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Effect of Alkyl Chain Stiffness and Branching on the Properties of Micelles Formed from 1-Methyl-4-(C_{12}-alkyl)pyridinium Iodide Surfactants

Jan Jaap H. Nusselder, Tjibbe-Jan de Groot, Michel Trimbos, and Jan B. F. N. Engberts*

Department of Organic Chemistry, University of Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands

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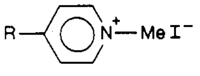
This paper describes a study of the micellization of four 1-methyl-4-(C_{12}-alkyl)pyridinium iodide surfactants in which C_{12}-alkyl is *n*-dodecyl (**1**), 9,9-dimethyldecyl (**2**), 1-methylundecyl (**3**), and 1-dodec-5-ynyl (**4**). Alkyl chain branching (**1**–**3**) exerts only a minor effect on the stability of the micelles (as indicated by the cmc's) and on the properties of the micellar surface (as indicated by counterion binding, charge-transfer absorption bands, and kinetic data for decarboxylation of micellar-bound 6-nitrobenzisoxazole-3-carboxylate). By contrast, chain packing is substantially affected as revealed by large differences in the surfactant concentration (second cmc) for transition of spherical into rodlike micelles. The latter effects are rationalized in terms of the packing parameter *P*, introduced by Israelachvili. The alkyl chain in surfactant **4** is more stiff and somewhat less hydrophobic, leading to a higher cmc and modified behavior of the micelles toward the kinetic probe.

Single-chain amphiphiles form micelles in aqueous solution above a critical concentration (cmc) and temperature (Krafft temperature). Since the introduction of the classical "oil drop" model for the structure of micelles,[1] a variety of alternative structural models have been proposed. These include the porous cluster model (Menger),[2] the surfactant block model (Fromherz),[3] the lattice model (Flory),[4] and the standard picture of ionic micelles (Gruen).[5] Appreciable controversy remains concerning such factors as water penetration into the micellar core and chain folding in the micellar aggregate.

Herein we describe a study of the aggregation behavior of four 1-methyl-4-(C_{12}-alkyl)pyridinium iodide surfactants: 1-methyl-4-*n*-dodecylpyridinium iodide (**1**), 1-methyl-4-(9,9-dimethyldecyl)pyridinium iodide (**2**), 1-methyl-4-(1-methylundecyl)pyridinium iodide (**3**), and 1-methyl-4-(1-dodec-5-ynyl)pyridinium iodide (**4**). In these structurally related surfactants, the C_{12} chain is varied through branching and the introduction of a triple bond in the middle of the chain. Since the hydrophobicity of the C_{12} chain in **1**–**4** varies only very little, it is assumed that differences in aggregation and micellar properties will mainly reflect differences in alkyl chain packing. We have concentrated our comparative study of **1**–**4** on (a) the critical micelle concentration (indicating the thermodynamic stability of the micelle), (b) the position of the first long-wavelength intramolecular charge-transfer absorption band (an intrinsic micropolarity reporter for the microenvironment in the Stern region),[6] (c) micellar catalysis of the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate[7] (a kinetic probe for the microenvironment at the micelle surface),[8] and (d) the micellar shape (spherical vs rodlike) as a function of the surfactant concentration.



1, R = $(CH_2)_{11}CH_3$
2, R = $(CH_2)_8C(CH_3)_3$
3, R = $CH(CH_3)(CH_2)_9CH_3$
4, R = $(CH_2)_4C{\equiv}C(CH_2)_5CH_3$

Table I. Comparison of Surfactant and Micellar Properties of 1–4

property	1	2	3	4
$\sum f_i$[a]	6.53	6.50	6.41	6.20
P[b]	0.36	0.53	0.29	
first cmc (25 °C), mol·kg^{-1}	2.45×10^{-3}	4.90×10^{-3}	4.17×10^{-3}	13×10^{-3}
second cmc (25 °C), mol·kg^{-1}	45×10^{-3}	25×10^{-3}	$>440 \times 10^{-3}$	
$(cmc)_2/(cmc)_1$	18.4	5.1	>105	
β,[c] %	83	84	80	78
λ_m^{CT} (CH_2Cl_2), nm	350	352	352	355
λ_m^{CT} (micelle) nm	286	292.5		
k_m,[d] s^{-1}	3.48×10^{-4}	4.18×10^{-4}	3.87×10^{-4}	4.1×10^{-4}
K/N[c]	1160	1430	1680	200

[a] Alkyl chain hydrophobicity in terms of Rekker's hydrophobic fragmental constants (f_{CH_2} = 0.530).[16] [b] Packing parameter.[15] [c] Counterion binding. [d] For the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate at 30 °C; see text. In water at 30 °C, $k_w = 2.1 \times 10^{-6}$ s^{-1}.

