[3+2] Cycloaddition of Diazocarbonyl Compounds to 1,1-Dinitroethenes: Synthesis of Functionalized *gem*-Dinitrocyclopropanes

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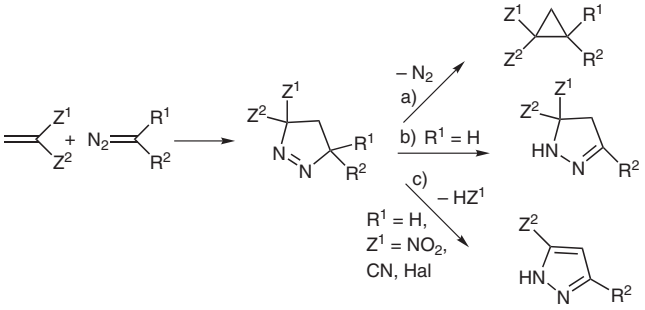
Abstract: The synthesis of functionalized *gem*-dinitrocyclopropanes via [3+2] cycloaddition of diazocarbonyl compounds with 1,1-dinitroethenes [in some cases in the presence of $Mo(CO)_6$ as catalyst] has been developed.

Key words: [3+2] cycloaddition, α-diazocarbonyl compound, 1,1-dinitroethene, 1,1-dinitrocyclopropane, hexacarbonylmolybdenum

Polynitrocyclopropanes are of particular interest as a new family of compounds with increased energy content and high potential synthetic utility.[1,2] Therefore, the development of new methods for the synthesis of these unique polyfunctionalized cyclopropanes is important. It is known that the direct interaction of carbenes with electron-deficient alkenes does not generally result in the formation of cyclopropanes.[3a] The reaction of diazo compounds with electron-deficient alkenes proceeds as a [3+2] cycloaddition (Scheme 1),[3–6] depending on the structure of the substrate employed, the resulting 1-pyrazolines can undergo the following transformations: (a) nitrogen elimination, by thermolysis or photolysis, followed by cyclopropane formation; (b) tautomerization to 2-pyrazolines (for $R^1 = H$); (c) elimination of HZ^1 ($Z^1 = NO_2$, CN, Hal) leading to aromatic pyrazole systems.[3–6]

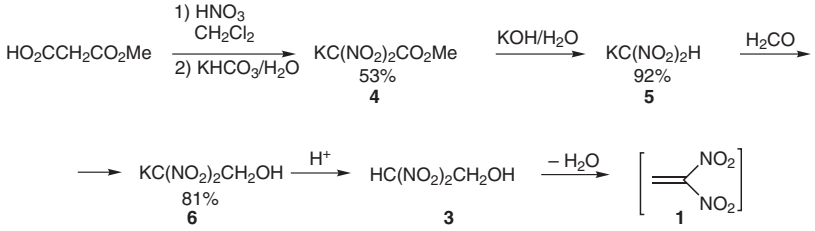


Scheme 1

Recently, we reported the first synthesis of the parent 1,1-dinitrocyclopropane by reaction of trinitromethane with diazomethane.[2b] Rationalization of this process includes the intermediacy of 1,1-dinitroethene (**1**), which, in turn, reacts with diazomethane through a [3+2] cycloaddition to yield 3,3-dinitropyrazoline as the second intermediate. The latter eliminates a molecule of nitrogen to form 1,1-dinitrocyclopropane. However, our mechanistic picture was in obvious contrast with the data of Fridman and coworkers,[7] who had reported that the reaction of 1,1-dinitroethene with diazocarbonyl compounds leads to substituted nitropyrazoles without the formation of 1,1-dinitrocyclopropane derivatives.

Thus, we decided to reinvestigate this [3+2]-cycloaddition process with the goal of finding a novel synthetic route to 1,1-dinitrocyclopropane derivatives via [3+2] cycloaddition of diazocarbonyl compounds to 1,1-dinitroethenes.

Two alkenes, namely 1,1-dinitroethene (**1**)[8] and β,β-dinitrostyrene (**2**)[9] were chosen as model *gem*-dinitroalkene substrates for the reaction with diazo compounds. Taking into consideration the instability of alkene **1**, we generated it in situ by spontaneous dehydration of 2,2-dinitroethanol (**3**) (Scheme 2).[8]



Scheme 2

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While the multistep synthesis of 1,1-dinitroethene (**1**) is known,[10] we improved some of its stages (see the experimental section).

