**d**.

alkoxycarbonyl-α-alkoxycarbonyl-α,*β*-olefinated carbonyl compounds may be regenerated from these products by cleavage of the hydrazono protecting group.[6] Furthermore, this investigation surprisingly offered a convenient route to 6-oxo-1,6-dihydropyridazine and 4-chloro-1-aminopyrrole derivatives according to classic domino-type sequenced reactions. In conclusion, this paper describes many cyclic and acyclic compounds of interest as products and intermediates in organic, biologial, pharmaceutical, and agricultural chemistry.

Experimental Section

General. 1,2-Diaza-1,3-butadienes **1a**−**e** were synthesized as standard *E*/*Z* isomer mixtures according to previously reported procedures.[16,17] Starting materials for the preparation of the above-mentioned reagents and bromonitromethane, dimethyl bromomalonate **4a**, diethyl bromomalonate **4b**, dimethyl chloromalonate **4c**, α,α-dichloroacetophenone, sodium methoxide, sodium hydride, sodium hydroxide, and solvents are commercially available materials (Lancaster, Carlo Erba and Aldrich). They were used without further purification with the exception of THF, which was distilled from sodium hydroxyde. Melting points were determined in open capillary tubes and are uncorrected. The products often decompose at their melting points. IR-FT spectra were performed in Nujol mull. MS spectra were made at an ionizing voltage of 70 eV. ^{1}H NMR spectra were recorded at 200 MHz, and ^{13}C NMR were at 50.32 MHz in DMSO-d_6. Chemical shifts (δ) are reported relative to TMS as internal standard, and the *J* values are in Hz. The multiplicities in ^{13}C NMR spectra were obtained by using 135 and 90° DEPT experiments. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; spt, septet; br, broad; all the NH and OH exchanged with D_2O. NOE enhancement factors were determined on degassed 0.01 M DMSO-d_6 solutions at 300 K, using a NOEDIFF pulse program. Generally, irradiation time was 2 s, with a power level of 30 low. Precoated 0.25 mm silica gel plates were employed for analytical thin-layer chromatography, and silica gel 35−70 mm was used for column chromatography. All new compounds showed satisfactory elemental analysis (C ± 0.35; H ± 0.30, N ± 0.30).

Preparation of α,*β*-Olefinated Hydrazones 3a−e. To a magnetically stirred solution of 1,2-diaza-1,3-butadienes **1a**−**e** (1 mmol) and bromonitromethane (1 mmol, 139.9 mg) in THF (6 mL) was added a catalytic amount of sodium methoxide (0.1 mmol, 5.4 mg). The reaction was stirred at room temperature for 3.0−6.0 h until the disappearance of the reagents (monitored by TLC). After evaporation of tetrahydrofuran under reduced pressure, products **3a**−**e** were obtained by crystallization from ethyl acetate/ethyl ether (70:30).

3a: mp 141−143 °C; IR ν_{max} 3379, 3224, 3104, 1735, 1711 cm^{-1}; ^{1}H NMR δ 2.05 (s, 3H), 3.82 (s, 3H), 6.04 and 6.69 (2 brs, 2H), 7.81 (s, 1H), 10.35 (s, 1H); ^{13}C NMR δ 12.3 (q), 52.9 (q), 136.4 (d), 138.8 (s), 142.8 (s), 155.5 (s), 164.1 (s); MS *m*/*z* 230 (1) [M$^+$], 183 (46), 157 (57), 140 (100). Anal. Calcd for $C_7H_{10}N_4O_5$: C, 36.53; H, 4.38; N, 24.34. Found: C, 36.41; H, 4.55; N, 24.42.

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(17) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 873. Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 671.

Product 5 from 1b and 4a: mp 131−134 °C from tetrahydrofuran; IR ν_{max} 3452, 3210, 1735, 1729, 1690 cm^{-1}; ^{1}H NMR δ 1.18 (t, 3H, J = 7.0), 2.26 (s, 3H), 3.69 (s, 6H), 4.40 (s, 1H), 4.11 (q, 2H, J = 7.0), 6.81 (brs, 2H), 10.21 (s, 1H); ^{13}C NMR δ 14.2 (q), 17.9 (q), 52.5 (q), 53.8 (d), 60.6 (t), 65.9 (s), 157.5 (s), 159.3 (s), 159.5 (s), 165.8 (s), 169.9 (s); MS m/z 398 (12) [M$^+$ + 2], 396 (12) [M$^+$], 316 (100). Anal. Calcd for $C_{12}H_{18}N_3O_7Br$: C, 36.38; H, 4.58; N, 10.61. Found: C, 36.41; H, 4.69; N, 10.41.

