mixtures 2,3 and 4,5 were measured (Varian MAT 731) after direct probe introduction. Spectra of derivative 7 and the free material were recorded with a Varian 731 instrument, 70 eV, source 250 °C, with direct probe sample introduction, at low resolution (EI and FD), and high resolution with photographic recording (EI).

Acetylation of Adenosine. Compound 1 (4 mg) in 0.2 mL of acetone was added to adenosine (2 mg) in 0.2 mL of water (adjusted to pH 7.4 with dilute NaOH) or in 0.2 mL of 0.1 M phosphate buffer, pH 7.4. After reaction overnight at 37 °C, the total mixture was applied to a preparative thin-layer chromatography plate (Analtech 2-mm silica gel GF). This was developed first in ethyl acetate to remove solvolysis products of 1 and then in ethyl acetate–methanol–acetic acid (89:7:4). Under these conditions, in either reaction 8% of the adenosine was converted to products identical in the two systems. These adducts have been previously reported.[6b] In phosphate buffer, however, an additional 12% was converted to material which did not leave the origin on TLC in ethyl acetate, but was the most mobile material in the secondary eluant. Two closely spaced bands appeared which, upon isolation, each gave rise to two bands on rechromatography, in addition to a trace of underivatized nucleoside. Each band had an ultraviolet spectrum like that of adenosine, with the same pK. The latter observation implies that the base was not altered or that any derivatization was immediately labile to acid and alkali. Gas chromatography–mass spectrometry of the silylated product from each TLC fraction showed a small amount of adenosine followed by two principal components having retention times 1.09 and 1.20 relative to adenosine,[17] areas 1.8:1, assigned to structures 2 and 3, respectively. Calcd exact mass for $C_{21}H_{29}N_5O_5Si_3$: 525.2258. Found for 2 + 3: 525.2264.

Acetylation of Guanosine. Compound 1 (13.5 mg) in 1 mL of acetone was added to 0.7 mg of guanosine in 1 mL of water or phosphate buffer. After reaction overnight at 37 °C, the reaction mixture was chromatographed on a preparative cellulose thin-layer plate (Analtech 1 mm Avicel F) in 1-butanol–acetic acid–water (50:11:25). In each reaction, 4% of the guanosine was converted to previously reported alkylation products,[6b] while in buffer another 4% was converted to new compound recognized as product running just ahead of guanosine on the plate. Like the adenosine product, it was a mixture of interconvertible materials with ultraviolet spectrum and pK like that of starting material. Gas chromatography–mass spectrometry of the silylated bands recovered from TLC produced a chromatographic pattern very similar to that of the adenosine product, consisting of guanosine and two major components; retention times relative to guanosine[17] 1.25, 1.37, areas 2.2:1, corresponding to 4 and 5, respectively. Calcd exact mass for $C_{24}H_{47}N_5O_6Si$: 613.2603. Found for 4 + 5: 613.2590.

Acetylation of Cytidine. Compound 6 (25 mg) in 0.5 mL of acetone was added to 2.5 mg of cytidine in 0.5 mL of water. After reaction overnight at 37 °C, the mixture was chromatographed in the same way as the adenosine–1 reaction mixture. A new compound was identified in about 6% yield, running just ahead of cytidine. This product had ultraviolet absorbance maxima (95% ethanol) at 247 and 299 nm (247/299 = 2.1), with no pK value between pH 2 and 10. In stronger base it was converted to a compound with UV characteristics of cytidine. Mass spectrometry of its trimethylsilyl derivative showed a component with a molecular weight of 501. Presence of three silyl groups was established from the mass spectrum of the corresponding $Si(CD_3)_3$ derivative. The assignment 7 was corroborated by the corresponding high-resolution mass spectrum (calcd exact mass for $C_{20}H_{39}N_3O_6Si_3$ 501.2146, found 501.2143), and field-desorption (FD) spectrum (MH^+ = 286). The FD mass spectrum also exhibited peaks consistent with the presence of lesser amounts of di- and triacetylcytidine (m/z 328, 370), which were not represented in the spectrum of 7, but were also found in the direct-probe EI spectrum of the underivatized cytidine product. Reinspection of the sample by analytical TLC (Analtech Uniplate, 0.25 mm SiO_2 GHLF; ethyl acetate–methanol–acetic acid, 89:7:4) revealed total detectable impurities to be less than 5% of the principal product, in agreement with the EI spectrum of the silylated compound.

