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Cycloaddition to 1,3-Dialkoxycarbonylallenes: One-Step Synthesis of Heterocyclic Compounds Containing a Dialkyl Glutaconate Structure

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A novel synthesis of alkyl 2-alkoxycarbonyl-3-pyridineacetates (**2**), alkyl 3-alkoxycarbonyl-4-pyrazoleacetate (**5**), and alkyl 5-alkoxycarbonyl-4-(1,2,3-triazole)acetate (**6**) is described. Diels–Alder reaction of 1,3-dialkoxycarbonylallenes (**3**) with 1-azadiene systems (**4**) gave **2**, and 1,3-dipolar cycloaddition of **3** to diazoalkanes and trimethylsilylazide gave **5** and **6**, respectively. The structures of the cycloadducts and the regiochemistry of the cycloadditions are discussed.

Keywords——1,3-dialkoxycarbonylallene; Diels–Alder reaction; 1,3-dipolar cycloaddition; alkyl 2-alkoxycarbonyl-3-pyridineacetate; alkyl 3-alkoxycarbonyl-4-pyrazoleacetate; alkyl 5-alkoxycarbonyl-4-(1,2,3-triazole)acetate

For our studies directed toward the synthesis of heterocycles (**1**) containing a glutaconic acid anhydride structure,[1] a versatile and general preparation of the corresponding glutaconates was essential. We have previously communicated[2] a convenient preparation of alkyl 2-alkoxycarbonyl-3-pyridineacetates (**2**) by means of a Diels–Alder reaction of 1,3-dialkoxycarbonylallenes (**3**) with 1-azadiene systems (**4**). We present here a full account of the work, as well as a demonstration of the synthetic utility of **3** for the preparation of five membered heterocycles containing a glutaconate structure by 1,3-dipolar cycloaddition.

Diels–Alder Reaction

The starting 1-azadiene system (**4**), which was recently shown to be useful as a diene component in the Diels–Alder reaction,[3] was prepared by direct hydrazone formation from the corresponding enones[4] or by a Hoffmann cleavage of the pyrazolinium iodide obtained from the corresponding enones.[5] The allenes (**3a**, **b**), which were conveniently prepared from 1,3-diethoxycarbonylacetone by the method of Bryson and Dolak,[6] readily reacted with **4**. A typical experimental procedure is as follows for the reaction of 1,3-dimethoxycarbonylallene (**3a**) with methacrolein *N*,*N*-dimethylhydrazone (**4a**). A solution of **3a** and **4a** in dry acetonitrile was heated at 80—90 °C for 2 d in a sealed tube, then the mixture was concentrated. Purification of the residue by usual silica gel column chromatography gave methyl 2-methoxycarbonyl-5-methyl-3-pyridineacetate (**2a**). The result of a nuclear Overhauser effect (NOE) experiment excluded the isomeric structure, methyl 3-methoxycarbonyl-5-methyl-2-pyridineacetate (**2a′**): irradiation of the methylene protons (CH_2CO_2Me) at δ 4.06 resulted in an enhancement of 29% in the integrated area of 4-H of the pyridine nucleus at δ 7.50, thereby demonstrating an *ortho* relationship of CH_2CO_2Me to 4-H of the pyridine nucleus. In a similar fashion, the allenes (**3a**, **b**) were reacted with other 1-azadienes (**4b**—**e**) to give the corresponding pyridineacetates (**2b**—**g**) in moderate yields. All these new acetates were characterized by nuclear magnetic resonance (^{1}H-NMR), infrared (IR), exact mass, and analytical data.

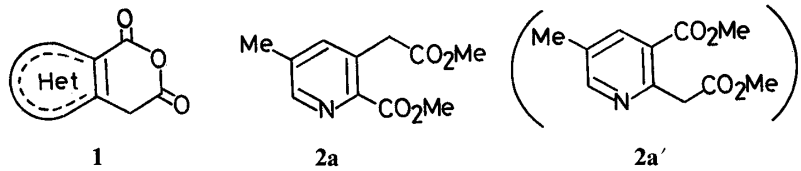
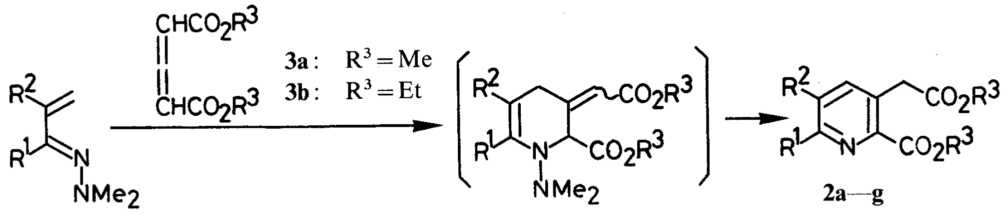


