dried ($MgSO_4$) and concentrated in vacuo. When $LiAl(O\text{-}t\text{-}Bu)_3H$ was used as the reducing agent, the hydrolyzed solution was washed several times with water to remove the *t*-BuOH, followed by a similar workup procedure. The mixture of crude products was subjected to two methods of analysis. In the NMR method, the residue was dissolved in $CDCl_3$ and with the aid of the LSR, $Eu(fod)_3$,[22] the methyl resonances were sufficiently separated so that an integration could be obtained. In the GLC method, dissolution of the residue in dry pyridine and silylation with a mixture of hexamethyldisilazane and trimethylchlorosilane[23] was followed by gas chromatography. Both of these procedures yielded the relative amounts of each stereoisomer.

$LiAlH_4$ Reduction of 1c in Benzene. To a properly dried reaction vessel was added 0.0747 g (0.394 mmol) of **1c** in 50 ml of dry benzene. The solution was heated to reflux and 0.22 ml (0.197 mmol) of a 0.9 M $LiAlH_4$ solution was added (the ether solvent was evaporated off immediately). After a 24-h reflux period, the reaction mixture was hydrolyzed with 15% NaOH, the mixture was concentrated in vacuo, and the crude product dissolved in ether. The ether solution was washed once with 60 ml of water and the aqueous layer thrice with 25 ml of ether. The combined ethereal layers were dried with $MgSO_4$, followed by concentration in vacuo, to yield an oil. Upon NMR analysis, the oil produced the same spectrum as the reduction run in diethyl ether, i.e., the trans hydroxy ether. A similar experiment with **1a**, the dione, failed to yield any of the reduction products.

Registry No.—**1a**, 17190-77-1; **1b**, 59269-93-1; **1c**, 59269-94-2; **1d**, 59269-95-3; **1e**, 59269-96-4; *cis*-**2a**, 54884-33-2; *trans*-**2a**, 54884-34-3; *trans*-**2c**, 59269-97-5; *cis*-**2d**, 59269-98-6; *trans*-**2d**, 59269-99-7; *cis*-**2e**, 59270-00-7; *trans*-**2e**, 59270-01-8; $LiAlH_4$, 16853-85-3; $LiAl(O\text{-}t\text{-}Bu)_3H$, 17476-04-9.

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Electrochemical Reduction of Geranial, Farnesal, and Crotonaldehyde[1]

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The electrolytic reduction of the α,β-unsaturated aldehydes **11**, **12**, and **13** was studied and the nature of the coupling products determined. Attempts at effecting substrate orientation by carrying out the reductions in micelles were unsuccessful. The reduction of crotonaldehyde was repeated and an earlier report[4] found to be in error.

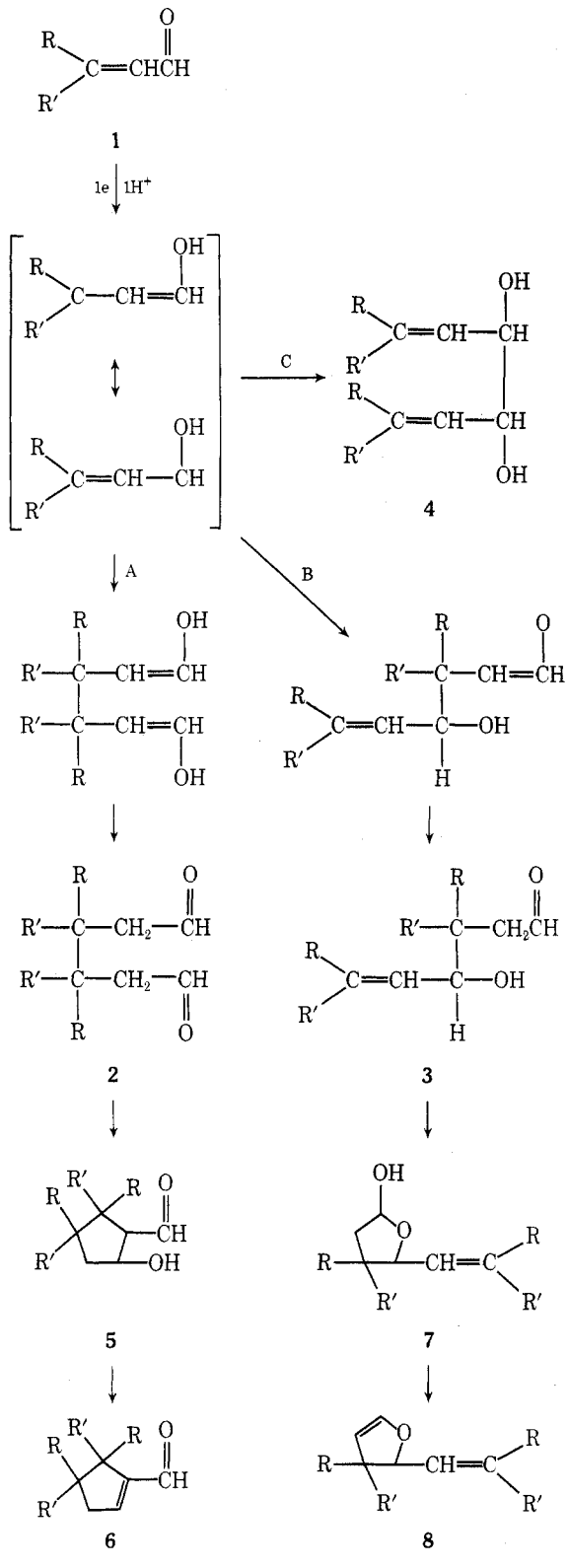
The electrochemical reduction of α,β-unsaturated aldehyde systems in acidic media results in the formation of a short-lived radical anion, which abstracts a proton from the solvent to produce an enol radical. Dimerization of this radical may take place via three different pathways:

