***cis*-Heneicosan-6,7-epoxy-11-one (10).** To a 0.45-g (1.46 mmol) sample of 1 dissolved in 20 ml of methylene chloride was added 0.504 g (2.92 mmol) of *m*-chloroperbenzoic acid which was stirred into solution before refrigerating at 5° for 15 hr.

The reaction mixture was transferred to a separatory funnel, 1.0 ml of dimethyl sulfide was added to destroy excess peracid, and the mixture was extracted with three 20-ml portions of saturated aqueous sodium bicarbonate solution and one 20-ml portion of water. The clear solution was dried over anhydrous magnesium sulfate and filtered, and the methylene chloride was removed. A 5-mg sample of this product was dissolved in methylene chloride for isomeric analysis. The remaining material was chromatographed, decolorized with activated charcoal, and recrystallized once from benzene–hexane to yield 0.23 g (48%) of **10:** mp 29–36°; ir (CCl_4 solution) 5.84 μ (C=O); NMR δ 2.35 (m, 4 H, CH_2C=O), 2.70 (m, 2 H, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 324 (19, $M^{\cdot+}$), 169 (42, $C_{10}H_{21}C{\equiv}O^+$), 156 [100, $(C_5H_{11}\overline{CHCHO}CH_2CH_2CH_2 + H)^{\cdot+}$].

Anal. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42. Found: C, 78.05; H, 12.33.

***trans*-Heneicosan-6,7-epoxy-11-one (11).** A 1.0-g (3.24 mmol) sample of **2** was epoxidized with 1.12 g (6.48 mmol) of *m*-chloroperbenzoic acid using the same procedure as described for the *Z* isomer. Isomeric analysis of this product was performed on a 5-mg sample before column chromatography and recrystallization from benzene–hexane. The remainder of the product, after one recrystallization, weighed 0.54 g (51%): mp 92–97°; ir (CCl_4 solution) 5.82 μ (C=O); NMR δ 2.30 (m, 4 H, CH_2C=O), 2.46 (m, 2 H, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 324 (19, $M^{\cdot+}$), 169 (42, $C_{10}H_{21}C{\equiv}O^+$), 156 [100, $(C_5H_{11}\overline{CHCHO}CH_2CH_2CH_2 + H)^{\cdot+}$].

Anal. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42. Found: C, 77.51; H, 12.42.

Stereochemical Analyses. Samples of **10, 11,** and a 1:2 mixture of **10** and **11** (all in methylene chloride solutions) were examined using a Varian 2700 gas chromatograph equipped with dual flame ionization detectors and a 12 ft × 0.125 in. stainless steel column packed with 10% Apolar 10C on 100/120 mesh Gas-Chrom Q (Applied Science Laboratories). After conditioning overnight at 260° the column was set isothermally at 165°. At this temperature the two isomers, **10** and **11,** were eluted at 19 and 21 min, respectively,[16] with near-baseline resolution (see Figure 1a). The detector output was recorded on two channels of a Gould Brush 260 recorder, the two channels differing in sensitivity by a factor of 10. This made it possible to measure and compare the peak areas of both isomers from a single injection. Duplicate runs were made for each isomer. Measurements of peak areas using peak height and width at half height show the *Z* isomer to be 97.60 and 97.63% pure and the *E* isomer to be 98.42 and 98.49% pure. Calculations using (1) a planimeter and (2) weights of cut-out peaks from photocopies of chromatograms gave values which do not differ by more than 0.3%.

Acknowledgment. Financial assistance was provided by U.S. Forest Service Pacific Northwest Forest and Range Experiment Station, Northwest Forest Pest Action Council, and State of Washington, Department of Natural Resources.

Registry No.—**1,** 54844-65-4; **2,** 54844-66-5; **4,** 54844-67-6; **5,** 54844-68-7; **6,** 54844-69-8; **7,** 54844-70-1; **8,** 54844-72-2; **9,** 54844-72-3; **10,** 54844-73-4; **11,** 54844-74-5; undecanal, 112-44-7; 1,3-propanedithiol, 109-80-8.

References and Notes

(1) R. G. Smith, G. E. Daterman, and G. D. Daves, Jr., *Science,* **188,** 63 (1975).
(2) For a recent paper describing the synthesis and utility of 1,3-dithianes as alkylating agents, see D. Seebach and E. J. Corey, *J. Org. Chem.,* **40,** 231 (1975).
(3) C. A. Brown and V. K. Ahuja, *J. Chem. Soc., Chem. Commun.,* 553 (1973).
(4) J. D. Warthen, Jr., and M. Jacobson, *Synthesis,* 616 (1973).
(5) D. J. Pasto and C. R. Johnson, "Organic Structure Determination", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 115.
(6) R. G. Smith, G. E. Daterman, G. D. Daves, Jr., K. D. McMurtrey, and W. L. Roelofs, *J. Insect Physiol.,* **20,** 661 (1974).
(7) J. A. Klun, O. L. Chapman, K. C. Mattes, P. W. Wojtkowski, M. Beroza, and P. E. Sonnett, *Science,* **181,** 661 (1973).
(8) Only a partial separation of **1** and **2** was achieved using a 50-ft SCOT column coated with DEGS and operated at 180°. We thank Dr. Iain Weatherston, Canadian Forestry Service, Sault Ste. Marie, Ontario, for this result.
(9) L. M. McDonough and D. A. George, *J. Chromatogr. Sci.,* **8,** 158 (1970).
(10) B. Loev and M. M. Goodman, *Chem. Ind. (London),* **48,** 2026 (1967).
(11) L. F. Fieser, *J. Am. Chem. Soc.,* **76,** 1945 (1954).
(12) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.,* **4,** 1075 (1965).
(13) F. D. Gunstone and M. Lie Ken Jie, *Chem. Phys. Lipids,* **4,** 1 (1970).
(14) K. Narasaka, T. Sakashita, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.,* **45,** 3724 (1972).
(15) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.,* **35,** 4000 (1970).
(16) The GLC retention times of a *Z* olefin and its epoxide are typically greater than those of the corresponding *E* isomers.[6,9] The reverse order in the present case is unexplained.

Fungal Extractives. IX.[1a] Synthesis of the Velleral Skeleton[1b] and a Total Synthesis of Pyrovellerolactone

Jan Froborg, Göran Magnusson,* and Svante Thorén

Organic Chemistry 2, Chemical Center, The Lund Institute of Technology, Box 740, S-220 07 Lund 7, Sweden

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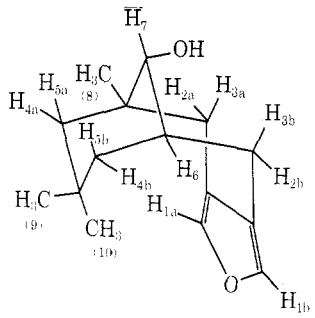
A synthetic route to the skeleton of the hydroazulenic sesquiterpene velleral (1) (from *Lactarius vellereus* and *L. Pergamenus;* Russulaceae, basidiomycetes) is described. The key intermediate 2,2,4-trimethylfuro[6,7-*c*]perhydroazulene (**13**) was transformed to the maleic anhydride derivative **18** by anodic oxidation of the furan ring to the corresponding 2,5-dihydroxy-2,5-dihydrofuran **17** followed by Jones oxidation. Two crystalline maleimides (**22** and **23**) were prepared for X-ray analysis by reaction of **18** with *p*-bromoaniline and **13** with *N*-(*p*-bromophenyl)maleimide. A $Eu(fod)_3$-induced chemical shift analysis was used to determine the stereostructure of 1,8,8-trimethylfuro[3,4-*c*]bicyclo[4.3.1]decan-10-ol (**7**). Hydrogenation of velleral gave a stereoisomer of **13**. A molecular force field calculation was used to determine the most stable conformer of a model precursor to **13**. A total synthesis of pyrovellerolactone (**3**) was accomplished using a new method for the preparation of lactones from furans (electrochemical oxidation followed by hydrolysis).