Fig. 1

TABLE I. Preparation of Alkyl 2-Alkoxycarbonyl-3-pyridineacetates (**2a**—**g**)



4a: $R^1=H$, $R^2=Me$
4b: $R^1=Me$, $R^2=H$
4c: $R^1=R^2=Me$
4d: $R^1=H$, $R^2=Et$
4e: $R^1=Et$, $R^2=H$

Compd.	R^1	R^2	R^3	mp °C or bp °C (Torr)[a)]	Yield[b)] (%)
2a	H	Me	Me	57—59	39
2b	Me	H	Me	145—150 (0.12)[c)]	31
2c	H	Me	Et	39—42	49
2d	Me	H	Et	140—145 (0.12)[c)]	45
2e	Me	Me	Et	130—135 (0.12)[c)]	35
2f	H	Et	Et	43—45	52
2g	Et	H	Et	135—140 (0.14)[c)]	35

a) Melting and boiling points are uncorrected. *b*) Yields of isolated products were based on the 1-azadiene **4**. *c*) Boiling points represent minimum bath temperature required for distillation.

Previous studies on the Diels–Alder reaction of 1,3-dialkoxycarbonylallenes (**3**) have been limited to ordinary carbon diene systems, such as 1-methoxycyclohexa-1,3-diene,[7)] furans,[8–10)] pyrroles,[8,9)] cyclopentadiene,[8)] 6-hydroxy-2-pyrone,[8)] and 1,3-butadienes,[11)] but we present here the first example of the reaction of **3** with hetero diene systems.

1,3-Dipolar Cycloaddition

The 1,3-dipolar cycloaddition reaction is one of the most useful reactions for the synthesis of five-membered heterocyclic compounds.[12)] Since diazoalkanes and trimethylsilylazide are a well-known and thoroughly investigated class of 1,3-dipoles, which generally provide pyrazolines and triazolines in high yields, we examined the cycloaddition of these 1,3-dipoles with allenes (**3a, b**).

Treatment of the allenes (**3**) with diazoalkanes resulted in 1,3-dipolar cycloaddition to give compounds of type **5**. Typical experimental conditions were as follows: a solution of the allene dicarboxylate (**3a**) in ether was reacted with diazomethane at room temperature overnight to give methyl 3-methoxycarbonyl-4-pyrazoleacetate (**5a**) regioselectively. The identity of the product was evident from the spectral data, especially from an NOE experiment: irradiation of the methylene protons (CH_2CO_2Me) at δ 3.84 resulted in a 16% enhancement of the integrated area of the proton at δ 7.71, thereby demonstrating an *ortho* relationship of CH_2CO_2Me to 5-H of the pyrazole nucleus. The double bond of **5a** appears to be in the endocyclic form (A) rather than the tautomeric exocyclic form (B) because the NMR spectrum exhibited two equivalent protons attributable to a CH_2CO_2Me group and there was no signal attributable to a vinyl proton. The allene (**3b**) also reacted readily with diazomethane to give ethyl 3-ethoxycarbonyl-4-pyrazoleacetate (**5b**).