Pathway A, the coupling of two β radicals ("tail to tail"), results in a dialdehydic compound (**2**), which may undergo an aldol condensation to produce compound **5** or **6**. Pathway B, the "head to tail" coupling of a carbonyl radical with a β radical, yields compound **3**, which may cyclize to form compound **7** or **8**. Finally, pathway C, the coupling of two carbonyl radicals ("head to head") affords a 1,2 diol (glycol), compound **4**.

One might expect steric factors to play a role in determining which pathway is favored. With acrolein (**9**) Misono[2] found compound **6** (R = R′ = H) to be the major product. This seems to indicate a preference for pathway A ("tail to tail") as the mode of coupling for the enol radical. Hindrance to the β position of acrolein should decrease products resulting from pathway A. Indeed, when the β position is subtituted with two methyl groups, as in 3-methylcrotonaldehyde (**11**) Miller[3] reported no products formed from pathway A. The methyl groups, however, are apparently not large enough to eliminate completely participation of the β radical in the coupling reaction, as evidenced by the fact that the major product from the electrochemical reduction of 3-methylcrotonaldehyde was that formed from pathway B.

We were interested to see whether increasing the size of one of the R groups at the β position would result in any decrease in the products resulting from pathway B ("head to tail" coupling) and thus make head to head coupling the prime route followed. To this end we repeated the reduction of 3-methylcrotonaldehyde,[3] and performed electrochemical reductions on geranial (**12**) and farnesal (**13**). Further, in order to determine what effect there would be in orienting the substrate during the electrochemical reduction, the electrolyses were repeated in micellar solutions. It seemed reasonable to assume that by using micelle solutions the β position would be buried in the micelle while the carbonyl position would be exposed to the reducing (aqueous) phase. This ideally would result in the formation of only the glycol (**4**).

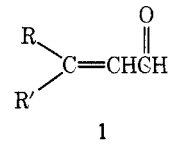
The aldehydes required for this investigation were available by short preparative schemes. 3-Methylcrotonaldehyde was prepared according to Miller.[3] Geranial was obtained by simple manganese dioxide oxidation of the corresponding commercially available alcohol. *trans,trans*-Farnesol was obtained by spinning band separation from commercially available farnesol, and was subsequently oxidized with man-



ganese dioxide to farnesal. All of the aldehydes were indicated to be of high purity by NMR and infrared analysis.

Polarographic runs were made on each of the aldehydes (**11, 12, 13**), 1×10^{-3} M in 1:1 ethanol–acetate buffer of pH 5. The half-wave potentials of all three aldehydes fell between −1.23 and −1.30 V (vs. SCE). Half-wave potentials for the aldehydes solubilized in the micelle solutions (0.05–0.50 M cetyltrimethylammonium bromide in pH 5 acetate buffer) were essentially the same, falling within the same narrow range.