During the last few years we have reported seven new sesquiterpenes from basidiomycetes of the genus *Lactarius.* Of these, isovelleral[1c] has the same basic skeleton as marasmic acid,[2] which has been the object of synthetic work by other groups;[3,4] lactaral,[5] a 4-substituted furan-3-aldehyde with a previously unknown carbon skeleton, has recently been synthesized by us;[6] the remaining five sesquiterpenes [velleral (**1**),[7] vellerolactone (**2**),[8,9] pyrovellerolactone (**3**),[8,9] and two furan alcohols[10]) have a hydroazulenic skeleton with a *gem*-dimethyl-substituted cyclopentane

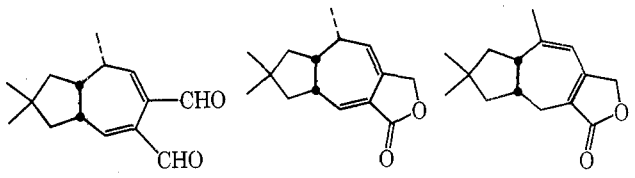
Table I
Eu(fod)$_3$-Induced Proton Chemical Shifts for 7 in Its Most Probable Conformation



Proton no.	Induced shift, Hz: Obsd[a]	Induced shift, Hz: Calcd[17]
1a	22	19
1b	22	20
2a	58	47
2b	48	41
3a	112	109
3b	124	124
4a	20[b]	32
4b	20[b]	36
5a	20[b]	17
5b	20[b]	30
6	90	89
7	240	241
8	69	96
9	18	14
10	12	5

[a] Sample containing 0.115 mol of Eu(fod)$_3$/mol of 7; $CDCl_3$ solution. [b] Average value; no unequivocal assignment could be made for protons 4 and 5.

ring. Three further sesquiterpenes of this type (all of basidiomycete origin) have been reported by other workers.[11-13]



1 velleral; 2 vellerolactone[a]; 3 pyrovellerolactone[a]

[a] We suggest these names for the previously unnamed lactones 2 and 3.

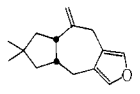
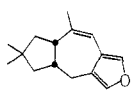
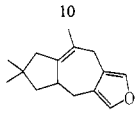
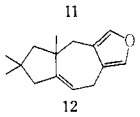
Syntheses of hydroazulenic sesquiterpenes have been concerned mainly with compounds containing guaiane-type skeletons;[14] no synthesis has hitherto been reported of a hydroazulenic compound containing the *gem*-dimethyl-substituted cyclopentane ring of velleral.

We now report an attempted synthesis of velleral, which has given a stereoisomer of a velleral derivative, and a total synthesis of pyrovellerolactone. As a primary synthetic goal we endeavored to prepare a furan derivative such as the velleral derivative **24** since we considered that this would be a suitable precursor to velleral because of the inherent functionality of the furan ring, and moreover the terpenes described in ref 10 and 13 have a furan ring in the same position. The product obtained was in fact the stereoisomer **13**.

The present synthesis (outlined in Scheme I) includes a solvolytic ring-contraction step following the general procedure used by Marshall and Partridge for their synthesis of bulnesol.[15] The synthesis starts with cycloalkylation of the enol acetate **4** with furan **5**, giving the ketone **6** in almost quantitative yield.[16] This compound was reduced with lithium aluminum hydride to give the alcohol **7** as the sole product.

Table II
Product Composition[a] for the Reaction

$$\mathbf{8} \xrightarrow{0.5\ M\ \text{RCOONa in RCOOH}} \mathbf{9\text{-}12}$$

Compd	R = CH_3	$(CH_3)_3C$	$(CH_3CH_2)_3C$	$(CH_3)_2CHCH_2$
 9	25	48	53	43
 10	26	20	15	20
 11	25	15	15	17
 12	24	17	17	20

[a] Determined from NMR integrals (%).

To determine the stereostructure of **7**, a lanthanide-induced chemical shift (LIS) analysis [Eu(fod)$_3$] was performed [LIS vs. amount of Eu(fod)$_3$ added gave almost linear plots for all protons]. However, the local symmetry in the molecule prevented a simple interpretation of the LIS experiment. This problem was circumvented by making a double-resonance experiment on the NMR sample containing the maximum amount of Eu(fod)$_3$. On irradiation of the methylene protons showing the largest LIS (H_2 and H_3 in Table I) there was a significant simplification of the signals in the furan region, indicating coupling. This was not observed on irradiation of H_4 and H_5. Thus the hydroxyl group in **7** should be situated closer to the methylene protons α to the furan ring (H_2 and H_3) than to the other methylene protons in the molecule. To prove the stereostructure of **7** unequivocally, a theoretical calculation was made of the induced chemical shifts for the two possible diastereomers (two conformers of each) using the newly developed LISRIT computer program.[17] The conformer shown in Table I had the best (lowest) agreement factor[18] (8%). The other three conformers could thus be rejected with high statistical significance[19] (>99.5%). The observed and calculated LIS's are shown in Table I for the most probable conformer.

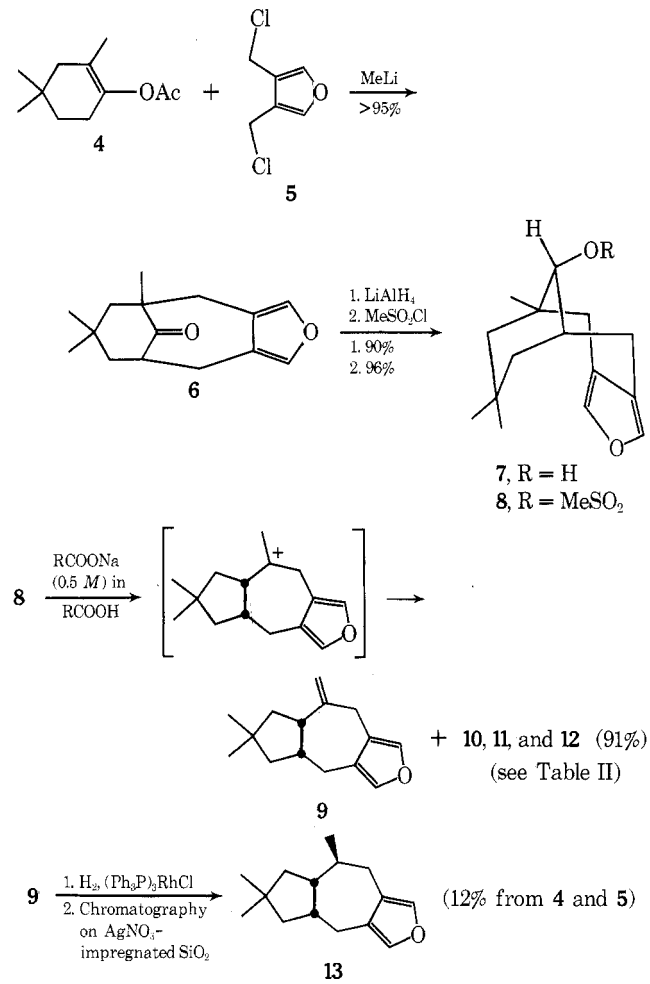
The alcohol **7** was converted to the mesylate **8** with mesyl chloride in pyridine.[15] Solvolytic ring contraction of **8** in a carboxylic acid–sodium carboxylate mixture (for specific details, see Table II) gave a mixture of isomeric furan olefins (**9–12**) presumably via (for **9–11**) the carbenium ion shown in Scheme I. The composition of the olefin mixture could be modified somewhat by choosing as base in the solvolysis step a sodium carboxylate of greater or lesser hindrance, as is shown in Table II. Although not generally appreciated in preparative work, it appears that the base used for removal of a proton from a carbenium ion is not unimportant and should be chosen with care.

