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Synthesis and Photochemical Decomposition of Pyrazolines from Homochiral Amino Pentenoates. A Laser Flash-Photolysis Study.

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Abstract. Optically pure pyrazolines have been synthesized by cycloaddition of diazomethane to homochiral amino pentenoates, facial diastereoselectivity being the opposite depending on the *Z*/*E* stereochemistry of the precursors. Photo-decomposition of these pyrazolines to the corresponding cyclopropanes has been shown to occur stereospecifically and has been studied in order to find the optimal conditions and to establish the influence of sensitizers. The transient behaviour of the pyrazoline triplet state has been analyzed by laser flash photolysis either after direct excitation or after energy transfer from benzophenone. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Photochemically induced decomposition of pyrazolines is an efficient method to synthesize cyclopropane derivatives, alternatively to their thermolysis that results in the production of insertion olefins. Although this synthetic protocol is well established,[1] mechanistic details on this photochemical process[2] as well as its photophysics have been the subject of few published works.[3]

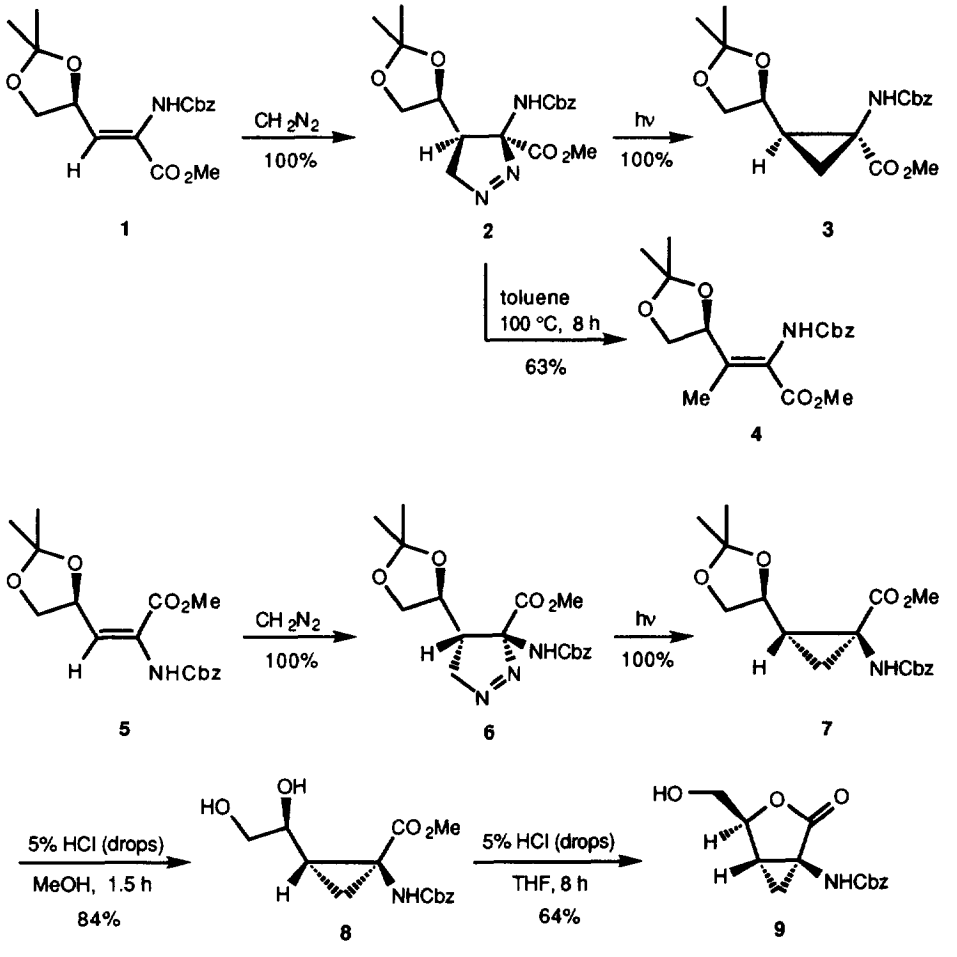
As a part of a research project on the synthesis of several kinds of cyclopropane products, we accomplished the 1,3-dipolar cycloaddition of diazomethane to the homochiral isomeric amino pentenoates **1** and **5**, the resultant pyrazolines **2** and **6** being respectively decomposed to furnish the corresponding cyclopropanes **3** and **7** (Scheme 1) which are synthetic precursors to a variety of products.[4] This purpose led us to explore the factors influencing the reactivity of these systems and the formation of by-products such as the cycloreversion and the insertion olefins, in order to optimize the reaction conditions.

