Reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with 2-pyrazolines

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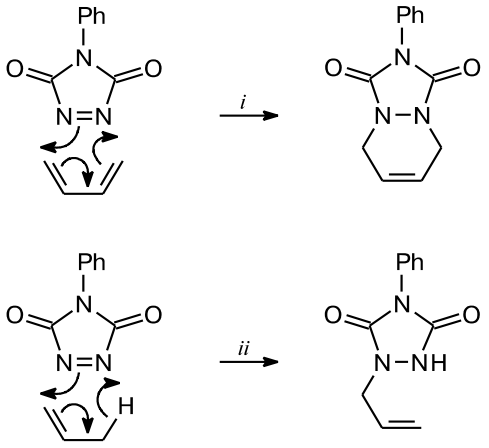
4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) acts as an efficient Michael acceptor in reactions with 1-unsubstituted 2-pyrazolines, giving substituted (3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-1-pyrazolines in quantitative yields. Through elimination of molecular nitrogen, the latter are easily transformed into the corresponding cyclopropanes. A reaction of methyl 5-methyl-2-pyrazoline-5-carboxylate with a twofold excess of PTAD leads to an intermediate bisadduct, which undergoes dediazotization to form a 1,3,5-triazabicyclo[3.3.0]octane-2,4-dione derivative. 1-Substituted 2-pyrazolines also add to PTAD with the exception that the 2-pyrazoline structure is retained in the product because of the migration of the C(3)H proton to PTAD.

Key words: 4-phenyl-1,2,4-triazoline-3,5-dione, ene reaction, pyrazoline, cyclopropane, dediazotization, stereoselectivity, NMR spectra.

4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) contains a highly reactive N=N bond and readily enters into the Diels—Alder reactions with various carbo- and heterodienes[1—6] and into ene reactions with substrates containing an allylic H atom[7—11] (Scheme 1). These reactions are of both synthetic[2—6,10,11] and mechanistic interest.[8—10,12,13] The wide use of PTAD in organic synthesis is due to a variety of accessible substrates, easily occurring and selective reactions, and high yields of reaction products.[2—6,10,11,14—18]

Scheme 1



i. [2+4] cycloaddition; *ii*. ene reaction.

Although much research has dealt with PTAD-involving transformations, its reactions with compounds containing the C=N or N=N bond have not been described hitherto. However, the study of such reactions could result in developing new approaches to the synthesis of various azaheterocycles. In connection with this, we studied reactions of PTAD with 2- and 1-pyrazolines containing the C=N and N=N bonds, respectively, and some transformations of the reaction products, out of which dediazotization to the corresponding cyclopropanes proved to be important.

Results and Discussion

We found that 1-unsubstituted 2-pyrazolines **1a—f** react with PTAD very rapidly even at 0 °C. The reaction was completed in less than 1 min, the bright red (because of PTAD) initial solution turning colorless. The first-step reaction products are substituted 1-pyrazolines **2a—f**, which were detected from the ^{1}H and ^{13}C NMR spectra of the reaction mixtures. The solutions of 1-pyrazolines **2** are stable at 0 °C for several hours. However, they eliminate molecular nitrogen even at room temperature, selectively giving cyclopropanes **3a—f** (Scheme 2). The dediazotization process largely depends on the substituents in the starting 2-pyrazolines and is substantially promoted in boiling chloroform or dichloroethane. No further purification of the resulting cyclopropanes is usually required; should the need arise, however, they can be recrystallized from diethyl ether or diethyl ether—hexane.

We studied reactions of PTAD with 2-pyrazolines containing the ester and phenyl groups in different positions of the heterocycle, as well as with a pyrazoline fused to a

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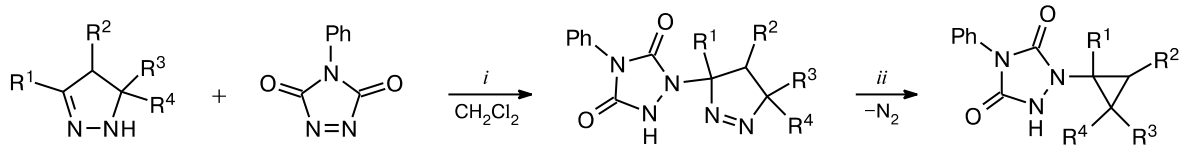
Scheme 2

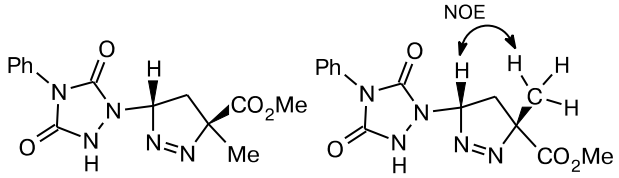


1a—f PTAD **2a—f** (>95%) **3a—f** (92—100%)

i. 0 °C, 1 min; *ii*. 20—60 °C.

Compound	R^1	R^2	R^3	R^4	Compound	R^1	R^2	R^3	R^4
a	CO_2Me	H	H	H	**d**	H	Ph	CO_2Me	CO_2Me
b	H	H	CO_2Me	Me	**e**	H	H	Ph	Ph
c	CO_2Me	H	CO_2Me	H	**f**	CO_2Me			H

norbornane fragment. A reaction of PTAD with disubstituted pyrazoline **1b** gives stereoisomeric pyrazolines *E*- and *Z*-**2b** in a ratio of ~3 : 1. The spatial arrangement of the substituents in these products was determined by 2D NOESY NMR spectroscopy. For the minor isomer, the spectrum shows a distinct coupling between the methyl protons and the C(3)H proton, which corresponds to isomer *Z*-**2b**.



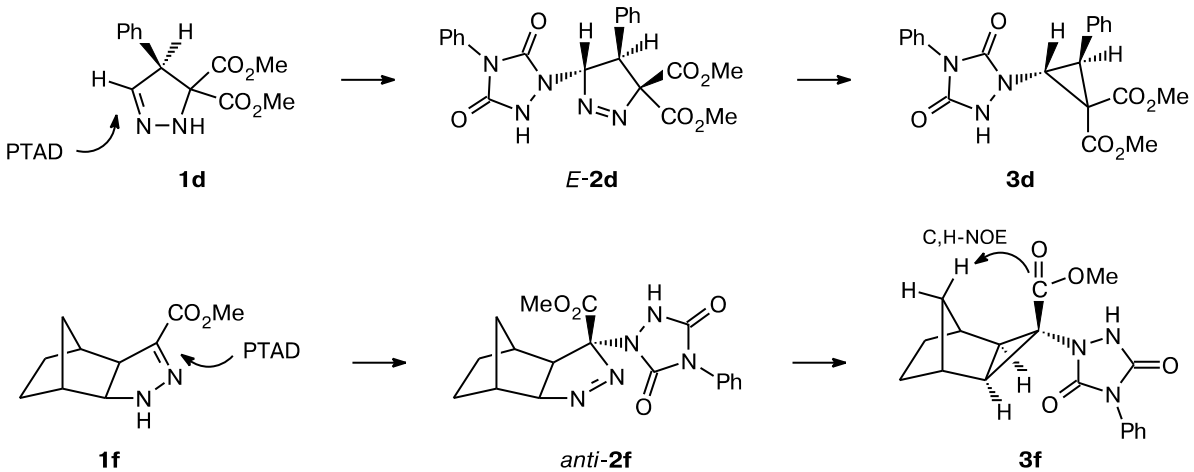
E-**2b** *Z*-**2b**

The stereochemistry of the addition of PTAD to the C=N bond of pyrazolines **1** is appreciably affected by steric factors due to the presence of the substituents in the pyrazoline ring. This effect is especially pronounced in pyrazolines **1d** and **1f**: their reactions with PTAD proceed stereospecifically to give stereoisomers *E*-**2d** and *anti*-**2f** only. Steric hindrances presented by the phenyl substituent and the norbornane framework preclude PTAD from approaching the pyrazoline ring on the side of these substituents, which allow its addition to the C(3) atom only from the less shielded side of the heterocycle (Scheme 3).