Preparation of α,*β*-Olefinated Hydrazones 6a−f. To a magnetically stirred solution of dimethyl bromomalonate **4a** (1 mmol, 211.0 mg) or diethyl bromomalonate **4b** (1 mmol, 239.0 mg) in THF (3 mL) with sodium hydride (1 mmol, 24.0 mg) was added dropwise a solution of 1,2-diaza-1,3-butadienes **1a−e** (1 mmol) in THF (3 mL). The disappearance of the reagents rapidly occurred (0.1 h, monitored by TLC). The reaction mixture was concentrated under reduced pressure, and the residue was dissolved with ethyl acetate (20 mL) and then washed with water (2 × 10 mL). The crude was chromatographed on a silica gel column (elution with cyclohexane/ethyl acetate mixtures from 100% cyclohexane to 100% ethyl acetate), affording α,*β*-olefinated hydrazones **6a−f**, which were crystallized from ethyl acetate/petroleum ether (40−60 °C, 70:30).

6a: mp 170−173 °C; IR ν_{max} 3476, 3234, 1742, 1729, 1698 cm^{-1}; ^{1}H NMR δ 1.24 (t, 3H, J = 7.0), 1.86 (s, 3H), 3.71 (s, 3H), 3.72 (s, 3H), 4.25 (q, 2H, J = 7.0), 6.01 and 6.52 (2 brs, 2H), 10.07 (s, 1H); ^{13}C NMR δ 19.5 (q), 19.8 (q), 58.6 (q), 58.9 (q), 67.8 (t), 143.7 (s), 150.0 (s), 161.8 (s), 168.7 (s), 170.9 (s), 171.0 (s), 171.1 (s); MS m/z 315 (1) [M$^+$], 213 (32), 181 (24), 167 (100). Anal. Calcd for $C_{12}H_{17}N_3O_7$: C, 45.72; H, 5.43; N, 13.33. Found: C, 45.61; H, 5.51; N, 13.28.

Preparation of Dialkyl 3-Methyl-6-oxo-1,6-dihydropyridazine-4,5-dicarboxylates 7a−f from 1a−c and 4b or 4c. To a magnetically stirred solution of 1,2-diaza-1,3-butadienes **1a−c** (1 mmol) and diethyl bromomalonate **4b** (1 mmol, 239.0 mg) or dimethyl chloromalonate **4c** (1 mmol, 166.5 mg) in THF (6 mL) was added a stoichiometric amount of sodium hydroxide (1 mmol, 40.0 mg). The reaction was stirred at room temperature for 0.1−0.5 h until 1,2-diaza-1,3-butadienes **1a−c** disappeared (monitored by TLC). After addition of methanol (3 mL), the reaction mixture was refluxed for 4.0−14.0 h until products **7a−f** were formed (monitored by TLC). After removal of the solvents under reduced pressure, the residue was dissolved in water (10 mL), neutralized with 2 N HCl (0.5 mL), and extracted with ethyl acetate (2 × 20 mL). Products **7a−c** were purified by chromatography on a silica gel column (elution with cyclohexane/ethyl acetate mixtures from 100% cyclohexane to 100% ethyl acetate) and then crystallized from ethyl acetate/petroleum ether (40−60 °C, 70:30); products **7d−f** were obtained directly by crystallization from ethyl acetate/petroleum ether (40−60 °C, 70:30).

Preparation of Dialkyl 3-Methyl-6-oxo-1,6-dihydropyridazine-4,5-dicarboxylates 7a−f from 6a−f. To a solution of α,*β*-olefinated hydrazones **6a−f** (1 mmol) dissolved in tetrahydrofuran (3 mL) and methanol (3 mL) was added a stoichiometric amount of sodium hydroxide (1 mmol, 40.0 mg). The reaction was refluxed for 3.0−6.0 h until products **6a−f** disappeared and products **7a−f** were formed (monitored by TLC). After removal of the solvents under reduced pressure, the residue was dissolved in water (10 mL), neutralized with 2 N HCl (0.5 mL), and extracted with ethyl acetate (2 × 20 mL). Products **7a−c** were purified by chromatography on a silica gel column (elution with cyclohexane/ethyl acetate mixtures from 100% cyclohexane to 100% ethyl acetate) and then crystallized from ethyl acetate/petroleum ether (40−60 °C, 70:30), and products **7d−f** were obtained directly by crystallization from ethyl acetate/petroleum ether (40−60 °C, 70:30).