In the preliminary planning of the synthesis we assumed that hydrogenation of the olefin mixture **9–11** would give

only a single saturated furan derivative by attack of hydrogen on the less hindered side of the double bonds, and thus would give a compound with the same stereostructure as in velleral (1). The best catalyst reported that allows the furan ring to be retained under hydrogenation conditions is palladium on strontium carbonate.[20] Nevertheless, even with this there was significant attack on the furan ring before complete saturation of the olefinic linkages was achieved and the product was a complex mixture difficult to separate. However, homogeneous phase hydrogenation with tris(triphenylphosphine)chlororhodium[21] as catalyst permitted a selective reduction of the exocyclic methylene of **9** without affecting the furan ring and also left the double bonds of **10, 11,** and **12** unreduced. Chromatography on silver nitrate impregnated silica gave a single saturated furan derivative (**13**) free of olefinic material. To summarize, **13** could be prepared from **4** and **5** in 12% total yield without purification of the intermediates **6–12** (Scheme I).

Compound **13** has a stereostructure different from that of velleral (see Scheme IV, compounds **13** and **24**). Catalytic hydrogenation can usually be expected to occur from the less hindered side, which would imply in the present case that the puckered conformation of **9** (cf. Figure 1) is unexpectedly the most stable and thus hydrogen will add on the side trans to the bridgehead hydrogens. To investigate the stabilities of the two conformers of **9**, a theoretical calculation of the internal strain energies was performed using the BIGSTRN computer program (molecular force field calculation) described by Andose, Mislow, Engler, and Schleyer.[22,23] Since the program did not accommodate furan ring parameters, the calculation was made on a cyclopentene model compound (Figure 1; the cyclopentene ring was "frozen" in furan geometry). This gave an energy difference of ca. 3 kcal/mol between **14** and **15** (**14** with lowest energy), suggesting an equilibrium in solution (strictly

Scheme I



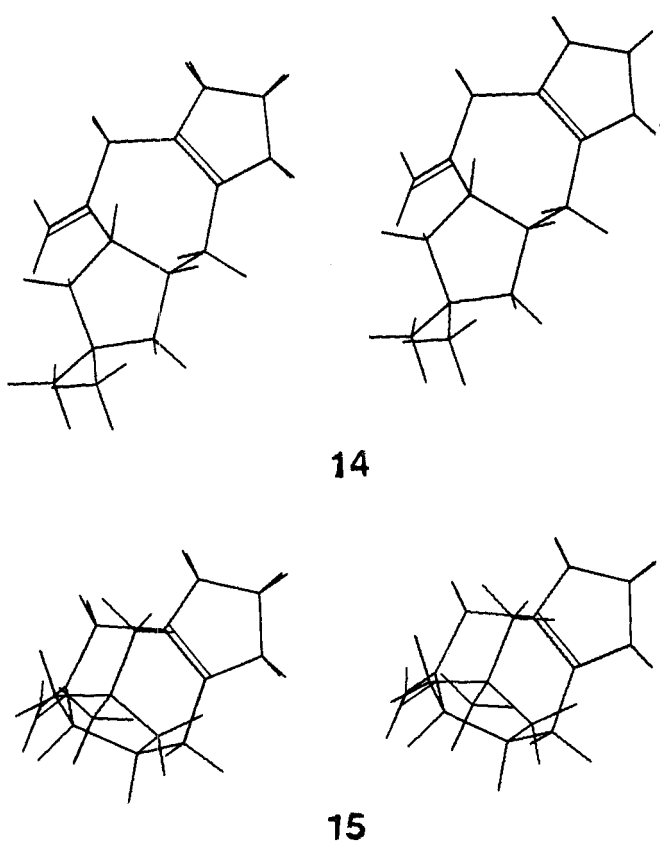
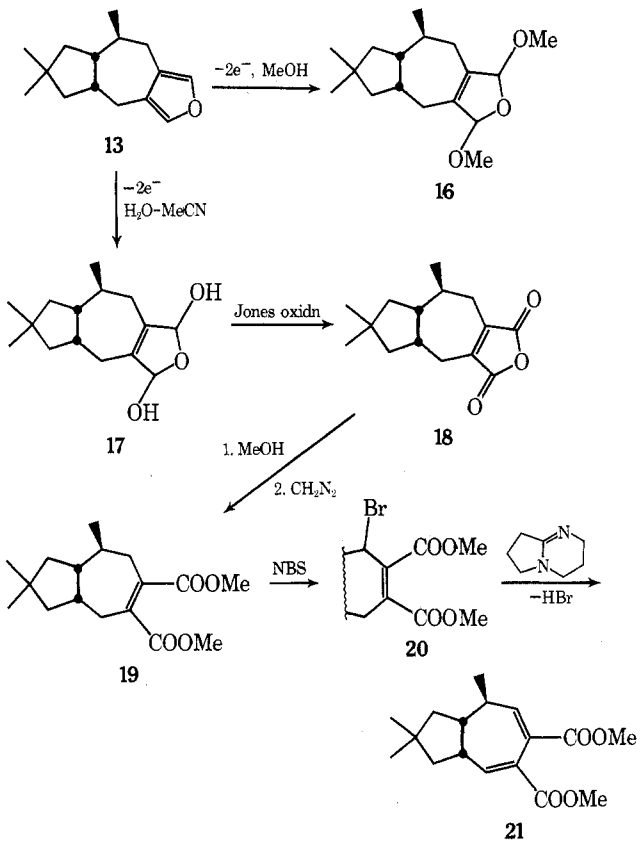


Figure 1. Stereoplots of the planar (**14**) and puckered (**15**) conformers of the cyclopentene model of **9**.

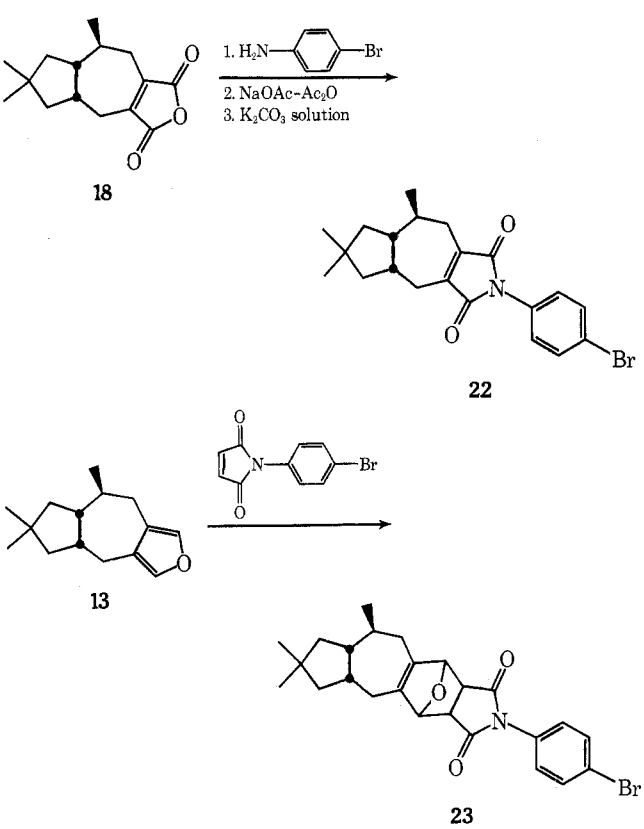
speaking in a gaseous phase) with the planar conformer (**14**) predominant. Thus it seems that only the minor component of the equilibrium mixture forms an effective substrate–catalyst complex[24] (this conclusion is supported by space-filling models and by the slow hydrogenation). Stereoplots (computer drawn[25]) of **14** and **15** are shown in Figure 1.

