The Birch Reduction of Heterocyclic Compounds. **IV** [1]. Birch Reduction of 3-Acylfurans. Competition between Ring Reduction, Carbonyl Reduction, and Dimer Formation

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The Birch reduction of 3-acylfurans **1**, **3** and **10** and their reaction path ways are described.
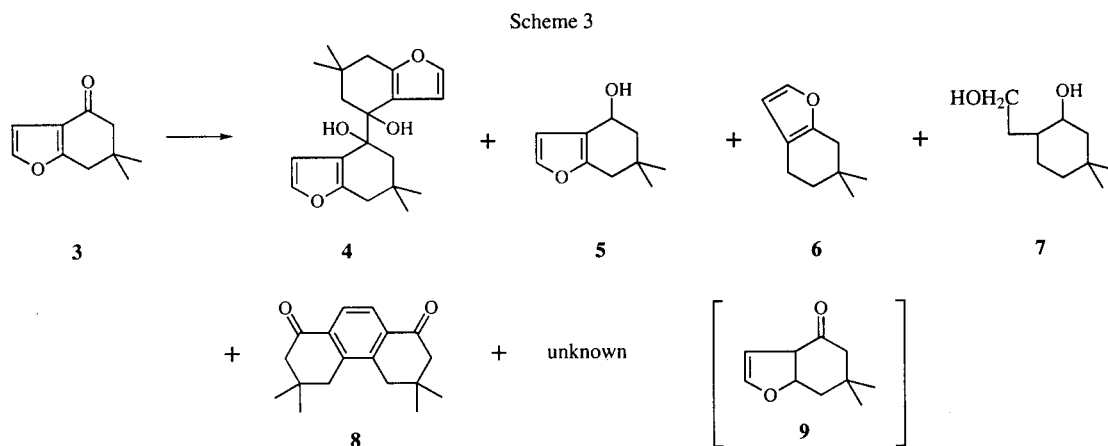
The metal-ammonia reduction of cyclic ketones has received considerable attention and is widely studied [2]. The Birch reduction of aryl ketones [3] involves greater complexity since, in principle, reduction may occur either at the carbonyl group or in the aromatic ring. In fact, the reduction of aryl ketones to alcohols and/or hydrocarbons has been known for some time, but nuclear reduction was first observed by Narisada and Watanabe [4]. As a part of our work, we now describe the Birch reduction of some 3-acylfurans and provide mechanistic insight into this complex process.

We have found that the reduction of 3-pentanoylfuran **1a** with 2 equivalent atoms of lithium gave the dihydro product **2a** (furan ring reduction) in 89% yield and the methyl dihydro product **2b** (reductive alkylation with iodomethane) in 50% yield, whereas the reduction of 3-(3-methoxybenzoyl)furan **1b** with 6 equivalent atoms of lithium in the presence of ethanol in ammonia afforded **2c**

(carbonyl and benzene ring reduction) in 95% yield (Scheme 1). Acid hydrolysis of **2c** with hydrochloric acid isomerized to the enone **2d**. A series of this reaction was applied to the synthesis of (±)-penlanfuran [5], a naturally occurring sesquiterpene. As shown in Scheme 2, many sesquiterpenoids [6] possess a novel skeleton, such as germacrenes and eudesmanes, as the structure **iii** which would be derived from **i**. We first examined the Birch reduction of model compound **3** since we succeeded in the ring reduction of **1a** to **2a**.

In the Birch reduction of **3** the expected product **9** could not be obtained; however, it produced as many as five different products, bis 4,4'-[6,6-dimethyl-4-hydroxytetra-hydrobenzo[*b*]furan] **4**, 6,6-dimethyl-4-hydroxytetra-hydrobenzo[*b*]furan **5**, 6,6-dimethyltetrahydrobenzo-[*b*]furan **6**, 5,5-dimethyl-2-(2-hydroxyethyl)cyclohexanol **7** and 3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydro-phenanthrene-1,8-dione **8**, including undetectable polar

Scheme 1

2a R = H   89%
2b R = CH₃ 50%

1

a : X = *n*-C₄H₉
b : X = 3-methoxyphenyl

2c

2d

Scheme 2

i   **ii**   **iii**
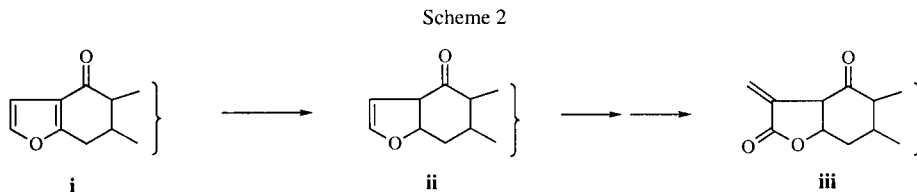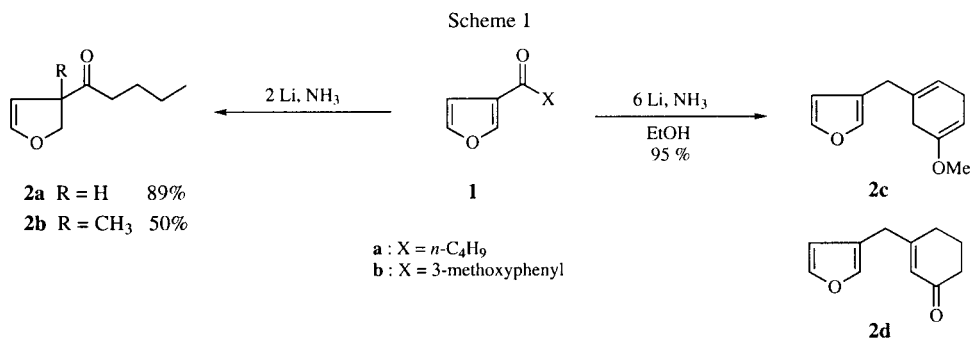
Scheme 3

compounds (Scheme 3). Moreover, the reaction is considerably sensitive to conditions as shown in the Table 4. Structures of these products were deduced from their nmr, ir and ms spectra, and the structure of **8** was finally confirmed by X-ray crystallography.