Previous studies on isomeric surfactants are rare and mostly involve only isomers in which the head group migrates along the alkyl chain.[9] Generally, amphiphiles with a branched alkyl chain possess a higher cmc than those with the corresponding *n*-alkyl chain.[10] Menger et al.[11] and Shobha et al.[12] have studied surfactants having an acetylenic moiety at the terminal position in the alkyl chain. Such a more hydrophilic chain end may function as a second head group. However, even a terminal methyl group may fold back for about 10% to the micellar surface.[5,13] Introduction of an alkene moiety in the alkyl chain is known to hamper micellization.[14]

Results and Discussion

Hydrophobicities and Packing Parameters for 1–4. Before turning to the micellar aggregation behavior of **1**–**4**, it is worthwhile to consider briefly two properties of the

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monomeric surfactants: the hydrophobicity of the isomeric C_{12} chains and the packing parameter (P), introduced by Israelachvili.[15] We compare the hydrophobicities of the C_{12} chains in terms of the sum of the hydrophobic fragmental constants proposed by Rekker[16] (Table I). The differences are particularly small for **1**–**3**; only **4** is slightly less hydrophobic. The packing parameter P is defined by

$$P = v/a_0 l$$

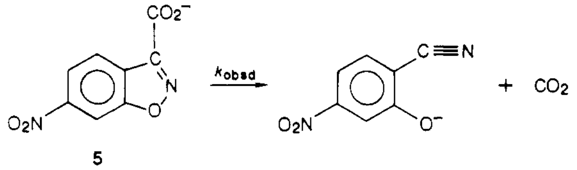
in which a_0 is the surface area per monomer, v is the volume of the hydrocarbon part of the surfactant, and l is the length of the alkyl chain.[15] If the volume of a cylinder with length l is taken for the volume v, then $P = a_c/a_0$, in which a_c is the area of the hydrophobic part of the surfactant. There is a relation between P and the type of aggregate formed.[15] When $P < {}^1/_3$, the surfactant assembles to spherical micelles, rodlike micelles are formed for $P = {}^1/_3$ to $P = {}^1/_2$, and $P > {}^1/_2$ leads to bilayers, vesicles, and inverted micelles. We have estimated P values for **1**–**3** using CPK molecular models. Two approximations were made: (i) the counterion binding is complete and (ii) the head groups are not hydrated. The results, given in Table I, show quite substantial differences. Branching at the end of the chain as in **2** leads to a definitely more cylindrical form of the surfactant. This effect is found to affect the morphology of the micelle at higher surfactant concentrations (vide infra).

Critical Micelle Concentration and Counterion Binding. Table I lists cmc's and counterion binding (β) values for the surfactants **1**–**4**. In the series **1**–**3** with almost equal hydrophobicity of the alkyl chain, the first cmc increases by a factor of about 2 upon branching. This will primarily reflect the decrease in surface area of the apolar part of the surfactant, leading to a decrease in the driving force for micellization.[17] Interestingly, the bulky end group in **2** exerts no dramatic effect on either the cmc or the counterion binding. Apparently the surfactant assembly is able to adjust the balance between attractive and repulsive interactions to retain its overall thermodynamic stability as determined to a large extent by chain packing.

A relatively large increase of the cmc and decrease of β is found for **4**. The effects seem to be larger than predicted by empirical rules.[18] We submit that the stiffness in the alkyl chain introduced by the acetylene moiety has a negative influence on effective chain packing in the micellar core. It appears that this effect is not so easily reconcilable in terms of the surfactant block model[3] for micelles. The slight decrease in the alkyl-chain hydrophobicity will also contribute to the increased cmc of **4** whereas the smaller β is indicative for a more open structure of the micelle. Second cmc's observed for **1** and **2** will be discussed below.