Controlled potential electrolytic reductions were performed on each aldehyde (**11, 12, 13**) in both the ethanol–pH 5 acetate buffer system and the micelle solutions. In all cases the reduction was complete within 2–3 h. After workup the crude oil from the reduction of each aldehyde was found to contain two dimeric products: a hydroxytetrahydrofuran of compound type **7**, resulting from "head to tail" coupling, and a 1,2-diol (glycol) of compound type **4**, resulting from "head to head" coupling. The results are summarized in Table I.



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9 (acrolein), R = H; R′ = H
10 (crotonaldehyde), R = CH_3; R′ = H
11 (3-methylcrotonaldehyde), R = CH_3; R′ = CH_3
12 (geranial), R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$
13 (farnesal), R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$

It is apparent that the micelle system is without effect on the course of dimerization. A possible explanation is that the reduction is occurring only on that small portion of aldehyde which is in the aqueous phase of the system. The resulting dimeric products could then be extracted into the micelles, more aldehyde could diffuse out, and the process continue. Alternatively it may be that the aldehyde is dissolved in the micelle system and is being reduced there, but the polarity of the α,β-unsaturated aldehyde results in the active site of the molecule being exposed to the aqueous phase. If the entire conjugated portion of the aldehyde were above the micellar surface, then little directing effect would be expected.

It may be seen from the results listed in Table I that while pathway B seems to be the preferred mode of coupling for a β,β-disubstituted acrolein system, increasing the size of one of the β substituents does decrease the amount of "head to tail" coupling. This could be attributed to an increased steric repulsion as the methyl group at the β position (compound **11**) is lengthened to a 6 (geranial) and 11 (farnesal) carbon chain.

A recent investigation[4] of crotonaldehyde (**10**) seems to contradict these trends. It was reported that reduction of crotonaldehyde in pH 4.7 acetate buffer yielded the glycol (compound **4**, R = CH_3; R′ = H) as the major product. Since this product was not isolated and characterized in that study, we felt that the reduction of crotonaldehyde required further investigation. We therefore repeated the reduction of crotonaldehyde and found, in accord with our other findings, that the major product (56.1% yield) was the hydroxytetrahydrofuran **7** (R = CH_3; R′ = H) resulting from pathway B. "Tail to tail" coupling (pathway A) accounted for 27.9% of the product (compound **5**, R = CH_3; R′ = H) and "head to head" coupling product (compound **4**, R = CH_3; R′ = H) was the minor constituent (16%). Thus, the previous report[4] was in error.

Experimental Section

Nuclear magnetic resonance spectra were recorded on the Varian Model EM-360 spectrometer using chloroform-*d* as solvent and tetramethylsilane as the internal standard. Infrared spectra were recorded on the Perkin-Elmer Model 257 spectrometer and were taken in solution (spectrograde chloroform) unless noted otherwise. pH was measured with a Corning Model 12 pH meter. Polarographic runs were made using a Princeton Applied Research Model 170 electrochemistry system with a dropping mercury electrode (DME) and saturated calomel electrode (SCE). The controlled potential electrolysis experiments were also carried out with this instrument, using the electrolysis cell described below.

3-Methylcrotonaldehyde (11). This aldehyde was prepared according to Miller:[3] NMR δ 2.0, 2.2 (s, 6 H), 5.85 (d, 1 H, J = 8 Hz), 9.85 (d, 1 H, J = 8 Hz); ir 2900 (m), 2750 (m), 1670 (s), 1450 (m), 1050 cm^{-1} (m).

Table I. Distribution of Electrolysis Products

Aldehyde	$E_{1/2}$,[a] V	Grams used	Solvent system	% yield[b]	% dimer	
					Furan	Glycol
3-Methylcrotonaldehyde	−1.27	0.50	EtOH–buffer[c]	54	85	15
3-Methylcrotonaldehyde	−1.30	0.50	0.1 M CTABr[d]	46	85	15
Geranial	−1.25	1.25	EtOH–buffer	54	66	34
Geranial	−1.25	1.25	0.0 M CTABr	70	62	38
Geranial	−1.23	1.25	0.1 M CTABr	43	62	38
Geranial	−1.25	1.25	0.5 M CTABr	67	64	36
Farnesal	−1.28	1.83	EtOH–buffer	51	64	36
Farnesal	−1.30	1.83	0.5 M CTABr	32	62	38

[a] Vs. SCE. [b] Yield of dimeric material. [c] 50:50 ethanol–0.25 M acetate buffer at pH 5, aqueous KCl as supporting electrolyte. [d] Cetyltrimethylammonium bromide in 0.25 M acetate buffer at pH 5.