We report herein the results of the study on the photolysis of these pyrazolines. It has been shown that the triplet transient behaviour of pyrazolines is not easy to follow by laser flash photolysis (LFP) under direct irradiation and, usually, sensitization is needed.[3b,c] In our systems, however, the transient absorption of the triplet has been recorded and analyzed either under direct irradiation or after energy transfer from benzophenone. Moreover, chirality of the pyrazolines and, by extension, the cyclopropanes **3** and **7** is the result of the facial diastereoselection in the cycloaddition, assuming that stereochemical homogeneity is secured throughout the process. This point is crucial to obtain enantio- and diastereomerically pure cyclopropane compounds and will also be considered.

RESULTS AND DISCUSSION

1. *Synthesis and characterization of pyrazolines 2 and 6, and cyclopropanes 3 and 7. Diastereofacial selectivity in the cycloaddition of diazomethane.*

Δ^1-Pyrazolines **2** and **6** were quantitatively synthesized by treatment of amino pentenoates **1** and **5**, respectively, with excess diazomethane at room temperature. In both cases, one single diastereoisomer was obtained and, surprisingly, facial diastereoselection was the reverse depending on the *Z*/*E* stereochemistry.



Scheme 1

Thus, pyrazoline **2** would be the result of the *syn*-attack of diazomethane to the double bond of **1**, assuming a preferential conformation such as that represented by **A** in Fig 1. Contrariwise, a similar conformation **B** would not explain the formation of **6** from **5**, the stereochemical outcome being justified by considering the *anti*-attack of the reagent to a conformer such as **C**.[5] Evidence for the conformations **A** and **C** has been obtained in solution by $^1H[^1H]$ n.O.e. measurements.

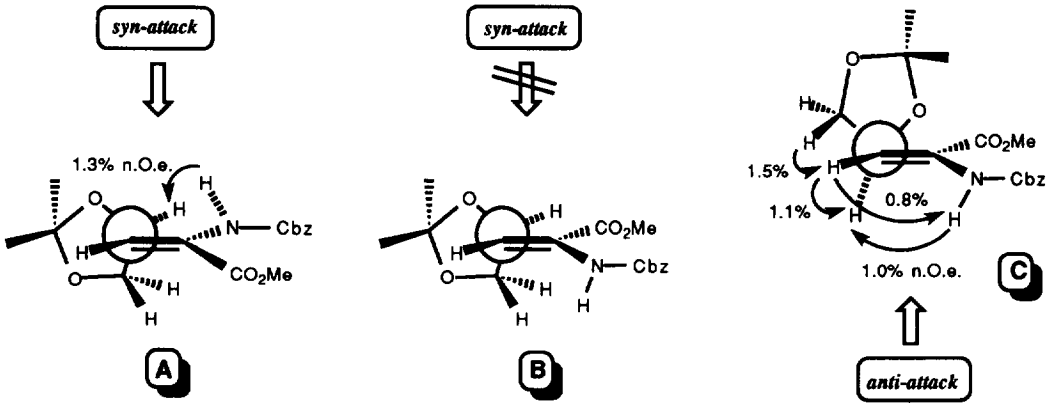


Fig 1. Active conformations proposed to justify syn/anti stereochemistry in the formation of pyrazolines 2 and 6.

The next step was conversion of **2** and **6** to cyclopropanes **3** and **7**, respectively. This transformation was not accomplished under thermal activation since thermolysis of **2** in toluene at 100 °C for 8 hours afforded the insertion olefin **4** in 63% yield as the only defined product.

Then, either pyrazolines **2** and **6** were photolyzed (*vide infra*) to the corresponding cyclopropane compounds, each one being also obtained as a single stereoisomer, as expected.

Configuration of the new stereogenic centers was determined in the case of **2** and **3** by X-Ray analysis of a convenient crystalline derivative.[4a] Stereochemistry of **6** and **7** was ascertained by their conversion into lactone **9** through diol **8**. Coupling constants in ^{1}H NMR and differential n.O.e. experiments confirmed the configuration stated in Scheme 1 (Fig 2). Thus, $J_{4,5}$ is near zero as expected for a dihedral angle of about 90 degrees corresponding to a *trans* disposition for these protons. This stereochemistry was also evidenced by n.O.e. enhancement for H_{6a} when H_4 was selectively irradiated. Moreover, selective irradiation of $H_{7a,b}$ enhanced significantly the H_5 absorption but not those of $H_{6a,b}$.