7a: mp 165−167 °C; IR ν_{max} 3150, 1758, 1742, 1652, 1600 cm^{-1}; ^{1}H NMR δ 1.25 (t, 3H, J = 7.0), 2.30 (s, 3H), 3.85 (s, 3H), 4.28 (q, 2H, J = 7.0), 13.58 (s, 1H); ^{13}C NMR δ 13.8 (q), 19.3 (q), 53.3 (q), 62.0 (t), 131.8 (s), 133.9 (s), 140.7 (s), 156.5 (s), 162.6 (s), 163.7 (s); MS m/z 240 (7) [M$^+$], 194 (19), 138 (51), 123 (29), 110 (100). Anal. Calcd for $C_{10}H_{12}N_2O_5$: C, 50.00; H, 5.04; N, 11.66. Found: C, 50.21; H, 5.18; N, 11.41.

Preparation of Alkyl 4-Chloro-2(chloromethyl)-5-phenyl-1*H*-aminopyrrole-3-carboxylates 9a−c. To a magnetically stirred solution of 1,2-diaza-1,3-butadienes **1a−c** (1 mmol) and α,α-dichloroacetophenone (1 mmol, 189.0 mg) in THF (6 mL) was added a catalytic amount of sodium hydride (0.1 mmol, 2.4 mg). The disappearance of 1,2-diaza-1,3-butadienes **1** occurred rapidly (monitored by TLC). Then, the reaction was heated under reflux for 1.0−2.5 h until products **9a−c** were formed (monitored by TLC). After evaporation of the reaction solvent, the residue was chromatographed on a silica gel column (elution with cyclohexane/ethyl acetate mixtures from 100% cyclohexane to 100% ethyl acetate), and products **9a−c** were crystallized from ethyl acetate/cyclohexane (80:20).

9a: mp 239−240 °C; IR ν_{max} 3457, 3343, 3204, 1711, 1676 cm^{-1}; ^{1}H NMR δ 3.82 (s, 3H), 4.67 and 5.08 (AB system, 2H, J = 11.9), 6.26 (s, 2H), 7.46 (s, 5H), 9.62 (s, 1H); ^{13}C NMR δ 34.5 (t), 51.4 (q), 108.4 (s), 109.2 (s), 127.5 (s), 128.2 (d), 128.7 (d), 129.9 (d), 132.6 (s), 134.3 (s), 156.3 (s), 162.5 (s); MS m/z 345 (3) [M$^+$ + 4], 343 (18) [M$^+$ + 2], 341 (27) [M$^+$], 308 (32), 306 (100). Anal. Calcd for $C_{14}H_{13}N_3O_3Cl_2$: C, 49.14; H, 3.83; N, 12.28. Found: C, 49.01; H, 3.97; N, 12.51.

Preparation of Alkyl 4-Chloro-2(methoxymethyl)-5-phenyl-1*H*-aminopyrrole-3-carboxylates 10a−d. To a magnetically stirred solution of 1,2-diaza-1,3-butadienes **1a−d** (1 mmol) and α,α-dichloroacetophenone (1 mmol, 189.0 mg) in THF (6 mL) was added a catalytic amount of sodium hydride (0.1 mmol, 2.4 mg). The disappearance of 1,2-diaza-1,3-butadienes **1** occurred rapidly (0.1 h, monitored by TLC). After evaporation of tetrahydrofuran, the reaction was heated under reflux in methanol (6 mL) for 0.5−2.0 h until products **10a−d** were formed (monitored by TLC). Products **10a,b,d** directly precipitated from the reaction medium, and product **10c** was crystallized from ethyl acetate/petroleum ether (40−60 °C, 70:30) after evaporation of the reaction solvent.

10a: mp 232−234 °C; IR ν_{max} 3418, 3280, 1716, 1681 cm^{-1}; ^{1}H NMR δ 3.26 (s, 3H), 3.81 (s, 3H), 4.37 and 4.73 (AB system, 2H, J = 11.9), 6.26 (s, 2H), 7.47 (s, 5H), 9.79 (s, 1H); ^{13}C NMR δ 51.1 (q), 57.5 (q), 61.9 (t), 107.6 (s), 109.8 (s), 128.0 (s), 128.1 (d), 128.3 (d), 130.0 (d), 131.9 (s), 135.3 (s), 156.8 (s), 163.0 (s); MS m/z 339 (6) [M$^+$ + 2], 337 (18) [M$^+$], 308 (6), 306 (18), 292 (9), 290 (27), 280 (32), 278 (100). Anal. Calcd for $C_{15}H_{16}N_3O_4Cl$: C, 53.34; H, 4.77; N, 12.44. Found: C, 53.51; H, 4.61; N, 12.31.

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