The molecular structure of **8** was unequivocally determined by X-ray crystallographic analysis as is shown in Figure 1. Details of the data collection are reported in Table 1. Atomic positional parameters, and bond distances and angles are listed in Table 2 and 3, respectively. The molecules have a non-crystallographic two-fold axis which bisects the C1-C2 and C4-C5 bonds. The ring system comprising a benzene and two cyclohexenones are planar within 0.122Å except C9 and C15 atoms. C9 and C15 deviate by 0.668 and 0.659Å on different sides of

this plane, indicating that cyclohexenone rings have an envelope shape with C9 and C15 as a flap. All bond distances and angles agree well with generally accepted values. The nonhydrogen atoms were refined anisotropically. All hydrogen atoms located on a difference Fourier map were included in the structure factor calculation but not refined. The final least-squares refinement resulted in residuals R = 0.055 and R_w = 0.088. The final difference Fourier map had no hole deeper than -0.19eÅ^{-3} and no peak greater than 0.12eÅ^{-3} [11].

Table 1

Crystallographic Data for 3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene-1,8-dione **8**

Crystal Dimensions (mm)	0.40 x 0.15 x 0.70
Space Group	$P2_12_12_1$
a/Å	11.9955(9)
b/Å	18.5340(9)
c/Å	6.9427(9)
V(Å^3)	1544.3(2)
fw	270.37
Z	4
d_{calc}(g/cm^3)	1.16
λ(Å)	1.54178
μ(cm^{-1})	5.81
$2\theta_{max}$(°)	120.2
R [a]	0.055
R_w [b]	0.088

[a] R = $\Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$

A suggested mechanism for a plausible explanation of the results is illustrated in Scheme 4. Stability of the initially formed anion radical would be in the order $A_3 > B_3 > C_3$.

Entry 1, 2, 3: In the absence of a proton donor, unstable intermediate C_3 abstracts a proton from ammonia followed by one-electron reduction to give anion D_3, which proceeded with β-elimination and ring opening [1] to produce an intermediate E_3. This process is fast. Subsequently, anion E_3 receives two electrons to give dianion F_3 which, on working-up, cyclizes and dehydrates

Figure 1. Perspective view and atom labeling of the crystal sturcture of **8**.

Table 2

Atomic Positional Parameters for the Atoms of 3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene-1,8-dione 8

atom	x	y	z	$B_{iso}(Å^2)$ [a]
O(1)	0.3089(2)	1.0391(1)	0.1481(4)	5.36(6)
O(2)	0.5439(3)	0.7413(2)	0.5955(4)	7.18(8)
C(1)	0.3998(2)	0.9211(2)	0.3403(5)	4.11(6)
C(2)	0.4463(3)	0.8625(2)	0.4279(4)	4.24(7)
C(3)	0.5369(3)	0.8277(2)	0.3453(4)	3.55(6)
C(4)	0.5809(2)	0.8514(1)	0.1697(4)	3.24(5)
C(5)	0.5356(2)	0.9132(1)	0.0813(4)	3.10(5)
C(6)	0.4435(2)	0.9467(2)	0.1672(5)	3.56(6)
C(7)	0.5872(3)	0.7643(2)	0.4469(5)	4.34(7)
C(8)	0.6897(3)	0.7323(2)	0.3645(5)	4.23(7)
C(9)	0.6872(3)	0.7321(1)	0.1435(5)	4.04(6)
C(10)	0.6749(3)	0.8099(1)	0.0739(4)	3.80(6)
C(11)	0.5895(3)	0.6861(2)	0.0740(5)	5.12(8)
C(12)	0.7973(3)	0.7014(2)	0.0678(6)	6.16(9)
C(13)	0.3881(2)	1.0095(2)	0.0706(5)	3.93(6)
C(14)	0.4308(3)	1.0318(2)	-0.1200(6)	4.70(7)
C(15)	0.5577(2)	1.0220(2)	-0.1411(6)	4.29(7)
C(16)	0.5840(2)	0.9422(2)	-0.1004(5)	3.84(6)
C(17)	0.6192(3)	1.0706(2)	0.0005(7)	5.97(9)
C(18)	0.5939(3)	1.0418(2)	0.3425(8)	6.25(10)
H(1)	0.5666	1.0105	-0.4123	
H(2)	0.6687	1.0336	-0.3645	
H(3)	0.5762	1.0903	-0.3882	
H(4)	0.6992	1.0678	-0.0029	
H(5)	0.6021	1.1154	0.0390	
H(6)	0.6066	1.0581	0.1351	
H(7)	0.6747	0.8142	-0.0730	
H(8)	0.7505	0.8341	0.0519	
H(9)	0.4096	0.8372	0.5540	
H(10)	0.3248	0.9326	0.3803	
H(11)	0.3879	0.9882	-0.2082	
H(12)	0.4082	1.0829	-0.1567	
H(13)	0.7525	0.7624	0.4196	
H(14)	0.7036	0.6763	0.4194	
H(15)	0.6631	0.9322	-0.1157	
H(16)	0.5615	0.9152	-0.2101	
M(17)	0.7991	0.7036	-0.0744	
H(18)	0.8110	0.6577	0.0904	
H(19)	0.8533	0.7281	0.0872	
H(20)	0.5870	0.6878	-0.0600	
H(21)	0.5141	0.6977	0.0820	
H(22)	0.5908	0.6392	0.1161	

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoids.

to afford 6. Compound 6 could not be obtained by the Birch reduction of the alcohol 5 which was separately prepared from 3 by sodium borohydride reduction. Radical anion A_3 would dimerize [7], via several steps, to finally produce 8. Since a lithium cation is harder relative to a sodium cation, the dianion F_3 is more stabilized to give 6 exclusively on work-up. In the case of the softer sodium cation the production of 6 is reduced and the dimers 4 and 8 are increased.