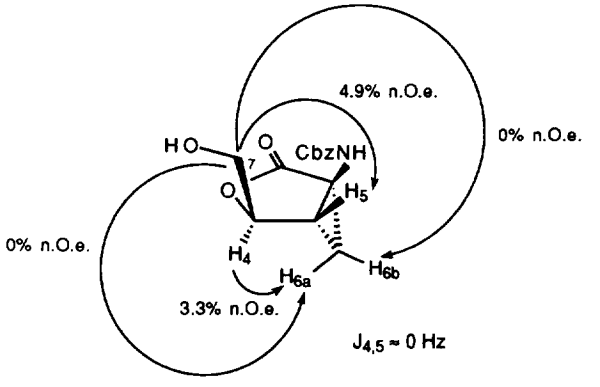


Fig 2. Relevant ^{1}H NMR data for the stereochemical assignment of lactone 9.

2. Photolysis of pyrazolines 2 and 6.

Pyrazoline **2** was photolyzed in several conditions to investigate the influence of solvent, concentration, temperature, and sensitizers on the reactivity and on the selectivity of the process. Irradiation was made as a solution contained in a Pyrex reactor by using a 125 W medium-pressure mercury-lamp. Table 1 summarizes the obtained results.

Inspection of Table 1 led us to conclude that reaction is faster when performed as diluted solutions at low temperature. Benzophenone, with a triplet quantum yield of essentially unity and a long (10^{-4} s) triplet half-life, was an excellent donor in dichloromethane solutions. Its use was crucial to increase the

Table 1. Direct and sensitized photolysis of pyrazoline 2 to cyclopropane 3.[a]

Solvent	Molar concentration	Sensitizer (eq)	Temp (°C)[b]	Time	3 % Yield	Other products[c] % Yield
Toluene	0.17	---	25	14 h	39	8
Toluene	0.11	---	25	10 h	54	13
Toluene	0.11	---	-78	50 min	81	7
Toluene	0.02	---	-78	35 min	80	5
Toluene	0.02	Ph_2CO (0.1)	-78	2.5 h	79	6
CH_2Cl_2	0.02	Ph_2CO (0.1)	25	1 h	86	3
CH_2Cl_2	0.09	Ph_2CO (0.1)	-78	25 min	97	2
CH_2Cl_2	0.02	Ph_2CO (0.1)	-78	13 min	100	--
CH_2Cl_2	0.02	---	-78	1 h	65[d]	traces
acetone	0.02	---	-78	2.5 h	60[d]	traces

[a] A 125 W lamp and pyrex reactors were used in all cases. [b] Referred to external temperature. [c] They include products **1** and **4**. Isolated yields are given. [d] Determined by ^1H NMR. 30-35% Starting pyrazoline **2** was recovered in these cases.

reaction rate as well as to improve yield and to avoid by-products such as **1** and **4**. These conditions also applied to pyrazoline **6** which was photolyzed as a 0.02M dichloromethane solution containing 0.1 eq of benzophenone, at -78 °C for 15 minutes, to yield quantitatively cyclopropane **7**. It is interesting to note that, according to the results listed in Table 1, the photolysis reaction was faster in toluene than in dichloromethane or acetone solutions, in absence of a sensitizer.

3. Laser flash-photolysis studies on pyrazolines 2 and 6.

In a next step we decided to study the photophysical behaviour of these systems by means of the LFP technique. The obtained results were useful to establish some mechanistic features of these processes. The ground state absorption of the pyrazolines **2** and **6** exhibited two main bands, one in the UV and the second in the near-UV-visible. As previously stated for similar systems,[3b,6] the longer wavelength absorption is due to a

π-π^* transition and the shorter wavelength absorption corresponds to an n-π^* transition. Spectral data of these bands are given in Table 2, the near-UV being the spectral region where excitation in LFP is usually achieved.

*Table 2. Spectroscopic data of pyrazolines **2**, and **6**.*

Pyrazoline	Solvent	$\lambda_{n-\pi}$ (nm)	ε (l mol^{-1} cm^{-1})	$\lambda_{\pi-\pi^*}$(nm)	ε (l mol^{-1} cm^{-1})
2	Dichloromethane	234	3.069 x 10^2	326	1.743 x 10^2
6	Dichloromethane	234	3.772 x 10^2	330	1.929 x 10^2

Experiments were made on degassed dichloromethane solutions exciting at 355 nm with laser pulses of 45 mJ (9 ns pulse width). An inconvenience was the low absorbance of the pyrazolines at this wavelength that forced us to use 0.03-0.04 M concentrations. Fig 3 shows the transient absorption difference spectra for pyrazolines **2** (3a) and **6** (3b) as well as for pure benzophenone (3c) and for a mixture of pyrazoline **2** and benzophenone (3d).