Geranial (12). Under a nitrogen atmosphere, 200 ml of benzene (dried over Na) and 20 g of fresh, activated MnO_2 (Winthrop Labs) were placed in a 500-ml flask equipped with a magnetic stirrer, Dean-Stark trap, and condensor. This mixture was refluxed for approximately 2 h until no more water was being collected. The flask contents were cooled to room temperature, the Dean-Stark trap removed, and 2.00 g of commercial geraniol in 5 ml of benzene was added. The mixture was stirred overnight at room temperature. The benzene solution was then filtered through Celite, the MnO_2 residue being washed with ethyl ether. The organic filtrates were combined and dried over anhydrous Na_2SO_4. Evaporation of this solution gave 1.91 g of geranial (96%). (It was found that lowering the ratio of oxidant from 10:1 to 5:1 did not significantly alter either the yield or quality of the product, as long as fresh MnO_2 was used.) NMR δ 1.65, 1.7 (s, 6 H), 2.2 (m, 7 H total), 5.1 (broad s, 1 H), 5.8 (d, 1 H, J = 8 Hz), 9.85 (d, 1 H, J = 8 Hz); ir 2920 (m), 1640 (s), 1635 (w), 1150 cm^{-1} (m).

Farnesal (13). Farnesal was prepared from *trans,trans*-farnesol by oxidation with fresh, activated MnO_2 using the same method as described for geranial. Farnesol (8.2 g) oxidized with 30 g of MnO_2 gave 6.74 g of farnesal (82%): NMR δ 1.6, 1.66 (s, 12 H), 2.1 (m, 8 H), 5.1 (m, 2 H), 5.8 (d, 1 H, J = 9 Hz), 9.9 (d, 1 H, J = 8 Hz); ir 2900 (s), 1660 (s), 1440 (m), 1360 (m), 1120 cm^{-1} (m).

Preparation of pH 5 Buffer. The buffer used in both the polarography and the electrolysis of the aldehydes (**11, 12, 13**) was a 0.25 M acetate system. It was prepared by adding sufficient 1 M acetic acid solution to 250 ml of 1 M NaOH to bring the pH near 5. The solution was then diluted to almost 1 l., and the pH was adjusted to 5. The solution was then diluted to exactly 1 l.

Purification of Surfactant. The cetyltrimethylammonium bromide was purified[5] by shaking with anhydrous ethyl ether and filtering through a Buchner funnel. This material was then dissolved in a minimum amount of hot methanol and cooled to crystallize. The solid was collected and redissolved in methanol to which ether was then added. This mixture was heated to redissolve the salt and cooled again to crystallize. The crystalline product was collected by suction filtration and dried in a vacuum desiccator at room temperature for 3 h (0.5 mmHg).

Polarography of Aldehydes (11, 12, 13). The polarographic measurements were made with a Princeton Applied Research Model 170 electrochemistry system, using a DME and SCE in a 10-ml H-type polarographic cell. The solutions, each 1.0×10^{-3} M in aldehyde, were purged with N_2 for 10–15 min before each run. The micelle systems foamed a good deal, but this did not seem to affect their polarographic behavior. In each case, a blank run on the solvent system (50:50 EtOH–0.25 M acetate buffer at pH 5) or micelle solution (0.05–0.50 M cetyltrimethylammonium bromide in 0.25 M acetate buffer at pH 5) alone was made to ensure that waves observed were actually due to the aldehyde. The half-wave potentials were closely grouped, falling between −1.23 and −1.30 V; the individual $E_{1/2}$ values are listed in Table I.

Controlled Potential Electrolysis of Aldehydes (11, 12, 13). The Princeton Applied Research Model 170 was also used for the controlled potential electrolyses. The electrolysis cell was a conventional three-electrode system: a mercury (instrument grade) pool working electrode (cathode), a saturated calomel reference electrode, and a Ag/AgCl auxiliary electrode (anode), which was separated from the solution by a fritted glass disk. All reductions were carried out under nitrogen atmosphere. The mercury pool was stirred rapidly throughout the electrolyses with a magnetic stirrer. In each case aqueous KCl was used as a supporting electrolyte. Prior to each electrolysis the system was purged with nitrogen for approximately 20 min until a steady background current for the solvent system, 150 ml of 50:50 ethanol–pH 5 acetate buffer (0.25 M), was obtained. The aldehyde (0.008 mol), which had been dissolved in 10 ml of ethanol, was then added slowly so as not to exceed a current of 1 A.