Entry 2, 3 and 4, 5: When a considerable amount of sodium was employed, with or without a proton source, the yield of 4 and 5 increased via a dimerization or protonation of the anion radical B_3 [2c] [3b].

Entry 6: When the reaction temperature is low, the radical coupling products 4 and 8 increase because of slow protonation.

Entry 7: In the case of a strongly acidic proton source, protonation takes place on the anion radical intermediate B_3 to produce 5 exclusively.

The Birch reduction of 10 yielded bis 1,1'-[1-hydroxy-1-(2-methyl-3-furyl)pentane 11, 3-(1-hydroxypentyl)-2-methylfuran 12, bis 3,3'-[2-methyl-3-pentanoyl-2,3-dihydrofuran] 13, and 2-methyl-2,3-dihydro-3-pentanoylfuran 14 as a ring reduction product (Table 5 and Scheme 5). The reaction pathway is shown in Scheme 6.

Judging from the reaction products of Birch reduction of 3-acylfurans, (i) non-substituted compound 1a gave the dihydrofuran 2a as a single product resulting from ring reduction; (ii) alkyl-substituted compound 10 yielded carbonyl reduction and dimer products along with the dihydrofuran 14; moreover, (iii) in the case of ring acylfuran 3 the reaction proceeded in a more complex way accompanied with carbonyl reduction, dimer formation and ring opening, and the normal expected product was not obtained at all.

These results would depend on the stability of the anion radicals initially generated as illustrated in Figure 2. Differences in the stability of these anion radicals can be explained by assuming the effects of an electron-donating group on the furan ring and ring strain. According to these considerations, the anion radical A_1 is evidently the most stable and the anion radical A_3 is the most unstable.

EXPERIMENTAL

Melting points were determined on a micro hot-stage and are uncorrected. Column chromatography was performed with silica gel (Merck NO. 7734; 63-200 μm), and thin-layer chromatography (tlc) was performed on a glass plate coated with Kieselgel 60 GF$_{254}$ (Merck), detected by uv light and followed by heating with anisaldehyde-acetic acid-sulfuric acid (1:100:2). The ir spectra were taken on a JASCO A-102 IR spectrophotometer. The ^1H and ^{13}C nmr (deuteriochloroform), and mass spectra were recorded on JEOL LA-300 (300 MHz) and JEOL AX-500 spectrometers, respectively.

3-Pentanoylfuran 1a.

To a stirred solution of N-methoxy-N-methyl-3-furamide [8] (2.33 g, 15 mmoles) in dry benzene (50 ml) was added dropwise the Grignard reagent prepared from 1-bromobutane (4.52 g, 33 mmoles) and magnesium (792 mg) in dry ether (75 ml) at 0°. After stirring for one hour at 0° and an additional 2 hours at room temperature, the reaction mixture was quenched by addition of water and acidified with dilute hydrochloric acid. The ether extract was chromatographed with n-hexane-ethyl acetate (10:1) to give 1a 2.0 g (88%), bp 70-72°/2 mm Hg, mp 21-22° [lit [9] mp 23°]; ir (neat): 1680, 1565, 1510, 1160, 870 cm^{-1}; ^1H nmr: δ 0.86 (t, 3H, J =7.9 Hz), 1.23-1.88 (m, 4H), 2.70 (t, 2H,
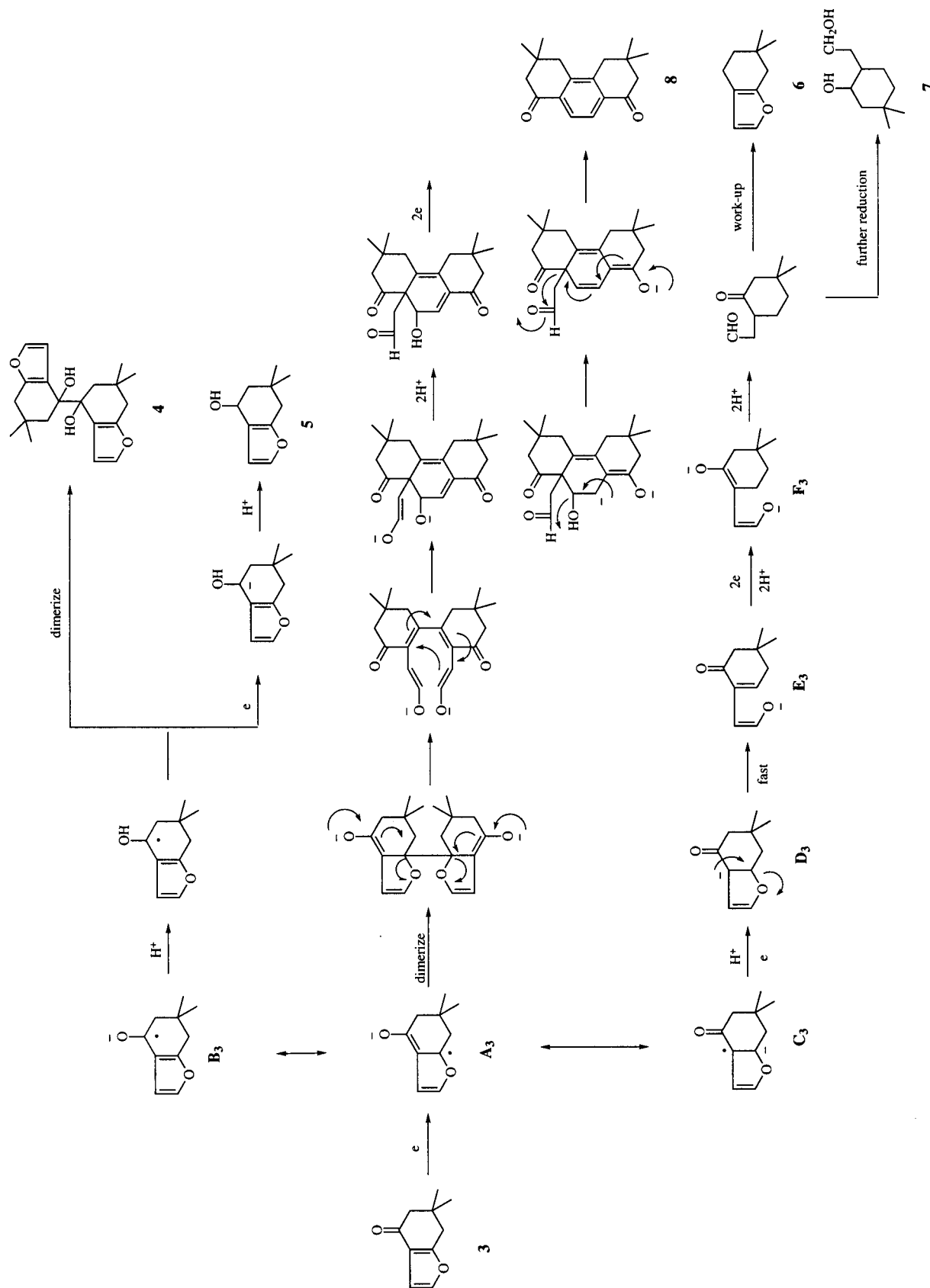
Scheme 4