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Registry No. 1, 26594-44-5; 2, 82064-45-7; 3, 82064-46-8; 4, 82064-47-9; 5, 82064-48-0; 6, 38105-25-8; 7, 82064-49-1; adenosine, 58-61-7; guanosine, 118-00-3; cytidine, 65-46-3.

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A Photochemical Ring Contraction of an Imino Lactam

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The photochemical rearrangement of three tetrahydro-2-pyrazinones in aqueous medium to imidazol-5-ones is described. 1,2,5,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (4) gives 1,2,2,4-tetramethyl-3-imidazolin-5-one (7), 1,2,5,6-tetrahydro-3,6,6-trimethyl-2-pyrazinone (5) gives 4-methyl-5-imidazolidinone (9), and 1,2,5,6-tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6) gives 1,4-dimethyl-5-imidazolidinone (8). A mechanism involving enediimine and isoimidazole intermediates is proposed in analogy with the mechanism for rearrangement of 5,6-dihydropyrazines to imidazoles.

Earlier we reported that an imino lactone, 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (1) undergoes photoreductive dimerization in 2-propanol solvent to give meso and *dl* dimers 2 and 3.[1] Because these dimers possess the interesting property of reacting as mild one- and two-electron reducing agents,[2,3] we have been synthesizing analogues as part of a structure reactivity study. We now report on an unusual photochemical ring contraction of the imino lactam analogue, 1,2,5,6-tetrahydro-3,5,5-trimethyl-2-pyrazinone (4), which occurs to the exclusion of

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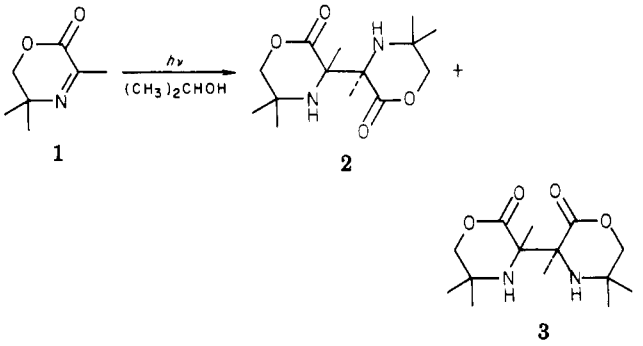
0022-3263/82/1947-3145$01.25/0

photoreductive dimerization in aqueous medium.



1 2 3

Results

Synthesis of Reactants. 1,2,5,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (4) was prepared by the reaction of ethyl pyruvate with 1,2-diamino-2-methylpropane. The regioisomer 1,2,5,6-tetrahydro-3,6,6-trimethyl-2-pyrazinone (5) was a byproduct of the condensation. Pyrazinone 4 was obtained pure in 40% isolated yield by two recrystallizations from ether. The regioisomers could not be separated by flash chromatography[4] of the mother liquor; however, a small sample of pure pyrazinone 5 was obtained by preparative GLC. The two pyrazinones were characterized from the spectral data and distinguished by ^1H NMR spectroscopy. In particular the methylene protons of 4 but not of 5 are coupled to the NH proton. Pyrazinone 4 was alkylated at the amide nitrogen with sodium hydride and methyl iodide to give 1,2,5,6-tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6).