It seemed that the diene dialdehyde system of velleral (**1**) might be best prepared from **13** via a maleic derivative (e.g., dialdehyde or diester) using an allylic bromination–1,4-elimination sequence. The relative instability of maleic dialdehydes[26] made us focus on maleic acid derivatives, which should be accessible from 2,5-dimethoxy-2,5-dihydrofurans (cf. **16**) by hydrolysis, followed by oxidation. However, this route gave mixtures containing much polymeric material (discussed in ref 27). We were thus forced to find a new procedure for the preparation of maleic acid derivatives from 3,4-disubstituted furans. Electrochemical oxidation to 2,5-dihydroxy-2,5-dihydrofurans[27] followed by Jones oxidation works well and this was used (Scheme II) for the preparation of anhydride **18** (**13** to **18**, ca. 80%). Methanolysis of **18** followed by diazomethane treatment gave the maleic diester **19**, which could be brominated with *N*-bromosuccinimide, giving a mixture, presumably of the four isomeric monobromo derivatives **20**. Treatment of **20** with 1,5-diazabicyclo[4.3.0]non-5-ene[28] gave the diester **21** (tentative structure; NMR two vinyl proton signals with J = 5.6 and 2.8 Hz, no allylic CH_3; uv λ_{max} 208 and 243 nm; no M^+, only $M^+ - 2$; for **25**, $M^+ - 2$ = 24% of M^+; for **19**, $M^+ - 2$ = 68% and $M^+ - 4$ = 108% of M^+) containing the basic unsaturated system of velleral. Attempts to reduce **21**

Scheme II



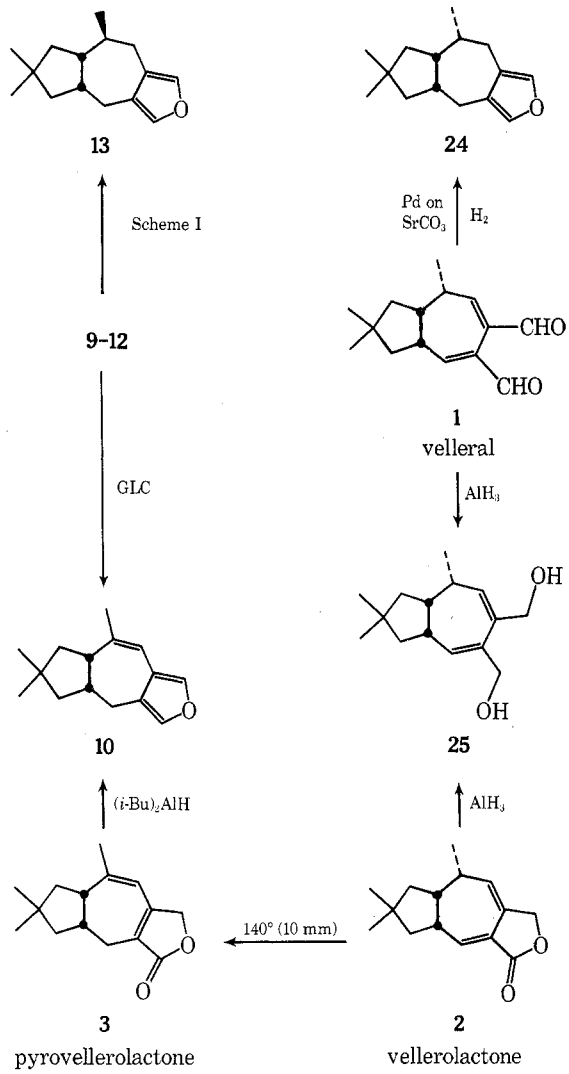
Scheme III



to the velleral dialdehyde system have so far been unsuccessful.

At this stage of the synthesis we succeeded in preparing the furan **24** by hydrogenation of velleral for comparison with furan **13**. Spectroscopic data (ir, NMR) showed small

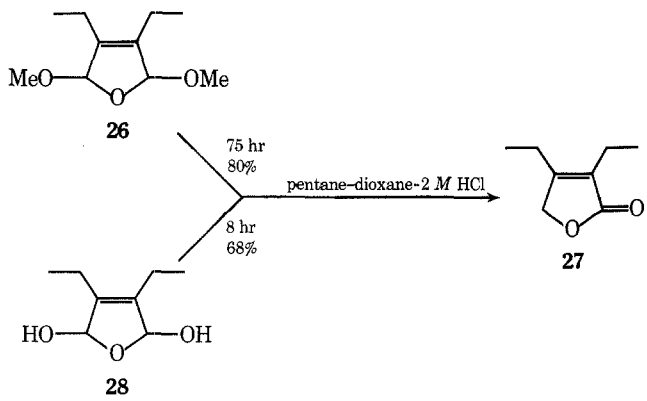
Scheme IV



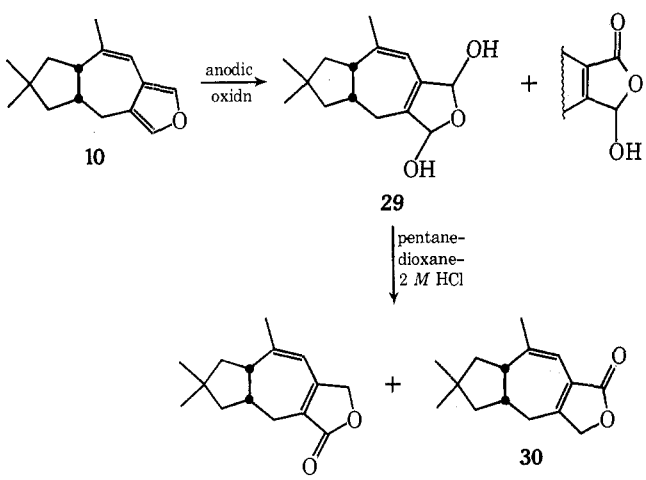
but significant differences, indicating that **13** had instead the stereostructure shown (MS practically identical). Two heavy-atom derivatives (**22** and **23**, Scheme III) were prepared[30,35,36] in order to settle the stereostructure of **13**, and thus of velleral, unequivocally by X-ray analysis.[29] Unfortunately, the crystals were thin leaflets rather unsuitable for single-crystal diffractometry. However, these two reactions offer convenient routes to heavy-atom derivatives of furans (cf. Scheme III) which may be useful elsewhere.

The unreduced mixture of olefins (**10–12** plus traces of **9**; separable by VPC on a 50-m OV-17 capillary column), obtained from the hydrogenation after removal of the dihydro compound **13**, was difficult to separate on a preparative scale. The synthetic component **10** was identical with semisynthetic **10** obtained by diisobutylaluminum hydride reduction (Scheme IV) of pyrovellerolactone (**3**) [same R_f values in VPC, identical mass spectra (VPC–MS) and ^{1}H NMR spectra (most of the signals from **10** were assigned previously in an independent analysis of the NMR spectra of the two olefin mixtures **10** plus **12** and **9–12**)]. The synthetic compounds **10** and **13** must have a cis ring junction because of the mechanism for solvolysis[15] of mesylate **8**. Velleral and vellerolactone have already been shown to have the same stereostructure [AlH_3 reduction to the same diol (**25**)[9]]. Vellerolactone has been transformed to pyrovellerolactone by heating[8] [140° (ca. 10 mm); presumably a 1,5-sigmatropic, suprafacial hydride shift]. These chemical transformations clearly show that velleral, vellerolactone,

Scheme V



Scheme VI



and pyrovellerolactone all have the *gem*-dimethylcyclopentane ring cis fused to the cycloheptadiene system. The difference between **13** and **24** must thus lie in the methyl group stereoarrangement. In velleral and vellerolactone this methyl group has been shown by NMR[7,9] to be trans to the bridgehead protons. It is hoped to obtain further confirmation by X-ray analysis (see above).