Table 3

Bond Distances (Å) and Angles (°) for 3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene-1,8-dione **8**

O(1)	C(13)		1.222(4)	C(6)	C(13)		1.499(4)
O(2)	C(7)		1.231(4)	C(7)	C(8)		1.480(5)
C(1)	C(2)		1.365(5)	C(8)	C(9)		1.535(4)
C(1)	C(6)		1.394(5)	C(9)	C(10)		1.528(4)
C(2)	C(3)		1.388(4)	C(9)	C(11)		1 527(5)
C(3)	C(4)		1.400(4)	C(9)	C(12)		1.532(5)
C(3)	C(7)		1.498(4)	C(13)	C(14)		1.479(5)
C(4)	C(5)		1.409(4)	C(14)	C(15)		1.541(4)
C(4)	C(10)		1.519(4)	C(15)	C(16)		1.539(4)
C(5)	C(6)		1.400(4)	C(15)	C(17)		1.524(5)
C(5)	C(16)		1.489(4)	C(15)	C(18)		1.509(6)
C(2)	C(1)	C(6)	120.0(3)	C(8)	C(9)	C(10)	108.4(3)
C(1)	C(2)	C(3)	120.4(3)	C(8)	C(9)	C(11)	109.4(3)
C(2)	C(3)	C(4)	120.6(3)	C(8)	C(9)	C(12)	109.1(3)
C(2)	C(3)	C(7)	119.1(3)	C(10)	C(9)	C(11)	110.7(2)
C(4)	C(3)	C(7)	120.4(3)	C(10)	C(9)	C(12)	109.0(3)
C(3)	C(4)	C(5)	119.3(3)	C(11)	C(9)	C(12)	110.2(3)
C(3)	C(4)	C(10)	120.1(3)	C(4)	C(10)	C(9)	114.4(2)
C(5)	C(4)	C(10)	120.6(2)	O(1)	C(13)	C(6)	119.8(3)
C(4)	C(5)	C(6)	118.6(3)	O(1)	C(13)	C(14)	122.5(3)
C(4)	C(5)	C(16)	120.8(2)	C(6)	C(13)	C(14)	117.7(3)
C(6)	C(5)	C(16)	120.6(2)	C (13)	C(14)	C(15)	113.2(3)
C(1)	C(6)	C(5)	120.9(3)	C (14)	C(15)	C(16)	107.3(3)
C(1)	C(6)	C(13)	118.9(3)	C (14)	C(15)	C(17)	110.3(3)
C(5)	C(6)	C(13)	120.2(3)	C (14)	C(15)	C(18)	110.1(3)
0(2)	C(7)	C(3)	119.7(3)	C (16)	C(15)	C(17)	110.5(3)
0(2)	C(7)	C(8)	122.4(3)	C (16)	C(15)	C(18)	110.2(3)
C(3)	C(7)	C(8)	117.8(3)	C (17)	C(15)	C(18)	108.4(3)
C(7)	C(8)	C(9)	111 8(3)	C(5)	C(16)	C(15)	115.0(3)

Table 4

Birch Reduction of **3**

Entry	Metal	Amount [a]	Proton donor	Temperature °C	Product % [b]					Recovered
					4	**5**	**6**	**7**	**8**	
1	Li	3	none	- 33	-	-	10	-	-	45
2	Na	3	none	-33	6	-	4	-	4	37
3	Na	6	none	- 33	16	2	6	-	6	23
4	Na	3	3 MeOH	-33	5	2	2	4	30	-
5	Na	6	8 MeOH	- 33	18	18	2	5	6	-
6	Na	3	3 MeOH	-78	27	13	1	-	24	-
7	Na	3	3 AcOH	-33	4	55	-	-	-	19