We have found, that the reaction of both 1,1-dinitroethenes **1** and **2** with diazocarbonyl compounds **7a–c**, containing a hydrogen atom in the α-position, leads to mixtures of the corresponding 1,1-dinitrocyclopropanes **8a–e** and nitropyrazoles **9a–e** in various ratios (Table 1).

We also studied the influence of hexacarbonylmolybdenum on the route of the reaction of dinitroalkenes **1** and **2** with diazocarbonyl compounds **7a–c**. This catalyst was proposed by Doyle et al. for the reactions of ethyl diazoacetate or α-diazoacetophenone with α,β-unsaturated compounds to increase the yields of the corresponding cyclopropane derivatives.[11a,b] In the absence of this catalyst 2-pyrazolines are the main products of these reactions.[11c]

According to the data presented in Table 1, the yields and the ratio of the products in the reaction of 1,1-dinitroethene (**1**) and ethyl diazoacetate (**7a**) do not notably depend on the use of the catalyst. At the same time, the result of the reaction of dinitroalkenes **1** and **2** with α-diazoacetophenone (**7b**) depends dramatically on the presence of the catalyst. Thus, the use of hexacarbonylmolybdenum affords dinitrocyclopropanes **8b** and **8e** as main products in good yields.

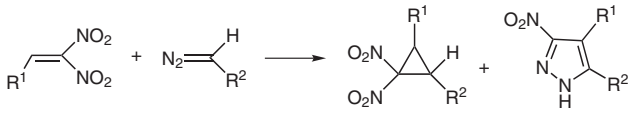
It is worth noting that tetraethyl 1*H*-pyrrole-2,3,4,5-tetracarboxylate (**10**) was formed as a byproduct (5–10% yield) in the reaction of diazoacetate **7a** with dinitroalkene **1** or **2**. Previously the formation of **10** was detected after heating diazoacetate in pyridine.[12] Phenylcyclopropanes **8d**,**e** were identified as mixtures of two diastereomers in 2.3:1 and 9:1 ratio, respectively. This is due to the stereoselectivity of the cyclopropane formation reaction. According to the NMR data, the stereochemistry of the major product has been assigned as having a *trans* arrangement of the phenyl group and the functional group and the minor product has been referred to as the *cis*-isomer (Figure 1).

The reactions of dinitroalkenes with disubstituted diazo compounds are less selective compared to monosubstituted diazo compounds. In fact, the reaction of 1,1-dinitroethene (**1**) with disubstituted diazo compounds **7d–f** leads to a complex mixture of products and dinitrocyclopropanes **8f–h** were isolated in moderate yields only after column chromatography (Table 2).

The molecular structures of **8a–h** and **9a–e** were also unambiguously proved by ^{1}H and ^{13}C NMR spectra (see experimental section).

The vicinal spin–spin coupling constants for rigid three-membered rings have a distinct Karplus-type dependence on the dihedral angle[13a] as it shown previously for monosubstituted cyclopropane compounds.[13b,c] We have found that the values of the coupling constants $^3J_{cis}$ and $^3J_{trans}$ of polysubstituted dinitrocyclopropanes **8a–e** are also significantly different: ^3J = 10.4–12.1 and 9.1–9.9 Hz, respectively; thus we were able to distinguish the isomers of

Table 1 Reaction of 1,1-Dinitroethenes with Diazocarbonyl Compounds Containing an α-Hydrogen

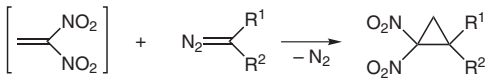


1, **2** **7a–c** **8a–e** **9a–e**

1,2	7	8,9	R^1	R^2	$Mo(CO)_6$, (mol%)	Solvent	Temp (°C)	Time (h)	Yield[a] (%)	
									8	**9**
1	**a**	**a**	H	CO_2Et	–	Et_2O	reflux	19	35	41
1	**a**	**a**	H	CO_2Et	4	Et_2O	reflux	19	37	40
1	**b**	**b**	H	COPh	–	benzene	55–60	6	30	40
1	**b**	**b**	H	COPh	5	benzene	60–65	10[b]	71	25
1	**c**	**c**	H	COMe	–	benzene	60	6	42	38
1	**c**	**c**	H	COMe	5	benzene	40–45	40[b]	54	38
2	**a**	**d**	Ph	CO_2Et	–	benzene	reflux	3	12	55
2	**a**	**d**	Ph	CO_2Et	10	benzene	reflux	3	41	44
2	**b**	**e**	Ph	COPh	–	benzene	reflux	0.5[c]	28	58
2	**b**	**e**	Ph	COPh	5	benzene	reflux	0.5[c]	70	15

[a] Yield of isolated product (column chromatography).
[b] Then reflux, 0.5 h.
[c] Then r.t., 2 d.