The reactions employing micelles were carried out in much the same fashion. The solvent system, 50 ml of 0.05–0.50 M cetyltrimethylammonium bromide in pH 5 acetate buffer (0.25 M) with aqueous KCl as supporting electrolyte, was purged slowly with nitrogen (foaming) until a steady background current was obtained. The aldehyde (0.008 mol) was dissolved in about 100 ml of the micelle solution and then added slowly to the electrolysis chamber. All of the electrolyses were conducted at −1.30 V vs. SCE and were complete in 2 h as indicated by a return to background levels of current. In all cases the workup involved extracting the aqueous solutions three times with ethyl ether (50 ml each). There was some tendency of the micelle solution to form emulsions, but these would separate if allowed to stand undisturbed. The ether extracts were combined for each reaction and washed with an aqueous solution of saturated NaCl. The organic extracts from each reduction were then dried over anhydrous Na_2SO_4 and concentrated to oils (often with odor of acetic acid). The results of each electrolysis are given in Table I. Separation and identification of the products is discussed below.

Product Isolation and Identification. 3-Methylcrotonaldehyde in EtOH–pH 5 Buffer. Electrolysis of 0.5 g (0.008 mol) as described previously and workup gave a yellow oil (0.55 g) which was chromatographed on 15 g of Silicar CC-7. Hexane, benzene/hexane, benzene, benzene/ether, ether, and then ethanol and methylene chloride were used as solvent. Two peaks were eluted. The first totaled 235 mg and was identified as the hydroxyfuran derivative (**7**, R = CH_3; R′ = CH_3); the second totaled 36 mg and proved to be the glycol (**4**, R = CH_3; R′ = CH_3) (ratio of 87:13 furan/glycol). Total isolated dimer was 271 mg (54% yield). A second run with 0.5 g of 3-methylcrotonaldehyde under the same conditions gave 242 mg of furan (**7**, R = CH_3; R′ = CH_3) and 48 mg of glycol (**4**, R = CH_3; R′ = CH_3) (ratio of 83:17) for a total of 290 mg (58% yield).

Peak 1. 4,4-Dimethyl-2-hydroxy-5-(2-methyl-1-propenyl)tetrahydrofuran[3] (**7**, R = CH_3; R′ = CH_3): NMR δ 1.05 (s, 6 H), 1.65 (m, 6 H), 2.1 (m, 2 H), 4.1 (m, 2 H), 4.4 (m, 1 H), 5.3 (m, 2 H); ir 3300 (broad), 2880 (s), 1685 (w), 1050 cm^{-1} (m).

Peak 2. 2,7-Dimethyl-2,6-octadiene-4,5-diol[3] (**4**, R = CH_3; R′ = CH_3): NMR δ 1.7 (s, 12 H), 2.25 (broad s, 2 H), 4.25 (m, 2 H), 5.25 (m, 2 H); ir 3550 (s), 2900 (s), 1660 (m), 1370 (m), 980 cm^{-1} (m).

3-Methylcrotonaldehyde in Micelle. Electrolysis of 0.5 g (0.008 mol) of aldehyde in 0.1 M cetyltrimethylammonium bromide as described in the general procedure previously gave an isolated yield of 197 mg of hydroxyfuran (**7**, R = CH_3; R′ = CH_3) and 34 mg of glycol (**4**, R = CH_3; R′ = CH_3) (product ratio of 85:15). Total isolated dimer was 231 mg (46% yield). The spectra of these materials were identical with those reported above. No other product was isolated from any of the runs with 3-methylcrotonaldehyde.

Geranial in EtOH–pH 5 buffer. Electrolysis of 1.25 g (0.008 mol) of geranial (**12**) in EtOH–buffer as described previously gave 0.9 g of crude reduction product on workup. This was chromatographed on 40 g of Silicar CC-7, eluting with hexane, ether/hexane, and ether with the percentage of ether increased in 5% increments. Two products were isolated. The first, totaling 412 mg, proved to be the hydroxyfuran [**7**, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$] and the second, 192 mg, was the glycol [**4**, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$]. Total isolated product was 604 mg (48% yield) with a ratio of furan to glycol

of 68:32. A second run employing the same quantity of geranial gave 480 mg of hydroxyfuran and 266 mg of glycol for a ratio of 64:36. Total yield in this case was 746 mg (60%).