Intramolecular Charge-Transfer Absorption Bands. The transition energy of the first intramolecular charge-transfer (CT) absorption band of **1**–**4** in their micellar aggregates functions as an intrinsic micropolarity probe for the microenvironment near the head groups.[6] Such an intrinsic micropolarity reporter group has definite advantages over extrinsic probes as discussed previously.[6,19] The use of *N*-alkylpyridinium iodides for probing micropolarities has been introduced by Kosower.[20] Observed CT absorption maxima (λ_m) for monomeric surfactants in CH_2Cl_2 and for the surfactants **1** and **2** in their micelles are given in Table I. Unfortunately no reliable λ_m values could be obtained for micelles of **3** and **4** as a result of overlap of the CT absorption band and the pyridinium $\pi \rightarrow \pi^*$ transition. For micellar **1**, λ_m is different from λ_m in bulk water but rather similar to λ_m in ethanol as the solvent (288 nm). For micelles of **2**, λ_m is definitely higher, indicative for a somewhat lower micropolarity. This was not anticipated on basis of the less effective chain packing for **2** than for **1**, which would lead to micelles in which the head groups are further apart. Therefore we suggest that this effect reflects folding back of the *tert*-butyl end group to the head-group region of the micelle.

Application of a Kinetic Probe. It is well-known that rate constants for the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (**5**) are extremely sensitive to changes in micropolarity of the medium.[7] Important molecular interactions contributing to these medium effects are hydrogen-bond stabilization of the initial state and London dispersion interactions stabilizing the highly polarizable transition state. The reaction has been employed to investigate microenvironmental effects in various types of surfactant aggregates, usually carrying a positive surface charge.[8,21] Micelles of **1**–**4** also catalyze the decarboxylation of **5**; rate accelerations are on the order of 10^2. The first-order rate constants determined at different surfactant concentrations were analyzed according to the Menger–Portnoy pseudophase model for micellar catalysis.[22] Values for the rate constants in the spherical micelle (k_m) and for K/N (K is the binding constant of **5** to the micelles, and **N** is the aggregation number) are listed in Table I. It turns out that the rate constants are rather similar and indicative for a micropolarity at the binding site(s) for **5** in the region between methanol ($k_{MeOH} = 2.5 \times 10^{-4}\ s^{-1}$)[7] and ethanol ($k_{EtOH} = 10.0 \times 10^{-4}\ s^{-1}$).[7] The K/N values are also not too different, except for **4**, where K/N is significantly lower. The latter result could indicate that hydrophobic bonding of **5** to micelles of **4** is reduced because of a more "open" structure of the micellar surface, but in that case one would expect that k_m would be significantly lower than for **1**–**3**. In the absence of N values, however, no definite interpretations can be given. In addition, it should be noted that the k_m and K/N values for **1**–**4** will also be modulated[21] by the (small) differences in β, since binding of **5** to the micelles competes with iodide counterion binding.[21] This effect may be smallest for micellar **4**.



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Spherical vs Rodlike Micelles. Depending on the structure of the apolar part of the surfactant and the hydrophobicity of the counterion, spherical micelles may be transformed[17] into rodlike micelles at the second cmc (= (cmc)$_2$), which is about 10–100 times the first cmc (= (cmc)$_1$) for surfactants such as sodium 4-*n*-octylbenzenesulfonate,[23] CTAB,[24] and *n*-dodecylammonium chloride.[25]

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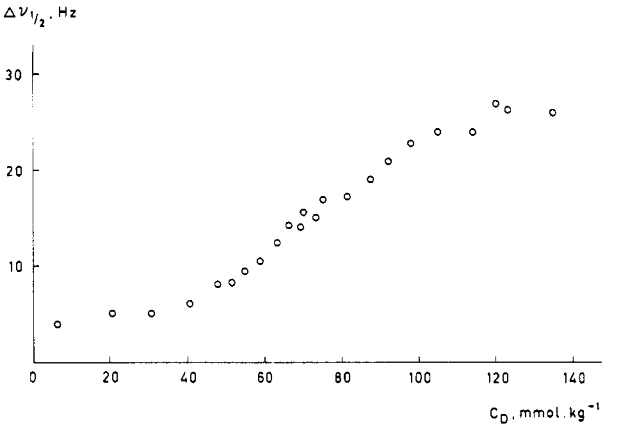

Figure 1. Line width at peak half-height of the alkyl resonance of surfactant 1 at ca. 1.2 ppm in D_2O solutions as a function of surfactant concentration at 30 ± 1 °C.