Table 2 Reaction 1,1-Dinitroethene with Disubstituted Diazocarbonyl Compounds



1 7d–f 8f–h

7	8	R^1	R^2	Solvent	Time (h)	Yield (%)
d	**f**	Me	CO_2Et	Et_2O	16	56
e	**g**	CH_2Ph	CO_2Me	benzene	10	15
f	**h**	CO_2Et	CO_2Et	chlorobenzene	4	35

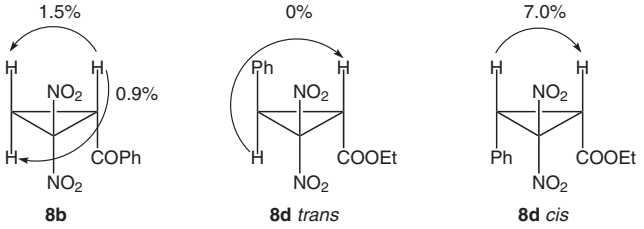


Figure 1 Representative NOE enhancements for compounds **8b**,**d**

8d,**e**. The correctness of the stereochemical assignment was unambiguously confirmed by the observation of NOE enhancements due to dipolar interaction between the hydrogens of compounds **8b**,**d**. The results of NOE measurements are presented in Figure 1. It is interesting to note that the hydrogen atoms of the three-membered rings of the compounds studied are shifted downfield ($\Delta\delta$ = 2.5–4.9) due to the influence of substituents. The $^1J_{CH}$ constants have rather large values (166–174 Hz).

In general, the efficiency of the method described for the synthesis of dinitrocyclopropanes depends on steric and electronic factors. For example, in the reaction of β,β-dinitrostyrene (**2**) with disubstituted diazocarbonyl compounds **7d**,**e**, cyclopropanes were found in small amounts and they could not be isolated. β,β-Dinitrostyrene (**2**) did not react with diethyl diazomalonate (**7f**). In addition, the reaction of the dinitroethenes **1** and **2** with ethyl diazonitroacetate did not result in the formation of cyclopropane derivatives.

In conclusion, reactions of 1,1-dinitroalkenes with α-diazocarbonyl compounds represent a useful approach for the synthesis of novel functionalized *gem*-dinitrocyclopropanes, readily able to undergo further chemical modifications.

NMR spectra (400 MHz) were recorded on a Bruker Avance-400 spectrometer at r.t. referenced to the solvent (^{1}H: $CDCl_3$, δ = 7.26, DMSO-d_6, δ = 2.50; ^{13}C: $CDCl_3$, δ = 77.1, DMSO-d_6, δ = 39.5). MS were recorded on the MALDI-TOF mass-spectrometer Bruker Ultraflex in positive mode, dithranol was used as a matrix. Melting points: Electrothermal 9100 capillary melting point apparatus, values uncorrected. Column chromatography was performed on silica gel 60 (230–400 mesh, Merck). Ethyl diazoacetate,[14] 2-diazo-1-phenylethanone,[15] 1-diazopropan-2-one,[16] ethyl 2-diazopropanoate,[16] methyl 2-diazo-3-phenylpropanoate,[17] and diazomalonic ester[18] were prepared by published procedures.

Methyl Dinitroacetate Potassium Salt (4)

To a stirred soln of fuming HNO_3 (77 mL, d = 1.50) in CH_2Cl_2 (57 mL) at –5 °C was added monomethyl malonate (23.9 g, 0.2 mol). The mixture was stirred at 5–7 °C for 3 h, then it was quenched with ice-water (120 mL). The organic layer was washed with ice-water (3 × 60 mL), then sat. aq $KHCO_3$ (170 mL) was added to the organic layer and the resulting mixture was stirred at 5–7 °C for 20 min. The thus-formed precipitate was filtered off and dried in air to give a cream-colored solid; yield: 21.4 g (53%); mp 209 °C (dec.).

^{1}H NMR (DMSO-d_6): δ = 3.69 (s, 3 H, CH_3).

