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.

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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]

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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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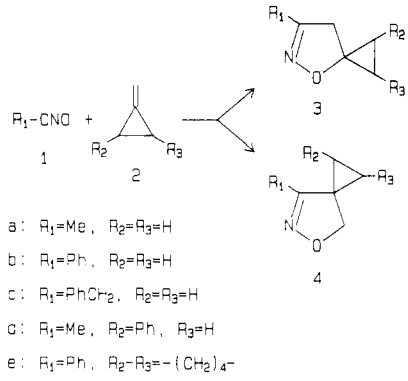
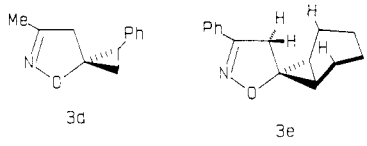
Scheme I



sis[7-10] of isoxazole and its (saturated) derivatives are in general assumed to involve primarily the weak N–O bond, we identified 5-spirocyclopropane compounds as suitable substrates.

Results and Discussion

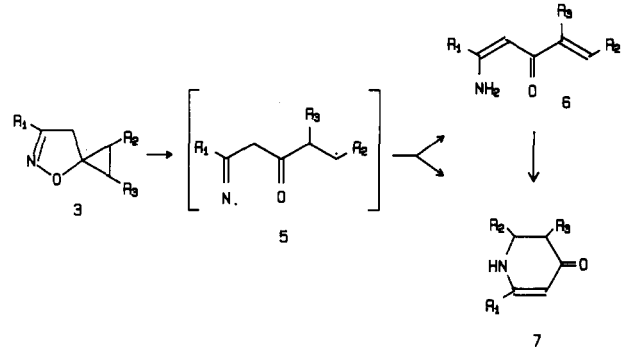
Synthesis of the Spiro Compounds 3. 4,5-Dihydroisoxazole-5-spirocyclopropanes **3** are easily accessible by cycloaddition of nitrile oxides **1** to methylenecyclopropane or its ring-substituted derivatives **2** (Scheme I): a high regioselectivity in favor of the 5-spiro isomers **3** is observed, as expected on the basis of previous findings concerning the cycloadditions of phenylazide to methylenecyclopropane[11] and of nitrile oxides to other methylenecycloalkanes.[12,13] Minor amounts of the regioisomers **4** are often detected in the crude reaction mixture by ^{1}H NMR spectroscopy (5%, **4a**; 4%, **4c**; 2%, **4e**). In addition, high diastereoselectivity is observed when substituents are present on the cyclopropane ring. Thus, only the depicted diastereoisomers **3d** and **3e** are detected, as a result of the



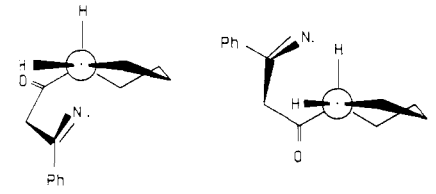
preferred approach of the dipole from the less hindered face of the dipolarophile ("anti" approach). The assignment of structure **3d** rests on the significant shielding effect of the phenyl ring on the isoxazoline methylene: ^{13}C δ 39.56 (43.17 in **3a**), ^{1}H δ 2.84 and 2.60 (2.98 in **3a**). Structure **3e** is supported by the lack of NOE on the protons of the isoxazoline methylene, due to the rapid conformational equilibrium of the boat-cyclohexane. Had the structure been that of the other diastereoisomer, a NOE would have been observed with the cyclopropane protons in a rigid conformation.

Rearrangement of Spiro Compounds 3. The rearrangement of the heterospiranes **3**, carried out under various exprimental conditions, leads in general to mixtures of enaminones **6** and pyridones **7** (Scheme II). As

Scheme II



Scheme III



already pointed out,[1] the enaminones **6** are not necessarily reaction intermediates, although they can be slowly converted into the isomers **7**.[14] In fact, during the rearrangement of **3b** in refluxing mesitylene, the molar ratio **7b**:**6b** changes from 1.04 (32% conversion) to 1.21 (78% conversion) and increases only if heating is prolonged after the disappearance of **3b**. However, it is not convenient to attempt completion of the process to **7b** by this route, as further decomposition becomes important.