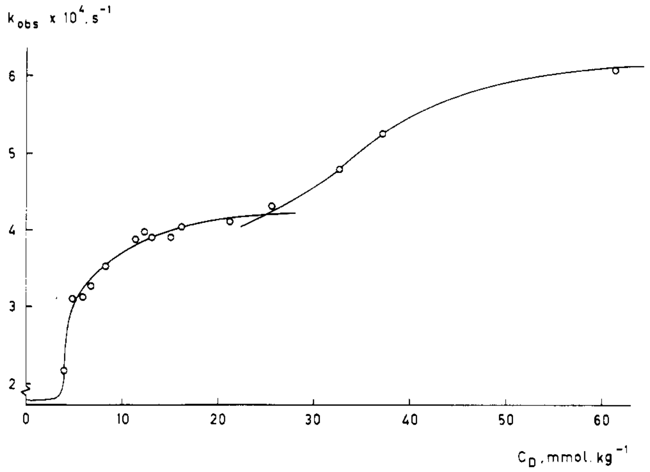

Figure 2. Plot of the unimolecular rate constant for decarboxylation of 5 as a function of the concentration of 2.

The ratio $(\mathrm{cmc})_2/(\mathrm{cmc})_1$ is still lower for hydrophobic counterions such as heptafluorobutyrate,[26] heptylsulfonate,[27] and salicylate.[28] The formation of rods is favorable in view of the reduction (theoretically by a factor of $^2/_3$) of the apolar surface area exposed to water. However, this effect is counteracted by an increase in head-group repulsion, which can be reduced by increasing the counterion hydrophobicity[26–28] or by adding salts.[29] The sphere-to-rod transition can be probed by NMR,[30] phosphorescence,[31] ESR,[32] viscometry,[33] electron microscopy,[34] SANS,[35] and light scattering [29,36] but not by conductivity measurements.[24] For the surfactants 1 and 2, an abrupt increase in the line width ($\Delta\nu_{1/2}$) of the ^{1}H NMR resonances is observed at a critical concentration, the second cmc (see Table I and Figure 1), which provides evidence for the formation of more anisotropic,[28] rodlike micelles (not disks).[28,37] For surfactant 2, the second cmc is also revealed by an abrupt increase in k_1 for decarboxylation of 5 at 24.4 mmol·kg^{-1} (Figure 2).[38] Apparently the micropolarity at the binding sites of 5 is lowered upon going to rodlike micelles,[39] consistent with measurements of the $E_T(30)$ parameter reported by Zachariasse et al.[40] For surfactant 1 the second cmc is higher by a factor of about 2 and cannot be detected kinetically with our decarboxylation reaction. Branching near the head groups as in 3 has a large effect and there is now no indication (NMR) for a transition to rods at surfactant concentrations as high as 105 times the first cmc. Thus it appears that branching of the alkyl chain in the series 1–3 is most strongly revealed by the ratio $(\mathrm{cmc})_2/(\mathrm{cmc})_1$ (Table I). These results can be rationalized by considering the packing parameters P (Table I). The small value of P for 3, as a result of the large surface area a_0, indicates that spherical packing is greatly favored over a rodlike arrangement of the surfactant molecules in the aggregate.[41] Branching at the chain end (2) leads to a more cylindrical form of the surfactant molecule and P increases to 0.53. Now rodlike micelles become more stable and $(\mathrm{cmc})_2/(\mathrm{cmc})_1$ is reduced to 5.1. A similar observation was made by Lattes et al.[42] upon introduction of bulky groups at the chain end. Surfactant 1 has a P value of 0.36 and $(\mathrm{cmc})_2/(\mathrm{cmc})_1$ is 18.4, which is a usual value for such a cationic surfactant.[17]

In conclusion, we note that branching of the alkyl chain (1–3) and introduction of an acetylenic bond (4) in the present series of surfactants have a modest effect on the properties of the micellar surface but a substantial effect on the chain packing in the micellar interior. Of course, the present results do not allow a choice between the different models for micellar structure, but in a first approximation it seems that the porous cluster model[2] and the model assuming the standard picture of ionic micelles[5] are best reconcilable with the micellar properties of 1–4 shown in Table I.

