Table III. Yields, Boiling Points, and Spectroscopic Data of Compounds 9[a,b]

compd	yield, %	bp, °C/mbar (lit. bp)
9a	82	80/7
9b	85	77/3
9c	79	74/2
9d	71	106/1013
9e	80	97/180 (44-46/15)[12]
9f	78	115/1013

[a] All compounds displayed a broad IR absorption between 3350 and 3250 cm^{-1} (film). [b] ^1H NMR data (δ) for 9a: 1.33 (br s, 1, NH), 2.38 (s, 3, CH_3N), 4.08 (d, 1, J = 7 Hz, CHN), 5.0-5.4 (m, 2, H_2C=), 5.7-6.3 (m, 1, HC=), 7.3 ("s", 5, C_6H_5). For 9b: 1.27 (br s, 1, NH), 1.6-1.7 (m, 3, CH_3), 2.32 (s, 3, CH_3N), 3.9-4.1 (m, 1, CHN), 5.5-5.8 (m, 2, 2CH=), 7.3 ("s", 5, C_6H_5). For 9c: 1.30 (br s, 1, NH), 1.50 (s, 3, CH_3), 2.25 (s, 3, CH_3N), 5.0-5.4 (m, 2, CH_2=), 5.8-6.3 (m, 1, CH=), 7.2-7.6 (m, 5, C_6H_5). For 9d: 1.00 (br s, 1, NH), 1.10 (d, 3, J = 6.5 Hz, CH_3C), 1.68 ("d", 3, J = 5 Hz, $CH_3C{\leqslant}$), 2.33 (s, 3, CH_3N), 2.8-3.3 (m, 1, CHN), 5.0-5.6 (m, 2, 2HC=). For 9e: 0.93 (br s, 1, NH), 1.3-2.2 (m, 6, $(CH_2)_3$), 2.43 (s, 3, CH_3N), 2.9-3.1 (m, 1, CHN), 5.75 ("s", 2, 2HC=). For 9f: 1.00 (br s, 1, NH), 1.60 (d, 3, J = 5 Hz, CH_3CH), 1.65 (s, 3, $CH_3C{\leqslant}$), 2.38 (s, 3, CH_3N), 3.12 (s, 2, CH_2N), 5.2-5.7 (m, 1, CH=). ^{13}C NMR data (δ) for 9a: 34.3 (q), 68.1 (d), 114.8 (t), 127.0 (d), 127.2 (d), 128.4 (d), 140.8 (d), 142.5 (s). For 9b: 17.7 (q), 34.3 (q), 67.5 (d), 126.0 (d), 126.9 (d), 127.1 (d), 128.4 (d), 134.2 (d), 143.5 (d). For 9c: 25.1 (q), 29.5 (q), 60.6 (s), 112.9 (t), 126.3 (d), 126.5 (d), 128.0 (d), 144.6 (d), 146.0 (s). For 9d: 17.7 (q), 21.8 (q), 34.0 (q), 57.8 (t), 125.3 (d), 135.5 (d). For 9e: 20.3 (t), 25.5 (t), 29.2 (t), 33.6 (q), 54.7 (d), 128.6 (d), 129.9 (d). For 9f: 13.2 (q), 14.4 (q), 35.8 (q), 60.1 (t), 120.2 (d), 134.3 (s).

Conversion of 7a into 8a by Iodotrimethylsilane. A solution of **7a** (6.5 g, 33 mmol), sodium iodide (14.0 g, 93 mmol), and iodotrimethylsilane (7.7 g, 71 mmol) in 70 mL of CH_3CN is refluxed under anhydrous conditions for 24 h. Thereupon, the mixture is chilled and acidified with 6 mL of concentrated hydrochloric acid. Volatile material is then removed on a rotating evaporator at ambient temperature. After being made alkaline with aqueous potassium hydroxide, the resultant emulsion is extracted with ether (3 × 50 mL). The combined ethereal extracts are washed successively with $Na_2S_2O_3$ solution and water, dried over anhydrous Na_2SO_4, and finally concentrated in vacuo. The product is purified by distillation to yield 3.6 g (81%).