Synthesis of Pyrovellerolactone. A convenient method for the preparation of α,β-unsaturated γ-lactones was found during attempts to prepare maleic dialdehydes from 2,5-dimethoxy-2,5-dihydrofurans (cf. **16**). Mild hydrolysis in a two-phase system (pentane–dioxane–2 *M* HCl) was used in order to keep the concentration of the expected dialdehyde low in the acid phase and thereby avoid some side reactions (e.g., polymer formation[27,31]). On testing a model compound (**26**) we found, however, that this gave exclusive formation of the α,β-unsaturated γ-lactone **27** (NMR for crude and distilled material almost identical). Compound **16** gave under the same conditions a good yield (ca. 70%) of lactones. Since the hydrolysis of the methoxy compound was slow (more than 3 days for compound **26**) we tried the same hydrolysis conditions on the 2,5-dihydroxy-2,5-dihydrofuran **28**.[27] This gave lactone **27** after 8 hr reaction time (Scheme V).

Having a method for the conversion of furans into lactones, we saw the possibility of making a total synthesis of (racemic) pyrovellerolactone (**3**) from the unsaturated furan **10**. This was obtained in pure form (optically active) by diisobutylaluminum hydride reduction of pyrovellerolactone (and in mixture with **12** by reverse-phase chromatography with silver fluoroborate eluent[32,33] of the furan mixture **9–12**). Anodic oxidation of **10** (from **3**) according to the method described earlier[27] gave a mixture of the 2,5-dihydroxy-2,5-dihydrofuran **29**, some lactol (presumably by further oxidation of **29**; ir ν 3420, 1740 cm^{-1}) and unreacted furan **10**. Hydrolysis of **29**, followed by chromatography, gave pyrovellerolactone (**3**) and apparently some (ca. 10%) of the isomeric lactone **30** (Scheme VI). The synthetic pyrovellerolactone was shown to be identical with the natural compound (R_f values in VPC and TLC, mass, ir, uv, and NMR spectra).

Experimental Section

NMR spectra were run on Varian T-60 and XL-100 instruments in $CDCl_3$ with Me_4Si as internal standard. Ir spectra were run as liquid films unless otherwise stated. Melting points are uncorrected.

1,8,8-Trimethylfuro[3,4-*c*]bicyclo[4,3,1]decan-10-ol (7). The ketone **6**[16] (28.4 g, 0.12 mol, crude product) in dry ether (500 ml) was added dropwise to a suspension of lithium aluminum hydride (13.7 g, 0.36 mol) in dry ether (700 ml) at 0° with mechanical stirring. After 1 hr, water (27 ml), sodium sulfate (5 g), and sodium hydroxide solution (10%, 22 ml) were added and stirring was continued for 1 hr to granulate the precipitated aluminum salts. Filtration and evaporation gave almost pure alcohol **7** (25.7 g, 90%). Recrystallization from hexane gave an analytical sample: mp 89.5–90.0°; ir (KBr) ν 3440 (OH), 1052, 1030, 873 (furan), 788 cm^{-1}; NMR δ 7.15 (2 H, s, H_{1a}, H_{1b}), 4.40 (1 H, t, broad, J = 6.0 Hz; with D_2O, d, J = 7.0 Hz, H_7), 3.03 (1 H, d, broad, J = 15.0 Hz, H_{3b}), 2.97 (1 H, d, J = 15.0 Hz, H_{3a}), 2.37 (1 H, m, H_6), 2.18 (1 H, d of d, J = 15.0 and 4.5 Hz, H_{2b}), 1.98 (1 H, d, J = 15.0 Hz, H_{2a}), 1.20–2.0 (4 H, m, H_4 and H_5), 1.19 (3 H, s, H_8), 1.09, 0.70 ppm (3 H each, s, H_{10} and H_9) [for proton numbering, see Table I; coupling constants from Eu(fod)$_3$-shifted sample]; mass spectrum *m/e* (rel intensity) 234 (M$^+$, 34, $C_{15}H_{22}O_2$), 216 (100, base peak), 201 (91).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.9; H, 9.5. Found: C, 76.5; H, 9.4.

1,8,8-Trimethylfuro[3,4-*c*]bicyclo[4.3.1]dec-10-yl Mesylate (8). The alcohol **7** (4.52 g, 19.3 mmol, crude product) in dry pyridine (70 ml) was cooled to 0°. Methanesulfonyl chloride (2.50 g, 22 mmol) in dry pyridine (25 ml) was added dropwise with stirring and the ice bath was removed. After 24 hr the reaction mixture was poured onto ice (150 g). Extraction with ether (4 × 75 ml), drying of the ether phase (Na_2SO_4), and evaporation gave almost pure mesylate **8** (5.78 g, 96%, spontaneous crystallization). Recrystallization from hexane gave an analytical sample: mp 104.5–105.5°; ir (KBr) ν 3019 (furan), 1346, 1335, 1170 (sulfonate), 942, 876 (furan), 797 cm^{-1}; NMR δ 7.15 (2 H, m, furan H), 5.47 (1 H, d, J = 7.0 Hz, OCH), 3.07 (3 H, s, SO_3CH_3), 1.22, 1.16, 0.73 ppm (3 H each, s, CCH_3); mass spectrum *m/e* (rel intensity) 312 (M$^+$, 2, $C_{16}H_{24}O_4S$), 216 (37), 201 (29), 86 (64), 84 (100, base peak).

Anal. Calcd for $C_{16}H_{24}O_4S$: C, 61.6; H, 7.7; S, 10.3. Found: C, 61.7; H, 7.7; S, 10.2.

Olefin Mixture (9–12). The mesylate **8** (4.00 g, 12.8 mmol, crude product) was heated in pivalic acid containing sodium pivalate (0.5 *M*, 50 ml) at 150° for ca. 30 min. The reaction was followed by TLC (SiO_2–toluene). The reaction mixture was cooled, made alkaline with sodium hydroxide solution (2 *M*, 350 ml), extracted with ether (3 × 100 ml), dried (Na_2SO_4), and evaporated. This gave (see Table II) the olefin mixture **9–12** (2.53 g, 91%): NMR in accord; mass spectrum *m/e* (rel intensity) 216 (M$^+$, 100, base peak, $C_{15}H_{20}O$), 201 (53).