Experimental Section

General. Melting points were measured on a Kofler hot stage and are uncorrected. ^{1}H NMR spectra (solutions in $CDCl_3$) were determined on a Hitachi Perkin-Elmer R-24B (60 MHz), Bruker WH-90-DS (90 MHz), or Nicolet NT-200 (200 MHz) instrument. ^{13}C NMR spectra were run on a Varian XL-100/15 (25 MHz) or a Nicolet NT-200 (50 MHz) instrument. Elemental analyses were carried out in the Analytical Section of our department by H. Draayer, J. Ebels, and J. E. Vos.

Cmc Measurements. Cmc's were measured conductometrically with a Philips PW 9501/01 conductivity meter with a Philips PW 9512/00 electrode. The conductivity cell was thermostated (±0.1 °C) and equipped with a magnetic stirring device. The counterion binding was determined as described previously.[6]

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[38] The effect is not due to a change in K/N since 5 is already completely bound to the spherical micelles below the second cmc.

[39] In a kinetic study using mixed micelles of SDS and 1-decanol, no change in micropolarity was noted in the transition from spherical to rodlike micelles: Ramesh, V.; Labes, M. M. *J. Am. Chem. Soc.* **1987**, *109*, 3228.

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Optical Absorption Measurements. Optical densities were measured between 260 and 420 nm with a Perkin-Elmer λ5 spectrophotometer. The charge-transfer absorption band maxima were determined by using Mukerjee's band-match method.[43]

NMR Line-Width Measurements. Line widths at peak half-height ($\Delta\nu_{1/2}$) were calculated from ^{1}H NMR spectra of the surfactant aggregate in D_2O solutions using a Bruker WH-90-DS spectrometer (90 MHz) operating in the FT mode at 30 ± 1 °C.

Kinetic Measurements. First-order rate constants for the decarboxylation of 5 were measured at 30.00 ± 0.01 °C by monitoring the increase in absorption at 410 nm using a Varian Cary 210 or Perkin-Elmer λ5 spectrophotometer. All reactions were followed for at least 3 half-lives, and the rate constants (reproducible to within 2%) were calculated by the Guggenheim method.[44] In a typical experiment 5 μL of a freshly prepared stock solution of 5[45] (8×10^{-2} M) was added to 2.5 mL of the surfactant solution (pH 11.3, NaOH) in the cell.

Syntheses. Surfactants 1–4 were prepared according to the general procedure described previously.[6] Thus, the anion of 4-methylpyridine (in ether at −30 °C) is reacted with the relevant 1-bromo- or 1-iodoalkane to provide the long-chain pyridine. Quaternization is performed with methyl iodide in acetone. The crude 1–4 were washed twice with dry ether and recrystallized 2–4 times from dry acetone at low temperature. The surfactants are light sensitive and should be stored under nitrogen. Below we report physical constants for the novel surfactants 2–4. The bromide used as a precursor in the synthesis of 2 was prepared by reacting the Grignard reagent of *tert*-butyl chloride with 1,7-dibromoheptane.[46] The procedure for introducing the 1-methyl group in 3 was similar to that employed in the synthesis of the long-chain pyridine, except that the reaction was performed at room temperature. 4-Undecyn-1-ol was synthesized according to the method of Brandsma[47] using 4-pentyn-1-ol and 1-iodohexane. The alcohol was converted into the corresponding iodide via the mesylate. Full synthetic details are available on request.

1-Methyl-4-*n*-dodecylpyridinium Iodide (1). This surfactant has been described previously.[6]

1-Methyl-4-(9,9-dimethyldecyl)pyridinium iodide (2): mp 112.5–113.5 °C; ^{1}H NMR δ 0.82 (s, 9 H), 1.25 (m, 12 H), 1.63 (t, *J* = 7.9 Hz, 2 H), 2.83 (t, *J* = 7.9 Hz, 2 H), 4.62 (s, 3 H), 7.85 (d, 2 H), 9.16 (d, 2 H); ^{13}C NMR δ 24.2, 28.9, 29.0, 29.2 (q), 29.3, 30.0 (s), 30.2, 35.7 (t), 44.0 (t), 48.5 (q), 127.6 (d), 144.8 (d), 163.0 (s). Anal. Calcd for $C_{18}H_{32}NI$: C, 55.53; H, 8.28, I, 32.59; N, 3.60. Found: C, 55.52; H, 8.32; I, 32.64; N, 3.39.