Peak 1. Hydroxyfuran [7, R = CH_3; R′ = $CH_2CH_2CCH{=}C(CH_3)_2$]. NMR δ 0.93 (d, 3 H, J = 7 Hz), 1.64 (s superimposed on multiplet, 18 H total), 2.07 (m, 6 H), 3.85 (broad singlet, 1 H), 4.35 (m, 1 H), 5.09 (m, 3 H), 5.51 (m, 1 H); ir 2500 (w), 2950 (s), 2920 (s), 1710 (w), 1640 (w), 1440 (m), 900 cm^{-1} (s).

Peak 2. Glycol [4, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$]. NMR δ 1.61, 1.7 (s, 18 H), 2.2 (m, 8 H), 4.25 (doublet of doublets, 2 H total), 5.12 (m, 4 H); ir 3550 (broad), 2900 (s), 1660 (m), 1440 (m), 1370 (m), 980 cm^{-1} (m).

Geranial in Micelles. In the manner described previously, geranial (**12**) was reduced in the presence of three different micelle concentrations. A 1.25-g portion reduced in 0.05 M cetyltrimethylammonium bromide gave, after chromatography, 544 mg of hydroxyfuran [**7**, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$] and 334 mg of glycol [**4**, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$] for a product ratio of 62:38. Total isolated yield was 878 mg (70%). The same quantity reduced in 0.1 M micelle solution gave 334 mg of the hydroxyfuran and 207 mg of the glycol (ratio 62:38). Total yield here was 541 mg (43%). An equal amount of geranial was also reduced in presence of 0.5 M micelle. This run gave 533 mg of the hydroxyfuran and 298 mg of the glycol (ratio 64:36). Total isolated yield was 831 mg (67%). The spectral properties are essentially those described in the previous section.

Farnesal in EtOH–pH 5 Buffer. Farnesal (**13**, 1.83 g, 0.008 mol) was reduced in the manner described previously. Upon workup (1.303 g of crude product) and chromatography on 60 g of Silicar CC-7 with the solvent system described for geranial, 601 mg of hydroxyfuran [**7**, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$] and 332 mg of glycol [**4**, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$] was isolated for a product ratio of 64:36 furan:glycol. Total isolated yield was 933 mg (51%).

Peak 1. Hydroxyfuran [7, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$]. NMR δ 0.93 (d, 3 H, J = 7 Hz), 1.63, 1.67 (s, 21 H), 2.05 (m, 16 H), 4.09 (m, 1 H), 4.51 (m, 1 H), 5.07 (m, 5 H), 5.39 (m, 1 H); ir 3400 (broad), 2920 (s), 1720 (w), 1660 (w), 1440 (m), 1380 (m), 1100 cm^{-1} (m).

Peak 2. Glycol [4, R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$]. NMR δ 1.63, 1.67 (s, 24 H), 2.09 (m, 16 H), 4.23 (doublet of doublet, 2 H), 5.12 (m, 6 H); ir 3400 (broad), 2960 (s), 2920 (s), 1620 (w), 1380 (s), 1080 cm^{-1} (m).

Farnesal in Micelles. Farnesal (1.83 g) was reduced in 0.5 M micelle–buffer solution in the manner described previously. Chromatography of the product on 60 g of Silicar CC-7 with the solvent system used for geranial gave 368 mg of the hydroxyfuran and 226 mg of the glycol. The product ratio was 62:38 furan:glycol. The yield of dimeric material totaled 594 mg (32%). These materials had the same spectral properties as described above for materials produced in a system without micelles.

Crotonaldehyde (10). Commercial crotonaldehyde was fractionally distilled (bp 104.5 °C) under N_2 to give a clear, colorless liquid. It was necessary to store the crotonaldehyde under N_2 in the refrigerator to prevent polymerization: NMR δ 2.05 (d of d, 3 H), 6.10 (m, 1 H), 7.00 (m, 1 H), 9.50 (d, 1 H); ir 2740 (w), 2810 (w), 1690 (s), 1645 cm^{-1} (m, sh).

Preparation of pH 4.7 Buffer. This buffer, used in both the polarography and electrolysis of crotonaldehyde, was prepared in exactly the same manner as the pH 5 buffer, except that the pH was adjusted to 4.7.