2,2,4-Trimethylfuro[6,7-*c*]perhydroazulene (13). The olefin mixture **9–12** (3.00 g, 13.9 mmol, crude product) was dissolved in ethanol (100 ml) in a dropping funnel with a pressure equilibration tube. This was mounted on a flask containing tris(triphenylphosphine)chlororhodium[21] (100 mg) in benzene (300 ml). The apparatus was evacuated and refilled with H_2 five times and then saturated with H_2 for 30 min, giving a yellow solution. The olefin solution was added in one lot and hydrogenation was continued until the exocyclic methylene compound **9** was consumed (ca. 30 hr). The other olefins did not react. Evaporation, extraction into hexane, filtration through alumina to remove catalyst, and reevaporation gave a mixture of furan **13** and unreduced olefins (2.8 g). Chromatography on silver nitrate impregnated silica (10%, 25 g, hexane) gave **13** (725 mg, 24%). Distillation gave an analytical sample: bp 71–73° (0.2 mm); n^{22}D 1.5113; ir ν 3150 (furan), 1388, 1371 (*gem*-dimethyl), 1045, 893 (furan), 775 cm^{-1}; NMR δ 7.06 (2 H, m, furan

H), 2.40–2.75 (4 H, m, furan CH_2), 1.05 (3 H, d, J = 7.0 Hz; $CHCH_3$), 0.98, 0.93 ppm (3 H each, s, CCH_3); ^{13}C NMR spectrum was in accord with a single substance of structure **13**; mass spectrum m/e (rel intensity) 218 (M^+, 87, $C_{15}H_{22}O$), 203 (15), 123 (100, base peak), 94 (68).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.5; H, 10.2. Found: C, 82.6; H, 10.1.

Elution of the column with ether gave compounds **10–12** containing traces of unreduced **9**.

2,2,4-Trimethyl(2,5-dimethoxy-2,5-dihydrofuro)[6,7-*c*]perhydroazulene (16). The furan **13** (720 mg, 3.3 mmol) was oxidized electrochemically[34] in methanol (40 ml) with boron trifluoride etherate (0.3 ml) as supporting electrolyte at −20° (Pt anode, Ni cathode, no diaphragm, constant current, 100 mA). After 1.5 times the theoretical reaction time, sodium methoxide in methanol (0.2 *M*, 15 ml) was added and the reaction mixture was evaporated. The residue was partitioned between ether (50 ml) and saturated sodium bicarbonate solution (20 ml) and the water phase was extracted with ether (2 × 15 ml). Drying, evaporation, and distillation gave a mixture of the cis and trans dimethoxydihydrofurans **16** (805 mg, 87%): bp 105–107° (0.2 mm); $n^{25}D$ 1.4892; ir ν 1467, 1388, 1369 (*gem*-dimethyl), 1198, 1100, 990, 957 cm^{-1}; NMR δ 5.64, 5.35 (2 H together, s, CH_3OCH), 3.36 ppm (6 H, s, OCH_3).

Anal. Calcd for $C_{17}H_{28}O_3$: mol wt, 280.2038. Found: mol wt, 280.2040 (M^+).

2,2,4-Trimethyl(2,5-dihydroxy-2,5-dihydrofuro)[6,7-*c*]perhydroazulene (17). The furan **13** (1040 mg, 4.56 mmol) was oxidized electrochemically as described in a previous paper.[27] After the theoretical reaction time (147 min) the reaction mixture was evaporated and the residue was partitioned between water and ether. The water phase was extracted with ether and the extract was dried (Na_2SO_4) and evaporated to give the dihydroxydihydrofuran **17** (1058 mg, 88%): ir ν 3380 (OH), 1387, 1372 (*gem*-dimethyl), 738 cm^{-1}; NMR δ 5.97, 5.86, 5.53, 5.43 ppm (2 H together, s, broad, HOCH).

2,2,4-Trimethyl-4,5-dihydro-1,3,8*H*-azulene-6,7-dicarboxylic Anhydride (18). The dihydroxydihydrofuran **17** (1058 mg, crude product) was dissolved in acetone (40 ml) and cooled with ice. Jones reagent [2.4 ml (10 g of CrO_3, 30 ml of H_2O, and 8.5 ml of concentrated H_2SO_4] was added dropwise with stirring (continued for 30 min). The precipitated chromium salts were filtered off and washed with acetone and the filtrate was evaporated. The residue was partitioned between water and ether, and the water phase was extracted with ether. The ether phases were dried (Na_2SO_4) and evaporated. The residue was dissolved in methylene chloride and treated with molecular sieve (Linde 3A) overnight. Filtration and evaporation gave the crude anhydride **18** (957 mg, 81%). An analytical sample was prepared by distillation [viscous oil which crystallized on cooling; bp 105–108° (0.2 mm); $n^{22}D$ 1.5129; ir ν 1857, 1780 (anhydride), 1385, 1370 (*gem*-dimethyl), 1280, 1260, 898, 730, 719, 707 cm^{-1}] followed by recrystallization from hexane: mp 120–121°; NMR δ 2.20–2.80 (4 H, m, $=CCH_2$), 1.10 (3 H, d, J = 6.0 Hz, $CHCH_3$), 1.01, 0.97 ppm (3 H each, s; CCH_3); mass spectrum m/e (rel intensity) 248 (M^+, 44, $C_{15}H_{20}O_3$), 233 (100, base peak).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.6; H, 8.1. Found: C, 72.4; H, 8.3.

2,2,4-Trimethyl-4,5-dihydro-1,3,8*H*-6,7-bis(methoxycarbonyl)azulene (19). The crude anhydride **18** (700 mg) was refluxed in methanol (15 ml) for 15 hr. Excess diazomethane (ca. 30 mmol) in ether was added to the methanol solution at 0°. After 15 min, acetic acid was added to destroy residual diazomethane. Evaporation gave crude (NMR 75% purity) dimethyl ester **19**. Chromatography on silica (60 g, CH_2Cl_2) gave pure **19** (486 mg, 50% from furan **13**). Distillation gave an analytical sample: bp 114–115° (0.07 mm); $n^{22}D$ 1.4959; ir ν 1735 (C=O), 1660 (C=C), 1387, 1370 cm^{-1} (*gem*-dimethyl); NMR δ 3.77 (6 H, s, OCH_3), 2.00–2.60 (4 H, m, $=CCH_2$), 1.06 (3 H, d, J = 6.0 Hz, $CHCH_3$), 1.00, 0.98 ppm (3 H each, s, CCH_3); mass spectrum m/e (rel intensity) 294 (M^+, 1, $C_{17}H_{26}O_4$), 262 (52), 158 (39), 139 (100, base peak).

Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.4; H, 8.9. Found: C, 69.5; H, 9.1.

Bromo Diester 20. The maleic ester **19** (470 mg) was dissolved in dry carbon tetrachloride (15 ml) and added to *N*-bromosuccinimide (425 mg, recrystallized and dried over P_2O_5) and azoisobutyronitrile (20 mg). The mixture was heated at 80° until the NBS had been consumed (ca. 1 hr). Cooling, removal of precipitated succinimide, and evaporation gave a mixture of brominated products. These were separated by preparative TLC (SiO_2, CH_2Cl_2) into three bands: R_f 0.55, 20 mg (dibrominated product); R_f 0.43, 385 mg (monobrominated product); R_f 0.30, 120 mg (starting material) [NMR (R_f 0.43) δ 4.80–5.45 (1 H, m, BrCH), 3.80 (6 H, s, OCH_3), 1.05, 0.93 ppm (3 H each, s, CCH_3); mass spectra of the three groups of compounds showed the isotopic distribution and fragmentation pattern expected].

2,2,4-Trimethyl-1,3,4*H*-6,7-bis(methoxycarbonyl)azulene (21). The bromo diester **20** (60 mg, 0.16 mmol) was dissolved in dry benzene (2 ml) and cooled with ice. 1,5-Diazabicyclo[4.3.0]non-5-ene[28] (20 mg, 0.16 mmol) in benzene (1 ml) was added dropwise with stirring (N_2). After 5 min (a white precipitate had formed) the reaction mixture was poured onto ice-cold sulfuric acid (2 *M*, 10 ml) and extracted with ether. Drying (Na_2SO_4) and evaporation gave almost pure diene diester **21** as a colorless oil (31 mg, 66%): uv λ_{max} (EtOH) 208 nm (ϵ 23,800), 243 (10,900); ir ν 1735 cm^{-1}; NMR δ 6.94 (1 H, d, broad, J = 5.6 Hz, =CH), 6.67 (1 H, d, broad, J = 2.8 Hz, =CH), 3.77 (6 H, s, OCH_3), 0.92 ppm (6 H, s, CCH_3); mass spectrum m/e (rel intensity) 290 (M^+ − 2, 38), 275 (25), 259 (52), 234 (54), 231 (55), 203 (100, base peak).