Photolytic cleavage of compound **3b** in solution leads to the same product mixture in molar ratio **7b**:**6b** = near 1, as further cyclization of **6b** to **7b** is apparently slow in these conditions. The results concerning the rearrangement of compounds **3a**, **3b**, and **3c** in solution are summarised in Table I of ref 1.

The same rearrangement can be profitably achieved by FVT (flash vacuum thermolysis) at 400 °C: by this procedure, the amount of enaminone **6** is considerably reduced (down to 0 in many cases), with increase in the yield of pyridone **7**.

The above results suggest that the two products **6** and **7** arise from a common intermediate, possibly the diradical **5**: unimolecular cyclization to **7** then competes with H-transfer to **6**, the last process (partially intermolecular) being favored in a condensed phase, the former in FVT conditions.

Structure of the Substituted Products 7d and 7e. Monosubstitution in the cyclopropane ring, as in **3d**, implies a regiochemical alternative in the rearrangement. The production of a single regioisomer (**7d**) indicates that the cyclopropane ring opening occurs selectively at the bond adjacent to R^2 = Ph, as a result of radical (or charge) stabilisation. The illustrated structure of **7d** is clearly supported by spectroscopic evidence (benzylic ^{1}H at δ 4.65, dd; ^{13}C at δ 58.21, d).

The rearrangement of compound **3e** affords a mixture of two diastereoisomers in molar ratio 6:1 (from ^{1}H NMR; 8:1 on the isolated isomers), identified as the cis-fused (major) and trans-fused (minor) isomers **7e** on the basis of ^{1}H NMR data. Decoupling experiments have shown in fact that the coupling constant between the protons of the

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two bridgehead CH groups is 3 Hz in the major and 13 Hz in the minor isomer. The observed selectivity in favor of *cis*-**7e** requires some comments.

Ring closure of the intermediate **5e** can take place by an axial (A) or an equatorial (E) attack on the cyclohexyl •CH by the N• atom: this intermediate **5e** is illustrated in Scheme III with the chain in the preferred equatorial position and in the conformation suitable for A- or E-attack. In analogous processes, the diastereoselectivity has been reported to be governed by the balance between *steric overcrowding* (which dominates with bulky reagents and favors the E-attack) and *torsional strain* (which dominates in the absence of reagents overcrowding and favors the A-attack).[15] The last applies to the intermediate **5e**: since the C–•CH–C plane lies above the adjacent equatorial ligands, an eclipsed conformation develops in the TS (transition state) under E-attack, whereas such a torsional strain will be absent in the case of A-attack.

Experimental Section

All reactions were carried out under nitrogen. Melting points were observed with a microscope RCH Kofler apparatus. Kugelrohr distillations were carried out by the Büchi GKR-50 distillator; the oven temperature is reported. Chromatographic separations were performed under pressure, using the flash-column technique[16] (silica gel); R_f values refer to TLC, carried out on 0.25-mm silica gel plates (Merck F_{254}), with the same eluant indicated for the column chromatography. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer, UV spectra on a Beckman DU-8B spectrophotometer, and NMR spectra ($CDCl_3$ solutions, unless otherwise stated) on Perkin-Elmer R 32 (^1H, 90 MHz), Varian XL 200 (^1H, 200 MHz) and Varian FT-80 A (^{13}C, 20 MHz) spectrometers: the chemical shifts are given in ppm from TMS. Coupling constants J (in Hz) refer to $^3J_{HH}$, but J_{gem} indicates $^2J_{HH}$. Mass spectra were recorded at 70 eV by GC inlet on a 5790A-5970A Hewlett-Packard instrument; only the most significant peaks are reported. Microanalyses were carried out with a Perkin-Elmer 240 C elemental analyzer. All chiral compounds are to be considered racemic.