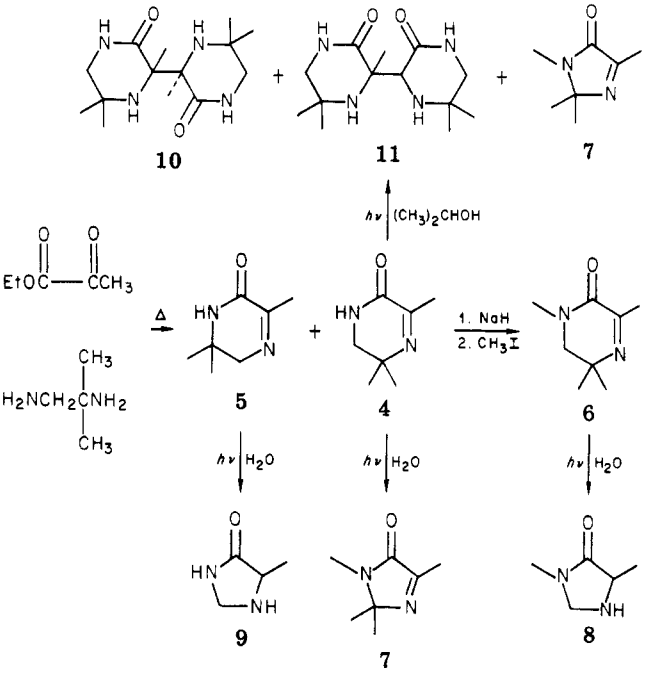
Photochemical Reactions. The pyrazinones 4–6 show weak transitions in the region of 310 nm. This band was assigned as an n–π^*-type transition consistent with the intensity and solvent shift data reported in the Experimental Section.

Irradiation of 1.0 g of pyrazinone 4 dissolved in water in a Pyrex immersion well apparatus with a 450-W mercury lamp for 32 h gave the isomer 1,2,2,4-tetramethyl-3-imidazolin-5-one (7) in 62% isolated yield. The imidazolinone was characterized from spectral and analytical data. In particular the ^1H NMR spectrum showed only three singlets and the IR spectrum showed the presence of carbon–oxygen and carbon–nitrogen double bonds. Irradiation of pyrazinone 4 under reducing conditions in 2-propanol solvent gave a mixture of the meso and *dl* dimers 10 and 11 analogous in structure to 2 and 3 as the major products and imidazolinone 7 as the minor product.[5]

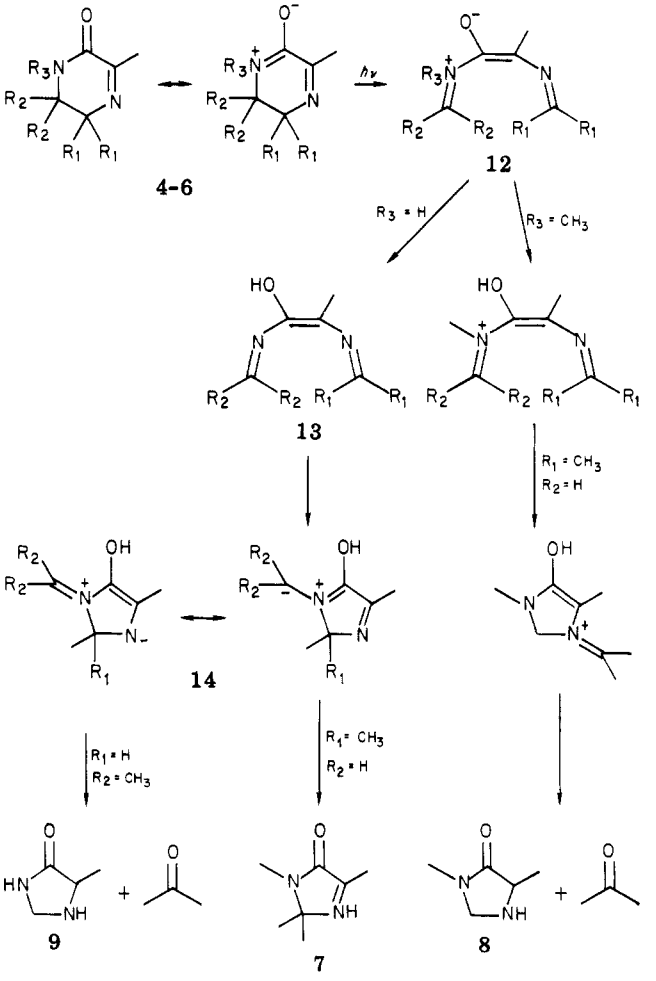
Similar irradiation of the *N*-methyl derivative 6 in water gave 1,4-dimethyl-5-imidazolidinone (8) in 58% isolated yield. The assigned structure was again established from the spectral data. Loss of the carbon–nitrogen double bond was evident in the IR, ^1H NMR, and ^{13}C NMR spectra. Acetone was shown to be a byproduct of the ring contraction by analytical GLC.