2,2,4-Trimethyl-4,5-dihydro-1,3,8*H*-6,7-dicarboximido(4-bromophenyl)azulene (22). The anhydride **18** (160 mg, 0.64 mmol) and *p*-bromoaniline (111 mg, 0.64 mmol) were dissolved in dry ether (10 ml) and stirred at room temperature (15 hr, a white precipitate was formed).[35] The ether was evaporated and the residue was heated (100°, 10 min) with acetic anhydride (10 ml) and sodium acetate (80 mg). The resulting yellow solution was cooled, poured into water, and extracted with ether. Drying (Na_2SO_4), evaporation, and chromatography (SiO_2–CH_2Cl_2) gave a yellow oil (**22** and the corresponding isomaleimide) (172 mg) which was treated with potassium carbonate solution[36] (44%, 15 ml) and dimethoxyethane (3 ml) for 2 hr. Extraction with ether, drying, evaporation, and sublimation (0.1 mm) gave pure **22** (90 mg, 35%): mp 168–169°; ir (KBr) ν 3110, 1780, 1716, 1498, 1385, 1080, 820, 722 cm^{-1}; NMR δ 7.10–7.70 (4 H, m, phenyl H), 2.30–2.60 (4 H, m, $=CCH_2$), 1.10 (3 H, d, J = 7.0 Hz, $CHCH_3$), 1.03, 0.98 ppm (3 H each, s, CCH_3); mass spectrum m/e (rel intensity) 401, 403 (M^+, 100, base peak, $C_{21}H_{24}NO_2Br$), 386, 388 (6), 278, 280 (91), 265, 267 (9). Recrystallization from ethanol gave crystals for X-ray analysis.

Anal. Calcd for $C_{21}H_{24}NO_2Br$: mol wt, 401.0990 and 403.0971. Found: mol wt, 401.0968 and 403.0978 (M^+).

***N*-(*p*-Bromophenyl)maleimide** was prepared by the method described for *N*-phenylmaleimide,[35] yield 70% (crude product). Recrystallization from cyclohexane gave an analytical sample: mp 118–120°; ir (KBr) ν 3100, 1728, 1500, 1408, 1392, 1155, 1070, 833, 710, 687 cm^{-1}; NMR δ 7.10–7.70 (4 H, m, phenyl H), 6.82 ppm (2 H, s, =CH); mass spectrum m/e 251, 253 (M^+, base peak, $C_{10}H_6NO_2Br$).

Diels–Alder Adduct 23. The furan **13** (50 mg, 0.23 mmol) and *N*-(*p*-bromophenyl)maleimide (40 mg, 0.16 mmol) were dissolved in ether (1.5 ml) and left at room temperature for 6 days.[30] A white precipitate (**23**, either or both of the two possible exo forms may be present, zero coupling) was formed which was filtered off and washed with cold ether, yield 55 mg (73%). Recrystallization from ethanol gave an analytical sample: mp 183–184°; ir (KBr) ν 1790, 1720, 1500, 1390, 1190, 1078, 871 cm^{-1}; NMR δ 7.00–7.65 (4 H, m, phenyl H), 5.07 (2 H, s, OCH), 2.94 ppm (2 H, s, COCH); the mass spectrum showed only furan **13** and *N*-(*p*-bromophenyl)maleimide (retro Diels–Alder reaction).

Anal. Calcd for $C_{25}H_{28}BrNO_3$: C, 63.8; H, 6.0. Found: C, 64.1; H, 6.0.

2,2,4-Trimethylfuro[6,7-*c*]perhydroazulene (24). Velleral (**1**, 70 mg) was dissolved in ethyl acetate (3 ml) and palladium on strontium carbonate[20] (3%, 15 mg) was added. Hydrogenation (1 atm, 2 equiv H_2 uptake) followed by column chromatography (SiO_2–hexane) gave the furan **24** (8 mg, 12%): $[\alpha]^{22}D$ + 39.1° (*c* 0.68, $CHCl_3$); ir ν 3150 (furan), 1390, 1375 (*gem*-dimethyl), 1058, 884 (furan), 783 cm^{-1}; NMR δ 7.12 (2 H, m, furan H), 2.30–2.65 (4 H, m, furan CH_2), 1.08, 1.00 ppm (3 H each, s, CCH_3); mass spectrum practically identical with that of furan **13**.

Anal. Calcd for $C_{15}H_{22}O$: mol wt, 218.1671. Found: mol wt, 218.1685 (M^+).

2,2,4-Trimethylfuro[6,7-*c*]-1,3,8*H*-azulene (10). Pyrovellerolactone (**3**, 440 mg, 1.9 mmol) was dissolved in dry ether (25 ml) and cooled with ice (magnetic stirring, N_2 atmosphere). Diisobutylaluminum hydride (2.5 mmol) in ether (2 ml) was added dropwise (syringe). After 60 min (0°) the reaction mixture was added with stirring to ice-cold hydrochloric acid (2 *M*, 10 ml) under nitrogen. The ether phase was washed with sodium bicarbonate solution and water, dried (Na_2SO_4), and evaporated. The residue (450 mg) was chromatographed (SiO_2–CH_2Cl_2), giving the furan **10** (210 mg, 51%): $[\alpha]^{22}D$ − 111.9° (*c* 0.90, $CHCl_3$); ir ν 3145 (furan), 1390, 1370 (*gem*-dimethyl), 1050, 885 (furan), 780 cm^{-1}; NMR δ 7.05, 7.16 (1 H each, s, broad, furan H), 6.05 (1 H, s, broad, =CH), 2.52 (2 H, s, broad, furan CH_2), 1.84 (3 H, d, J = 1.0 Hz, $=CCH_3$), 1.07,

1.02 ppm (3 H each, s, CCH_3); mass spectrum *m/e* (rel intensity) 216 (M^+, 100, base peak, $C_{15}H_{20}O$), 201 (50), 187 (20), 173 (11), 145 (32), 131 (35).

Conventional column and thin layer chromatography (SiO_2, $AgNO_3$-impregnated SiO_2) of the furan mixture **9–12** (after hydrogenation and isolation of **13**) did not give any separation of the four compounds. However, a reversed phase partition chromatography method (using a $AgBF_4$ solution as eluent) described by Wickberg and Westfelt[32,33] gave partial separation both on thin layer and column chromatography. R_f values (TLC) for the compounds follow: **9**, 0.8; **10** and **12**, 0.33; and **11**, 0.22. Compounds **10** and **12** could thus be isolated free of other material. Compounds **9–12** could be separated by VPC (OV-17, 50-m capillary column, 180°). Attempted preparative VPC (10% Reoplex 400 on Gas-Chrom Q, 60–80 mesh, 160°, 6-m steel column) was unsuccessful owing to aerosol formation and destruction on the column.