Nitrile oxides 1 were generated in situ from the appropriate precursors: acetonitrile oxide (1, R^1 = Me) from nitroethane,[17] benzonitrile oxide (1, R^1 = Ph) from benzohydroxamoyl chloride, and phenylacetonitrile oxide (1, R^1 = $PhCH_2$) from phenylacetohydroxamoyl chloride.[18] **Methylenecyclopropane** (2, R^2 = R^3 = H) was prepared as reported[19] or purchased from Fluka. **1-Methylene-2-phenylcyclopropane** (2, R^2 = Ph, R^3 = H) was prepared as reported.[20] **7-Methylenenorcarane** (2, R^2, R^3 = $-(CH_2)_4-$) was prepared as reported[21] from 7,7-dibromonorcarane.[22]

Spiro[4,5-dihydro-3-methylisoxazole-5,1′-cyclopropane] (3a). A solution of nitroethane (5 mmol) and triethylamine (1.2 mmol) in anhydrous diethyl ether (5 mL) was added to a cold (–50 °C) solution of methylenecyclopropane (5.5 mmol) and phenyl isocyanate (10 mmol) in the same solvent (5 mL), under stirring. After 6 h at 0 °C and 10 h at room temperature, the mixture was passed over a pad of silica gel and the clear solution concentrated (Vigreux column) and distilled to give **3a**, bp 80 °C at 12 Torr, yield 35%.

3a. Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 63.03; H, 8.20; N, 12.86.[23] MS, m/e (rel intensity): 111 (**3a**$^{•+}$, 11), 55 (**3a**$^{•+}$ – C_3H_4O, 23), 42 (100). ^1H NMR: 2.98 (s, 2 H), 2.00 (s, 3 H), 1.10 (m, 2 H), 0.70 (m, 2 H). ^{13}C NMR: 155.78, 64.53, 43.17, 13.25, 11.12. UV ($CDCl_3$) λ_{max} 220 nm.

4a. MS, m/e (rel intensity): 111 (**4a**$^{•+}$, 33), 83 (31), 82 (100), 69 (19), 68 (10), 55 (17), 42 (36), 39 (15). ^1H NMR: 4.25 (s, 2 H), 1.65 (s, 3 H), 1.10 (m, 2 H), 0.70 (m, 2 H). ^{13}C NMR: 74.08, 10.82, 10.64, 10.04. The NMR signals are those identified in the crude reaction mixture.

Spiro[4,5-dihydro-3-phenylisoxazole-5,1′-cyclopropane] (3b). A solution of methylenecyclopropane (47 mmol) in anhydrous diethyl ether (23 mL) was prepared at –50 °C. After triethylamine addition (30.8 mmol), the temperature was allowed to reach 0 °C and a solution of benzohydroxamoyl chloride (30.8 mmol) in the same solvent (40 mL) added slowly (4.5 h) under stirring. Stirring was continued at room temperature overnight, then the precipitate was removed, the volume was reduced in vacuo, and the product **3b** was collected and washed with cold light petroleum ether: 3.04 g (R_f 0.43), TLC pure. After complete solvent removal, the residue was column-chromatographed (eluant: methylene chloride + light petroleum ether, 2:1) to give more product (0.78 g). Overall yield 3.82 g (72%).

3b: mp 94–95 °C, from ligroin. Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.56; H, 6.43; N, 8.14. MS, m/e (rel intensity): 173 (**3b**$^{•+}$, 27), 172 (45), 144 (76), 117 (**3b**$^{•+}$ – C_3H_4O, 100). ^1H NMR: 7.7–7.3 (m, 5 H), 3.36 (s, 2 H), 1.20 (m, 2 H), 0.80 (m, 2 H). ^{13}C NMR: 156.8, 129.8, 128.4, 126.7, 126.2, 65.9, 39.7, 11.58. IR ($CDCl_3$): 1570, 1370, 1010 cm^{-1}.

Spiro[4,5-dihydro-3-benzylisoxazole-5,1′-cyclopropane] (3c). The procedure described above for **3b** was applied to phenylacetohydroxamoyl chloride (19.5 mmol), added during 6.5 h to methylenecyclopropane (33.7 mmol) and triethylamine (19.8 mmol) in anhydrous diethyl ether (50 mL). The residue, after removal of the solvent in vacuo, was passed over a short-path column (silica gel, eluant methylene chloride) in order to remove most dibenzylfuroxan and then column-chromatographed (same eluant) to give **3c**, 1.31 g, 7 mmol (36%), R_f 0.43; distilled with Kugelrohr at 170 °C and 0.8 Torr.

