mm). Glpc analysis showed the distillate to contain 74% of **5** and 26% of **6**. Smaller scale experiments gave mixtures containing 80–90% **5** and 10–20% **6**.

B.—A solution of 220 mg (1 mmol) of freshly distilled aluminum isopropoxide in 10 ml of anhydrous isopropyl alcohol (distilled from calcium hydride) was heated to reflux and 73.2 mg (0.44 mmol) of **7** in 0.5 ml of anhydrous isopropyl alcohol was added by syringe over 15 min. The isopropyl alcohol was distilled slowly through a Claisen head over 2 hr keeping the volume in the reaction flask constant by the addition of fresh isopropyl alcohol (25 ml was distilled after 2 hr). The remaining isopropyl alcohol was removed on the rotary evaporator at ~1 mm. Ether (20 ml) and water (5 ml) were added and the mixture was acidified with dilute hydrochloric acid. The organic layer was dried ($MgSO_4$) and concentrated to yield a colorless oil (65.5 mg, 90%) which was shown by glpc to contain 84% of **5** and 16% of **6**.

Registry No.—**1**, 17190-71-5; **2**, 17190-72-6; **3**, 17190-73-7; **5**, 17190-74-8; **6**, 17190-75-9; **7**, 17190-76-0.

Acknowledgment—We thank Dr. A. Steyermark and his staff for the microanalyses, Dr. F. Vane for the mass spectra, Dr. T. Williams for the nmr spectra, Dr. V. Toome for the uv spectra, Mr. S. Traiman for the ir spectra, and Mr. H. Jenny for the gas–liquid partition chromatography. We are indebted to Dr. A. Brossi for his encouragement during the course of this work.

Synthesis of $\Delta^{\alpha,\beta}$-Butenolides[1]

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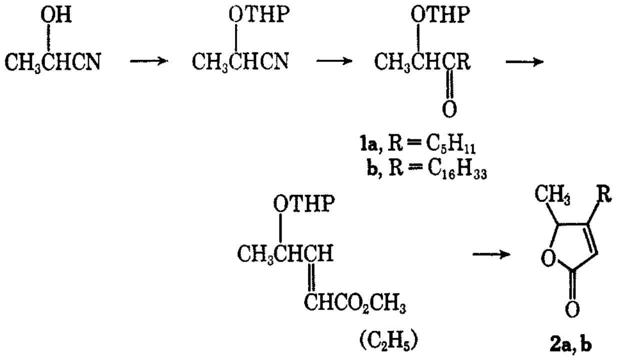
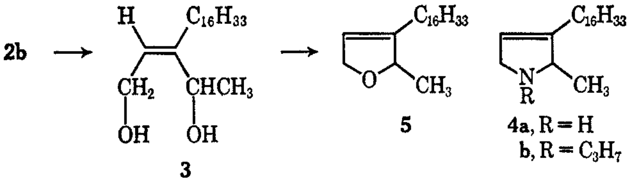
A relatively useful method for the preparation of β,γ-dialkyl-$\Delta^{\alpha,\beta}$-butenolides (γ-lactones of 3,4-dialkyl-4-hydroxycrotonic acids) has been devised in which aldehydes or aldehyde cyanohydrins and alkyl halides are used as starting materials. The condensation reaction between **1** and the Wadsworth–Emmons reagent[2]



THP = tetrahydropyranyl

is expected to provide a mixture of geometrical isomers. Hence, a considerable quantity of substituted *trans*-4-hydroxycrotonic acid should be present. Further treatment of the acid residue with HCl did not provide any lactone. Recently Epstein and Sonntag[3] transformed methyl *trans*-4-hydroxy-3-methylcrotonate into the γ-lactone of the *cis* isomer by irradiation, in the presence of a trace of HCl, in a quartz cell with a high-pressure mercury arc. We found that treatment with BF_3 etherate in benzene under reflux produced a mixture of polyester and $\Delta^{\alpha,\beta}$-butenolide from which the latter could be distilled. Since the acid fraction may have contained γ-keto acid (5.84 μ) as well as the expected *trans*-4-hydroxycrotonic acid (5.96, 6.09 μ) and the former can be cyclized to $\Delta^{\beta,\gamma}$-butenolides it is not certain that isomerization of the *trans*-4-hydroxycrotonic acid occurred.