Polarography of Crotonaldehyde. This was conducted with the same apparatus that was used for the polarographic studies of the aldehydes (**11, 12, 13**). After the system was purged with N_2 for approximately 15 min, a blank run was made on the solvent system, 0.25 M acetate buffer at pH 4.7, 5% EtOH. No reduction of the solvent occurred in the potential range −0.10 to −1.60 V. A solution of 1.0×10^{-3} M crotonaldehyde in 0.25 M acetate buffer at pH 4.7, 5% EtOH was placed in the polarographic H cell and purged with N_2 for approximately 15 min. The polarogram was run, and the half-wave potential of crotonaldehyde was determined to be −1.25 V vs. SCE.

Controlled Potential Electrolysis of Crotonaldehyde. The same apparatus employed in the reduction of the other aldehydes (**11, 12, 13**) was used for the electrolysis of crotonaldehyde. pH 4.7 buffer, 5% EtOH (200 ml) was placed in the electrolysis cell with Hg and magnetic stirrer. The system was purged with N_2 for 15–20 min, and the electrodes were connected. The potential was set at −1.30 V. After a stable background current was obtained, 2.00 g (0.286 mol) of crotonaldehyde dissolved in 10 ml of EtOH was added at a rate such that a current of 1 A was not exceeded. The mercury pool was stirred vigorously during the electrolysis. Aqueous KCl was added periodically to prevent electrical overloading. The reduction was complete in 2 h, as indicated by a return to background level of current.

The pH of the aqueous solution was adjusted to 8 by the addition of saturated Na_2CO_3. The solution was extracted five times with chloroform (50 ml each). The organic extracts were combined and dried over anhydrous $MgSO_4$. The chloroform solution was concentrated to a clean, colorless, viscous liquid weighing 1.73 g (86.5%). It was necessary to store the oil under N_2 and in the cold. GC analysis showed that three products were present in the oil (none of which were starting material). This crude (0.95 g) was chromatographed on 70 g of Silicar CC-7, eluting successively with hexane, ether/hexane, and ether. Three peaks were obtained totaling 900 mg (94.7%). The first peak, 505 mg (56.1%), was eluted in 40% ether/hexane and was identified as the hydroxytetrahydrofuran (**7**, R = CH_3; R′ = H) by NMR and ir analysis. The second peak, 251 mg (27.9%), eluted in 60% ether/hexane was identified as the aldol (**5**, R = CH_3; R′ = H). The final peak, 144 mg (16.0%), eluted in 90% ether/hexane was identified as the glycol (**4**, R = CH_3; R′ = H). The evidence for these compounds is given below.

Peak 1. Hydroxytetrahydrofuran (7, R = CH_3; R′ = H) NMR δ 1.00 (d, 3 H, J = 6 Hz), 1.75 (d, 3 H, J = 5 Hz), 4.70 (m, 1 H), 5.55 (m, 2 H); ir 1670 (w), 1710 (w), 3380–3600 cm^{-1} (m).

Peak 2. Aldol (5, R = CH_3; R′ = H). NMR δ 1.00 (d, 6 H, J = 4 Hz), 3.20 [s (broad), 1 H], 4.48 (m, 1 H), 9.75 (d, 1 H, J = 4 Hz); ir 1720 (s), 2720 (w), 3400–3600 cm^{-1} (m).

Peak 3. Glycol (4, R = CH_3; R′ = H). NMR δ 1.75 (d, 6 H, J = 5 Hz), 4.05 (d, 2 H, J = 6 Hz), 5.65 (m, 4 H); ir 1670 (m), 1700 (w), 3400–3600 cm^{-1} (s).

Registry No.—**4** (R = R′ = CH_3), 28405-69-8; **4** (R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)_2$), 18927-19-0; **4** (R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$), 59015-27-9; **4** (R = CH_3; R′ = H), 4486-59-3; **5** (R = CH_3; R′ = H), 25801-68-7; **7** (R = R′ = CH_3), 28405-68-7; **7** (R = CH_2; R′ = $CH_2CH_2CH{=}C(CH_3)_2$), 59015-28-0; **7** (R = CH_3; R′ = $CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$), 59015-29-1; **7** (R = CH_3; R′ = H), 59015-30-4; **10**, 4170-30-3; **11**, 107-86-8; **12**, 141-27-5; **13**, 502-67-0; *trans,trans*-farnesol, 106-28-5; geraniol, 106-24-1.

References and Notes

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