^{13}C NMR (DMSO-d_6): δ = 52.6 (CH_3O), 131.04 [$C(NO_2)_2$], 161.49 (CO_2CH_3).

Potassium Dinitromethane (5)

Methyl dinitroacetate potassium salt (15.0 g, 0.074 mol) was added to a stirred soln of KOH (5.56 g, 0.1 mol) in H_2O (56 mL) and the mixture was heated at 65–70 °C for 30 min. Then the resulting mixture was allowed to cool to 0 °C, the yellow solid was filtered off, washed with ice-water (2 × 10 mL), and dried in air; yield: 9.80 g (92%).

^{1}H NMR (DMSO-d_6): δ = 3.46 (s, 1 H, CH).

^{13}C NMR (DMSO-d_6): δ = 122.7 (CH).

Potassium 2,2-dinitroethanol (6)

A suspension of potassium dinitromethane (6 g, 0.042 mol) and 40% aq formaldehyde (6 mL) in H_2O (10 mL) was heated at 90 °C for 15 min and the resulting soln was cooled to 0–5 °C. The yellow solid was filtered off, washed with ice-water (2 mL) and MeOH (2 mL), and dried in air; yield: 5.90 g (81%), mp 148–150 °C (Lit.[8] 152 °C).

^{1}H NMR (DMSO-d_6): δ = 4.52 (t, ^3J = 6.1 Hz, 1 H, OH), 4.72 (d, ^3J = 6.1 Hz, 2 H, CH_2).

^{13}C NMR (DMSO-d_6): δ = 57.4 (CH_2OH), 136.4 [$C(NO_2)_2$].

2,2-Dinitroethanol (3)

Potassium 2,2-dinitroethanol (0.5 g, 2.9 mmol) was dissolved in ice-water (2 mL), then soln of concd H_2SO_4 (0.08 mL) in H_2O (2.5 mL) was added at 3 °C under stirring. The aqueous soln was extracted with cold Et_2O (5 × 3 mL) and the combined organic layers were dried (anhyd $MgSO_4$). Then benzene (5 mL) (or Et_2O, chlorobenzene) was added to the ether soln and the soln was concentrated to 5 mL in vacuo. The crude dinitroethanol was utilized without purification.

Reaction of 1,1-Dinitroethene (1) with Diazo Compounds 7a–c; General Procedure

The mixture of the diazo compound (2.9 mmol) in benzene (or Et_2O for diazoacetate) (5 mL), $Mo(CO)_6$ (0.030 g, 4 mol%), and 2,2-dinitroethanol [obtained from potassium 2,2-dinitroethanol (2.9 mmol) in benzene (5 mL)] was heated at reflux with activated 4 Å molecular sieves for several hours (Table 1). After cooling the resulting mixture was concentrated in vacuo. The products **8a–c**, **9a–c,** and **10** were isolated by column chromatography (*n*-hexane–$CHCl_3$, 1:1).

Ethyl 2,2-Dinitrocyclopropanecarboxylate (8a)

Oil; R_f = 0.7 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.30 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.55 (dd, ^2J = 7.8, ^3J = 10.6 Hz, 1 H, CH_2CHCO_2Et), 2.78 (dd, ^2J = 7.8,

^3J = 9.1 Hz, 1 H, CH_2CHCO$_2$Et), 3.41 (dd, ^3J = 10.6, 9.1 Hz, 1 H, CH$_2$CHCO$_2$Et), 4.25 (m, 2 H, CH$_2$O).

^{13}C NMR (CDCl$_3$): δ = 13.7 (CH$_3$), 22.3 ($^1J_{CH}$ = 174 Hz, CH$_2$), 31.3 ($^1J_{CH}$ = 176 Hz, CH$_2$), 63.2 (CH$_2$O), 97.3 [C(NO$_2$)$_2$], 164.7 (*C*O$_2$Et).

Anal. Calcd for $C_6H_8N_2O_6$: C, 35.30; H, 3.95; N, 13.72. Found: C, 35.25; H, 3.70; N, 13.59.

Ethyl 5-Nitro-1*H*-pyrazole-3-carboxylate (9a)[7]
Crystals; mp 155 °C (CHCl$_3$) [Lit.[7] 155–156 °C]; R_f = 0.2 (CHCl$_3$).