As noted above, the dediazotization of pyrazolines **2** smoothly occurs when they are kept at 20 °C for several hours or refluxed in chloroform, though variation in the reaction conditions for some of them leads to somewhat different outcomes (Table 1).

For instance, the dediazotization of pyrazoline **2a** containing no substituents in positions 4 and 5 of the pyrazoline ring at 40 °C gives *gem*-disubstituted cyclopropane **3a** in a quantitative yield. However, this reaction in boiling 1,2-dichloroethane is nonselective, producing cyclo-

Scheme 3



1d *E*-**2d** **3d**

1f *anti*-**2f** **3f**

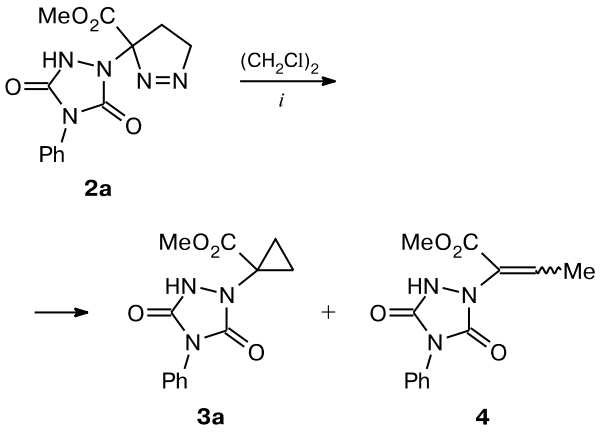
Table 1. Reactions of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) with 2-pyrazolines[a]

Starting pyrazoline	Solvent	Step 1,[b] product	Step 2[c]			
			T/°C	*t*/min	Product	Yield[d] (%)
1a	CH_2Cl_2	**2a**	40	150	**3a**	98
1a	$(CH_2Cl)_2$	**2a**	83	15	**3a** + *E*-**4** + *Z*-**4** (~10 : 4 : 1)	98
1b	$CHCl_3$	*E*-**2b** + *Z*-**2b** (3 : 1)	60	15	*E*-**3b** + *Z*-**3b** (2.9 : 1)	96
1c	$CHCl_3$	*E*-**2c** + *Z*-**2c** (2.8 : 1)	25	180	*E*-**3c** + *Z*-**3c** (4.9 : 1)	95
1c	$CHCl_3$	*E*-**2c** + *Z*-**2c** (2.8 : 1)	60	15	*E*-**3c** + *Z*-**3c** (2.6 : 1)	97
1d	$CHCl_3$	*E*-**2d**	60	15	*E*-**3d**	92
1e	$CHCl_3$	**2e**	60	15	**3e**	96
1f	$(CH_2Cl)_2$	*anti*-**2f**	83	30	*anti*-**3f**	98

[a] The molar ratio is 1 : 1.
[b] The first step (0 °C, 1—2 min) is the formation of 1-pyrazolines **2** in >95% yields. Their yields were determined from the ^{1}H NMR spectra of the reaction mixtures.
[c] The second step is dediazotization to cyclopropanes **3**.
[d] The yields of cyclopropanes **3** and unsaturated compounds **4** are given with respect to the gross amount of the dediazotization products isolated.

propane **3a** (up to 33% yield) and unsaturated compounds **4** as a ~4 : 1 mixture of *E*- and *Z*-isomers (Scheme 4).

Scheme 4



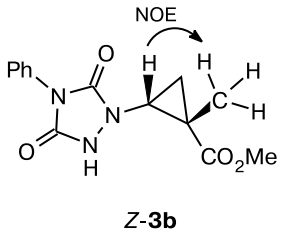
i. 83 °C, 15 min.

Isomeric pyrazolines **2b** (*E* : *Z* = 3 : 1) are transformed into cyclopropanes *E*- and *Z*-**3b**, regardless of the dediazotization conditions. The stereochemistry of the substituents remains nearly the same (2.9 : 1) as that in the starting pyrazolines **2b**. Likewise, isomerically pure pyrazolines *E*-**2d** and *anti*-**2f** with substantial steric effects of the substituents undergo dediazotization to the corresponding isomerically pure cyclopropanes *E*-**3d** and *anti*-**3f** in high yields. In contrast to other pyrazolines **2**, the complete conversion of fused pyrazoline **2f** can be attained only under more drastic conditions (dichloroethane, reflux, 30 min). The spatial arrangement of the substituents in cyclopropane **3f** was determined by 2D NMR experiments (^{1}H,^{13}C HOESY: Heteronuclear Overhauser Effect Spectroscopy). The C atoms of the ester group show a characteristic ^{1}H,^{13}C NOE peak with the C(8)H proton of the norbornane framework (see Scheme 3).

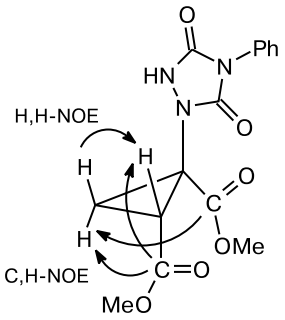
At the same time, the stereoselectivity of the dediazotization of isomeric pyrazolines **2c** varies with the reaction conditions. For instance, a mixture of pyrazolines *E*- and *Z*-**2c** (2.8 : 1) in boiling chloroform is completely transformed into a mixture of cyclopropanes *E*- and *Z*-**3c** (~2.6 : 1), while the same pyrazolines at 20 °C (complete conversion in 3 h) yield cyclopropanes **3c** with *E* : *Z* = = 4.9 : 1 (see Table 1).

Apparently, the dediazotization of the 1-pyrazolines studied proceeds through a biradical transition state in which the configuration of the substituents can be partially changed by rotation about the single C—C bond. The stereochemical outcome of these transformations depends in a complicated manner[19] on the electronic and steric effects of the substituents in the transition state.

The *E*- and *Z*-isomers of cyclopropane **3b** were identified from 2D NOESY data. The presence of a coupling between the methyl protons and the C(1)H proton was indicative of the minor isomer. In the case of cyclopropanes **3c**, ^{1}H,^{1}H-NOESY and ^{1}H,^{13}C-HOESY NMR experiments revealed couplings of the C atoms of both ester groups with the same *cis*-vicinal proton of the cyclopropane ring in the major isomer *E*-**3c**.



Z-**3b**

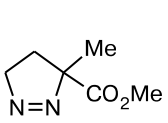


E-**3c**

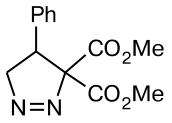
A reaction of 2-pyrazoline **1b** with a twofold excess of PTAD gives 1,3,5-triazabicyclo[3.3.0]octane-2,4-dione **5** through an intermediate bisadduct (Scheme 5). The reaction occurs in boiling $CHCl_3$ for 30 min. Recrystallization from diethyl ether gives functionalized triazabicyclooctanes *E*- and *Z*-**5** (~10 : 1) in 82% yield. Their structures were determined from 2D NOESY experiments. As expected, the major product is isomer *E*-**5**, which is sterically least hindered.

When the reaction temperature is lowered to 30 °C and the reaction time is extended to 2 h, the formation of triazabicyclooctane *E*-**5** becomes less selective. The ratio *E*-**5** : *Z*-**5** is nearly the same (~3 : 1) as that for isomeric pyrazolines *E*- and *Z*-**2b**. It should be noted that a specially prepared mixture of cyclopropanes *E*- and *Z*-**3b** does not react with PTAD in boiling $CHCl_3$, nor yielding bicyclic products of the type **5**. Apparently, the first step involves a rapid reaction of 2-pyrazoline **1b** with PTAD followed by addition of a second PTAD molecule to 1-pyrazoline **2b** (in the form of a biradical intermediate), which leads to compounds *E*- and *Z*-**5**. The reaction mechanism proposed above (see Scheme 5), according to which the elimination of N_2 follows the addition of the second PTAD molecule, is confirmed by the absence of isomeric cyclopropanes **3b**.