General Procedure for the Preparation of 2-Alkenylmethylamines 9. A solution of the corresponding **7** (0.1 mol) in 75 mL of dry ether is slowly added to a stirred suspension of $LiAlH_4$ (5.7 g, 0.15 mol) in 150 mL of ether. After completion of addition the mixture is refluxed for 4 h. Thereupon, excess $LiAlH_4$ is carefully quenched with water (quenching with ethyl acetate would afford a tertiary amine[9]), followed by filtration of the resultant inorganic salts. The filtrate is dried over anhydrous Na_2SO_4 and fractionated by distillation. Yields, physical constants, and spectroscopic data for products **9** are given in Table III. All compounds **7-9** gave satisfactory combustion analytical data.

Methyl *N*-(1-Phenyl-1-propenyl)carbamate (10a). Compound **7a** (3.0 g, 16 mmol), KO-*t*-Bu (2.5 g, 22 mmol), and catalytic amounts of dibenzo-18-crown-6 in 50 mL of dry ether are stirred for 60 h at ambient temperature. Thereupon, undissolved material is collected by filtration, and the filter cake is suspended in 50 mL of ether and dissolved by addition of 50 mL of water. The organic layer is rapidly separated, washed with water (3 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo (15 mbar). The residue is recrystallized from CH_2Cl_2/pentane (1:4) to yield 1.9 g (63%) of white needles: mp 72 °C; ^1H NMR ($CDCl_3$) δ 1.78 (d, 3, J = 7 Hz, CH_3CH), 3.67 (s, 3, CH_3O), 5.85 (q, 1, J = 7 Hz, CH=), 6.2 (br s, 1, NH), 7.2-7.7 (m, 5, C_6H_5). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.96; H, 6.98; N, 6.97.

Methyl *N*-(1-phenyl-1-butenyl)carbamate (10b) was obtained from **7b** (1.7 g, 8.3 mmol), potassium *tert*-butoxide (3.0 g, 27 mmol), and dibenzo-18-crown-6 in 40 mL of dry ether as described for **10a**. In this case, however, not the filter cake but the filtrate is subjected to further workup: yield 0.9 g (53%); mp 43 °C; ^1H NMR ($CDCl_3$) δ 1.08 (t, 3, J = 7 Hz, CH_3CH_2), 2.23 (quint, 2, J = 7 Hz, CH_2), 3.70 (s, 3, CH_3O), 5.73 (t, 1, J = 7 Hz, CH=), 7.2-7.6 (m, 5, C_6H_5). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.36; N, 6.82. Found: C, 70.05; H, 7.42; N, 6.65.

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Registry No. **1a**, 300-57-2; **1b**, 1560-06-1; **1c**, 934-10-1; **1d**, 109-68-2; **1e**, 110-83-8; **1f**, 513-35-9; **1g**, 557-93-7; **5**, 16762-82-6; **7a**, 86766-60-1; **7b**, 86766-61-2; **7c**, 86766-62-3; **7d**, 86766-63-4; **7e**, 86766-64-5; **7f**, 86766-65-6; **7g**, 86766-66-7; **8a**, 4393-21-9; **8b**, 4393-18-4; **8c**, 86766-67-8; **8d**, 86766-68-9; **8e**, 1541-25-9; **8f**, 86766-69-0; **9a**, 86766-70-3; **9b**, 86766-71-4; **9c**, 86766-72-5; **9d**, 86766-73-6; **9e**, 86766-74-7; **9f**, 86766-75-8; **10a**, 86766-76-9; **10b**, 86766-77-0; SCl_2, 10545-99-0; methyl *N*,*N*-dichlorocarbamate, 16487-46-0; iodotrimethylsilane, 16029-98-4.