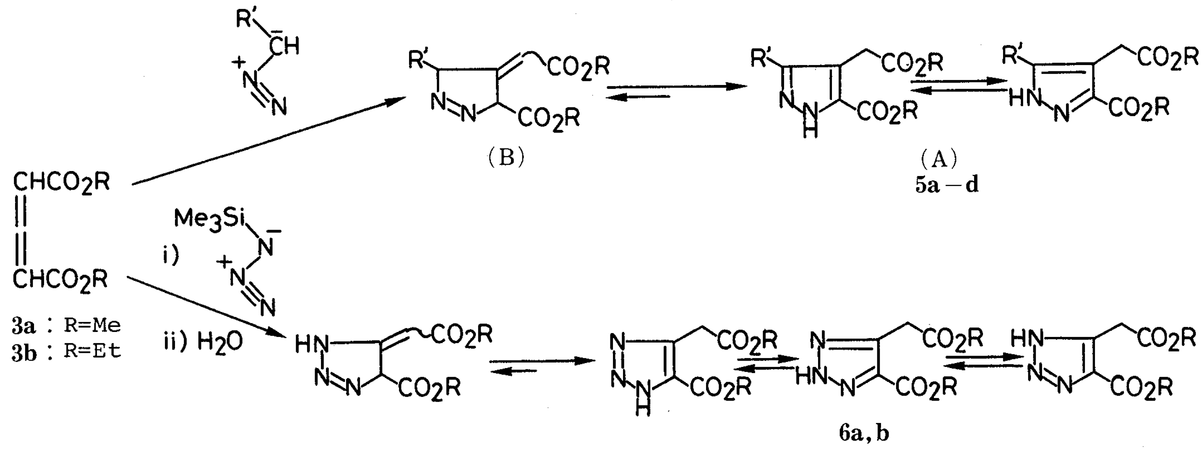
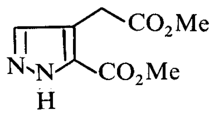
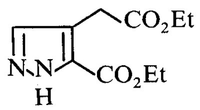
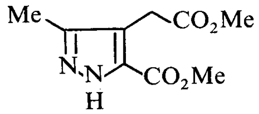
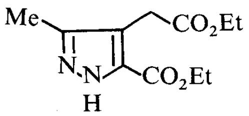
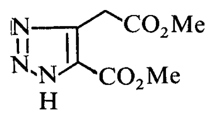
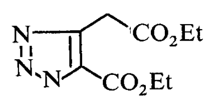


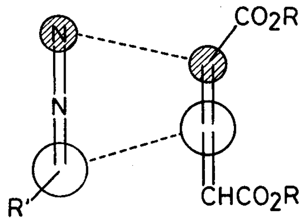
Chart 1

TABLE II. Cycloaddition of 1,3-Dialkoxycarbonylallenes (**3a, b**) to 1,3-Dipoles

Compd.		Reaction conditions	Yield[a] (%)	mp (°C)[b]
	**5a**	**3a**, CH_2N_2 r.t., 1 d	68	137—138
	**5b**	**3b**, CH_2N_2 r.t., 1 d	52	103—104
	**5c**	**3a**, CH_3CHN_2 r.t., 1 d	64	122—125
	**5d**	**3b**, CH_3CHN_2 r.t., 1 d	41	94—97
	**6a**	**3a**, Me_3SiN_3 110—120 °C, 12 h	10	129—131
	**6b**	**3b**, Me_3SiN_3 110—120 °C, 12 h	15	86—87

a) Yields of isolated products are based on the allene **3**. *b*) Melting points are uncorrected.

Similarly, the allenes (**3a, b**) were treated with other 1,3-dipoles, diazoethane and trimethylsilylazide, to give the corresponding 1,3-dipolar cycloadducts (**5c, d** and **6a, b**). High temperature (110—120 °C) was required for the 1,3-dipolar cycloaddition of trimethylsilylazide to **3a, b**, whereas diazoalkanes effected cycloaddition of **3a, b** at low temperature (0 °C—room temperature). The compounds used and the results obtained are summarized in



HOMO LUMO

Fig. 2

Table II.

The 1,3-dipolar cycloadditions can generally be regarded as pericyclic reactions under the control of both HOMO and LUMO of the 1,3-dipole. The former predominates with electron-attracting substituted olefins, and the latter with olefins bearing electron-donating substituents. The regiochemical control leading to the crucial 4-pyrazoleacetates (**5**) was secured by the presence of the alkoxycarbonyl residue of the allene, which causes a definite polarization of the coefficients determining the nature of the HOMO dipole–LUMO dipolarophile transition state (visualized in Fig. 2).