[a] Millimoles of metal per 1.0 mmole of **3** (2 mmoles of metal in the minimum required for complete reduction: an overall two-electron process). [b] Isolated yield by column chromatography.
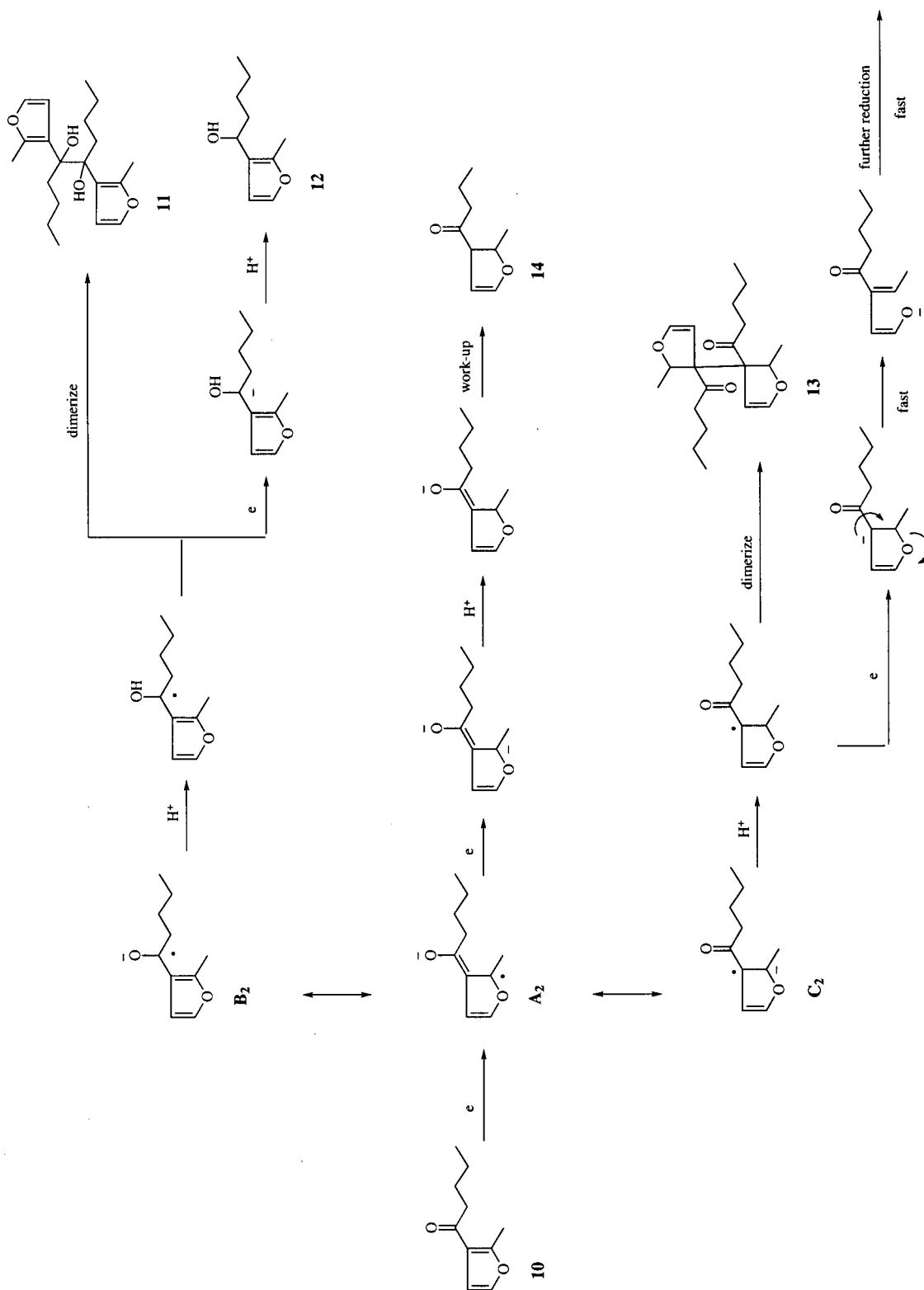
Scheme 5

10　　　　**11**　　　　**12**　　　　**13**

14
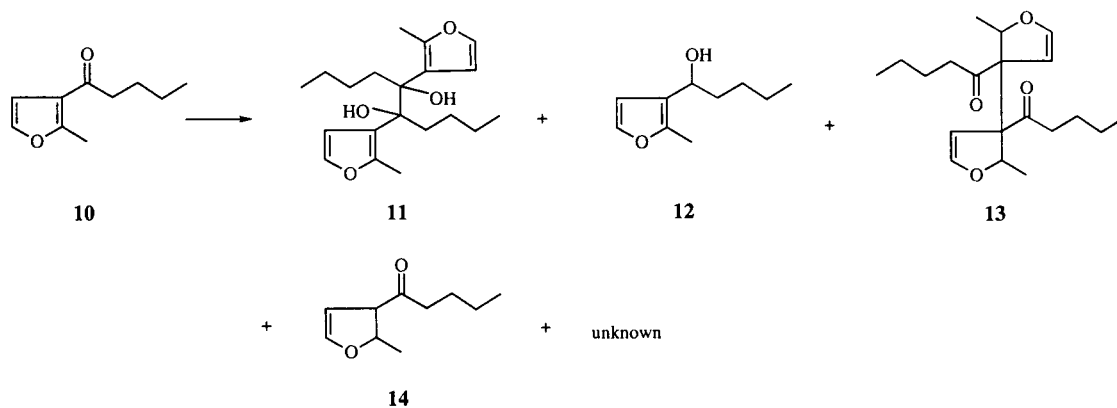
Scheme 6

Table 5

Birch Reduction of **10**

Entry	Metal	Amount [a]	Proton donor	Temperature °C	**11**	**12**	**13**	**14**	Recovered
1	Li	3	none	- 33	6	5	3	18	10
2	Na	3	none	- 33	10	-	-	12	22
3	K	3	none	- 33	4	22	-	19	8
4	Na	3	none	- 78	8	2	7	1	25
5[c]	Na	3	none	- 33	13	3	9	15	17
6	Na	1	none	- 33	6	-	-	7	38
7	Na	3	8MeOH	- 33	5	8	2	-	7
8	Na	3	8MeOH	- 78	6	7	7	-	13
9	Na	3	3 AcOH	- 33	11	70	-	-	3

The header "Product % [b]" spans columns 11, 12, 13.