3c. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.62; H, 7.16; N, 7.19. MS, m/e (rel intensity): 187 (**3c**$^{•+}$, 4), 117 (21), 91 (100). ^1H NMR (CCl_4): 7.23 (s, 5 H), 3.64 (s, 2 H), 2.75 (s, 2 H), 1.15–0.95 (m, 2 H), 0.7–0.45 (m, 2 H). ^{13}C NMR: 158.3, 135.4, 128.5, 126.8, 65.0, 41.0, 34.4, 11.3. IR (neat): 1620, 1362, 1010, 700 cm^{-1}.

4c. MS, m/e (rel intensity): 187 (**4c**$^{•+}$, 18), 130 (34), 117 (19), 91 (100). ^1H NMR: 7.34 (s, 5 H), 4.28 (s, 2 H), 3.45 (s, 2 H), 0.99–0.83 (m, 4 H).

Spiro[4,5-dihydro-3-methylisoxazole-5,1′-2′-phenylcyclopropane] (3d). A solution of nitroethane (22 mmol) and triethylamine (2.6 mmol) in anhydrous benzene (11 mL) was added dropwise (1 h) to a refluxing solution of 1-methylene-2-phenylcyclopropane (14.5 mmol) and phenyl isocyanate (23 mmol) in the same solvent (10 mL), under stirring. Stirring was continued overnight at room temperature, the precipitate was removed, and the solution was concentrated in vacuo. The unreacted 1-methylene-2-phenylcyclopropane was recovered by Kugelrohr distillation (45–65 °C at 0.5 Torr) and the product **3d** was isolated by column chromatography (eluant: methylene chloride): 1.095 g (40%), R_f 0.22, mp 85 °C from diethyl ether.

3d. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.85; H, 7.01; N, 7.29. MS, m/e (rel intensity): 187 (**3d**$^{•+}$, 10), 186 (5), 158 (6), 104 (100). ^1H NMR: 7.5–6.95 (m, 5 H), AB system [2.84 (d, J_{gem} = 19, 1 H), 2.60 (d, J_{gem} = 19, 1 H)], 2.54 (dd, J_{trans} = 8, J_{cis} = 11, 1 H), 1.91 (s, 3 H), 1.66 (dd, J_{cis} = 11, J_{gem} = 7, 1 H), 1.19 (dd, J_{trans} = 8, J_{gem} = 7, 1 H). ^{13}C NMR: 155.6, 137.0, 128.3, 127.1, 126.0, 70.1, 39.6, 27.4, 16.1, 13.3. IR ($CDCl_3$): 1610, 1392 cm^{-1}.

Spiro[4,5-dihydro-3-phenylisoxazole-5,7′-bicyclo[4.1.0]-heptane] (3e). A solution of benzohydroxamoyl chloride (41 mmol) in anhydrous ether (60 mL) was added dropwise (1.5 h) under stirring to a cold (0 °C) solution of 7-methylenenorcarane (26.3 mmol) and triethylamine (48 mmol) in the same solvent (60 mL). Stirring was continued 1 h at room temperature, then the precipitate was removed, the solution was concentrated in vacuo, and the product was extracted with light petroleum ether, bp 30–50 °C, in order to remove most of the diphenylfuroxan. The solution was concentrated and the residue column-chromatographed (eluant: pentane + methylene chloride 1:1) to give the product **3e** as an oil (yield 37%), R_f 0.20, which solidified.

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3e: mp 67–68 °C, from pentane. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.60; H, 7.48; N, 5.94. MS, *m/e* (rel intensity): 227 (**3e**$^{\bullet+}$, 10), 226 (6), 198 (9), 145 (33), 117 (**3e**$^{\bullet+}$ – $C_7H_{10}O$, 100). ^{1}H NMR: 7.9–7.2 (m, 5 H), 3.3 (s, 2 H), 2.0–0.8 (m, 10 H). ^{13}C NMR: 156.0, 130.0, 129.7, 128.4, 126.2, 72.3, 32.3, 21.0, 17.9, 16.1. IR ($CDCl_3$): 1570, 1355 cm^{-1}.

4e. MS, *m/e* (rel intensity): 227 (**4e**$^{\bullet+}$, 63), 226 (17), 198 (44), 144 (48), 130 (100). ^{1}H NMR: 4.3 (s, 2 H), identified in the crude reaction mixture.