Experimental

The infrared (IR) absorption spectra were recorded on a JASCO HPIR-102 spectrometer, and proton nuclear magnetic resonance (^{1}H-NMR) spectra on a Hitachi R-20A (60 MHz) or a Hitachi R-22 (90 MHz) spectrometer (with tetramethylsilane as an internal standard). Low- and high-resolution mass spectra (MS) were obtained with a JEOL JMS D-300 instrument with a direct-inlet system at 70 eV. Column chromatography was carried out on Merck Silica-gel 60.

General Procedures for the Diels–Alder Reaction of 1,3-Dialkoxycarbonylallenes (3a, b) with 1-Azadienes (4a—e) Leading to Alkyl 2-Alkoxycarbonyl-3-pyridineacetates (2a—g)——A solution of 1,3-dialkoxycarbonylallene (**3**, 1.5 mmol) and the *N*,*N*-dimethylhydrazone (**4**, 1.0 mmol) was heated at 80—90 °C for 2 d in a sealed tube. The reaction mixture was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel with the appropriate eluting solvent to give a pure product (compound **2a**, ether–ethanol 19 : 1; **2b**, ether–benzene 9 : 1; **2c**, ether–benzene 2 : 3; **2d**, benzene–ethyl acetate 4 : 1; **2e**, ether–benzene 4 : 1; **2f**, ether–benzene 1 : 1; **2g**, benzene–ethyl acetate 4 : 1).

Methyl 2-Methoxycarbonyl-5-methyl-3-pyridineacetate (2a)——Compound **2a** (870 mg) was prepared from **3a** (2.34 g, 15 mmol) and **4a** (1.12 g, 10 mmol). Recrystallization from AcOEt : *n*-hexane gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 2.45 (s, 3H, $=\dot{C}-CH_3$), 3.75 (s, 3H, $CH_2CO_2C\underline{H}_3$), 4.01 (s, 3H, $=\dot{C}-CO_2CH_3$), 4.06 (s, 2H, $C\underline{H}_2CO_2CH_3$), 7.50 (s, 1H, 4-H), 8.52 (s, 1H, 6-H). Exact mass calcd for 223.0845. Found: 223.0860. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.32; H, 5.83; N, 6.50.

Methyl 2-Methoxycarbonyl-6-methyl-3-pyridineacetate (2b)——Compound **2b** (277 mg) was prepared from **3a** (936 mg, 6 mmol) and **4b** (448 mg, 4 mmol). Distillation under reduced pressure gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 2.60 (s, 3H, $=\dot{C}-CH_3$), 3.71 (s, 3H, $CH_2CO_2C\underline{H}_3$), 3.90 (s, 3H, $=\dot{C}-CO_2CH_3$), 4.25 (s, 2H, $C\underline{H}_2CO_2CH_3$), 7.09 (d, 1H, $J=7$ Hz, 5-H), 8.15 (d, 1H, $J=7$ Hz, 4-H). Exact mass calcd for 223.0845. Found: 223.0819. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.27; H, 5.95; N, 6.47.

Ethyl 2-Ethoxycarbonyl-5-methyl-3-pyridineacetate (2c)——Compound **2c** (615 mg) was prepared from **3b** (1.38 g, 7.5 mmol) and **4a** (560 mg, 5 mmol). Recrystallization from AcOEt : *n*-hexane gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.25 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.41 (t, 3H, $J=7$ Hz, $=\dot{C}-CO_2CH_2C\underline{H}_3$), 2.38 (s, 3H, $=\dot{C}-CH_3$), 3.95 (s, 2H, $C\underline{H}_2CO_2-CH_2CH_3$), 4.17 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.40 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.35 (s, 1H, 4-H), 8.40 (s, 1H, 6-H). Exact mass calcd for 251.1158. Found: 251.1173. *Anal.* Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.06; H, 6.89; N, 5.63.

Ethyl 2-Ethoxycarbonyl-6-methyl-3-pyridineacetate (2d)——Compound **2d** (565 mg) was prepared from **3b** (1.38 g, 7.5 mmol) and **4b** (560 mg, 5 mmol). Distillation under reduced pressure gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.29 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.37 (t, 3H, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 2.58 (s, 3H, $=\dot{C}-CH_3$), 4.16 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.22 (s, 2H, $C\underline{H}_2CO_2CH_2CH_3$), 4.32 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.11 (d, 1H, $J=8$ Hz, 5-H), 8.13 (d, 1H, $J=8$ Hz, 4-H). Exact mass calcd for 251.1158. Found: 251.1161. *Anal.* Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.21; H, 6.82; N, 5.66.