[a] Millimoles of metal per 1.0 mmole of **10** (2 mmoles of metal m the minimum required for complete reduction: an overall two-electron process). [b] Isolated yield by column chromatography. [c] Metal added frst.
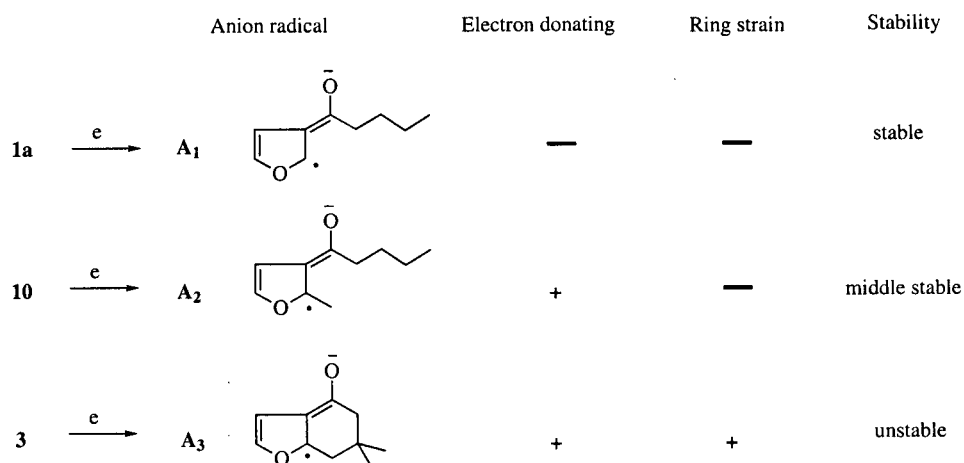
Figure 2. The relative stability of the initially formed anion radicals.

J = 8.0 Hz), 6.70 (dd, 1H, J = 0.8 Hz, J = 1.9 Hz), 7.37 (dd, 1H, J = 1.5 Hz, J = 1.9 Hz), 7.96 (dd, 1H, J = 0.8 Hz, J = 1.5 Hz); ^{13}C nmr: δ 13.9 (q), 22.4 (t), 26.6 (t), 40.0 (t), 108.5 (d), 144.1 (d), 147.0 (d), 157.1 (s), 196.2 (s).

3-(3-Methoxybenzoyl)furan **1b**.

This compound was prepared from N-methoxy-N-methyl-3-furamide and 3-methoxyphenylmagnesium bromide, as in the preparation of **1a** in 78% yield as a viscous oil; ir (neat): 1640, 1580, 1315, 1250, 1160, 750 cm^{-1}; ^{1}H nmr: δ 3.91 (s, 3H), 6.91 (d, 1H, J = 1.0 Hz), 7.13 (ddd, 1H, J = 1.7 Hz, J = 2.8 Hz, J = 7.7 Hz), 7.38 (m, 2H), 7.42 (dd, 1H, J = 1.7 Hz, J = 2.4 Hz), 7.50 (t, 1H, J = 1.8 Hz), 7.94 (t, 1H, J = 1.0 Hz); ^{13}C nmr: δ 55.4 (q), 110.2 (d), 113.3 (d), 118.8 (d), 121.3 (d), 126.5 (s), 129.5 (d), 140.1 (s), 143.9 (d), 148.6 (d), 159.7 (s), 189.1 (s); hrms: Calcd. for $C_{12}H_{10}O_3$: (M$^+$) 202.0630. Found: m/z 202.0655.

3-Pentanoyl-2,3-dihydrofuran **2a**.

Lithium (104 mg, 2 equivalents) was added to the stirred liquid ammonia (80 ml) in small pieces at -78°. 3-Pentanoylfuran **1a** (1.31 g, 7.45 mmoles) and ethanol (1.8 ml) in tetrahydrofuran (3 ml) was added to the blue solution,

and the resulting yellow solution was stirred for 30 minutes. After removal of ammonia, the mixture was extracted with ether. Chromatography with n-hexane-ethyl acetate (4:1) gave **2a** as an oil (1.18 g, 89%); ir (neat): 1720, 1615, 1145, 1060 cm^{-1}; ^{1}H nmr: δ 0.92 (t, 3H, J = 7.8 Hz), 1.12-1.65 (m, 4H), 2.48 (t, 2H, J = 8.0 Hz), 3.65-3.85 (m, 1H), 4.30 (t, 1H, J = 10.1 Hz), 4.74 (dd, 1H, J = 6.4 Hz, J = 10.1 Hz), 5.02 (t, 1H, J = 2.5 Hz), 6.39 (t, 1H, J = 2.5 Hz); ^{13}C nmr: δ 13.7 (q), 22.3 (t), 25.5 (t), 40.1 (t), 54.5 (d), 70.1 (t), 98.5 (d), 147.7 (d), 208.3 (s).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.89; H, 9.18.

3-Methyl-3-pentanoyl-2,3-dihydrofuran **2b**.

This compound was obtained by the Birch reductive alkylation [8] as an oil in 50% yield; ^{1}H nmr: δ 0.90 (t, 3H, J = 7.3 Hz), 1.30 (sext, 2H, J = 7.3 Hz), 1.31 (s, 3H), 1.56 (quint, 2H, J = 7.8 Hz), 2.52 (t, 2H, J = 7.6 Hz), 3.94 (d, 1H, J = 9.4 Hz), 4.74 (d, 1H, J = 9.4 Hz), 4.99 (d, 1H, J = 2.8 Hz), 6.39 (d, 1H, J = 2.8 Hz); ^{13}C nmr: δ 13.9 (q), 22.3 (t), 23.5 (q), 25.9 (t), 37.5 (t), 58.8 (s), 77.6 (t), 105.3 (d), 147.5 (d), 211.3 (s). hrms: Calcd. for $C_{10}H_{16}O_2$: (M$^+$) 168.1150. Found: m/z 168.1155.