^{1}H NMR (DMSO-d_6): δ = 1.32 (t, ^3J = 7.2 Hz, 3 H, CH$_3$), 4.36 (q, ^3J = 7.2 Hz, 2 H, CH$_2$O), 7.48 (s, 1 H, CH), 15.19 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 14.4 (CH$_3$), 62.2 (CH$_2$O), 105.1 (CH), 136.3 (C), 156.4 (C), 158.2 (*C*O$_2$Et).

Tetraethyl 1*H*-Pyrrole-2,3,4,5-tetracarboxylate (10)[12]
Oil; R_f = 0.5 (CHCl$_3$).

^{1}H NMR (CDCl$_3$): δ = 1.31 (t, ^3J = 7.2 Hz, 6 H, 2 CH$_3$), 1.35 (t, ^3J = 7.2 Hz, 6 H, 2 CH$_3$), 4.36 (q, ^3J = 7.2 Hz, 4 H, 2 CH$_2$), 4.42 (q, ^3J = 7.2 Hz, 4 H, 2 CH$_2$).

(2,2-Dinitrocyclopropyl)phenylmethanone (8b)
Crystals; mp 89 °C; R_f = 0.6 (CHCl$_3$).

^{1}H NMR (CDCl$_3$): δ = 2.61 (dd, ^2J = 7.6, ^3J = 10.4 Hz, 1 H, CH_2CHCOPh), 3.05 (dd, ^2J = 7.6, ^3J = 9.2 Hz, 1 H, CH_2CHCOPh), 4.36 (dd, ^3J = 10.4, 9.2 Hz, 1 H, CH$_2$CHCO$_2$Et), 7.50–7.60 (m, 2 H, Ph), 7.66–7.74 (m, 1 H, Ph), 7.98–8.04 (m, 2 H, Ph).

^{13}C NMR (CDCl$_3$): δ = 22.3 ($^1J_{CH}$ = 173 Hz, CH$_2$), 33.3 ($^1J_{CH}$ = 171 Hz, CH$_2$), 98.8 [C(NO$_2$)$_2$], 128.8 (2 CH, Ph), 129.2 (2 CH, Ph), 135.0 (CH, Ph), 135.3 (C, Ph), 188.8 (CO).

Anal. Calcd for $C_{10}H_8N_2O_5$: C, 50.85; H, 3.41; N, 11.86. Found: C, 50.82; H, 3.19; N, 11.63.

(5-Nitro-1*H*-pyrazol-3-yl)phenylmethanone (9b)[7]
Crystals; mp 186 °C (CHCl$_3$) [Lit.[7] 186–187 °C].

^{1}H NMR (DMSO-d_6): δ = 7.45 (s, 1 H, CH), 7.52–7.60 (m, 2 H, Ph), 7.63–7.72 (m, 1 H, Ph), 7.91–7.98 (m, 2 H, Ph), 15.19 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 106.0 (CH), 129.1 (2 CH, Ph), 129.4 (2 CH, Ph), 134.0 (CH, Ph), 136.1 (C, Ph), 141.6 (C), 156.2 (C), 183.8 (CO).

1-(2,2-Dinitrocyclopropyl)ethanone (8c)
Crystals; mp 62–63 °C; R_f = 0.5 (CHCl$_3$).

^{1}H NMR (CDCl$_3$): δ = 2.49 (dd, ^2J = 7.8, ^3J = 10.4 Hz, 1 H, CH_2CHCOCH$_3$), 2.50 (s, 3 H, CH$_3$), 2.79 (dd, ^2J = 7.8, ^3J = 9.2 Hz, 1 H, CH_2CHCOCH$_3$), 3.67 (dd, ^3J = 10.4, 9.2 Hz, 1 H, CH$_2$CHCOCH$_3$).

^{13}C NMR (CDCl$_3$): δ = 22.3 ($^1J_{CH}$ = 173 Hz, CH$_2$), 31.7 (CH$_3$), 36.2 ($^1J_{CH}$ = 172 Hz, CH), 98.6 [C(NO$_2$)$_2$], 197.3 (CO).

Anal. Calcd for $C_5H_6N_2O_5$: C, 34.49; H, 3.47; N, 16.09. Found: C, 34.52; H, 3.35; N, 16.02.

1-(5-Nitro-1*H*-pyrazol-3-yl)ethanone (9c)[7]
Crystals; mp 131–132 °C (CHCl$_3$) [Lit.[7] 136–137 °C].