Ethyl 2-Ethoxycarbonyl-5,6-dimethyl-3-pyridineacetate (2e)——Compound **2e** (186 mg) was prepared from **3b** (552 mg, 3 mmol) and **4c** (252 mg, 2 mmol). Distillation under reduced pressure gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.22 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.34 (t, 3H, $J=$ 7 Hz, $CO_2C\underline{H}_2CH_3$), 2.29 (s, 3H, C=C–CH_3), 2.49 (s, 3H, N=C–CH_3), 4.12 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.17 (s, 2H, $C\underline{H}_2CO_2CH_2CH_3$), 4.29 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.94 (s, 1H, 4-H). Exact mass calcd for 265.1314. Found: 265.1344. *Anal.* Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.26; H, 7.27; N, 5.57.

Ethyl 2-Ethoxycarbonyl-5-ethyl-3-pyridineacetate (2f)——Compound **2f** (692 mg) was prepared from **3b** (1.38 g, 7.5 mmol) and **4d** (630 g, 5 mmol). Recrystallization from AcOEt : *n*-hexane gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.23 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.27 (t, 3H, $J=$ 7 Hz, $CO_2CH_2C\underline{H}_3$), 1.41 (t, 3H, $J=8$ Hz, =C–$CH_2C\underline{H}_3$), 2.71 (q, 2H, $J=8$ Hz, =C–$C\underline{H}_2CH_3$), 3.98 (s, 2H, $C\underline{H}_2CO_2CH_2CH_3$), 4.15 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.40 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.39 (s, 1H, 4-H), 8.45 (s, 1H, 6-H). Exact mass calcd for 265.1314. Found: 265.1317. *Anal.* Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.16; H, 7.31; N, 5.46.

Ethyl 2-Ethoxycarbonyl-6-ethyl-3-pyridineacetate (2g)——Compound **2g** (468 mg) was prepared from **3b** (1.38 g, 7.5 mmol) and **4e** (630 mg, 5 mmol). Distillation under reduced pressure gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.24 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.29 (t, 3H, $J=8$ Hz, =C–$CH_2C\underline{H}_3$), 1.35 (t, 3H, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 2.85 (q, 2H, $J=8$ Hz, =C–$C\underline{H}_2CH_3$), 4.16 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.20 (s, 2H, $C\underline{H}_2CO_2CH_2CH_3$), 4.32 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.10 (d, 1H, $J=8$ Hz, 5-H), 8.16 (d, 1H, $J=8$ Hz, 4-H). Exact mass calcd for 265.1314. Found: 265.1295. *Anal.* Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.35; H, 7.33; N, 5.53.

General Procedures for the 1,3-Dipolar Cycloaddition of 1,3-Dialkoxycarbonylallenes (3a, b) to Diazoalkanes Leading to Alkyl 3-Alkoxycarbonyl-4-pyrazoleacetates (5a—d)——A solution of 1,3-dialkoxycarbonylallene (**3**, 2.4 mmol) in ether (1 ml) was added to a solution of diazoalkane (10—12 mmol) in ether (10 ml), and the mixture was allowed to stand at room temperature overnight. *n*-Hexane was added to the mixture, and the resulting crystals were collected and recrystallized to give pure **5**.

Methyl 3-Methoxycarbonyl-4-pyrazoleacetate (5a)——Compound **5a** (328 mg) was prepared from **3a** (375 mg, 2.4 mmol) and diazomethane (12 mmol). Recrystallization from benzene gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 3.71 (s, 3H, $CH_2CO_2C\underline{H}_3$), 3.84 (s, 2H, $C\underline{H}_2CO_2CH_3$), 3.93 (s, 3H, CO_2CH_3), 7.71 (s, 1H, N=C–H), 12.0 (br s, 1H, exchangeable with D_2O, NH). MS *m/e*: 198 (M^+). *Anal.* Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.45; H, 5.08; N, 13.93.