The rate constants k_d for the decay of the pyrazoline transients were determined at 410 nm from the respective absorbance plots. They showed a sharp slope at very short times not depending on the laser pulse energy while a rather flattened decay was observed at longer times (see insets in Fig 3a and 3b). Such results suggested the existence of two transient species for each pyrazoline, each one with a different decay constant. These transients probably are, in every case, the pyrazoline triplet and the biradical resultant from extrusion of nitrogen prior to the formation of the C-C bond of the cyclopropane ring. Table 3 shows the values for k_{d1} and k_{d2} determined for both pyrazolines **2** and **6**.

In a similar manner, k_d for the benzophenone triplet was determined from the monoexponential decay of its transient absorption at 530 nm in a 2x10^{-3}M dichloromethane solution and found to be 5.5x10^5 s^{-1} (Fig 3c).

*Table 3. Rate constants k_d for the decay of the pyrazoline transients for **2** and **6**.*

Pyrazolines	λ_{max} (nm)	k_{d1} (s^{-1}) x 10^5	k_{d2} (s^{-1}) x 10^5
2	410	83	4.6
6	410	38	1.9

Fig 3d shows the time-resolved spectrum for a mixture of pyrazoline **2** and benzophenone. As shown in the inset, there is a very fast decay for the benzophenone triplet as a consequence of an efficient energy transfer to the acceptor (*i.e.* pyrazoline). It is observed that appearance of an absorption in the 390-450 nm