^{1}H NMR (CD$_3$OD): δ = 2.60 (s, 3 H, CH$_3$), 7.59 (s, 1 H, CH).

^{13}C NMR (DMSO-d_6): δ = 27.0 (CH$_3$), 104.5 (CH), 142.2 (C), 156.5 (C), 188.0 (CO).

1-Substituted 2,2-Dinitro-3-phenylcyclopropanes 8d,e; General Procedure
A mixture of β,β-dinitrostyrene (**2**, 0.5 g, 2.6 mmol), diazo compound **7a** or **7b** (2.6 mmol), and Mo(CO)$_6$ was refluxed in benzene (5 mL) for several hours (Table 1). After cooling, the resulting mixture was concentrated in vacuo. The products **8d**,**e** and **9d**,**e** were isolated by column chromatography (*n*-hexane–EtOAc, 20:1).

Ethyl 2,2-Dinitro-3-phenylcyclopropanecarboxylate (8d)
Oil; ratio *trans*/*cis* 70:30; R_f = 0.6 (CHCl$_3$).

***trans*-Isomer**
^{1}H NMR (CDCl$_3$): δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, CH$_3$), 4.01 (d, ^3J = 9.9 Hz, 1 H, CH), 4.31 (q, ^3J = 7.1 Hz, 2 H, CH$_2$), 4.39 (d, ^3J = 9.9 Hz, 1 H, CH), 7.31 (m, 2 H, Ph), 7.39 (m, 3 H, Ph).

^{13}C NMR (CDCl$_3$): δ = 13.9 (CH$_3$), 33.9 ($^1J_{CH}$ = 169 Hz, CH), 38.8 ($^1J_{CH}$ = 168 Hz, CH), 63.4 (CH$_2$), 101.0 [C(NO$_2$)$_2$], 127.1 (C, Ph). 128.1 (2 CH, Ph), 129.2 (2 CH, Ph), 129.7 (CH, Ph), 164.3 (C).

***cis*-Isomer**
^{1}H NMR (CDCl$_3$): δ = 1.19 (t, ^3J = 7.1 Hz, 3 H, CH$_3$), 3.69 (d, ^3J = 12.1 Hz, 1 H, CH), 4.09 (d, ^3J = 12.1 Hz, 1 H, CH), 4.19 (q, ^3J = 7.1 Hz, 2 H, CH$_2$), 7.31 (m, 2 H, Ph), 7.39 (m, 3 H, Ph).

^{13}C NMR (CDCl$_3$): δ = 13.7 (CH$_3$), 33.8 ($^1J_{CH}$ = 173 Hz, CH), 38.5 ($^1J_{CH}$ = 166 Hz, CH), 62.7 (CH$_2$), 98.9 [C(NO$_2$)$_2$], 126.4 (C, Ph), 128.5 (2 CH, Ph), 129.0 (2 CH, Ph), 129.8 (CH, Ph), 162.8 (C).

Anal. Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.42; H, 4.20; N, 10.01.

(2,2-Dinitro-3-phenylcyclopropyl)phenylmethanone (8e)
Oil; ratio *trans*/*cis* 90:10; R_f = 0.7 (CHCl$_3$).

***trans*-Isomer**
^{1}H NMR (CDCl$_3$): δ = 4.64 (d, ^3J = 10.1 Hz, 1 H, CH), 4.89 (d, ^3J = 10.1 Hz, 1 H, CH), 7.34 (m, 2 H, Ph), 7.42 (m, 3 H, Ph), 7.59 (m, 2 H, CH, Ph-CO), 7.73 (m, 1 H, CH, Ph-CO), 8.10 (m, 2 H, CH, Ph-CO).

^{13}C NMR (CDCl$_3$): δ = 36.6 ($^1J_{CH}$ = 165 Hz, CH), 38.3 ($^1J_{CH}$ = 167 Hz, CH), 102.2 [C(NO$_2$)$_2$], 127.7 (C, Ph). 128.1 (2 CH, Ph), 128.9 (2 CH, Ph), 129.3 (2 CH, Ph), 129.3 (2 CH, Ph), 129.7 (CH, Ph), 130.6 (C, Ph), 135.2 (CH, Ph), 188.1 (C=O).