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Identification of Configurational Isomers of Fluorochloridone

C. K. Tseng* and R. D. Gless, Jr.

de Guigne Technical Center, Stauffer Chemical Company, Richmond, California 94804

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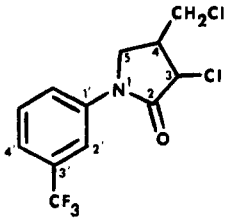
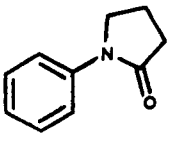
The experimental herbicide Fluorochloridone[1] (3-chloro-4-(chloromethyl)-1-[3-(trifluoromethyl)phenyl]-2-pyrrolidinone) was reported[2] to reduce chlorophyll production in corn. This compound can exist as both a cis and a trans isomer. These isomers were separated, and the configuration of each isomer was determined. Initial structural assignments were unsuccessful due to ambiguous results obtained in ^1H and ^{13}C NMR studies. X-ray crystallographic studies of the major isomer (**1a**) subsequently allowed its assignment as the trans isomer.



1a (trans)
1b (cis)



2

Proton NMR. The proton NMR parameters for **1a** and **1b** are listed in Table I. The chloromethyl group of **1a** exhibited a doublet with a coupling constant of 5.4 Hz whereas that of **1b** exhibited a multiplet. The ring proton H3 of **1a** showed a doublet at 4.48 ppm with a coupling constant of 8.82 Hz and that of **1b** a double at 4.55 ppm

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0022-3263/83/1948-3564$01.50/0

Table I. Proton NMR Parameters of 1a and 1b

compd	shift, δ (multiplicity) H_3	H_4	H_5	CH_2	Ar	$J_{3,4}$, Hz
1a	4.48 (d)	3.00 (m)	3.6–4.1 (m)	3.79 (d)	7.3–7.8 (m)	8.82
1b	4.55 (d)	3.08 (m)	3.5–4.2 (m)	3.5–4.2 (m)	7.4–7.8 (m)	6.30

Table II. Carbon-13 NMR Parameters of 2-Pyrrolidinones

atom	chemical shift,[b,d] 1a	1b	2
C2	168.05 (s)	168.31 (s)	173.6 (174.0,[a] s)
C3	57.46 (d)	58.55 (d)	32.4 (32.7,[a] t)
C4	44.29 (d)	40.18 (d)	17.6 (17.8,[a] t)
C5	48.48 (t)	49.61 (t)	48.3 (48.5,[a] t)
CH_2	43.06 (t)	41.84 (t)	
C1′	139.08 (s)	139.04 (s)	139.0[c] (s)
C2′	116.53 (4.0, d)	116.59 (4.0, d)	119.4[c] (d)
C3′	131.31 (32.4, s)	131.53 (33.4, s)	128.2[c] (d)
C4′	121.93 (3.7, d)	122.06 (4.0, d)	123.8[c] (d)
C5′	129.78 (d)	129.77 (d)	128.2[c] (d)
C6′	122.88 (d)	123.07 (d)	119.4[c] (d)
CF_3	123.93 (272.5, s)	123.85 (273.6, s)	

[a] Reference 6. [b] CF coupling constants expressed in hertz and multiplicities are given in parentheses. [c] The chemical shift assignments for the aromatic carbons in 2 were based on comparison with the reported values (ppm) for acetanilide[7] (C1′, 139.5; C2′, 119.3; C3′, 128.7; C4′, 123.2). [d] Multiplicities are from SFORD.

with a coupling of 6.30 Hz. Proton NMR studies for 1-phenyl-2-pyrrolidinone (**2**)[3] and 4-phenyl-5-carboxy-2-pyrrolidinone,[4] as well as a number of other five-membered-ring compounds[5] reported that cis vicinal coupling constants were larger than trans coupling constants. On the basis of these data, the cis configuration would be assigned to the major isomer, **1a**, and the trans configuration to **1b**.