In contrast to pyrazoline **1b**, pyrazolines **1a** and **1c** react with two equivalents of PTAD (60 °C, 30 min) to yield no products resulting from double addition of PTAD (like triazabicyclooctane **5**). Under these conditions, as with one equivalent of PTAD, the reaction products are compounds **3a** and **4** or cyclopropane **3c**; the second equivalent of PTAD remains intact. Obviously, the resulting pyrazolines **2a** and **2c** tend to undergo intramolecular transformations (ring closure into cyclopropanes **3a** and **3c** or formation of isomeric olefins **4**) rather than react with PTAD. It should be noted that 1-pyrazolines **6a**,**b** (see Refs 20—22) deprived of the 3,5-dioxo-4-phenyl-1,2,4-triazolidine substituent do not react with PTAD in such a way as to produce compounds like triazabicyclooctane **5**. Below 130 °C, the reaction does not occur at all; at higher temperatures, either starting component decomposes independently. Pyrazolines **6a**,**b** are mainly transformed into cyclopropanes and isomeric alkenes (similar transformations have been described earlier[22,23]), while PTAD yields a 1,3,5,7-tetraazabicyclo[3.3.0]octane derivative.[24]



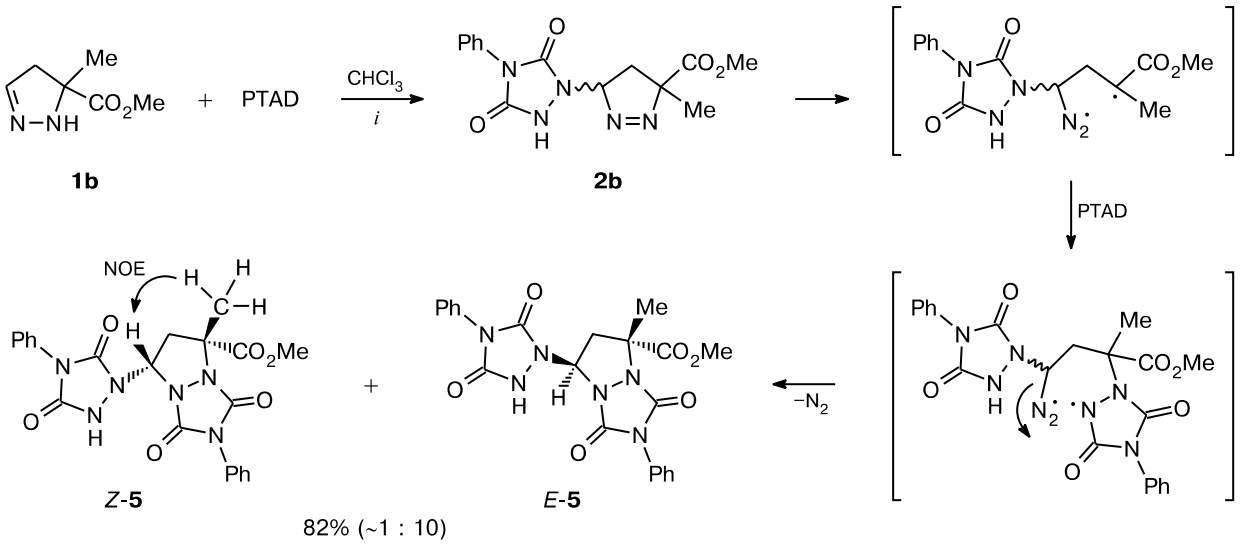
6a



6b

Strange as it may seem, PTAD also reacts with *N*-substituted 2-pyrazolines to give, in high yields, products for-

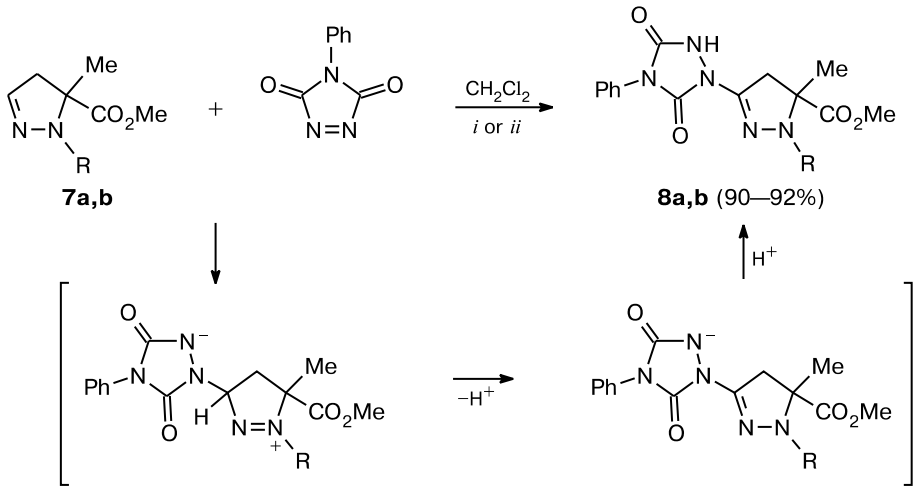
Scheme 5



82% (~1 : 10)

i. 60 °C, 30 min.

Scheme 6



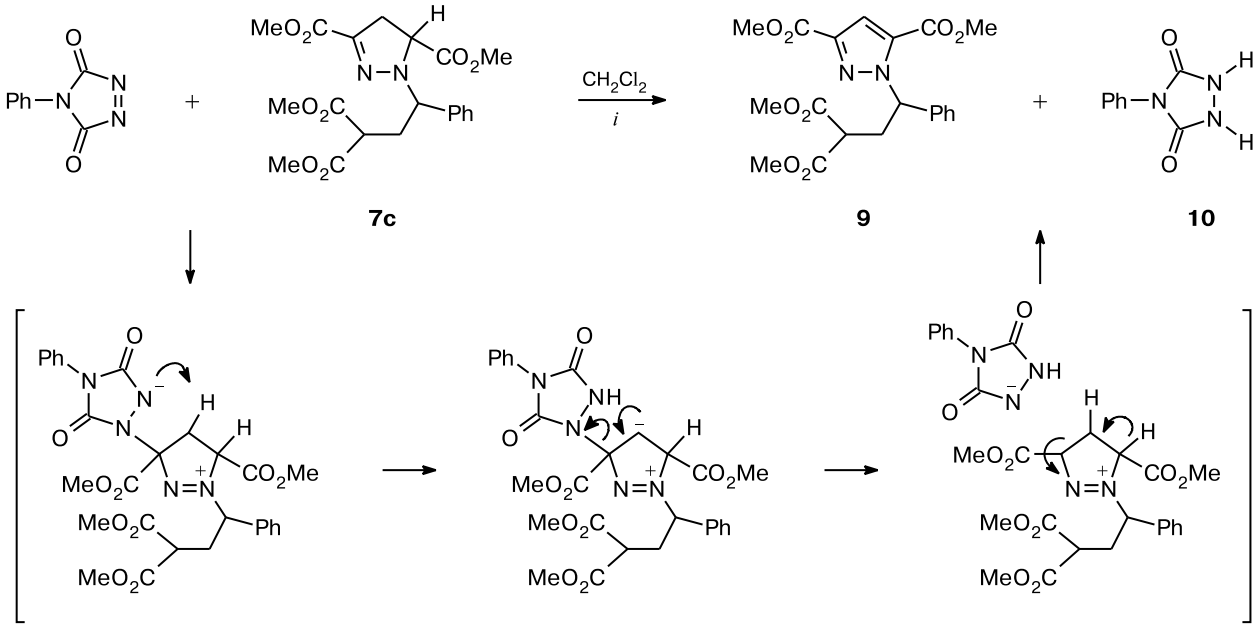
R = $CHPhCH_2CH(CO_2Me)_2$ (**a**), COPh (**b**)

Reaction conditions and products: *i*. 20 °C, 30 min, **8a**; *ii*. 35 °C, 90 h, **8b**.

mally derived by addition of PTAD to the H—C(3) bond of 2-pyrazolines **7a,b** (Scheme 6). Since the formation of the 1-pyrazoline structure is impossible, the C—N bond formation is followed by proton transfer from the pyrazoline fragment to the triazoline one and thus the 2-pyrazoline structure is retained in the reaction product.