The $\Delta^{\alpha,\beta}$-butenolides would appear to be useful synthetic intermediates for other partially dehydrogenated heterocyclic ring systems such as 2,5-dihydrofurans and 3-pyrrolines. In particular, a route was sought to 2-methyl-3-hexadecyl-3-pyrroline which has been proposed[4] as the structure of a component of the venom of the imported fire ant, *Solenopsis saevissima richteri* (Faril). Treatment of **2b** with lithium aluminum hydride gave diol **3** which, with *p*-toluenesulfonyl chloride and excess pyridine, yielded the corresponding 2,5-dihydrofuran. As we had been unable to convert 2-methyl-3-hexadecylpyrrole into its 3-pyrroline,[5] we attempted to prepare it from **3** in analogy to the method of Bobbitt, *et al.*[6] Reaction of **3** with thionyl chloride and pyridine, followed by heating in propylamine, produced **4b**. The 3-pyrroline **4a**, however, was not obtained by similar treatment of **3** with ammonia.



Experimental Section

Infrared spectra were determined on both Perkin-Elmer Model 137 and 521 infrared spectrophotometers. Ultraviolet spectra were obtained with a Beckman DK-2 spectrophotometer. Nmr spectra were obtained with a Varian HA 100 instrument and chemical shifts are reported in parts per million from tetramethylsilane; carbon tetrachloride was employed as the solvent unless otherwise indicated. Gas chromatograms were obtained with Aerograph Model A-700 and Varian Aerograph Model 204 B instruments employing various columns as indicated below. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

2-[(Tetrahydropyranyl)oxy]propionitrile.—Lactonitrile[7] (142 g, 2.00 mol) was converted into its tetrahydropyranyl ether in the usual manner. The product was distilled through an 8-in. column packed with helices. After a small forerun, 264 g (85.3%) of product was obtained, bp 58–64° (0.35 mm). The ir spectrum (film) lacked OH absorption, CN was undetectable,[8] and a series of intense bands appeared between 970 and 1120 cm^{-1}. The nmr spectrum showed bands at 1.44 and 1.48 (2 CH_3 doublets—compound is a mixture of diastereomers), 4.28 and 4.48 (two quartets—the H on the neighboring carbon), and 4.72 ppm (multiplet—H on carbon bonded to two oxygens).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 62.18; H, 8.49; N, 8.81.

2-[(Tetrahydropyranyl)oxy]-3-octanone (1a).—Pentylmagnesium bromide (from 58.1 g of 1-bromopentane, 9.72 g of magnesium turnings, and 1 l. of anhydrous ether), in a nitrogen at-

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[1] See P. E. Sonnet, *Chem. Ind.* (London), 1296 (1967), for a preliminary communication.

[2] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

[3] W. W. Epstein and A. C. Sonntag, *J. Org. Chem.*, **32**, 3390 (1967).

[4] G. A. Adrouny, *Bull. Tulane Univ. Med. Fac.*, **25** (1), 67 (1966).

[5] P. E. Sonnet, *Science*, **156**, 1759 (1967).

[6] J. M. Bobbitt, L. H. Amundsen, and R. I. Steiner, *J. Org. Chem.*, **25**, 2230 (1960).

[7] Obtained from Columbia Organic Chemicals, Inc., Columbia, S. C.

[8] The presence of an oxygenated group, especially on the same carbon that bears CN, results in marked "quenching" of the CN absorption intensity: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 266.

mosphere, was cooled in an ice bath and the 2-[(tetrahydropyranyl)oxy]propionitrile was added dropwise at such a rate as to maintain a gentle reflux. The solution was then refluxed for an additional 0.5 hr, chilled in an ice bath, and treated with a cold solution of 7 ml of H_2SO_4 and 84 ml of H_2O added in a steady stream. The mixture was swirled until the gummy deposit disappeared, and the desired product was obtained by decanting and washing the aqueous phase several times with ether. The combined ether layers were shaken with small quantities of dilute HCl until the washes were acidic. Considerable imine (1640 cm^{-1}) remained if this latter procedure was not carried out. The organic phase was dried ($MgSO_4$), concentrated, and distilled to give 2.8 g of forerun and 46.0 g (79.2%) of **1a**: bp 79–83° (0.09 mm); ir spectrum (CCl_4), 1720 cm^{-1}; nmr spectrum, 0.93 (CH_3 triplet), 1.15 and 1.24 (diastereomeric CH_3 doublets), 4.0 (overlapping quartets for adjacent **CH**), 2.44 (multiplet CH_2 adjacent to carbonyl), and 4.5 ppm (multiplet H on carbon bonded to two oxygens).