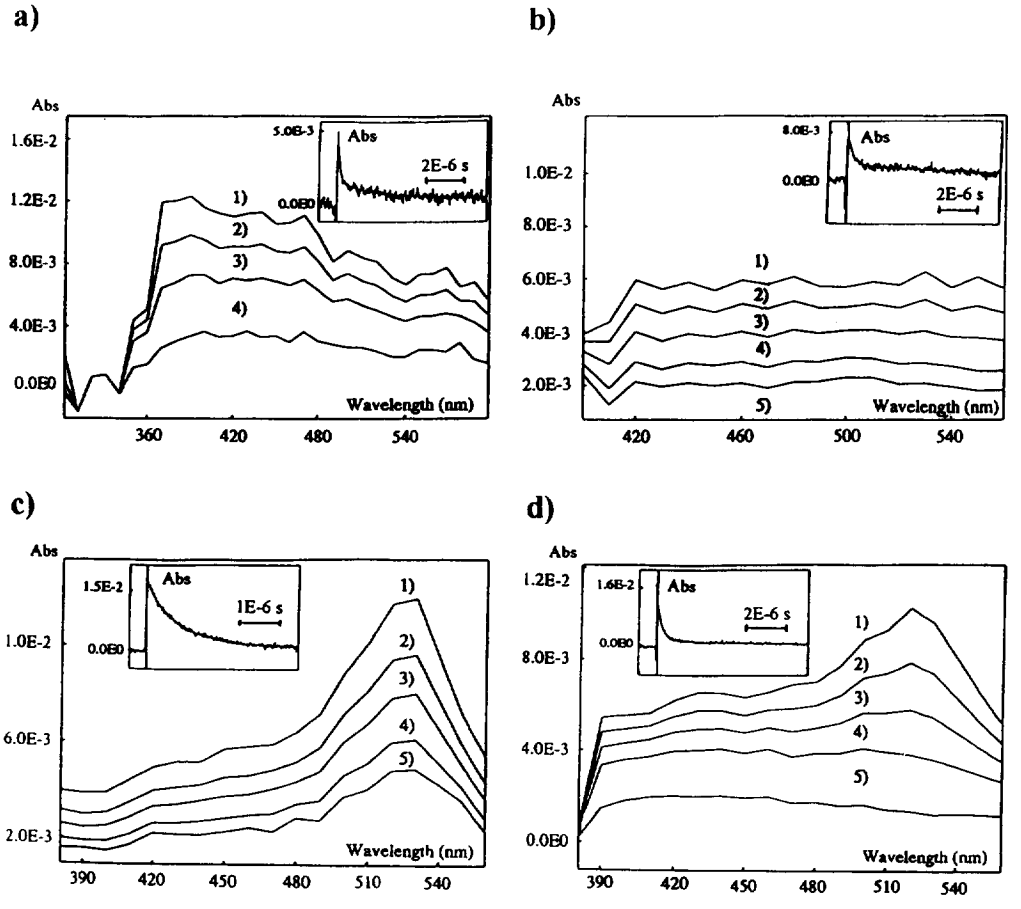


Fig 3. Transient absorption spectra (λ_{ex}=355 nm) of nitrogen-purged dichloromethane solutions of: ***a)*** *pyrazoline* ***2****, (1) 8.0x10^{-8}, (2) 16x10^{-8}, (3) 28x10^{-8} and (4) 180x10^{-8} s after laser flash; Inset: decay trace at 410 nm.* ***b)*** *pyrazoline* ***6****, (1) 10x10^{-8}, (2) 21x10^{-8}, (3) 42x10^{-8}, (4) 130x10^{-8} and (5) 250x10^{-8} s after laser flash; Inset: decay trace at 410 nm.* ***c)*** *benzophenone, (1) 9.2x10^{-8}, (2) 26x10^{-8}, (3) 44x10^{-8}, (4) 74x10^{-8} and (5) 120x10^{-8} s after laser flash; Inset: decay trace at 530 nm.* ***d)*** *benzophenone-pyrazoline* ***2****, (1:20), (1) 7.0x10^{-8}, (2) 12x10^{-8}, (3) 18x10^{-8}, (4) 27x10^{-8} and (5) 44x10^{-8} s after laser flash; Inset: decay trace at 530 nm.*

range parallels the disappearance of the transient absorption of benzophenone centered at 530 nm, thus suggesting the efficient formation of excited pyrazoline. From this spectrum, k_{obs} for the decay of benzophenone triplet is obtained for different amounts of pyrazoline. In the Stern-Volmer graph k_{obs} is plotted *vs* molarity of **2**, allowing the determination of the quenching rate constant. This value, k_q = 1.7 (±0.2) x 10^9 s^{-1} mol^{-1} dm^3, affords a quantitative measure for the efficiency of the photosensitization process.

Pyrazoline **6** was similarly studied, k_q for the sensitized process (1.2 (±) x 10^9 s^{-1} mol^{-1} dm^3) being slightly lower than that determined for the case of **2**.

(c) Mechanistic conclusions.

From the results obtained in the above studies we can propose that pyrazoline **2**, in absence of benzophenone, is excited to a singlet state from which a part of the energy is transmitted to T_1 *via* intersystem crossing and another part activates the formation of photoproducts such as the insertion olefin **4** or the cycloreversion product **1**, among other unidentified substances. Triplet, in turn, evolves through loss of nitrogen to a biradical species that leads finally to the cyclopropane. In the presence of benzophenone as a sensitizer, obtention of by-products is avoided, since pyrazoline triplet is actually originated from benzophenone triplet, the pyrazoline being not excited to a singlet state (Fig 4). Similar conclusions can be deduced for the production of cyclopropane **7** from pyrazoline **6**.

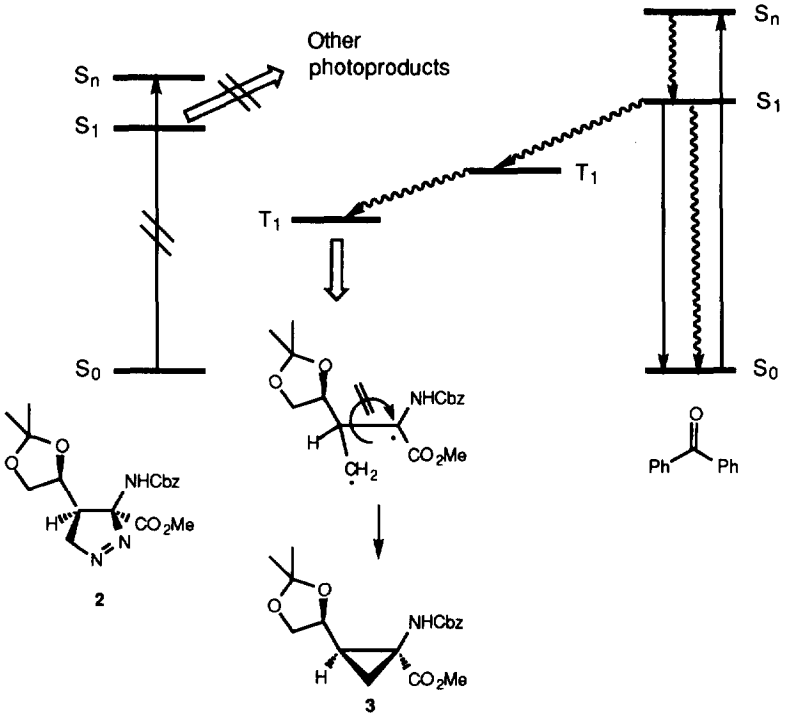


***Fig 4** . State energy diagram for the sensitized photodecomposition of pyrazoline **2** to cyclopropane **3**.*

It is noteworthy that collapse of this transient biradical must be faster than rotation around the C_2-C_3 bond, thus ensuring that chirality of the stereogenic centers remains unaltered throughout the process. This observation is in agreement with previously reported results[2a] on the stereospecificity involved in the photochemical decomposition of Δ^1-pyrazolines. Accordingly, in our case cyclopropanes **3** and **7** are stereospecifically produced from (*Z*)- and (*E*)-amino pentenoates **1** and **5**, respectively, through the corresponding pyrazoline intermediates **2** and **6**.