In the case of *N*-alkylpyrazoline **7a** prepared from dimethyl 2-phenylcyclopropane-1,1-dicarboxylate and methyl 3-methyl-1-pyrazoline-3-carboxylate in the presence of scandium triflate,[25] the reaction occurs at room temperature and is completed in about 30 min, giving substituted 2-pyrazoline **8a**. The presence of the electron-withdrawing benzoyl substituent at the N atom in pyrazoline **7b** makes this compound appreciably less reactive: its reaction with PTAD at 35 °C takes 4 days and a twofold excess of PTAD is required for complete conversion of compound **7b**.

Scheme 7



i. 20 °C, 30 min.

Replacement of the proton in position 3 of the pyrazoline ring by a methoxycarbonyl group (as in, *e.g.*, 2-pyrazoline **7c** (see Ref. 25)) causes its reaction with PTAD to follow a redox pattern. As a result, 1,3,5-trisubstituted pyrazole **9** and 4-phenyl-1,2,4-triazolidine-3,5-dione (**10**),[26,27] which is insoluble in dichloromethane, are obtained in quantitative yields (Scheme 7). Apparently, in this case too, the first step involves addition of PTAD to the double bond of 2-pyrazoline **7c**, which is followed by double proton transfer from the pyrazoline ring in a bipolar intermediate to the N=N bond of PTAD and the formation of pyrazole **9**.

To sum up, 4-phenyl-1,2,4-triazoline-3,5-dione show high efficiency in reactions with various substituted 2-pyrazolines. Under slight heating, the resulting 1-pyrazolines can be smoothly transformed into dioxotriazolidinylcyclopropanes. After an appropriate transformation of the triazolidine ring (reduction or hydrolysis),[3—6,10] the latter can be of interest for the synthesis of substituted aminocyclopropanes or cyclopropylhydrazines.

Experimental

^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.1, 100.6, and 40.5 MHz, respectively) for solutions in $CDCl_3$ or CD_2Cl_2 containing 0.05% Me_4Si as the internal standard. For ^{15}N NMR spectra, CD_3NO_2 was used as the standard. The signals were assigned and the isomers of the compounds obtained were distinguished by homo- and heteronuclear 2D correlation techniques (DEPT, COSY, NOESY, HSQC, HMBC, and HOESY). ^{13}C,^{1}H-HOESY NMR spectra were recorded using a pulse "hoesy" program (AMX version[28]) for Bruker spectrometers with a mixing time of 2.0 s. Mass spectra were measured on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet probe). Pyrazolines **1a**,[29] **1b**,[30,31] **1c**,[32] **1d**,[33] **1e**,[34] and **1f** (see Ref. 35) were prepared by 1,3-dipolar cycloaddition reactions of diazo compounds with alkenes as described earlier; *N*-substituted pyrazolines **7a—c** were prepared according to our own procedures.[25] 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) was purchased from Aldrich. Solvents (reagent grade, >99.5%) were used without further purification.

Synthesis of (3,5-dioxotriazolidinyl)-1-pyrazolines 2a—f (general procedure). Powdery PTAD (105 mg, 0.6 mmol) was added in one portion at 0 °C to a solution of 2-pyrazoline **1** (0.6 mmol) in CH_2Cl_2 (5—7 mL). The reaction mixture was stirred for ~1 min to complete homogenization and decoloration. The resulting solutions of virtually pure pyrazolines **2a—f** are stable at 0 °C for several hours and can be used for further chemical transformations. For recording ^{1}H and ^{13}C NMR spectra, analogous reactions were carried out in an NMR tube by adding powdery PTAD (0.1 mmol) in one portion at 0 °C to a solution of 2-pyrazolines **1a—f** (0.1 mmol) in CD_2Cl_2 or $CDCl_3$ (0.5 mL). The reaction mixture was stirred at 0 °C for ~1 min and NMR spectra were recorded at the same temperature. The yields of 1-pyrazolines **2a—f** were >95%.

Methyl 3-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-4,5-dihydro-3*H*-pyrazole-3-carboxylate (2a). ^{1}H NMR ($CDCl_3$), δ: 2.35 (ddd, 1 H, H_a(4), ^2J = 14.0 Hz, ^3J = 8.4 Hz, ^3J = 4.3 Hz); 2.40 (ddd, 1 H, H_b(4), ^2J = 14.0 Hz, ^3J = 8.5 Hz, ^3J = 7.5 Hz); 3.79 (s, 3 H, OMe), 4.66 (ddd, 1 H, H_a(5), ^2J = 18.2 Hz, ^3J = 8.4 Hz, ^3J = 7.5 Hz); 5.01 (ddd, 1 H, H_b(5), ^2J = 18.2 Hz, ^3J = 8.5 Hz, ^3J = 4.3 Hz); 7.34—7.50 (m, 5 H, Ph); 8.05 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 27.4 (C(4)); 53.9 (OMe); 79.8 (C(5)); 106.5 (C(3)); 126.0 (C_o); 128.8 (C_p); 129.3 (C_m); 130.7 (C_{ipso}); 154.0, 154.6 (C=O); 166.1 (COO).

Methyl 5-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-3-methyl-4,5-dihydro-3*H*-pyrazole-3-carboxylate (2b). A 3 : 1 mixture of *E*- and *Z*-isomers. *E*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 1.55 (s, 3 H, Me); 1.95 (dd, 1 H, H_a(4), ^2J = 13.7 Hz, ^3J = 8.8 Hz); 2.18 (dd, 1 H, H_b(4), ^2J = 13.7 Hz, ^3J = 7.9 Hz); 3.80 (s, 3 H, OMe); 6.67 (dd, 1 H, H(5), ^3J = 8.8 Hz, ^3J = 7.9 Hz); 7.34—7.53 (m, 5 H, Ph); 7.80 (br.s, 1 H, NH). *Z*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 1.58 (s, 3 H, Me); 1.42 (dd, 1 H, H_a(4), ^2J = 13.7 Hz, ^3J = 8.8 Hz); 2.51 (dd, 1 H, H_b(4), ^2J = 13.7 Hz, ^3J = 8.8 Hz); 3.79 (s, 3 H, OMe); 6.58 (dd, 1 H, H(5), $^3J_1 \approx {}^3J_2$ = 8.8 Hz); 7.35—7.51 (m, 5 H, Ph); 7.80 (br.s, 1 H, NH).

Dimethyl 3-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-4,5-dihydro-3*H*-pyrazole-3,5-dicarboxylate (2c). A 2.8 : 1 mixture of *E*- and *Z*-isomers. *E*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 2.56 (dd, 1 H, H_a(4), ^2J = 14.5 Hz, ^3J = 5.6 Hz); 2.83 (dd, 1 H, H_b(4), ^2J = 14.5 Hz, ^3J = 9.4 Hz); 3.82, 3.84 (both s, 3 H each, 2 OMe); 5.77 (dd, 1 H, H(5), ^3J = 9.4 Hz, ^3J = 5.6 Hz); 7.39—7.54 (m, 5 H, Ph); 8.45 (br.s, 1 H, NH). ^{13}C NMR (CD_2Cl_2), δ: 30.3 (C(4)); 54.7, 55.6 (OMe); 94.9 (C(5)); 108.9 (C(3)); 127.5 (C_o); 130.4 (C_p); 130.8 (C_m); 132.2 (C_{ipso}); 155.4, 155.8 (C=O); 167.4, 168.3 (COO). *Z*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 2.58 (dd, 1 H, H_a(4), ^2J = 14.1 Hz, ^3J = 9.1 Hz); 2.77 (dd, 1 H, H_b(4), ^2J = 14.1 Hz, ^3J = 8.3 Hz); 3.79, 3.88 (both s, 3 H each, 2 OMe); 5.47 (dd, 1 H, H(5), ^3J = 9.1 Hz, ^3J = 8.3 Hz); 7.39—7.54 (m, 5 H, Ph); 8.45 (br.s, 1 H, NH). ^{13}C NMR (CD_2Cl_2), δ: 32.4 (C(4)); 54.2, 55.7 (OMe); 94.5 (C(5)); 109.4 (C(3)); 127.6 (C_o); 130.4 (C_p); 130.8 (C_m); 132.4 (C_{ipso}); 155.6, 156.2 (C=O); 166.6, 168.8 (COO).