***cis*-Isomer**
^{1}H NMR (CDCl$_3$): δ = 4.25 (d, ^3J = 12.1 Hz, 1 H, CH), 4.54 (d, ^3J = 12.1 Hz, 1 H, CH), 7.34 (m, 2 H, Ph), 7.42 (m, 3 H, Ph), 7.59 (m, 2 H, *m*-CH, Ph-CO), 7.73 (m, 1 H, *p*-CH, Ph-CO), 8.10 (m, 2 H, *o*-CH, Ph-CO).

Anal. Calcd for $C_{16}H_{12}N_2O_5$: C, 61.54; H, 3.85; N, 8.97. Found: C, 61.38; H, 3.85; N, 8.66.

Ethyl 5-Nitro-4-phenyl-1*H*-pyrazole-3-carboxylate (9d)
Yellow oil; R_f = 0.1 (CHCl$_3$).

^{1}H NMR (CDCl$_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 3 H, CH$_3$), 4.23 (q, ^3J = 7.1 Hz, 3 H, CH$_2$), 7.35–7.70 (m, 5 H, Ph).

MS-MALDI-TOF: *m*/*z* = 261 [M]$^+$.

(5-Nitro-4-phenyl-1*H*-pyrazol-3-yl)phenylmethanone (9e)
Yellow oil; R_f = 0.1 (CHCl$_3$).

^{1}H NMR (CDCl$_3$): δ = 7.35–7.70 (m, 10 H, Ph).

Anal. Calcd for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.75; N, 14.33. Found: C, 65.71; H, 3.95; N, 14.58.

Reaction of 1,1-Dinitroethene with Disubstituted Diazo Compounds 7d–f; General Procedure
A mixture of the diazo compound (2.9 mmol) in a solvent (5 mL) and 2,2-dinitroethanol [obtained from potassium 2,2-dinitroethanol (2.9 mmol) in the same solvent] was heated at reflux with activated 4 Å molecular sieves for several hours (Table 2). After cooling the

resulting mixture was concentrated in vacuo. The products were isolated by column chromatography (*n*-hexane–$CHCl_3$, 1:1).

Ethyl 1-Methyl-2,2-dinitrocyclopropanecarboxylate (8f)
Oil; R_f = 0.6 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.30 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 2.49 (d, ^2J = 8.3 Hz, 1 H, CH_2), 2.90 (d, ^2J = 8.3 Hz, 1 H, CH_2), 4.20–4.35 (m, 2 H, OCH_2).

^{13}C NMR ($CDCl_3$): δ = 13.7 (CH_3), 15.01 (CH_3), 26.4 ($^1J_{CH}$ = 171 Hz, CH_2), 37.9 (C), 63.8 (CH_2O), 101.2 [$C(NO_2)_2$], 166.2 (CO_2Et).

Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.54; H, 4.62; N, 12.84. Found: C, 38.58; H, 4.49; N, 12.70.

Methyl 1-Benzyl-2,2-dinitrocyclopropanecarboxylate (8g)
Oil; R_f = 0.6 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.66 (d, ^2J = 8.6 Hz, 1 H, CH_2), 2.93 (d, ^2J = 8.6 Hz, 1 H, CH_2), 3.74 (s, 3 H, CH_3), 3.83 (s, 2 H, CH_2), 7.30–7.55 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 25.6 ($^1J_{CH}$ = 170 Hz, CH_2), 34.8 (CH_2), 44.8 (C), 51.8 (CH_3), 100.5 [$C(NO_2)_2$], 128.1 (2 CH, Ph), 128.9 (2 CH, Ph), 130.3 (CH, Ph), 134.3 (C, Ph), 167.9 (CO_2CH_3).

Anal. Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.09; H, 3.95; N, 10.20.

Diethyl 2,2-Dinitrocyclopropane-1,1-dicarboxylate (8h)
Oil; R_f = 0.8 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.30 (t, ^3J = 7.1 Hz, 6 H, CH_3), 2.99 (s, 2 H), 4.29 (q, ^3J = 7.1 Hz, 4 H, CH_2O).

^{13}C NMR ($CDCl_3$): δ = 13.7 (2 CH_3), 25.9 ($^1J_{CH}$ = 174 Hz, CH_2), 44.3 (C), 64.1 (2 CH_2O), 98.0 [$C(NO_2)_2$], 161.8 (2 CO_2Et).

Anal. Calcd for $C_9H_{12}N_2O_8$: C, 39.14; H, 4.38; N, 10.14. Found: C, 39.46; H, 4.28; N, 9.98.

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