EXPERIMENTAL SECTION

LFP experiments were performed by using an LKS50 instrument from Applied Photophysics. The second harmonic (532 nm) of a Q-switched Nd:YAG laser (Spectron Laser Systems, UK; pulse width *ca.* 9 ns) was used for laser flash excitation.

Flash column chromatography was carried out on silica gel (240-400 mesh). Melting points were determined on a hot stage and are uncorrected. Electron-impact mass spectra were recorded at 70 eV. Chemical shifts in NMR spectra are given in ppm relative to internal TMS (δ scale).

Cycloaddition of diazomethane to pentenoates 1 and 5: Synthesis of pyrazolines 2 and 6. The general procedure is described for the synthesis of **6**. An ethereal solution of excess diazomethane was distilled on amino pentenoate **5** (286 mg, 0.8 mmol) in 4 mL of ether. The light-protected resultant solution was stirred at room temperature for 3 h, then excess diazomethane and solvent were removed and the oily residue was chromatographed (1:1 ethyl acetate-hexane) to give quantitatively pyrazoline **6** (319 mg). In a similar manner, the already described pyrazoline **2**[4c] was prepared. The new pyrazoline **6** was characterized as follows.

Methyl (3*S*,4*S*,4'*S*)-(+)-3-[*N*-benzyloxycarbonylamino]-4-(2',2'-dimethyl-1',3'-dioxolan-4'-yl)-1-pyrazoline-3-carboxylate, 6. Oil, $[\alpha]_D$ +70.5 (c=2.0, chloroform): IR (film) 3500-3100 (broad), 1733 (broad) cm^{-1}; MS, m/e (%) 169 (11), 137 (16), 108 (35), 107 (21), 101 (21), 91 (100), 79 (28), 77 (17), 72 (25), 43 (45); 250-MHz ^1H NMR ($CDCl_3$) 1.28 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 2.85 (m, 1H, H_4), 3.55 (m, 1H, $H_{5'a}$), 3.74 (s, 3H, OCH_3), 3.89-4.00 (complex absorption, 2H, $H_{5'b}$+$H_{4'}$), 4.41 (dd, 1H, $J_{5a,5b}$=17.7 Hz, $J_{5a,4}$=9.0 Hz, 1H, H_{5a}), 5.03 (d, J_{gem}=12.1 Hz, 1H, CH_2Ph), 5.09 (d, J_{gem}=12.1 Hz, CH_2Ph), 5.17 (dd, $J_{5b,5a}$=17.7 Hz, $J_{5b,4}$=8.6 Hz), 6.59 (broad s, 1H, N-*H*), 7.33 (s, 5H, Ph); 62.5-MHz ^{13}C NMR ($CDCl_3$) 25.21 (CH_3), 26.37 (CH_3), 43.22 (C_4), 53.41 (CH_3O), 67.12 (CH_2Ph), 67.99 ($C_{5'}$), 73.63 ($C_{4'}$), 79.37 (C_5), 100.61 (C_3), 109.28 ($C_{2'}$), 128.26 ($2C_o$), 128.42 (C_p), 128.45 ($2C_m$), 135.38 (C_{ipso}), 153.64 (HN*C*=O), 166.0 (*C*=O). Anal. Calcd. for $C_{18}H_{23}N_3O_6$: C, 57.29; H, 6.14; N, 11.13. Found: C, 57.16; H, 6.09; N, 10.73.

Pyrolysis of pyrazoline 2. A stirred solution of pyrazoline **2** (63 mg, 0.2 mmol) in toluene (5 mL) was heated at 100 °C for 9 h. Then solvent was removed and the yellowish residue was chromatographed (1:1 ethyl acetate-hexane) to afford methyl (*Z*)-(4'*S*)-[*N*-benzyloxycarbonylamino]-3-(2',2'-dimethyl-1',3'-dioxolan-4'-yl)butenoate, **4**, as an oil (36 mg, 63% yield) which was identified by their NMR spectral data. 250-MHz ^1H NMR ($CDCl_3$) 1.33 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 3.89 (m, 1H), 4.30 (m, 1H), 4.72 (m, 1H), 5.16 (s, coalescent AB system, 2H, CH_2Ph), 6.93 (broad s, N-*H*), 7.30 (complex absorption, 5H, Ph); 62.5-MHz ^{13}C NMR ($CDCl_3$) 15.44 (CH_3), 25.32 (CH_3), 26.55 (CH_3), 52.31 (CH_3O), 67.22 (CH_2Ph), 67.21 ($C_{5'}$), 72.66 ($C_{4'}$), 109.88 ($C_{2'}$), 126.74 (C_2), 127.98 ($2C_o$), 128.16 (C_p), 128.35 ($2C_m$), 131.09 (C_2), 135.47 (C_{ipso}), 148.44 (C_3), 154.79 (HN*C*=O), 165.77 (*C*=O).