Dimethyl (*E*)-5-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-4-phenyl-4,5-dihydro-3*H*-pyrazole-3,3-dicarboxylate (2d). ^{1}H NMR ($CDCl_3$), δ: 3.40, 3.85 (both s, 3 H each, 2 OMe); 4.20 (d, 1 H, H(4), ^3J = 10.4 Hz); 6.90 (d, 1 H, H(5), ^3J = 10.4 Hz); 7.03—7.65 (m, 11 H, 2 Ph, NH).

5-(3,5-Dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-3,3-diphenyl-4,5-dihydro-3*H*-pyrazole (2e). ^{1}H NMR ($CDCl_3$), δ: 2.18 (dd, 1 H, H_a(4), ^2J = 13.2 Hz, ^3J = 10.1 Hz); 2.93 (dd, 1 H, H_b(4), ^2J = 13.2 Hz, ^3J = 7.3 Hz); 6.30 (dd, 1 H, H(5), ^3J = 10.1 Hz, ^3J = 7.3 Hz); 7.21—7.53 (m, 15 H, Ph); 7.60 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 34.1 (C(4)); 95.7 (C(5)); 100.3 (C(3)); 125.7 (C_o, Ph—N); 126.6, 126.8 (C_o, Ph—C); 128.0, 128.3 (C_p, Ph—C); 128.7 (C_p, Ph—N), 128.8, 129.0 (C_m, Ph—C); 129.3 (C_m, Ph—N); 130.9 (C_{ipso}, Ph—N); 139.8, 143.7 (C_{ipso}, Ph—C); 153.1, 154.3 (C=O).

Methyl 5-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-*exo*-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-3-ene-5-carboxylate (2f). ^{1}H NMR (CD_2Cl_2), δ: 0.77, 0.97 (both m, 1 H each, $H_2C(10)$, ^2J = 11.1 Hz); 1.15, 1.26, 1.48, 1.62 (all m, 1 H each, $H_2C(8)$, $H_2C(9)$); 2.01, 2.93 (both m, 1 H each, H(1), H(7)); 2.46 (m, 1 H, H(6), $J_{2,6}$ = 5.9 Hz); 3.75 (s, 3 H, OMe); 4.85 (m, 1 H, H(2), $J_{2,6}$ = 5.9 Hz); 7.32—7.51 (m, 5 H, Ph); 8.85 (br.s, 1 H, NH). ^{13}C NMR (CD_2Cl_2), δ: 25.2, 28.7, 32.7 (C(8), C(9), C(10)); 37.8, 38.0, 44.6 (C(1), C(6), C(7)); 53.2 (OMe); 99.3 (C(2)); 107.2 (C(5)); 125.7 (C_o); 128.7 (C_p); 129.2 (C_m); 130.6 (C_{ipso}); 153.8, 154.2 (C=O); 165.7 (COO).

Synthesis of (3,5-dioxotriazolidinyl)cyclopropanes 3a—f (general procedure). Powdery PTAD (105 mg, 0.6 mmol) was added at 20 °C to a solution of 2-pyrazoline **1** (0.6 mmol) in chloroform (7 mL). The reaction mixture was stirred for ~1 min to complete homogenization and decoloration and then refluxed for 15 min (~60 °C) until gas evolution ceased. For compound **1a**, the reaction was carried out at 40 °C for 2.5 h; in specific cases, the reaction medium was boiling dichloroethane (see Table 1). Then the reaction mixture was filtered through a cotton plug and concentrated *in vacuo*. If required, the residue was recrystallized from diethyl ether or Et_2O—hexane (2 : 1) and dried *in vacuo* (0.01 Torr). The yields of cyclopropanes **3a—f** were 92—98%, colorless crystals.

Methyl 1-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)cyclopropane-1-carboxylate (3a), m.p. 138—140 °C. Found (%): C, 56.73; H, 4.76; N, 15.07. $C_{13}H_{13}N_3O_4$. Calculated (%): C, 56.25; H, 4.72; N, 14.71. MS, *m/z* (I_{rel} (%)): 275 (15) $[M]^+$, 260 (1) $[M - Me]^+$, 243 (7) $[M - OMe]^+$, 232 (35), 216 (13) $[M - CO_2Me]^+$, 200 (13) $[M - Ph]^+$, 177 (12), 172 (21), 156 (12), 145 (26), 141 (50), 134 (14), 127 (9), 119 (100), 96 (19), 91 (31), 84 (13), 77 (13), 69 (11), 64 (18), 59 (17). ^{1}H NMR ($CDCl_3$), δ: 1.45 (m, 2 H, $H_a(2)$, $H_a(3)$); 1.58 (m, 2 H, $H_b(2)$, $H_b(3)$); 3.69 (s, 3 H, OMe), 7.32—7.55 (m, 5 H, Ph); 8.3 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 16.4 (CH_2CH_2); 39.7 (C(1)); 53.0 (OMe); 126.0 (C_o); 128.5 (C_p); 129.2 (C_m); 131.2 (C_{ipso}); 154.2, 154.3 (C=O); 170.6 (COO).

Methyl 2-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-1-methylcyclopropane-1-carboxylate (3b). A 2.9 : 1 mixture of *E*- and *Z*-isomers, m.p. 53—54 °C. Found (%): C, 57.69; H, 5.12; N, 14.67. $C_{14}H_{15}N_3O_4$. Calculated (%): C, 58.13; H, 5.23; N, 14.53. MS, *m/z* (I_{rel} (%)): 289 (19) $[M]^+$, 257 (26) $[M - MeOH]^+$, 230 (7) $[M - CO_2Me]^+$, 214 (12), 187 (11), 177 (24), 154 (21), 138 (25), 119 (100), 112 (97), 91 (39), 69 (35). *E*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 1.37 (s, 3 H, Me); 1.37 (dd, 1 H, $H_a(3)$, ^2J = 5.8 Hz, ^3J = 4.9 Hz); 1.70 (dd, 1 H, $H_b(3)$, ^2J = 5.8 Hz, ^3J = 8.3 Hz); 3.66 (dd, 1 H, H(2), ^3J = 8.3 Hz, ^3J = 4.9 Hz); 3.67 (s, 3 H, OMe); 7.33—7.51 (m, 5 H, Ph); 8.40 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.6 (Me); 20.9 (C(3)); 25.2 (C(1)); 40.6 (C(2)); 52.4 (OMe); 125.7 (C_o); 128.5 (C_p); 129.2 (C_m); 131.1 (C_{ipso}); 153.2, 153.5 (C=O); 173.5 (COO). *Z*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 1.25 (dd, 1 H, $H_a(3)$, ^2J = 6.3 Hz, ^3J = 7.9 Hz); 1.35 (s, 3 H, Me); 2.10 (dd, 1 H, $H_b(3)$, ^2J = 6.3 Hz, ^3J = 5.1 Hz); 3.13 (dd, 1 H, H(2), ^3J = 7.9 Hz, ^3J = 5.1 Hz); 3.68 (s, 3 H, OMe); 7.33—7.51 (m, 5 H, Ph); 8.40 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 18.7 (Me); 20.9 (C(3)); 26.2 (C(1)); 42.2 (C(2)); 52.8 (OMe); 125.7 (C_o); 128.4 (C_p); 129.2 (C_m); 131.2 (C_{ipso}); 152.6, 154.5 (C=O); 172.7 (COO).