Because reasonable quantities of the pure regioisomer 5 could not be obtained, pyrazinone 5 was irradiated in water as a 52:48 mixture with pyrazinone 4. After 90% destruction of the pyrazinone mixture, 4-methyl-5-imidazolidinone (9) was isolated in 25% yield from pyrazinone 5 and imidazolinone 7 was isolated in 54% yield from pyrazinone 4. Structure 9 is consistent with spectral data which are comparable with spectral data for imidazolidinone 8. These photochemical ring contraction reactions are summarized in Scheme I.

Scheme I



Scheme II



Discussion

A mechanism consistent with the observed photochemical ring contraction is shown in Scheme II. The excited

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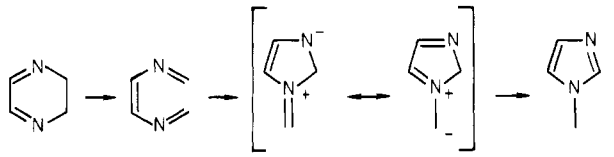
pyrazinone undergoes ring opening at the 5,6 bond to give an enediimine zwitterion **12**. Proton rearrangement of the zwitterion when possible gives the enediimine **13** which cyclizes regioselectively to form the isoimidazole ring. Final product structure is a function of protonation of the ambient zwitterion **14**. When proton rearrangement of the initial zwitterion **12** is not possible, the regiochemistry of the cyclization is reversed and occurs by attack of the imine nitrogen on the carbon of the iminium ion functional group.

The mechanism finds precedent in the photorearrangement of 5,6-dihydropyrazines as initially observed by Beak and Miesel[6] and further described by Arnold and co-workers.[7] Beak and Miesel observed that six 5,6-dihydropyrazines photorearrange to imidazoles and proposed the intermediacy of an enediimine and a zwitterionic isoimidazole. An intermediate assigned the enediimine structure was observed in low-temperature photolysis of 2,3,5,5-tetramethyl-5,6-dihydropyrazine by Arnold and co-workers.[7]



The enediimine is also accessible from photolysis of 1,3-diazabicyclo[3.1.0]hex-3-enes.[8] Imidazolines are isolated products in alcoholic medium;[8] furthermore, colored intermediates assigned the zwitterionic isoimidazole structure have been detected spectroscopically at low temperature and trapped with dipolarophiles.[9]

Because of the similarity with the photorearrangement of the 5,6-dihydropyrazines, the iminol tautomers of pyrazinones **4** and **5** are reasonable precursors for this photorearrangement. However, the presence of the iminol tautomer was not detected in the NMR spectra of **4** and **5** or in the UV spectrum of **4** compared with the UV spectrum of **6** as a function of solvent (Experimental Section). Similar photorearrangement of pyrazinone **6** for which tautomerism is impossible suggests that the amino carbonyl form is the reactive species.

The dihydropyrazines and the tetrahydropyrazinones react via population of an n–π^*-type excited state. Arnold and co-workers[7] note that the UV spectrum of cyclic molecules bearing the 1,4-diaza-1,3-diene chromophore is a function of ring size. 2,3-Diphenyl-5,6-dihydropyrazine shows a band at 364 nm (ϵ 440) in ethanol solvent; whereas, 2,2-dimethyl-4,5-diphenylisoimidazole shows no long-wavelength absorption band. They attributed the long-wavelength absorption band to a transition between the ground state of the 5,6-dihydropyrazine and the excited state of the enediimine which bears a node between C-5 and C-6. We note a similar absence of the long-wavelength absorption band when the imino lactam functionality is in a five-membered ring. We propose that the long-wavelength absorption band of **4–6** results from the promotion of an electron in an in-plane orbital involving at least the 5, 6 σ bond and the imine nitrogen nonbonding orbital to the lowest π^* orbital. The excited state can then participate in homolysis of the C-5,C-6 bond or hydrogen atom abstraction from solvent at the imine nitrogen. Bond homolysis then occurs to the exclusion of photoreductive dimerization in aqueous medium where hydrogen atom abstraction is inhibited by the water O–H bond strength.

In summary we have described a photochemical rearrangement of some tetrahydro-2-pyrazinones to imidazolones analogous to the rearrangement of dihydropyrazines to imidazoles and note the utility of aqueous medium in facilitating this photochemical reaction.