3,4-Diethyl-2,5-dimethoxy-2,5-dihydrofuran (26) was prepared from 3,4-diethylfuran[27] by the same method as for the synthesis of **16** (1.2 times the theoretical reaction time): yield 53%; bp 90–93° (11 mm); $n^{22}D$ 1.4462; ir ν 1470, 1200, 1100, 997, 930, 910, 862, 808 cm^{-1}; NMR δ 5.74, 5.45 (2 H, s, MeOC**H**), 3.38 (6 H, s, OCH_3), 2.18 (4 H, q, broad, J = 7.0 Hz, CH_2), 1.05 ppm (6 H, t, J = 7.0 Hz, CH_2CH_3); mass spectrum *m/e* (rel intensity) 186 (M^+, 18, $C_{10}H_{18}O_3$), 155 (100, base peak).

2,3-Diethyl-2-penten-5-olide (27). The 2,5-dimethoxy-2,5-dihydrofuran **26** or the 2,5-dihydroxy-2,5-dihydrofuran **28**[27] (ca. 200 mg) was stirred in pentane–dioxane–2 *M* HCl (20:3:3 ml) for 75 or 8 hr, respectively. Extraction with ether, drying (Na_2SO_4), evaporation, and distillation gave the lactone **27**: yield 80% (from **26**) and 68% (from **28**); bp 51–52° (0.2 mm); $n^{21}D$ 1.4695; ir ν 1756, 1678, 1465 cm^{-1}; NMR δ 4.70 (2 H, s, OCH_2), 2.50 (2 H, q, J = 7.0 Hz, $=CCH_2$), 2.32 (2 H, q, J = 7.0 Hz, $=CCH_2$), 1.17 (3 H, t, J = 7.0 Hz, CH_3), 1.10 ppm (3 H, t, J = 7.0 Hz, CH_3); mass spectrum *m/e* (rel intensity) 140 (M^+, 100, base peak, $C_8H_{12}O_2$), 125 (26), 111 (74).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.6; H, 8.6; mol wt, 140.0836. Found: C, 68.0; H, 8.6; mol wt, 140.0832 (M^+).

Pyrovellerolactone (3).[8,9] The furan **10** (170 mg) was oxidized electrolytically,[27] giving a mixture of the 2,5-dihydroxy-2,5-dihydrofuran **29** with other material as a yellow oil. This was stirred in pentane–dioxane–2 *M* HCl (20:3:3 ml) for 15 hr. Standard work-up and chromatography (SiO_2–CH_2Cl_2) gave pyrovellerolactone (**3**) and some (ca. 10%) of, presumably, an isomer (**30**) in a total yield of 25 mg (14%). Compounds **3** and **30** were separated by VPC (GE SF-96, 50-m capillary column, 220°), **3** showing the same retention time as the natural compound. Identity was further shown by ir, NMR, uv, and mass spectrometry.

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Registry No.—**1**, 50656-61-6; **3**, 51276-29-0; (±)-**3**, 54823-66-4; **6**, 50388-42-6; **7**, 54823-67-5; **8**, 54823-68-6; **9**, 54823-69-7; **10**, 54823-70-0; (±)-**10**, 54823-71-1; **11**, 54823-72-2; **12**, 54823-73-3; **13**, 54823-74-4; **16**, 54823-75-5; **17**, 54823-76-6; **18**, 54823-77-7; **19**, 54823-78-8; **20**, 54823-79-9; **21**, 54823-80-2; **22**, 54823-81-3; **23**, 54823-82-4; **24**, 54868-47-2; **26**, 54823-83-5; **27**, 54823-84-6; **28**, 54823-85-7; **29**, 54823-86-8; methanesulfonyl chloride, 124-63-0; *N*-bromosuccinimide, 128-08-5; *p*-bromoaniline, 106-40-1; *N*-(*p*-bromophenyl)maleimide, 13380-67-1; 3,4-diethylfuran, 53059-82-8.

References and Notes

(1) (a) Part VIII: see ref 10. (b) Presented at 15:e Nordiska Kemistmötet, Tammerfors, Finland, June 1974. (c) G. Magnusson, S. Thorén and B. Wickberg, *Tetrahedron Lett.*, 1105 (1972).
(2) J. J. Dugan, P. de Mayo, M. Nisbet, J. R. Robinson, and M. Anchel, *J. Am. Chem. Soc.*, **88**, 2838 (1966).
(3) D. Helmlinger, P. de Mayo, M. Nye, L. Westfelt, and R. B. Yeats, *Tetrahedron Lett.*, 349 (1970).
(4) S. R. Wilson and R. B. Turner, *J. Org. Chem.*, **38**, 2870 (1973).
(5) G. Magnusson and S. Thorén, *Tetrahedron*, **30**, 1431 (1974).
(6) J. Froborg, G. Magnusson and S. Thorén, *Acta Chem. Scand, Ser. B*, **28**, 265 (1974).
(7) G. Magnusson, S. Thorén, and T. Drakenberg, *Tetrahedron*, **29**, 1621 (1973).
(8) G. Magnusson and S. Thorén, *Acta Chem. Scand.*, **27**, 1573 (1973).
(9) G. Magnusson and S. Thorén, *Acta Chem. Scand.*, **27**, 2396 (1973).
(10) G. Magnusson, S. Thorén, J. Dahmén, and K. Leander, *Acta Chem. Scand., Ser. B*, **28**, 841 (1974).
(11) W. M. Daniewski and M. Kocòr, *Bull. Acad. Pol. Sci., Ser. Chim.*, **19**, 553 (1971).
(12) W. M. Daniewski, B. Zółtowska, and M. Kocòr, *Bull. Acad. Pol. Sci., Ser. Chim.*, **21**, 785 (1973).
(13) S. Nozoe, H. Matsumoto, and S. Urano, *Tetrahedron Lett.*, 3125 (1971).
(14) C. H. Heathcock in J. ApSimon, Ed., "The Total Synthesis of Natural Products", Vol. 2, Wiley-Interscience, New York, N.Y., 1974. For a fuller account of syntheses of nonbridged hydroazulenes, see also G. Magnusson, Dissertation, Lund, Sweden, 1975.
(15) J. A. Marshall and J. J. Partridge, *Tetrahedron*, **25**, 2159 (1969).
(16) J. Froborg, G. Magnusson, and S. Thorén, *J. Org. Chem.*, **39**, 848 (1974).
(17) P. Stilbs, *Chem. Scr.*, **7**, 59 (1975).
(18) R. E. Davis and M. R. Willcott, III, *J. Am. Chem. Soc.*, **94**, 1744 (1972).
(19) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(20) R. J. Rallings and J. C. Smith, *J. Chem. Soc.*, 618 (1953).
(21) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(22) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).
(23) J. D. Andose and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2168 (1974).
(24) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967).
(25) Program written by P. Stilbs, Physical Chemistry 2, Chemical Center, Lund, Sweden.
(26) D. L. Hufford, D. S. Tarbell, and T. R. Koszalka, *J. Am. Chem. Soc.*, **74**, 3014 (1952).
(27) J. Froborg, G. Magnusson, and S. Thorén, *J. Org. Chem.*, **40**, 122 (1975).
(28) H. Oediger, F. Möller, and K. Eiter, *Synthesis*, 591 (1972).
(29) X-Ray work was performed by Dr. Christer Svensson, Inorganic Chemistry 2, Chemical Center, Lund, Sweden.
(30) H. Kwart and I. Burchuk, *J. Am. Chem. Soc.*, **74**, 3094 (1952).
(31) J. A. Hirsch and A. J. Szur, *J. Heterocycl. Chem.*, **9**, 523 (1972).
(32) B. Wickberg, *J. Org. Chem.*, **27**, 4652 (1962).
(33) L. Westfelt and B. Wickberg, *Ark. Kemi*, **26**, 545 (1967).
(34) N. Elming, *Adv. Org. Chem.* **2**, 67 (1960).
(35) M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 944.
(36) R. Pummerer and G. Dorfmüller, *Ber.*, **45**, 292 (1912).