Dimethyl 1-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)cyclopropane-1,2-dicarboxylate (3c). The ratio of *E*- and *Z*-isomers in the product was 2.6 : 1 (60 °C, 15 min; m.p. 45—46 °C) or 4.9 : 1 (20 °C, 3 h (see Table 1); m.p. 51—52 °C). Found (%): C, 53.89; H, 4.69; N, 12.75. $C_{15}H_{15}N_3O_6$. Calculated (%): C, 54.06; H, 4.54; N, 12.61. MS, *m/z* (I_{rel} (%)): 333 (16) $[M]^+$, 302 (6) $[M - OMe]^+$, 290 (6), 274 (6) $[M - CO_2Me]^+$, 258 (2), 231 (5), 215 (2), 199 (3), 183 (11), 177 (12), 157 (86), 156 (70), 119 (100), 91 (55), 59 (80). IR, ν/cm^{-1} ($CHCl_3$): 3360 (NH), 1784, 1728 (O=CO, NC=O), 1600, 1504, 1440, 1428. *E*-isomer. ^{1}H NMR ($CDCl_3$), δ: 1.83 (dd, 1 H, $H_a(3)$, ^2J = 6.1 Hz, ^3J = 10.0 Hz); 2.15 (dd, 1 H, $H_b(3)$, ^2J = 6.1 Hz, ^3J = 8.5 Hz); 2.71 (dd, 1 H, H(2), ^3J = 10.0 Hz, ^3J = 8.5 Hz); 3.71, 3.73 (both s, 3 H each, 2 OMe); 7.35—7.51 (m, 5 H, Ph); 8.95 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 19.2 (C(3)); 30.5 (C(2)); 44.7 (C(1)); 52.8, 53.3 (OMe); 125.8 (C_o); 128.6 (C_p); 129.2 (C_m); 131.0 (C_{ipso}); 154.0, 154.4 (C=O); 167.5, 167.9 (COO). ^{15}N NMR ($CDCl_3$), δ: −254.54 (1 N); −254.59 (2 N). *Z*-isomer. ^{1}H NMR ($CDCl_3$), δ: 2.02 (dd, 1 H, $H_a(3)$, ^2J = 6.1 Hz, ^3J = 9.1 Hz), 2.29 (dd, 1 H, $H_b(3)$, ^2J = 6.1 Hz, ^3J = 7.9 Hz), 2.77 (dd, 1 H, H(2), ^3J = 9.1 Hz, ^3J = 7.9 Hz); 3.70, 3.75 (both s, 3 H each, 2 OMe); 7.35—7.51 (m, 5 H, Ph); 8.95 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 20.6 (C(3)); 28.8 (C(2)); 44.7 (C(1)); 53.0, 53.6 (OMe); 126.0 (C_o); 128.6 (C_p); 129.2 (C_m); 131.1 (C_{ipso}); 154.0, 154.4 (C=O); 168.5, 168.8 (COO). ^{15}N NMR ($CDCl_3$), δ: −254.54 (1 N); −254.59 (2 N).

Dimethyl (*E*)-2-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-3-phenylcyclopropane-1,1-dicarboxylate (3d), m.p. 68—69 °C. Found (%): C, 61.25; H, 4.88; N, 10.65. $C_{21}H_{19}N_3O_6$. Calculated (%): C, 61.61; H, 4.68; N, 10.26. MS, *m/z* (I_{rel} (%)): 409 (1) $[M]^+$, 377 (3) $[M - MeOH]^+$, 345 (31), 318 (11), 279 (43), 232 (40), 219 (28), 187 (31), 173 (40), 159 (33), 145 (21), 131 (33), 119 (100), 116 (66), 103 (50), 91 (100), 77 (60), 59 (56). ^{1}H NMR ($CDCl_3$), δ: 3.50, 3.84 (both s, 3 H each, 2 OMe); 3.96 (d, 1 H, H(3), ^3J = 6.1 Hz); 4.27 (d, 1 H, H(2), ^3J = 6.1 Hz); 7.15—7.55 (m, 11 H, 2 Ph, NH). ^{13}C NMR ($CDCl_3$), δ: 36.7 (C(3)); 42.1 (C(1)); 45.0 (C(2)); 52.8, 53.8 (OMe); 125.7 (C_o, Ph—N); 128.1, 128.3 (C_p); 128.6, 128.7, 129.2 (C_o, Ph—C, both C_m); 131.0, 132.0 (C_{ipso}); 153.5, 154.0 (C=O); 165.4, 167.3 (COO).

1-(3,5-Dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-2,2-diphenylcyclopropane (3e), m.p. 87—89 °C. MS, *m/z* (I_{rel} (%)): 250 (2) $[M - PhNCO]^+$, 249 (3), 219 (2), 183 (36), 177 (28), 165 (17), 152 (9), 119 (34) $[PhNCO]^+$, 105 (93), 77 (100), 51 (53). HRMS: found *m/z* 368.1381; calculated for $C_{23}H_{19}N_3O_2$: $[M - H]^+$ 368.1394. ^{1}H NMR ($CDCl_3$), δ: 1.71 (dd, 1 H, $H_a(3)$, ^2J = 6.6 Hz, ^3J = 8.2 Hz); 2.33 (dd, 1 H, $H_b(3)$, ^2J = 6.6 Hz, ^3J = 4.3 Hz); 3.64 (dd, 1 H, H(1), ^3J = 6.6 Hz, ^3J = 4.3 Hz), 7.18—7.51 (m, 15 H, 3 Ph), 7.61 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 18.4 (C(3)); 37.1 (C(2)); 41.5 (C(3)); 125.6 (C_o, Ph—N); 127.2, 127.5 (C_o, Ph—C); 128.4 (C_p, Ph—N); 128.83, 128.85, 129.1, 129.2, 129.4 (C_p, Ph—C, C_m); 131.1 (C_{ipso}, Ph—N); 138.8, 143.2 (C_{ipso}, Ph—C); 153.6, 154.0 (C=O).

Methyl 3-*anti*-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-*exo*-tricyclo[3.2.1.0^{2,4}]octane-3-carboxylate (3f), m.p. 65—66 °C. Found (%): C, 63.31; H, 5.85; N, 12.55. $C_{18}H_{19}N_3O_4$. Calculated (%): C, 63.33; H, 5.61; N, 12.31. MS, *m/z* (I_{rel} (%)): 341 (30) $[M]^+$, 309 (4) $[M - MeOH]^+$, 298 (6) $[M - CO_2Me]^+$, 282 (4), 268 (3), 255 (4), 239 (8), 207 (14), 179 (9), 177 (9), 163 (12), 119 (100), 105 (22), 91 (59), 77 (45), 66 (32), 59 (26). ^{1}H NMR ($CDCl_3$), δ: 0.83, 0.87 (both m, 1 H each, $H_2C(8)$, ^2J = 13.0 Hz); 1.30 (m, 2 H, $H_{endo}(6)$, $H_{endo}(7)$); 1.52 (m, 2 H, $H_{endo}(6)$, $H_{endo}(7)$); 1.82 (m, 2 H, H(1), H(5)); 2.68 (m, 2 H, H(2), H(4)); 3.75 (s, 3 H, OMe); 7.33—7.54 (m, 5 H, Ph); 8.40 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 28.7 (C(6), C(7)); 30.3 (C(8)); 30.7 (C(2), C(4)); 35.9 (C(1), C(5)); 43.6 (C(3)); 52.9 (OMe); 125.7 (C_o); 128.3 (C_p); 129.1 (C_m); 131.2 (C_{ipso}); 151.4, 152.9 (C=O); 168.3 (COO).