Experimental Section

Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 337 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with Varian EM 390 and JEOL PFT-100 spectrometers, respectively. Chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. Mass spectra data were obtained with a Varian Mat CH-5 mass spectrometer. A Varian Aerograph Series 1700 gas chromatograph with thermal conductivity detector was used for preparative and analytical gas chromatography. A Cary 219 spectrophotometer was used to obtain ultraviolet and visible spectra. Microanalyses were performed by Atlantic Microlab, Atlanta, GA.

1,2,3,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (4). A 500-mL, three-neck flask was equipped with an addition funnel, nitrogen inlet and outlet, magnetic stirring apparatus, Dean–Stark trap, condenser, and heating mantle. A solution of freshly distilled 1,2-diamino-2-methylpropane (22.0 g, 0.250 mol; Aldrich) in 200 mL of toluene was added to the reaction flask and heated to reflux under a nitrogen atmosphere. Freshly distilled ethyl pyruvate (29.0 g, 0.250 mol; Aldrich) was then added dropwise over a 20-min period. The reaction mixture was refluxed overnight maintaining the nitrogen atmosphere. GLC analysis of the solution with a 5.7 m by 0.63 cm column of 5% FS-1265 on 60/80 mesh Diatoport S at 160 °C (He 60 mL/min) showed only solvent, 1,2,5,6-tetrahydro-3,5,5-trimethyl-2-pyrazinone (**4**; retention time, 4.0 min), and 1,2,5,6-tetrahydro-3,6,6-trimethyl-2-pyrazinone (**5**; retention time, 4.6 min) in the ratio 2.7:1, uncorrected for differences in detector response. The solvent was removed by rotary evaporation and the resultant solid recrystallized twice from ether. Pyrazinone **4** (14.0 g) was obtained in 40% yield as colorless needles, mp 106–108 °C and characterized from the following spectral and analytical data: IR (KBr) 3.12, 3.23, 3.26, 3.38, 3.43, 3.49, 5.94, 6.12 μm; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 6 H), 2.21 (s, 3 H), 3.33 (d, J = 3 Hz, 2 H, collapses to a singlet upon addition of deuterium oxide), 6.70 (br, 1 H); mass spectrum (70 eV), m/e (relative intensity) 141 (6), 140 (57), 111 (12), 97 (17), 82 (62), 71 (17), 70 (10), 55 (19), 43 (22), 42 (100), 41 (56), 39 (14); UV (H_2O) 240 nm (ϵ 1560), 305 nm (sh, 125); (CH_2Cl_2) 239 nm (ϵ 1570), 323 (sh, 139); ^{13}C NMR ($CDCl_3$) δ 21.0, 26.2, 49.2, 54.4, 158.2, 160.0.

Anal. Calcd for $C_7H_{12}N_2O$: C, 59.98; H, 8.63; N, 19.98. Found: C, 59.85; H, 8.62; N, 19.93.

1,2,5,6-Tetrahydro-3,6,6-trimethyl-2-pyrazinone (5). A small sample of pyrazinone **5** as prepared above was isolated via preparative GLC of the mother liquor resulting from the recrystallization of the regioisomer **4**. The same column and conditions as described above were used for the GLC separation. The pyrazinone **5** (mp 96–99 °C) was characterized from the following spectral and analytical data: IR (KBr) 3.16, 3.25, 3.38, 3.43, 5.95, 6.12 μm; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 6 H), 2.23 (m, 3 H), 3.63 (m, 2 H), 6.40 (br, 1 H); UV (H_2O) 243 nm (ϵ 1400), 304 (sh, 139); mass spectrum (70 eV), m/e (relative intensity) 141 (6) 140 (67), 111 (18), 96 (41), 56 (100), 42 (45).

Anal. Calcd for $C_7H_{12}N_2O$: C, 59.98; H, 8.63; N, 19.98. Found: C, 59.81; H, 8.64; N, 19.92.