Photolysis of pyrazolines 2 and 6. The general procedure for benzophenone sensitized processes is described for the decomposition of **6**.

A stirred solution of pyrazoline **6** (350 mg, 0.9 mmol) and benzophenone (17 mg, 0.09 mmol) in anhydrous dichloromethane (62 mL) contained in a Pyrex reactor under nitrogen atmosphere, cooled at -78 °C, was irradiated with a 125 W medium-pressure mercury-lamp for 14 minutes (UV monitoring). Solvent was removed and the residue was chromatographed (1:1:1 dichloromethane-ether-hexane) to afford quantitatively cyclopropane **7** (320 mg).

Cyclopropane **3** was previously described.[4c] Representative data for new cyclopropane **7** follow.

Methyl (1*S*,2*S*,4'*S*)-(+)-1-[*N*-benzyloxycarbonylamino]-2-(2',2'-dimethyl-1',3'-dioxolan-4'-yl)cyclopropanecarboxylate, 7. Colorless oil; $[\alpha]_D$ +14.54 (c=0.55, chloroform); IR (film) 3318 (broad), 1736, 1652 cm^{-1}; MS, m/e (%) 349 (M, 1), 101 (14), 91 (100), 43 (17); 250-MHz ^1H NMR (acetone-d_6) 1.29 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.43 (dd, $J_{3b,2}$=9.1 Hz, $J_{3b,3a}$=4.7 Hz, 1H, H_{3b}), 1.58 (dd, $J_{3a,2}$=8.3 Hz, $J_{3a,3b}$=4.7 Hz, 1H, H_{3a}), 1.68 (m, 1H, H_2), 3.62 (s, 3H, OCH_3), 3.86-4.00 (complex absorption, 2H, $H_{5'a/b}$), 4.11 (ddd, $J_{4',2}$=8.5 Hz, $J_{4',5'a}$=$J_{4',5'b}$=6.4 Hz, 1H, $H_{4'}$), 5.05 (t, J_{gem}=13.1 Hz, 2H, CH_2Ph), 7.14 (broad s, N-*H*), 7.29-7.37 (complex absorption, 5H, Ph); 100-MHz ^{13}C NMR ($CDCl_3$) 22.98 (C_3), 25.83 (*C*H_3), 27.17 (*C*H_3), 34.58 (C_2), 38.37 (C_1), 52.69 (*C*H_3O), 66.57 (*C*H_2Ph), 69.15 ($C_{5'}$), 75.75 ($C_{4'}$), 109.33 (C_2), 128.43 ($2C_o$), 128.58 (C_p), 129.13 ($2C_m$), 138.05 (C_{ipso}), 157.33 (HN*C*=O), 172.62 (*C*=O). Anal. Calcd. for $C_{18}H_{23}NO_6$: C, 61.86; H, 6.64; N, 4.01. Found: C, 61.82; H, 6.96; N, 4.05.

Hydrolysis of acetonide 7: Methyl (1*S*,2*R*,4'*S*)-(-)-1-[*N*-(benzyloxycarbonylamino]-2-(1',2'-dihydroxyethyl)cyclopropanecarboxylate, 8. A mixture of 7 (250 mg, 0.7 mmol) and 3 drops of 5% HCl in methanol (10 mL) was stirred at r.t. for 1.5 h. Solvent was removed and the residue was chromatographed (4:1 ethyl acetate-hexane) to furnish diol **8** (185 mg, 84% yield) and 10 mg (5% yield) of lactone **9**. Diol **8** is an oil; IR (film) 3560-2900 (broad), 1754, 1701cm^{-1}; 250-MHz ^1H NMR (acetone-d_6) 1.38-1.52 (complex absorption, 2H, $H_{3a/b}$), 2.35 (m, 1H, H_2), 3.66 (s, 3H, OCH_3), 3.67-3.74 (complex absorption, 2H, $H_{2'a/b}$), 4.72 (m, 1H, $H_{1'}$), 5.09 (s, 2H, CH_2Ph), 6.56 (broad s, N-*H*), 7.30-7.42 (complex absorption, Ph); 62.5-MHz ^{13}C NMR ($CDCl_3$) 20.42 (C_3), 34.30 (C_2), 37.80 (C_1), 52.56 (*C*H_3O), 65.90 (*C*H_2Ph), 67.00 ($C_{5'}$), 69.49 ($C_{4'}$), 127.83 ($2C_o$), 128.04 (C_p), 128.29 ($2C_m$), 135.67 (C_q), 157.39 (HN*C*=O), 171.67 (*C*=O).