Carbon-13 NMR. The carbon-13 NMR parameters for **1a**, **1b**, and pyrrolidinone **2** are listed in Table II. The aromatic carbon shifts of the *m*-(trifluoromethyl)phenyl group in **1a** and **1b** can be calculated from the aromatic carbon shifts of **2** by using substituent chemical shift values of monosubstituted benzenes.[8] The calculated values (in ppm: C1′, 138.8; C2′, 116.1; C3′, 130.8; C4′, 120.5; C5′, 127.9; C6′, 122.6) are in good agreement with the observed aromatic carbon shifts of **1a** and **1b**. The shifts of C2′, C3′, and C4′ were further confirmed by their coupling constants with the fluorine atoms of the trifluoromethyl group. The chemical shift assignments for the carbons in the pyrrolidinone ring of **1a** and **1b** were readily made with an SFORD experiment. Among the methine carbons, C3, which is directly attached to chlorine, should have a lower field shift (57.46 ppm for **1a** and 58.55 ppm for **1b**), and thus the 44.29-ppm absorption would be assigned to C4 in **1a** and the 40.18 ppm absorption to C4 in **1b**. This is in agreement with the estimated shift for C4 (41.9 ppm) on using reported substituent parameters.[9] The methylene carbons at 48.48 and 39.61 ppm were assigned to C5 for **1a** and **1b**, respectively, based on reported shifts for pyrrolidinone **2**. The remaining absorptions at 43.06 and 41.84 ppm would then be assigned to the chloromethyl carbons for **1a** and **1b**, respectively. On the basis of the γ-compression shift data,[10] **1a** would be assigned a trans configuration and **1b** a cis configuration. The results thus contradict those derived from the proton NMR studies.

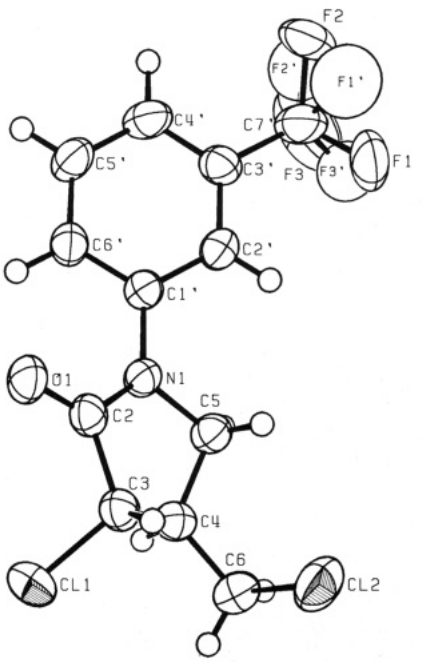

Figure 1. Molecular structure of Fluorochloridone (**1a**).

X-ray. The crystal of **1a** consists of well-separated molecules stacked in sheets roughly parallel to the *a*–*c* plane. The pyrrolidinone ring is in the envelope configuration with N1, C2, C3, and C5 in the plane and C4 out of the plane as shown in Figure 1. The four-atom plane is planar to +0.03 Å and C4 is 0.53 Å below it. The angle between the plane N1,C2,C3,C5 and the plane C3,C4,C5

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is 33.8°. The configurations around atom C3 and C4 are such that C3–H3 and C4–H4 bonds are approximately perpendicular to the plane, and the C3–Cl1 and C4–H4 bonds are approximately parallel to the plane. The torsional angles for N1–C2–C3–C4 and N1–C5–C4–C3 are −17.0° and −33.9°, respectively. The corresponding torsional angles for unsubstituted pyrrolidinone were reported[13] to be −6.1° and −6.5°. The substituents at C3 and C4 in **1a** significantly amplify the distortion of the pyrrolidinone ring.

Conclusion

The major product **1a** is a trans isomer, and the minor product **1b** is a cis isomer. The distortion of the pyrrolidinone ring in **1a** causes H3 and H4 to be oriented at a dihedral angle such that the trans coupling constant becomes larger than the cis coupling constant. The low torsional angle for Cl1–C3–C4–C6 (−77.8°) in **1a** can be used to explain why the γ-compression shift between **1a** and **1b** is lower than that between *cis*- and *trans*-1,2-dimethylcyclopentane. This study points out that configurational assignments based solely on proton NMR coupling constants may lead to erroneous results.

Experimental Section

Fluorochloridone was prepared as described in the literature.[1] The major isomer was isolated by bulb to bulb distillation of the crude product [bp 180 °C (0.4 mmHg)] followed by recrystallization in MeOH to give colorless plates, mp 80–81 °C. Anal. Calcd for $C_{12}H_{10}Cl_2F_3NO$: C, 46.17; H, 3.23; N, 4.49. Found: C, 46.07; H, 3.23; N, 4.36. The minor isomer was isolated from the mother liquor by recrystallization from CS_2 to give very small white crystals, mp 54–55 °C.