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.28; H, 10.49.

2-[(Tetrahydropyranyl)oxy]-3-nonadecanone (1b).—The reaction of the tetrahydropyranyl ether of lactonitrile with hexadecylmagnesium bromide was conducted as above. The crude reaction product was allowed to stand in acetone overnight and filtered to remove most of the dotriacontane, mp 69–71°, formed in the reaction. Attempts to distil the product were unsuccessful (decomposition) and it was purified by filtration through alumina. An analytical sample was prepared by refiltration, ir spectrum 1720 cm^{-1}.

Anal. Calcd for $C_{24}H_{46}O_3$: C, 75.34; H, 12.12. Found: C, 75.19; H, 12.08.

4-Hydroxy-4-methyl-3-pentylcrotonic Acid γ-Lactone (2a).—Triethyl phosphonoacetate (59.0 g, 0.263 mol) was converted into its sodio derivative with 11.6 g (0.27 mol) of 55.8% sodium hydride in 600 ml of anhydrous 1,2-dimethyoxyethane as previously described[2] (the sodium hydride had been washed with hexane to remove the mineral oil). The ketone, **1a**, (40.0 g, 0.175 mol) was added, and the mixture was kept at 70° in a nitrogen atmosphere for 20 hr, cooled, concentrated on a flash evaporator, diluted with H_2O, and extracted with ether. The crude ester was saponified with KOH in aqueous ethanol, and the acid which was obtained was dissolved in 2:1 dioxane–H_2O containing a little HCl. The mixture was warmed at 50–55° for 18 hr and then worked up to give a mixture of **1a** and the $\Delta^{\beta,\gamma}$ isomer. The ir spectrum had a very broad carbonyl absorption covering the area from 1750 to 1800 cm^{-1} and a rather weak 1640-cm^{-1} band. Gas chromatograms obtained with an SE 30 column (5% on base-washed Chromosorb P, 6 ft × 0.125 in.) revealed two major peaks. The earlier peak predominated (2:1), and treatment with base or alumina caused the latter peak to grow at the expense of the former. Distillation of the mixture through a packed column gave 13.4 g of liquid [bp 76–80° (0.10 mm)], 6.6 g of which was passed through 130 g of alumina with 1:1 ether–petroleum ether (exothermic) to give 4.8 g of pure **2a**: bp 85–87° (0.10 mm); ir spectrum (CCl_4), 1763, sh 1780, 1643 cm^{-1} s; nmr spectrum, 1.34 (CH_3 doublet), 4.85 (quartet for adjacent CH), 5.63 (singlet for vinyl H); uv spectrum (ethanol), strong end absorption.

Anal. Calcd for $C_{10}H_{16}O$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.62.

The yield of **2a** from the ketone was ~33%. Filtration yields were optimum when the material was allowed to traverse the column fairly rapidly.

Treatment of the Acid Residue to Obtain 2a.—The acidic material recovered from the above lactonization (13.3 g) was dissolved in 35 ml of benzene, and 4 ml of BF_3 etherate was added. The resulting solution was heated under reflux for 20 hr (~1 ml of H_2O was collected). The mixture was poured into H_2O and extracted with ether, and the latter was dried ($MgSO_4$) and concentrated: ir spectrum (film), 1760 and 1725 cm^{-1}. Short path distillation gave 6.6 g of light yellow liquid, bp 73–104° (0.10 mm), which was >80% pure by glpc. Further treatment of the undistilled residue (saponification, BF_3 treatment, distillation) provided another 0.5 g. Therefore, by glpc, a further 20% yield of **2a** from the acid portion of the above reaction is possible. Two distillations through a packed column provided material of 96–97% purity.

4-Hydroxy-4-methyl-3-hexadecylcrotonic Acid γ-Lactone (2b).—Crude ketone **1b** was converted directly into **2b** in an analogous manner. No effort was made to improve the yield by conversion of *trans*-hydroxy acid; the over-all yield from lactonitrile was 30%: ir spectrum (CCl_4), 1768 and 1643 cm^{-1}.