Rearrangement of 3a: 5-Aminohexa-1,4-dien-3-one (6a) and 5,6-Dihydro-2-methyl-4-pyridone (7a). A solution of **3a** in anhydrous benzene (183 mg in 7.26 mL, 0.227 M) was heated in a sealed tube at 200 °C for 30 min. The solvent was then removed and the residue column-chromatographed (eluant: methylene chloride + methanol, 10:1) to give recovered **3a**, R_f 0.69, 11 mg (6%); **6a**, R_f 0.50, 47 mg (26%): **7a**, R_f 0.30, 99 mg (55%).

6a: mp 89–92 °C, from ligroin. Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.35; H, 8.16; N, 12.17. MS, *m/e* (rel intensity): 111 (**6a**$^{\bullet+}$, 82), 110 (65), 84 (100). ^{1}H NMR: 10.20 (br), 6.40 (dd, J_{cis} = 9, J_{trans} = 17, 1 H, A part of an ABX system), 6.10 (dd, J_{gem} = 3, J_{trans} = 17, 1 H, B part of an ABX system), 5.49 (dd, J_{gem} = 3, J_{cis} = 9, 1 H, X part of an ABX system), 5.18 (s, 1 H), 1.95 (s, 3 H). ^{13}C NMR: 187.3, 163.4, 137.8, 123.0, 95.0, 22.2. IR ($CDCl_3$): 3500, 1610, 1530 cm^{-1}.

7a: mp 38–40 °C. Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.36; H, 8.34; N, 11.93. MS, *m/e* (rel intensity): 111 (**7a**$^{\bullet+}$, 99), 82 (39), 68 (50), 42 (100). ^{1}H NMR: 6.87 (br s, 1 H), 4.92 (s, 1 H), 3.55 (t, *J* = 8, 2 H), 2.38 (t, *J* = 8, 2 H), 2.00 (s, 3 H). ^{13}C NMR: 191.9, 163.7, 97.8, 41.25, 34.6, 20.6. IR ($CDCl_3$): 3450, 1630, 1590, 1532 cm^{-1}.

Rearrangement of 3b: 1-Amino-1-phenylpenta-1,4-dien-3-one (6b) and 5,6-Dihydro-2-phenyl-4-pyridone (7b). (a) Thermolysis in Solution. A solution of **3b** in anhydrous acetonitrile (346 mg in 10 mL, 0.2 M) was heated in a sealed tube at 200 °C for 1 h. **7b** precipitated in part on cooling (105 mg). The solution was then concentrated and the residue column-chromatographed (eluant: methylene chloride + methanol, 20:1) to give **6b**, R_f 0.49, 131 mg (38%); more **7b**, R_f 0.28, 100 mg (overall 205 mg, 59%); no starting material **3b**. In refluxing mesitylene, after 10 h, 36.5% **7b** and 39% **6b** were isolated. During the rearrangement, the following mixture compositions were observed by GC (in diphenyl ether): 1.5 h, **3b** 67.5%, **7b** 13.8%, **6b** 13.3%; 4.5 h, **3b** 21.9%, **7b** 32.4%, **6b** 26.7%.

(b) Photolysis in Solution. A solution of **3b** in anhydrous acetonitrile (345 mg in 4 mL, 0.5 M) was exposed for 1 day to the UV light of a low-pressure Hg lamp (λ_{max} 253 nm) and the precipitated **7b** was collected (78 mg). The solution was worked up as above to give **6b**, 140 mg (41%), and more **7b**, 79 mg (overall 157 mg, 45%); benzonitrile was detected as a byproduct.

(c) Flash Vacuum Thermolysis (FVT). The vapors of **3b** (172 mg) were passed under 0.04 Torr through a quartz tube heated at 400 °C and then led into a cold trap. After washing with methylene chloride, solid **7b** was collected from the condensed vapors (75 mg) and the solution was worked up as above to give starting material **3b**, R_f 0.69, 22 mg (with residual 8 mg in the starting flask, overall 30 mg, 17%), **6b**, 20 mg (12%), and more **7b**, 19 mg (overall 94 mg, 54%).