1,2,2,4-Tetramethyl-3-imidazolin-5-one (7). A solution of 1.00 g (7.09 mmol) of 1,2,5,6-tetrahydro-3,5,5-trimethyl-2-pyrazinone (**4**) in 50 mL of distilled, deionized water was irradiated with a 450-W Hanovia mercury lamp in a Pyrex immersion well. The reaction mixture was continuously degassed with nitrogen and monitored by silica gel TLC, eluting with 10% methanol in methylene chloride and visualizing with UV light (product, R_f 0.48; starting material, R_f 0.32). After 32 h the reaction was complete. The solution was then saturated with sodium chloride and continuously extracted with methylene chloride for 2.5 days. The extract was dried over sodium sulfate and the methylene chloride

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removed by rotary evaporation to afford 0.622 g (4.45 mmol, 62%) of pure 1,2,2,4-tetramethyl-3-imidazolin-5-one as determined by ^{1}H NMR spectroscopy. Vacuum distillation at 95–97 °C (18 torr) gave crystaline material with mp 42–44 °C. The pure imidazolinone had the following spectral properties: IR (KBr) 2.88, 3.37, 3.42, 5.88, 6.10 μm; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6 H), 2.28 (s, 3 H), 3.01 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 14.6, 24.3, 25.5, 84.0, 162.8, 165.5; mass spectrum (70 eV), *m/e* (relative intensity) 140 (27.7), 125 (12.0), 83 (13.9), 82 (18.6), 71 (23.6), 56 (100), 43 (10.3), 42 (48.4); UV (H_2O) 239 nm (ε 3570); (CH_2Cl_2) 234 nm (ε 3380).

Anal. Calcd for $C_7H_{12}N_2O$: C, 59.98; H, 8.63; N, 19.98. Found: C, 60.03; H, 8.66; N, 19.94.

1,2,5,6-Tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6). Sodium hydride (0.373 g as a 50% oil dispersion, 7.76 mmol) was added to 100 mL of tetrahydrofuran and the solution cooled to 0 °C. 1,2,5,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (1.00 g, 7.14 mmol) as a saturated tetrahydrofuran solution was then added dropwise with a nitrogen atmosphere via a Hirschberg dropping funnel. Following a 10-min stirring period 0.55 mL (8.83 mmol) of methyl iodide in 10 mL of tetrahydrofuran was added. The reaction mixture was allowed to warm to ambient temperature with stirring overnight. The contents of the flask were transferred to a round-bottom flask, rinsing with methanol, and the solvents were removed by rotary evaporation. The product mixture was transferred to a separatory funnel with 20 mL of water and 15 mL of methylene chloride and extracted 10 times with 15 mL of methylene chloride. The combined methylene chloride extracts were then dried over sodium sulfate, and the methylene chloride was removed by rotary evaporation to yield 1.10 g (100%) of 1,2,5,6-tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6). The pure pyrazinone had the following spectral properties: IR ($CHCl_3$) 3.36, 3.39, 3.44, 3.52, 6.00, 6.13 μm; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 6 H), 2.14 (s, 3 H) 2.95 (s, 3 H), 3.20 (s, 2 H); mass spectrum, *m/e* (relative intensity) 154 (62), 111 (13), 82 (86), 56 (100), 42 (86), 41 (31); UV (H_2O) 254 nm (ε 1768), 308 (sh, 200); (CH_2Cl_2) 253 nm (ε 1490), 316 (sh, 110).

1,4-Dimethyl-5-imidazolidinone (8). A solution of 1.76 g (11.4 mmol) of 1,2,5,6-tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6) in 140 mL of distilled, deionized water was irradiated with a 450-W Hanovia lamp in a Pyrex immersion well. The solution was continuously degassed with nitrogen, and progress of the reaction was monitored by analytical silica gel TLC, eluting with 10% methanol in methylene chloride (product, R_f 0.29; starting material, R_f 0.54) and visualizing with UV light and 10% phosphomolybdic acid in ethanol. After 96 h the reaction was complete. The solution was saturated with sodium chloride and continuously extracted with methylene chloride for 8 days. The methylene chloride extract was dried over sodium sulfate and the methylene chloride removed by rotary evaporation. The residue was 0.756 g (6.63 mmol, 58%) of 1,4-dimethyl-5-imidazolidinone (8), which was characterized from the following spectral data: IR ($CHCl_3$) 3.05, 3.36, 3.43, 3.51, 5.92 μm; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 7 Hz, 3 H), 2.87 (s, 3 H), 2.60 (br, 1 H), 3.53 (q, J = 7 Hz, 1 H), 4.33 (s, 2 H); ^{13}C NMR ($CDCl_3$) with off-resonance decoupling 16.2 (q), 26.9 (q), 54.3 (d), 63.8 (t), 174.9 (s); mass spectrum, *m/e* (relative intensity) 114 (41), 113 (11), 99 (12), 57 (88), 56 (34), 44 (100), 43 (20), 42 (44). The imidazolidinone 8 could not be sufficiently purified for combustion analysis because of instability.