Proton and carbon-13 NMR spectra were obtained on a Varian T60A spectrometer and a Varian CFT-20 NMR spectrometer, respectively. All spectra were measured in $CDCl_3$ with tetramethylsilane as an internal reference.

X-ray analysis was carried out on an Enraf-Nonius CAD-4 automated diffractometer. Crystals were thin transparent colorless plates. A crystal of **1a** grown from methanol (size 0.15 × 0.28 × 0.36 mm) was mounted on glass fibers in air by using cyanoacrylate cement. The crystal was triclinic, space group $P\bar{1}$ with cell parameters as follows: a = 6.7569 (9) Å; b = 8.8525 (14) Å; c = 11.7367 (17) Å; α = 78.638 (13)°; β = 73.121 (12)°; γ = 75.870 (12)°; V = 645.4 (2) Å^3; Z = 2; d(calcd) = 1.606 g/cm^3; μ(calcd) = 5.28 cm^{-1}.

The structure was solved by using the MULTAN 79 direct methods program package.[11] Standard least-squares refinement and Fourier techniques revealed the positions of the hydrogen atoms and the disordered configuration of the trifluoromethyl group. The hydrogen atoms were included in structure factor calculations at their idealized positions (C–H distance = 0.95 Å) with isotropic thermal parameters set to 5.0 Å. The disordered fluorine atoms, F1′, F2′, and F3′, were given an occupancy of 0.25 based on the height of the peaks in the difference Fourier map. The initially discovered fluorine atoms, F1, F2, and F3, were assigned an occupancy of 0.75. All nonhydrogen atoms were then allowed to refine in the least-squares analysis. All atoms except the low-occupancy fluorine atoms were given anisotropic thermal parameters. In the final cycles of the least-squares analysis a secondary extinction parameter[12] was allowed to refine.

The structure was determined by using 1700 reflections, and the R value for all 1700 data was 5.12%.

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Registry No. **1a**, 61213-60-3; **1b**, 61213-59-0; **2**, 4641-57-0.

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Supplementary Material Available: Listings of intramolecular angles and distances, selected torsional angles, general temperature factor expressions, root-mean-squares amplitudes of thermal vibration, positional and thermal parameters, and a unit cell crystal structure diagram (8 pages). Ordering information is given on any current masthead page.

Efficient Method for a One-Carbon Homologation of Aldehydes and Benzophenone to Carboxylic Acids

Kazumasa Takahashi,* Kenichiro Shibasaki, Katsuyuki Ogura, and Hirotada Iida

Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 260, Japan

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We report here an efficient sequence for the one-carbon homologation of aldehydes and benzophenone to carboxylic acids (Scheme I). The present method for the homologation has been established by employing reactions of α-(*N*-methylanilino)acetonitrile with aldehydes or benzophenone to form α-cyano enamines, which could be easily converted into the corresponding carboxylic acids by acid hydrolysis in high yields.

Available methodology for the transformation of carbonyl compounds to carboxylic acids has relied on the intermediacy of (a) α-acetoxyacrylonitriles,[1] (b) cyanohydrins,[2] (c) nitriles,[3] (d) ketene thioacetal,[4] (e) α,β-unsaturated sulfones,[5] (f) α,β-unsaturated phosphonates,[6] (g) enol ethers,[7] (h) thioenol ethers,[8] (i) enamines,[9] (j) epoxides,[10] or (k) glycidic ethers[11] to introduce the requisite one-carbon unit. Most of these approaches involve production of an intermediate aldehyde which is subsequently oxidized to the carboxylic acid. Many of these methods, however, lack effective procedures for hydrolysis of the intermediates in each step or require starting materials which are difficulty to synthesize.

The α-cyano enamine synthon is known to be synthetically equivalent to an acyl cyanide in which the carbonyl group is masked as an enamine.[12] There is, however, no information about a general synthesis of α-cyano enamines

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