Synthesis of methyl (*E*)- and (*Z*)-2-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)but-2-enoates (*E*- and *Z*-4) in a mixture with cyclopropane 3a. Powdery PTAD (105 mg, 0.6 mmol) was added in one portion at 20 °C to a solution of 2-pyrazoline **1a** (77 mg, 0.6 mmol) in dichloroethane (7 mL). The reaction mixture was stirred for ~1 min to complete homogenization and decoloration and refluxed until gas evolution ceased (83 °C,

~30 min). After cooling, the mixture was filtered through a cotton plug, concentrated *in vacuo*, and dried (0.01 Torr). The yield of the product was 161 mg (98%), colorless powdery solid, m.p. 146—149 °C. According to ^{1}H and ^{13}C NMR data, the product consists of cyclopropane **3a** and unsaturated compounds *E*- and *Z*-**4** in a ratio of ~10 : 4 : 1. These compounds are inseparable by chromatography on SiO_2 or crystallization. Isomer *E*-**4**. ^{1}H NMR ($CDCl_3$), δ: 2.16 (d, 3 H, Me, ^3J = 7.5 Hz); 3.80 (s, 3 H, OMe); 6.72 (q, 1 H, H(3), ^3J = 7.5 Hz); 7.36—7.53 (m, Ph); 8.40 (br.s, NH). ^{13}C NMR ($CDCl_3$), δ: 14.8 (Me); 52.5 (OMe); 125.9 (C_o); 127.0 (C(2)); 128.6 (C_p); 129.3 (C_m); 131.2 (C_{ipso}); 145.7 (C(3)); 154.1, 154.5 (C=O); 162.9 (COO). Isomer *Z*-**4**. ^{1}H NMR ($CDCl_3$), δ: 1.94 (d, 3 H, Me, ^3J = 7.1 Hz); 3.91 (s, 3 H, OMe); 7.21 (q, 1 H, H(3), ^3J = 7.1 Hz); 7.36—7.53 (m, Ph); 8.40 (br.s, NH). ^{13}C NMR ($CDCl_3$), δ: 14.2 (Me); 52.2 (OMe); 125.8 (C_o); 126.9 (C(2)); 128.6 (C_p); 129.3 (C_m); 131.2 (C_{ipso}); 145.4 (C(3)); 154.0, 154.4 (C=O); 163.0 (COO).

Methyl (*E*)- and (*Z*)-6-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-8-methyl-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.3.0]-octane-8-carboxylate (5). Powdery PTAD (123 mg, 0.7 mmol) was added at 20 °C to a solution of 2-pyrazoline **1a** (50 mg, 0.35 mmol) in chloroform (7 mL). The reaction mixture was stirred for 1 min to complete homogenization and then refluxed for 30 min until gas evolution ceased. The solvent was removed *in vacuo* and the product was recrystallized from diethyl ether. The yield of triazabicyclo[3.3.0]octane **5** as a ~10 : 1 mixture of *E*- and *Z*-isomers was 134 mg (82%), colorless crystals, m.p. 111—112 °C. Found (%): C, 56.97; H, 4.52; N, 18.06. $C_{22}H_{20}N_6O_6$. Calculated (%): C, 56.89; H, 4.34; N, 18.10. MS, *m/z* (I_{rel} (%)): 288 (47) $[M - PhC_2HN_3O_2]^+$, 230 (15), 177 (23) $[PhC_2H_2N_3O_2]^+$, 169 (13), 141 (100), 119 (84), 109 (18), 97 (21), 91 (44), 77 (26), 64 (27). IR, ν/cm^{-1} ($CHCl_3$): 3352 (NH), 1772, 1728 (O=C), 1600, 1504, 1412. *E*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 1.73 (s, 3 H, Me); 2.95 (dd, 1 H, H_a(7), ^2J = 13.8 Hz, ^3J = 7.1 Hz); 3.04 (dd, 1 H, H_b(7), ^2J = 13.8 Hz, ^3J = 9.0 Hz); 3.73 (s, 3 H, OMe); 6.16 (dd, 1 H, H(6), ^3J = 9.0 Hz, ^3J = 7.1 Hz); 7.30—7.52 (m, Ph); 8.55 (br.s, NH). ^{13}C NMR ($CDCl_3$), δ: 21.9 (Me); 42.4 (C(7)); 53.9 (OMe); 67.1 (C(6)); 67.5 (C(8)); 125.9, 126.0 (C_o); 128.77, 128.82 (C_p); 129.4 (C_m); 130.7, 131.2 (C_{ipso}); 152.9, 153.2, 153.8, 155.3 (C=O); 171.3 (COO). *Z*-isomer. ^{1}H NMR (CD_2Cl_2), δ: 1.76 (s, 3 H, Me); 2.80 (dd, 1 H, H_a(7), ^2J = 13.7 Hz, ^3J = 3.2 Hz); 3.59 (dd, 1 H, H_b(7), ^2J = 13.7 Hz, ^3J = 8.3 Hz); 3.77 (s, 3 H, OMe); 6.25 (dd, 1 H, H(6), ^3J = 8.3 Hz, ^3J = 3.2 Hz); 7.30—7.52 (m, Ph); 8.55 (br.s, NH). ^{13}C NMR ($CDCl_3$), δ: 22.6 (Me); 45.8 (C(7)); 54.3 (OMe); 64.5 (C(8)); 67.1 (C(6)); 125.69, 125.74 (C_o); 128.6, 128.7 (C_p); 129.4 (C_m); 130.8, 131.2 (C_{ipso}); 153.75, 153.76, 154.98, 154.99 (C=O); 172.2 (COO).

Dimethyl 2-{2-[3-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-5-methoxycarbonyl-5-methyl-4,5-dihydro-1*H*-pyrazol-1-yl]-2-phenylethyl}malonate (8a). Powdery PTAD (35 mg, 0.2 mmol) was added at 20 °C to a solution of 2-pyrazoline **7a** (a ~1 : 1 mixture of two diastereomers;[25] 75 mg, 0.2 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min, filtered through a cotton plug, concentrated *in vacuo*, and dried (0.01 Torr). The yield of compound **8a** as a ~1 : 1 mixture of two diastereomers (90—94% purity, ^{1}H NMR) was 110 mg, colorless oil. Attempted purification by preparative TLC on SiO_2 only contaminated the product. Isomer *S*,R**-**8a**. ^{1}H NMR ($CDCl_3$), δ: 1.51 (s, 3 H, Me); 2.34 (ddd, 1 H, H_a(1′), ^2J = 14.3 Hz, ^3J = 8.4 Hz, ^3J = 5.7 Hz); 2.71 (ddd, 1 H, H_b(1′), ^2J = 14.3 Hz, ^3J = 9.3 Hz, ^3J = 6.2 Hz); 2.98 (s, 3 H, OMe); 3.21, 3.85 (both d, 1 H each, H_2C(4″), ^2J = 17.3 Hz); 3.56 (dd, 1 H, H(2′), ^3J = 8.4 Hz, ^3J = 6.2 Hz); 3.73, 3.74 (both s, 3 H each, 2 OMe); 4.13 (dd, 1 H, H(2′); ^3J = 9.3 Hz, ^3J = 5.7 Hz); 7.20—7.55 (m, 2 Ph and NH). Isomer *R*,R**-**8a**. ^{1}H NMR ($CDCl_3$), δ: 1.09 (s, 3 H, Me); 2.31 (ddd, 1 H, H_a(1′), ^2J = 14.4 Hz, ^3J = 9.5 Hz, ^3J = 4.9 Hz); 2.67 (ddd, 1 H, H_b(1′), ^2J = 14.4 Hz, ^3J = 9.9 Hz, ^3J = 5.1 Hz); 3.22, 3.84 (both d, 1 H each, H_2C(4″), ^2J = 17.6 Hz); 3.70 (dd, 1 H, H(2′), ^3J = 9.5 Hz, ^3J = 5.1 Hz); 3.71, 3.75, 3.80 (all s, 3 H each, 3 OMe); 4.32 (dd, 1 H, H(2′), ^3J = 9.9 Hz, ^3J = 4.9 Hz); 7.20—7.55 (m, 2 Ph, NH).

Methyl 1-benzoyl-3-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-5-carboxylate (8b). Powdery PTAD (52 mg, 0.3 mmol) was added to a solution of 2-pyrazoline **7b** (74 mg, 0.3 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred under argon at room temperature for ~90 h, while adding PTAD as rapidly as it was being consumed (decoloration of the solution); the total amount of PTAD added was 122 mg (0.7 mmol). The reaction mixture was filtered through a cotton plug and concentrated *in vacuo*. The residue was dissolved in diethyl ether—hexane (1 : 1) and the product was precipitated with hexane and dried *in vacuo* (0.01 Torr). The yield of compound **8b** was 113 mg (90%), colorless crystals, m.p. 110—113 °C. Found (%): C, 59.36; H, 4.64; N, 16.16. $C_{21}H_{19}N_5O_5$. Calculated (%): C, 59.85; H, 4.54; N, 16.62. MS, *m/z* (I_{rel} (%)): 421 (1) $[M]^+$, 362 (1) $[M - CO_2Me]^+$, 177 (4), 141 (1), 119 (14), 105 (100), 91 (9), 77 (37). ^{1}H NMR ($CDCl_3$), δ: 1.87 (s, 3 H, Me); 3.46, 3.79 (both d, 1 H each, H_2C(4), ^2J = 18.4 Hz); 3.81 (s, 3 H, OMe); 7.28—7.56 (m, 9 H, Ph, C_m, C_p, Bz, NH); 7.82 (m, 2 H, C_o, Bz). ^{13}C NMR ($CDCl_3$), δ: 22.0 (Me); 44.3 (C(4)); 55.2 (OMe); 68.3 (C(5)); 125.8 (C_o, Bz); 127.9 (C_o); 129.1 (C_p); 129.5, 129.6 (C_m); 130.3 (C_{ipso}); 131.2 (C_p, Bz); 133.7 (C_{ipso}, Bz); 144.0, 147.4 (C=O); 150.8 (C(3)); 166.2 (C=O); 171.3 (COO).