6b. Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.28; H, 6.40; N, 8.21. MS, *m/e* (rel intensity): 173 (**6b**$^{\bullet+}$, 60), 172 (100), 146 (85). ^{1}H NMR: 10.4 (br), 7.7–7.4 (m, 5 H), 6.48 (dd, J_{trans} = 18, J_{cis} = 10, 1 H), 6.18 (dd, J_{trans} = 18, J_{gem} = 3, 1 H), 5.57 (dd, J_{cis} = 10, J_{gem} = 3, 1 H), 5.60 (s, 1 H). ^{13}C NMR: 188.3, 162.8, 138.0, 137.0, 130.6, 128.9, 126.1, 123.6, 94.5. IR ($CDCl_3$): 3495, 1605, 1528 cm^{-1}.

7b: mp 183–184 °C, from acetonitrile. Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.58; H, 6.39; N, 8.38. MS, *m/e* (rel intensity): 173 (**7b**$^{\bullet+}$, 100), 172 (45), 144 (55). ^{1}H NMR: 7.50 (m, 5 H), 5.55 (br s, 1 H), 5.42 (s, 1 H), 3.72 (dt, *J* = 9, 2, 2 H), 2.50 (t, *J* = 9, 2 H). ^{13}C NMR: 192.8, 162.1, 135.4, 130.7, 128.8, 126.0, 98.2, 41.0, 35.3. IR ($CDCl_3$): 3460, 1625, 1565, 1522 cm^{-1}.

Rearrangement of 3c: 5-Amino-6-phenylhexa-1,4-dien-3-one (6c) and 5,6-Dihydro-2-benzyl-4-pyridone (7c). A solution of **3c** in anhydrous acetonitrile (176 mg in 4.7 mL, 0.2 M) was heated in a sealed tube at 200 °C for 1 h. The solvent was then removed and the residue column-chromatographed (eluant: methylene chloride + methanol, 20:1) to give **7c**, R_f 0.22, 95 mg (54%), and **6c**, R_f 0.44, 21 mg (12%).

6c. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 77.22; H, 6.66; N, 7.54. MS, *m/e* (rel intensity): 187 (**6c**$^{\bullet+}$, 100), 186 (73), 160 (23). ^{1}H NMR: 10 (br), 7.50–7.20 (m, 5 H), 6.4 (dd, J_{trans} = 17, J_{cis} = 9, 1 H), 6.12 (dd, J_{gem} = 3, J_{trans} = 17, 1 H), 5.52 (dd, J_{cis} = 9, J_{gem} = 3, 1 H), 5.27 (s, 1 H), 3.55 (s, 2 H). ^{13}C NMR: 187.9, 164.6, 137.8, 135.3, 129.1, 128.8, 127.3, 123.4, 95.4, 42.1. IR (CCl_4): 3490, 1520 cm^{-1}.

7c: mp 116 °C. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.84; H, 7.32; N, 7.31. MS, *m/e* (rel intensity): 187 (**7c**$^{\bullet+}$, 100), 186 (19), 158 (40). ^{1}H NMR: 7.45–7.2 (m, 5 H), 5.07 (s, 1 H), 3.55 (s, 2 H), 3.48 (t, *J* = 8, 2 H), 2.39 (t, *J* = 8, 2 H). ^{13}C NMR: 192.3, 164.3, 135.3, 128.9, 128.8, 127.2, 99.4, 41.8, 40.9, 35.1. IR ($CDCl_3$): 3430, 1630 cm^{-1}.

Rearrangement of 3d: 5,6-Dihydro-2-methyl-6-phenyl-4-pyridone (7d). The intermediate **3d** (260 mg) was submitted to FVT, as described for **3b**. Washing with light petroleum ether (bp 30–50 °C) gave solid **7d**, 216 mg (83%) and, after removal of the solvent, a residual oil identified as benzylideneacetone, 22 mg (8.5%).

7d: mp 162 °C, from chloroform + light petroleum ether. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.79; H, 6.85; N, 7.56. MS, *m/e* (rel intensity): 187 (**7d**$^{\bullet+}$, 53), 186 (8), 104 (100). ^{1}H NMR: 7.5 (s, 5 H), 5.03 (br s, 1 H), 4.96 (s, 1 H), 4.65 (dd, J_{cis} = 6.5, J_{trans} = 13, 1 H), 2.57 (dd, J_{trans} = 13, J_{gem} = 16, 1 H), 2.31 (dd, J_{cis} = 6.5, J_{gem} = 16, 1 H), 2.05 (s, 3 H). ^{13}C NMR: 191.6, 162.1, 140.1, 128.8, 128.2, 126.5, 99.3, 58.2, 43.3, 20.9. IR ($CDCl_3$): 3430, 1630, 1590, 1520 cm^{-1}.