(1*S*,4*S*,5*R*)-(+)-1-[*N*-(benzyloxycarbonylamino]-4-hydroxymethyl-3-oxabicyclo[3.1.0]hexan-2-one, 9. A mixture of diol **8** (185 mg, 0.6 mmol) and 5 drops of 5% HCl in THF (5 mL) was stirred at r.t. for 8 h. Solvent was removed and the residue was chromatographed (1:2 ethyl acetate-hexane) to give lactone **9** (86 mg, 64% yield) as an oil; [α]D +33.3 (c=0.6, chloroform), IR (film) 3600-3100, 1778, 1708 cm^{-1}; 250-MHz 1H NMR (acetone-d_6) 1.23 (t, $J_{6a,5}$=5.1 Hz, $J_{6a,6b}$=5.1 Hz, 1H, H_{6a}), 1.60 (dd, $J_{6b,2}$= 8.4 Hz, $H_{6b,6a}$=5.1 Hz, 1H, H_{6b}), 2.39 (dd, $J_{5,6b}$=8.4 Hz, $J_{5,6a}$=5.1 Hz, 1H, H_5), 2.87 (broad s, O-*H*), 3.78-3.86 (complex absorption, 2H, $H_{7a/b}$), 4.30 (m, 1H, H_4), 5.09 (s, 2H, CH_2Ph), 7.29-7.37 (complex absorption, 5H, Ph), 7.50 (broad s, N-*H*); 62.5-MHz ^{13}C NMR (acetone-d_6) 18.35 (C_6), 25.50 (C_5), 38.29 (C_1), 64.18 (C_7), 67.77 (*C*H_2Ph), 79.53 (C_4), 128.23 ($2C_o$), 128.43 (C_p), 128.57 ($2C_m$), 135.37 (C_{ipso}), 156.89 (HN*C*=O), 173.46 (*C*=O). Anal. Calcd. for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.83; H, 5.51; N, 4.90.

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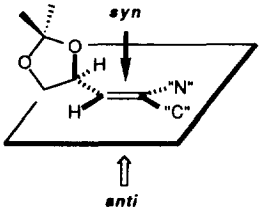
REFERENCES AND NOTES

1. March, J. *Advanced Organic Chemistry*, J. Wiley & Sons, 4th ed. **1992**, p.1045-1046, and references therein.
2. See, for instance: (a) Van Auken, T. V.; Rinehart Jr., K. L. *J. Am. Chem. Soc.*, **1962**, *84*, 3736. (b) Engel, P. S.; Nalepa, C. L. *Pure and Appl. Chem.* **1980**, *52*, 2621. (c) Reedich, D. E.; Sheridan, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 3697.
3. For representative works, see: (a) Wilkinson, F.; Kelly. G. P. *J. Photochem. Photobiol., A: Chem.* **1988**, 45, 223. (b) Wilkinson, F.; Kelly. G. P.; Michael, C. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 309. (c) Blair, J. T.; Sahyun, M. R. V.; Sharma, D. K. *J. Photochem. Photobiol., A: Chem.* **1994**, *77*, 133.
4. (a) Jiménez, J. M.; Casas, R.; Ortuño, R. M. *Tetrahedron Lett.* **1994**, *35*, 5945. (b) Jiménez, J. M.; Rifé, J.; Ortuño, R. M. *Tetrahedron: Asymmetry*, **1995**, *6*, 1849. (c) Jiménez, J. M.; Rifé, J.; Ortuño, R. M. *Tetrahedron: Asymmetry*, **1996**, *7*, 537. (d) Jiménez, J. M.; Ortuño, R. M. *Tetrahedron: Asymmetry*, **1996**, *7*, 3203.
5. A detailed study on the factors influencing the *syn/anti* diastereoselectivity involved in the cycloadditions of diazomethane to pentenoates **1** and **5**, and other related chiral substrates is being carried out in our laboratory. This study also includes theoretical calculations of the active conformations, as well as the geometries and the energy barriers associated with the transition states leading to each stereoisomer.

   Syn/anti is a notation used in this work to distinguish the two facial diastereoisomers. Thus, *syn* facial diastereoselection refers to the attack of diazomethane on the π-face of the double bond marked by the black arrow, fixing the conformation for the dioxolane ring as represented for **1** in the figure. *Anti* orientation is stated by the white arrow to occur by attack on the opposite side of the plane.



6. Nurmukhametor, R. N.; Tishchenko, V. G. *Opt. Spectrosc.*, **1967**, *23*, 83.

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