5-[(Furan-3-yl)methyl]-1-methoxy-1,4-cyclohexadiene 2c.

This compound was obtained by the similar procedure as in the case of 1b in 95% yield as an oil; ^{1}H nmr: δ 2.60 (t, 2H, J = 7.5 Hz), 2.81 (m, 2H), 3.11 (m, 2H), 3.54 (s, 3H), 4.62 (s, 1H), 5.50 (d, 1H, J = 1.4 Hz), 6.25 (d, 1H, J = 1.4 Hz), 7.24 (t, 1H, J = 1.7 Hz), 7.34 (t, 1H, J = 1.7 Hz); ^{13}C nmr: δ 26.8 (t), 31.3 (t), 32.4 (t), 53.8 (q), 90.2 (d), 111.4 (d), 119.7 (d), 122.3 (s), 133.0 (s), 139.7 (d), 142.8 (d), 152.9 (s); ms: m/z (%) 190 (M[+], 25), 188 (M[+]-H$_2$, 100), 159 (M[+]-OMe, 40), 109 (M[+]-H$_2$-C$_6$H$_4$OMe, 90). hrms; Calcd. for C$_{12}$H$_{14}$O$_2$: (M[+]) 190.0994. Found: m/z 190.1007. Calcd. for C$_{12}$H$_{12}$O$_2$; (M[+]-H$_2$) 188.0837. Found: m/z 188.0839.

3-[(Furan-3-yl)methyl]cyclohex-2-enone 2d.

To a solution of 2c (1.2 g, 6.3 mmoles) in methanol (20 ml) was added a catalytic amount of 3N hydrochloric acid at room temperature. After stirring for 12 hours, the mixture was neutralized with sodium bicarbonate, and extracted with ether. The residue was chromatography (hexane-ethyl acetate; 4:1) to give 2d as a viscous oil (1.0 g, 94%); ir (neat): 1660, 1620, 1250, 1010, 860 cm^{-1}; ^{1}H nmr: δ 1.98 (dt, 2H, J = 6.4 Hz, J = 13.0 Hz), 2.29 (t, 2H, J = 5.5 Hz), 2.37 (t, 2H, J = 6.4 Hz), 3.32 (s, 2H), 5.90 (t, 1H, J = 1.3 Hz), 6.24 (d, 1H, J = 0.7 Hz), 7.29 (t, 1H, J = 0.7 Hz), 7.39 (t, 1H, J = 1.7 Hz); ^{13}C nmr: δ 22.6 (t), 29.2 (t), 33.4 (t), 37.3 (t), 111.1 (d), 120.0 (s), 126.4 (d), 140.1 (d), 143.3 (d), 164.0 (s), 199.9 (s); hrms: Calcd. for C$_{11}$H$_{12}$O$_2$: (M[+]) 176.0837. Found: m/z 176.0830.

Birch Reduction of Acylfurans 3 and 10. General Procedure.

To a mixture of acylfuran (5 mmoles in tetrahydrofuran 5 ml) and *ca.* 3 or 8 molar equivalents of alcohol in liquid ammonia (*ca.* 10 ml per mmole of substrate) was added 3 equivalent atoms of metal little by little with constant stirring under reflux. The mixture was stirred for an additional hour. In the absence of alcohol excess of ammonium chloride was added. After evaporation of liquid ammonia at room temperature, the residue was extracted with ether or dichloromethane (3 x 40 ml). The combined organic extracts were washed with water and brine, and dried with sodium sulfate. Removal of solvent *in vacuo* afforded the crude product. Silica gel chromatography (hexane-ethyl acetate) gave the product.

6,6-Dimethyl-6,7-dihydrobenzo[b]furan-4(5H)-one 3.

This compound was prepared according to the reported procedure [10], bp 113-115°/1.5 mm Hg [lit bp 88°/10[-2] Torr]; ^{1}H nmr: δ 1.14 (s, 6H), 2.38 (s, 2H), 2.75 (s, 2H), 6.67 (d, 1H, J = 2.0 Hz), 7.34 (d, 1H, J = 2.0 Hz); ^{13}C nmr: δ 28.6 (q, Me x 2), 35.3 (s), 37.4 (t), 52.1 (t), 106.3 (d), 119.9 (s), 142.9 (d), 166.3 (s), 194.0 (s).

Bis 4,4'-[6,6-dimethyl-4-hydroxytetrahydrobenzo[b]furan] 4.

This compound had mp 163-164°; ir (nujol): 3590, 3510, 1300, 1035, 740 cm^{-1}; ^{1}H nmr: δ 1.07 (s, 3H), 1.09 (s, 3H), 1.18 (d, 1H, J = 14.8 Hz), 1.32 (d, 1H, J = 14.8 Hz), 2.33 (d, 1H, J = 15.9 Hz), 2.41 (d, 1H, J = 15.9 Hz), 2.83 (s, 1H, OH), 6.70 (d, 1H, J = 2.0 Hz), 7.26 (d, 1H, J = 2.0 Hz); ^{13}C nmr: δ 27.2 (q), 32.2 (q), 32.2 (s), 36.8 (t), 48.7 (t), 76.0 (s), 109.9 (d), 118.3 (s), 140.7 (d), 152.3 (s); ms: m/z (%) 312 (M[+]-H$_2$O, 65), 294 (M[+]-2H$_2$O, 85), 279 (M[+]-2H$_2$O-Me, 100), 165 (80).

Anal. Calcd. for C$_{20}$H$_{26}$O$_4$: C, 72.70; H, 7.93. Found: C, 72.39; H, 7.95.