Rearrangement of 3e: 3-Amino-1-(1-cyclohexen-1-yl)-3-phenyl-2-propen-1-one (6e) and 5,6,7,8,9,10-Hexahydro-2-phenyl-4(1*H*)-quinolinone (7e, Two Isomers). The mixture of products obtained by FVT from 378 mg of **3e** condensed in part in the cold trap (24 mg, identified by GC/MS as an equimolar mixture of benzonitrile and 1-acetylcyclohexene) and mainly in the quartz tube, outside the oven (301 mg). This fraction was dissolved in methylene chloride and column-chromatographed (eluant: ethyl acetate + light petroleum ether, 2:1) to give **6e**, R_f 0.79, 18 mg (5%), **7e** (trans isomer), R_f 0.49, 31 mg (8%), **7e** (cis isomer), R_f 0.26, 241 mg (64%).

6e. MS, *m/e* (rel intensity): 227 (**6e**$^{\bullet+}$, 61), 226 (24), 146 (100). ^{1}H NMR: 7.7–7.4 (m, 5 H), 6.8 (m, 1 H), 5.85 (s, 1 H), 2.45–2.2 (m, 4 H), 1.9–1.6 (m, 4 H).

7e, major isomer (cis): mp 174–175 °C, from benzene. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.25; H, 7.42; N, 6.33. MS, *m/e* (rel intensity): 227 (**7e**$^{\bullet+}$, 41), 226 (11), 198 (27), 172 (100), 104 (8). ^{1}H NMR: 7.8–7.3 (m, 5 H), 5.4 (br s, 1 H), 5.35 (s, 1 H), 3.9 (m, 1 H; becomes br d, *J* = 3, on irradiation at δ 1.57), 2.5–1.15 (m, 9 H). ^{13}C NMR: 196.2, 160.9, 135.4, 130.4, 128.5, 126.0, 96.2, 52.4, 45.9, 28.1, 24.2, 23.6, 21.3. IR ($CDCl_3$): 3445, 3420, 1620, 1565, 1518 cm^{-1}.

7e, minor isomer (trans). MS; identical with that of the cis isomer. ^{1}H NMR: 7.7–7.3 (m, 5 H), 5.45 (d, *J* = 2, 1 H), 5.1 (br d, *J* = 2, 1 H), multiplet centered at 3.4 (1 H; becomes br d, *J* = 13, on irradiation at δ 1.65), 2.6–1.05 (m, 9 H). ^{13}C NMR: 194.8, 160.7, 135.4, 130.4, 128.5, 126.0, 98.1, 57.4, 47.7, 31.6, 25.0, 24.1, 24.0. IR ($CDCl_3$): 3445, 3420, 1625, 1570, 1512 cm^{-1}.

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Registry No. **1** (R_1 = Me), 7063-95-8; **1** (R_1 = Ph), 873-67-6; **1** (R_1 = $PhCH_2$), 71494-99-0; **2** (R_2 = R_3 = H), 6142-73-0; **2** (R_2 = Ph, R_3 = H), 29817-09-2; **2** (R_2, R_3 = $(CH_2)_4$), 54211-14-2; **3a**, 101960-34-3; **3b**, 101960-35-4; **3c**, 101960-36-5; **3d**, 112712-47-7; **3e**, 112712-48-8; **4a**, 112712-45-5; **4c**, 112712-46-6; **4e**, 112712-49-9; **6a**, 101960-37-6; **6b**, 101960-38-7; **6c**, 101960-39-8; **6e**, 112712-50-2; **7a**, 59636-08-7; **7b**, 101960-40-1; **7c**, 101960-41-2; **7d**, 26674-16-8; *cis*-**7e**, 112712-51-3; *trans*-**7e**, 112712-52-4; $MeCH_2NO_2$, 79-24-3; PhNCO, 103-71-9; PhC(Cl)=NOH, 698-16-8; $PhCH_2C(Cl)$=NOH, 701-72-4; PhCH=CHCOMe, 122-57-6.