Anal. Calcd for $C_{21}H_{38}O_2$: C, 78.20; H, 11.88. Found: C, 78.35; H, 11.93.

***trans*-3-(1-Hydroxyethyl)-2-nonadecen-1-ol (3).**—Lactone **2b** (3.5 g, 10.9 mmol) was added to a suspension of 0.57 g (15 mmol) of lithium aluminum hydride in ether and the resulting mixture was heated under reflux for 2 hr. Excess hydride was destroyed with H_2O. The crude diol was chromatographed on a column containing 65 g of alumina. Diol **3** (2.6 g) was obtained. It could be sublimed to a wax: mp 40–44°; ir spectrum (CCl_4), 3610 w, 3340 cm^{-1} broad; nmr spectrum, 1.2 (CH_3 doublet partially obscured), 4.58 (quartet for adjacent CH), 4.1 (multiplet CH_2OH), and 5.34 (multiplet vinyl H).

Anal. Calcd for $C_{21}H_{42}O_2$: C, 77.23; H, 12.97. Found: C, 77.22; H, 12.97.

A less polar isomeric diol was also obtained (36 mg), mp 81–83.5° (ether–petroleum ether).

Anal. Calcd for $C_{21}H_{42}O_2$: C, 77.23; H, 12.97. Found: C, 77.08; H, 12.97.

3-Hexadecyl-2,5-dihydro-2-methylfuran (5).—The diol **3** (0.30 g, 9.2 mmol) was added to a slurry of 100 mg of hexane-washed sodium hydride in 25 ml of ether under nitrogen. The mixture was heated under reflux for 1 hr and cooled. Then 0.20 g of *p*-toluenesulfonyl chloride was added in portions with stirring. The mixture was heated under reflux for 2 hr. The product was worked up in the usual way. Excess sulfonyl chloride was removed by briefly treating the crude product with pyridine (5 min). Purification was achieved by filtration through alumina (Brockman, activity 1). A colorless oil was obtained (0.15 g, 54%): ir spectrum (film), 1080 cm^{-1} (2,5-dihydrofuran itself exhibits a band at 1075 cm^{-1}); nmr spectrum, 4.44 (**CH**$_2$–O multiplet), 4.60 (CH_3**CH**–O multiplet), and 5.26 (vinyl H multiplet).

Anal. Calcd for $C_{21}H_{40}O$: C, 81.75; H, 13.07. Found: C, 81.94; H, 13.27.

3-Hexadecyl-2-methyl-1-propyl-3-pyrroline (4b).—The diol **3** was converted into the dichloride by treatment with dry pyridine and thionyl chloride at 0°. The crude dihalide was heated under reflux in propylamine for 16 hr. After barium hydroxide had been added, the mixture was filtered, and the precipitate was washed with ether. The mother liquors were thoroughly stripped of propylamine, and the residue was dissolved in anhydrous ether. Dry HCl gas was then passed in, and the mixture was chilled. A total of 205 mg (29%) of the hydrochloride could be obtained as an amorphous solid: mp 115.5–117° (methanol–ether). The free base obtained by molecular distillation was a colorless mobile oil which absorbed CO_2 rather readily: nmr spectrum, 2.57 (triplet CH_2CH_2N) 3.24 (doublet ring **CH**$_2$–N), 4.28 (quartet CH_3**CH**–N), and 5.15 ppm (broadened triplet vinyl H).

Anal. Calcd for $C_{24}H_{48}ClN \cdot CH_3OH$: C, 71.86; H, 12.54; Cl, 8.48; N, 3.35. Found: C, 71.90; H, 12.54; Cl, 8.82; N, 3.68.

Registry No.—2-[(Tetrahydropyranyl)oxy]propionitrile, 17224-04-3; **1a**, 17223-97-1; **1b**, 17223-98-2; **2a**, 17223-99-3; **2b**, 17224-00-9; **3**, 17224-01-0; **4b**, 17224-05-4; **4b**·HCl, 17224-02-1; **5**, 17224-03-2.

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The Structure of an Alleged Triazetidine

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Datta and Chatterjee reported in 1922[1] that hydrolysis of the chlorination product of urethane gave a

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(1) R. L. Datta and B. C. Chatterjee, *J. Amer. Chem. Soc.*, **44**, 1538 (1922).