Dimethyl 2-(3,5-dimethoxycarbonyl-1*H*-pyrazol-1-yl)-2-phenylethylmalonate (9). Powdery PTAD (42 mg, 0.24 mmol) was added to a solution of *N*-substituted pyrazoline-3,5-dicarboxylate **7c** (*R*,R**-diastereomer;[25] 100 mg, 0.24 mmol) in chloroform (5 mL). The reaction mixture was stirred at room temperature for 15 min. The precipitate of 4-phenyl-1,2,4-triazolidine-3,5-dione (**10**) that formed was filtered off (m.p. 206—207 °C; the ^{1}H and ^{13}C NMR spectra agree with the literature data[34,35]). The mother liquor was concentrated *in vacuo* and the residue was dried (0.01 Torr). The yield of pyrazole **9** was 100 mg (~100%), colorless oil. Found (%): C, 57.18; H, 5.33; N, 6.88. $C_{20}H_{22}N_2O_8$. Calculated (%): C, 57.40; H, 5.30; N, 6.70. MS, *m/z* (I_{rel} (%)): 418 (7) $[M]^+$, 387 (2) $[M - OMe]^+$, 319 (1), 295 (2), 287 (70), 273 (85), 255 (16), 235 (12), 213 (21), 203 (14), 185 (44), 171 (28), 153 (17), 121 (65), 115 (100), 103 (26), 91 (27), 77 (27), 59 (82). ^{1}H NMR ($CDCl_3$), δ: 2.82—2.91 (m, 1 H, H_a(1′)); 3.13—3.25 (m, 2 H, H_b(1′), H(2)); 3.70, 3.72, 3.85, 3.93 (all s, 3 H each, 4 OMe); 6.60 (m, 1 H, H(2′)); 7.26 (m, 1 H, HC_p); 7.30 (m, 2 H, HC_m); 7.34 (s, 1 H, H(4″)); 7.41 (m, 2 H, HC_o). ^{13}C NMR ($CDCl_3$), δ: 34.4 (C(1′)); 48.9 (C(2)); 52.15, 52.23, 52.67, 52.71 (4 OMe); 61.8 (C(2′)); 114.6 (C(4″)); 127.3 (C_o); 128.4 (C_p); 128.7 (C_m); 133.9 (C(5″)); 138.9 (C(3″)); 142.6 (C_{ipso}); 159.5 (C(5″) COO); 162.1 (C(3″) COO); 168.9, 169.1 (2 COO).

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References

1. E. L. Clennan, A. D. Earlywine, *J. Am. Chem. Soc.*, 1987, **109**, 7104.
2. T. Sheradsky, R. Moshenberg, *J. Org. Chem.*, 1984, **49**, 587.
3. J. Nakayama, R. Hasemi, *J. Am. Chem. Soc.*, 1990, **112**, 5654.
4. K. Makino, Y. Henmi, M. Terasawa, O. Hara, Y. Hamada, *Tetrahedron Lett.*, 2005, **46**, 555.
5. L. McElwee-White, D. A. Dougherty, *J. Am. Chem. Soc.*, 1982, **104**, 4722.
6. J. W. Morzycki, R. R. Sicinski, *Acta Chim. Hung.*, 1985, **120**, 239.
7. C. C. Cheng, F. D. Greene, *J. Org. Chem.*, 1984, **49**, 2917.
8. Z. Syrgiannis, F. Koutsianopoulos, K. W. Muir, Y. Elemes, *Tetrahedron Lett.*, 2009, **50**, 277.
9. C. C. Cheng, C. A. Seymour, M. A. Petti, F. D. Greene, *J. Org. Chem.*, 1984, **49**, 2910.
10. A. H. Gau, G. L. Lin, B. J. Uang, F. L. Liao, S. L. Wang, *J. Org. Chem.*, 1999, **64**, 2194.
11. E. Corey, B. Snider, *Tetrahedron Lett.*, 1973, **14**, 277.
12. Y. Elemes, C. S. Foote, *J. Am. Chem. Soc.*, 1992, **114**, 6044.
13. J. S. Chen, K. N. Houk, C. S. Foote, *J. Am. Chem. Soc.*, 1997, **119**, 9852.
14. A. Christoforou, G. Nicolaou, Y. Elemes, *Tetrahedron Lett.*, 2006, **47**, 9211.
15. K. A. Ajaj, L. Hennig, M. Findeisen, S. Giesa, D. Müller, P. Welzel, *Tetrahedron*, 2002, **58**, 8439.
16. R. M. Wilson, A. Hengge, *J. Org. Chem.*, 1987, **52**, 2699.
17. R. Breslow, R. J. Corcoran, B. B. Snider, R. J. Doll, P. L. Khanna, R. Kaleya, *J. Am. Chem. Soc.*, 1977, **99**, 905.
18. G. Nicolaou, Y. Elemes, *Tetrahedron Lett.*, 2008, **49**, 6324.
19. P. S. Engel, *Chem. Rev.*, 1980, **80**, 99.
20. R. Touillaux, B. Tinant, M. V. Meerssche, J. M. Dereppe, *J. Chim. Phys. Phys. Chim. Biol.*, 1980, **77**, 319.
21. K. Auwers, F. König, *Liebigs Ann. Chem.*, 1932, **496**, 27.
22. J. Martelli, R. Gree, *J. Chem. Soc., Chem. Commun.*, 1980, 355.
23. M. P. Doyle, R. L. Dorow, W. H. Tamblyn, *J. Org. Chem.*, 1982, **47**, 4059.
24. H. Wamhoff, K. Wald, *Chem. Ber.*, 1977, **110**, 1699.
25. Yu. V. Tomilov, R. A. Novikov, O. M. Nefedov, *Tetrahedron*, 2010, **66**, 9151.
26. B. T. Gilles, J. D. Hagarty, *J. Org. Chem.*, 1966, **32**, 330.
27. R. A. Izydore, A. A. Ribeiro, I. H. Hall, *J. Org. Chem.*, 1996, **61**, 3733.
28. C. Yu, G. C. Levy, *J. Am. Chem. Soc.*, 1984, **106**, 6533.
29. J. A. Moore, *J. Org. Chem.*, 1955, **20**, 1607.
30. E. Buchner, A. Papendieck, *Liebigs Ann. Chem.*, 1893, **273**, 232.
31. M. P. Doyle, M. R. Colsman, R. L. Dorow, *J. Heterocycl. Chem.*, 1983, **20**, 943.
32. A. A. Ouyahia, G. Leroy, J. Weiler, R. Touillaux, *Bull. Soc. Chim. Belg.*, 1976, **85**, 545.
33. R. Tuloup, R. Danion-Bougot, D. Danion, J. P. Pradere, *Tetrahedron Lett.*, 1988, **29**, 6249.
34. E. E. Schweizer, C. S. Kim, *J. Org. Chem.*, 1971, **36**, 4033.
35. V. A. Gorpinchenko, E. A. Yatsynich, D. V. Petrov, L. T. Karachurina, R. U. Hisamutdinova, N. Zh. Baschenko, V. A. Dokichev, Yu. V. Tomilov, M. S. Yunusov, O. M. Nefedov, *Pharm. Chem. J. (Russ.)*, 2005, **39**, 9.

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