Irradiation of a Mixture of 1,2,5,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (4) and 1,2,5,6-Tetrahydro-3,6,6-trimethyl-2-pyrazinone (5). A solution of 0.77 g (5.55 mmol) of a 48:52 mixture of 4 and 5 in 50 mL of distilled, deionized water was irradiated with a 450-W Hanovia mercury lamp in a Pyrex immersion well. The reaction was continuously degassed with nitrogen and monitored by silica gel TLC, eluting with ethyl acetate (imidazolinone, R_f 0.68; starting materials, R_f 0.49; imidazolidinone, R_f 0.12) and visualizing with UV light and a solution of 0.3% ninhydrin and 3% acetic acid in 1-butanol. After 97 h of irradiation the reaction was stopped even though some starting material was still present. The solution was saturated with sodium chloride and continuously extracted with methylene chloride for 94 h. The majority of the methylene chloride was rotary evaporated and the residue flash chromatographed through a 15 cm by 3 cm column of dry-packed 32–63-μm silica gel. The column was eluted with 5% methanol in methylene chloride for the first 15 20-mL fractions and then with 20% methanol in methylene chloride for the next 12 20-mL fractions followed by 28% methanol in methylene chloride for the last 10 20-mL fractions. 1,2,2,4-Tetramethyl-3-imidazolin-5-one (7; 0.199 g, 1.42 mmol, 54% from pyrazinone 4) was obtained in fractions 7–10; starting pyrazinones (0.068 g, 0.48 mmol, 9%) in the ratio of 65:35 (4/5) as determined by ^{1}H NMR spectroscopy was obtained in fractions 11–16; and 4-methylimidazolidinone (9; 0.072 g, 0.52 mmol, 25% from pyrazinone 5) was obtained in fractions 28–35. The imidazolidinone was characterized from the following spectral properties: IR ($CHCl_3$) 3.00, 3.36, 3.43, 3.51, 5.91 μm; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 7.5 Hz, 3 H), 2.30 (br, 1 H), 3.48 (q, J = 7.5 Hz, 1 H), 4.40 (s, 2 H), 8.10 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 180.2, 58.8, 54.4, 16.5; mass spectrum, *m/e* (relative intensity) 100 (30), 85 (39), 84 (12), 83 (70), 72 (14), 57 (78), 56 (28), 51 (25), 49 (100), 44 (45), 43 (14), 42 (16). The imidazolidinone 9 could not be sufficiently purified for combustion analysis because of instability.

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Registry No. 4, 82043-97-8; 5, 82043-98-9; 6, 82043-99-0; 7, 82044-00-6; 8, 82044-01-7; 9, 82044-02-8; 10, 82044-03-9; 11, 82044-04-0; 1,2-diamino-2-methylpropane, 811-93-8; ethyl pyruvate, 617-35-6.

Synthesis with Hypochlorous Acid Functionalization of an Isopropenyl Group. Syntheses of (+)-Bilobanone and the Juvabiones

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The two-phase reaction of HOCl with (+)-carvone and (+)-limonene monooxide affords 10-chlorocarvone (2) and 10-chlorolimonene monooxide (10), respectively. The organozinc reagents derived from these halides react with isovaleraldehyde to yield homoallylic alcohols with a bisabolane skeleton, which can be readily converted to (+)-bilobanone (8) and keto epoxide 13, which has previously been used as an intermediate in the synthesis of juvabione (14).

In a recent communication[1] we described the two-phase reaction of hypochlorous acid with certain olefins leading to the formation of allylic chlorides. We now demonstrate that this reaction can be employed to functionalize an isopropenyl group in the presence of other reactive functional groups as illustrated in syntheses of (+)-bilobanone (8) and the juvabiones (14).

10-Chlorocarvone (2) is obtained in high yield by the reaction of HOCl with (+)-carvone (1).[1] Formation of an

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