Ethyl 3-Ethoxycarbonyl-4-pyrazoleacetate (5b)——Compound **5b** (279 mg) was prepared from **3b** (442 mg, 2.4 mmol) and diazomethane (12 mmol). Recrystallization from benzene : *n*-hexane gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.26 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.38 (t, 3H, $J=$ 7 Hz, $CO_2C\underline{H}_2CH_3$), 3.84 (s, 2H, $C\underline{H}_2CO_2CH_2CH_3$), 4.18 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.41 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.57 (s, 1H, =C–H), 11.5 (br s, 1H, exchangeable with D_2O, NH). *Anal.* Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 53.09; H, 6.22; N, 12.27.

Methyl 3-Methoxycarbonyl-5-methyl-4-pyrazoleacetate (5c)——Compound **5c** (327 mg) was prepared from **3a** (375 mg, 2.4 mmol) and diazoethane (10 mmol). Recrystallization from benzene gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 2.27 (s, 3H, N=C–CH_3), 3.73 (s, 3H, $CH_2CO_2C\underline{H}_3$), 3.77 (s, 2H, $C\underline{H}_2CO_2CH_3$), 3.91 (s, 3H, CO_2CH_3), 5.7 (br s, 1H, exchangeable with D_2O, NH). MS: *m/e* 212 (M^+). *Anal.* Calcd for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.70; N, 13.20. Found: C, 50.84; H, 5.16; N, 13.14.

Ethyl 3-Ethoxycarbonyl-5-methyl-4-pyrazoleacetate (5d)——Compound **5d** (238 mg) was prepared from **3b** (442 mg, 2.4 mmol) and diazoethane (10 mmol). Recrystallization from benzene : *n*-hexane gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.28 (t, 3H. $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.38 (t, 3H, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 2.27 (s, 3H, N=C–CH_3), 3.77 (s, 2H, $C\underline{H}_2CO_2CH_2CH_3$), 4.17 (q, 2H, $J=7$ Hz, $CH_2CO_2C\underline{H}_2CH_3$), 4.36 (q, 2H, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 9.3 (br s, 1H, exchangeable with D_2O, NH). MS: *m/e* 240 (M^+). *Anal.* Calcd for $C_{11}H_{16}N_2O_4$: C, 54.99; H, 6.71; N, 11.66. Found: C, 54.88; H, 6.76; N, 11.54.

General Procedures for the 1,3-Dipolar Cycloaddition of 1,3-Dialkoxycarbonylallenes (3a, b) to Trimethylsilyl Azide Leading to Alkyl 5-Alkoxycarbonyl-4-(1,2,3-triazole)acetates (6a, b)——A solution of 1,3-dialkoxycarbonylallene (**3**, 4 mmol) and trimethylsilylazide (460 mg, 4 mmol) was heated at 110—120 °C for 16 h and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with ether : ethanol = 10 : 1 as the eluting solvent to give pure **6**.

Methyl 5-Methoxycarbonyl-4-(1,2,3-triazole)acetate (6a)——Compound **6a** (79 mg) was prepared from **3a** (624 mg, 4 mmol). Recrystallization from benzene gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 3.78 (s, 3H, $CH_2CO_2C\underline{H}_3$), 3.96 (s, 3H, CO_2CH_3), 4.13 (s, 2H, $C\underline{H}_2CO_2CH_3$), 10.5 (br s, 1H, exchangeable with D_2O, NH). MS: *m/e* 199 (M^+). *Anal.* Calcd for $C_7H_9N_3O_4$: C, 42.21; H, 4.55; N, 21.10. Found: C, 41.98; H, 4.49; N, 20.88.

Ethyl 5-Ethoxycarbonyl-4-(1,2,3-triazole)acetate (6b)——Compound **6b** (134 mg) was prepared from **3b** (736 mg, 4 mmol). Recrystallization from benzene : *n*-hexane gave an analytical sample. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.28 (t, 3H, $J=7$ Hz, $CH_2CO_2CH_2C\underline{H}_3$), 1.39 (t, 3H, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 4.11 (s, 2H,

$CH_2CO_2CH_2CH_3$), 4.22 (q, 2H, J=7 Hz, $CH_2CO_2CH_2CH_3$), 4.42 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$), 10.2 (br s, 1H, exchangeable with D_2O, NH). MS: *m/e* 227 (M^+). *Anal.* Calcd for $C_9H_{13}N_3O_4$: C, 47.57; H, 5.77; N, 18.49. Found: C, 47.42; H, 5.77; N, 18.34.

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