1-Methyl-4-(1-methylundecyl)pyridinium iodide (3): mp 76–78 °C; ^{1}H NMR δ 0.80 (m, 3 H), 1.17 (m, 19 H), 1.56 (m, 2 H), 2.88 (q, 1 H), 4.61 (s, 3 H), 7.77 (d, 2 H), 9.24 (d, 2 H); ^{13}C NMR δ 13.7 (q), 20.2 (q), 22.4 (t), 27.0 (t), 28.9 (t), 29.1 (t), 31.45 (t), 36.8 (t), 39.9 (d), 48.2 (q), 126.3 (d), 144.9 (d), 167.7 (s). Anal. Calcd for $C_{18}H_{32}NI$: C, 55.53; H, 8.28; I, 32.59. Found: C, 54.88; H, 8.23; I, 32.59.

1-Methyl-4-(1-dodec-5-ynyl)pyridinium iodide (4): mp 33–45 °C; ^{1}H NMR δ 0.8–2.3 (m, 17 H), 2.9 (t, 2 H), 4.6 (s, 3 H), 7.80 (d, 2 H), 9.20 (d, 2 H); ^{13}C NMR δ 13.4 (q), 17.8 (t), 18.1 (t), 21.8 (t), 27.7 (t), 27.8 (t), 28.4 (t), 30.6 (t), 34.7 (t), 48.2 (q), 78.2 (s), 80.6 (s), 127.3 (d), 144.5 (d), 162.2 (s). Anal. Calcd for $C_{18}H_{28}NI$: C, 56.11; H, 7.32; I, 32.93; N, 3.63. Found: C, 55.70; H, 7.37; I, 32.53; N, 3.57.

Registry No. 1, 62541-13-3; 2, 113893-20-2; 3, 113893-21-3; 4, 113893-22-4; 5, 42540-91-0.

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Rearrangement of Isoxazoline-5-spiro Derivatives. 1. Synthesis of 4,5-Dihydroisoxazole-5-spirocyclopropanes and Their Rearrangement to 5,6-Dihydro-4-pyridones[1]

Antonio Guarna,[†] Alberto Brandi,[†] Francesco De Sarlo,*[†] Andrea Goti,[‡] and Fabio Pericciuoli[†]

Dipartimento di Chimica organica "Ugo Schiff", Università di Firenze, Firenze, Italy, and Centro di studio sulla chimica e la struttura dei composti eterociclici e loro applicazioni, CNR, Firenze, Italy

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The title spiroheterocycles 3 are prepared by cycloaddition of nitrile oxides to methylenecyclopropane or its ring-substituted derivatives. Thermolysis of the cycloadducts 3 affords, presumably via N–O bond homolysis, the title pyridones 7 besides minor amounts of the isomeric enaminones 6: the amounts of 6 relative to 7 are reduced when thermolysis is carried out by FVT rather than in solution. Similar results are obtained by photolysis of 3b in solution. Phenyl substitution in the cyclopropane ring selectively causes the C(spiro)–C(benzylic) bond fission with production of a single regioisomer, 7d. The rearrangement of the cycloadduct 3e from methylenenorcarane is selective, too: the cis-fused quinolinone 7e predominates over the trans-fused isomer, as a result of "torsional strain" in the latter transition state.

Recent reviews extensively illustrate the synthetic potential of a strained ring undergoing ring-opening and eventual recyclization to sterically relieved products.[2-4] A variety of adjacent functionalities modulate both the reacting conditions and the reaction output, the combination of strain and reactivity normally introducing a high degree of selectivity.[3]

Thus, the nonselective thermal ring-opening of isoxazoline derivatives, leading to product mixtures (mainly arising from 1–2 and 3–4 or 1–2 and 4–5 bond fissions), could be directed toward a definite pathway by the presence of a strained ring. Since thermolysis[5-7] or photoly-

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[†] Dipartimento di Chimica organica.

[‡] Centro CNR.

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