6,6-Dimethyl-4-hydroxytetrahydrobenzo[b]furan 5.

This compound was obtained as a viscous oil, bp 120°/3 mm Hg; ir (neat): 3350, 1210, 1030, 890 cm^{-1}; ^{1}H nmr: δ 0.98 (s, 2H), 1.13 (s, 3H), 1.46 (dd, 1H, J = 8.3 Hz, J = 12.8 Hz), 1.60 (bs, 1H, OH), 1.92 (ddd, 1H, J = 1.3 Hz, J = 5.7 Hz, J = 12.8 Hz), 2.35 (d, 1H, J = 16.3 Hz), 2.48 (d, 1H, J = 16.3 Hz), 4.70 (m, 1H), 6.44 (d, 1H, J = 2.0 Hz), 7.29 (d, 1H, J = 2.0 Hz); ^{13}C nmr: δ 26.5 (q), 30.8 (q), 32.9 (s), 36.7 (t), 46.8 (t), 64.4 (d), 108.5 (d), 119.1 (s), 141.4 (d), 151.5 (s). hrms: Calcd. for C$_{10}$H$_{14}$O$_2$: (M[+]) 166.0994. Found: m/z 166.0990.

6,6-Dimethyl-tetrahydrobenzo[b]furan 6.

This compound was obtained as an oil. Neither a carbonyl group nor a hydroxyl group was observed in ir spectrum; ^{1}H nmr: δ 1.00 (s, 6H), 1.50 (t, 2H, J = 6.4 Hz), 2.34 (bs, 2H), 2.51 (bt, 2H, J = 6.4 Hz), 5.98 (dd, 1H, J = 2.6 Hz, J = 2.8 Hz), 6.63 (dd, 1H, J = 2.4 Hz, J = 2.6 Hz); ^{13}C nmr: δ 28.2 (Me x 2), 20.2 (t), 30.7 (s), 36.6 (t), 36.9 (t), 107.0 (d), 115.2 (s), 115.8 (d), 126.6 (s).

5,5-Dimethyl-2-(2-hydroxyethyl)cyclohexanol 7.

This compound was obtained as a viscous oil; ^{1}H nmr: δ 0.90 (s, 3H), 0.95 (s, 3H), 1.06-1.39 (m, 5H), 1.55-1.80 (m, 4H), 2.82-3.20 (bs, 2H), 3.45 (m, 1H), 3.65 (m, 1H), 3.80 (m, 1H); ^{13}C nmr: δ 24.9 (q), 29.0 (t), 32.2 (s), 32.9 (q), 37.9 (t), 38.5 (t), 44.7 (t), 48.6 (t), 61.8 (t), 72.1 (d).

Diacetate of 7; ^{1}H nmr: δ 0.95 (s, 3H), 0.97 (s, 3H), 1.00-1.26 (m, 3H), 1.35-1.54 (m, 2H), 1.64-1.83 (m, 4H), 2.02 (s, 3H), 2.05 (s, 3H), 4.02 (dt, 1H, J = 4.7 Hz, J = 11.4 Hz), 4.04 (dt, 1H, J = 4.7 Hz, J = 11.4 Hz), 4.83 (dt, 1H, J = 4.2 Hz, J = 10.8 Hz).

3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene-1,8-dione 8.

This compound had mp 146°; ir (nujol): 1675, 1265 cm^{-1}; ^{1}H nmr: δ 1.11 (s, 6H), 2.54 (s, 2H), 2.77 (s, 2H), 7.99 (s, 1H); ^{13}C nmr: δ 28.5 (q), 33.0 (s), 40.4 (t), 51.6 (t), 124.5 (d), 135.1 (s), 141.1 (s), 198.3 (s); ms: m/z (%) 270 (M[+], 100).

Anal. Calcd. for C$_{18}$H$_{22}$O$_2$: C, 79.96; H, 8.20. Found: C, 79.76; H, 8.32.

X-Ray Crystallography of Compound 8.

Colorless crystals of 8 were recrystallized from ethyl acetate. Single crystal data for X-ray studies were collected at room temperature on a Rigaku AFC7R diffractometer with graphite monochromated Cu-Kα radiation. Cell constants were obtained from a least-squares refinement using setting angles of 25 carefully centered reflections in the range 55.27<2θ<59.46°. The diffraction data were collected for 1371 unique reflections with *h* from 0 to 13, *k* from 0 to 20, and *l* from 0 to 7. The full-matrix least-squares refinement was based on 1271 observed reflections (I>2σ(I)). An empirical absorption correction, based on azimuthal scans of several moderately intense reflections, resulted in transmission factors of 0.84-1.00. All the calculations were carried out with the use of the TEXSAN crystallographic software package [11].

2-Methyl-3-pentanoylfuran 10.

N-Methoxy-*N*-methyl-2-methyl-3-furamide (prepared from 2-methyl-3-furoylchloride and *N,O*-dimethylhydroxylamine hydrochloride) was treated as in the preparation of 1a to give 10 in 92% yield, bp 74-75°/3 mm Hg; ir (neat): 1670, 1575, 1230, 920 cm^{-1}; ^{1}H nmr: δ 0.94 (t, 3H, J = 7.1 Hz), 1.36 (sext, 2H, J =

7.3 Hz), 1.67 (quint, 2H, J = 7.3 Hz), 2.59 (s, 3H), 2.71 (t, 2H, J = 7.3 Hz), 6.62 (d, 1H, J = 2.0 Hz), 7.23 (d, 1H, J = 2.0 Hz); ^{13}C nmr: δ 13.9 (q), 14.3 (q), 22.4 (t), 26.1 (t), 40.9 (t), 110.0 (d), 120.9 (s), 140.1 (d), 158.4 (s), 196.9 (s); hrms. Calcd. for $C_{10}H_{14}O_2$: (M$^+$) 166.0994, Found: m/z 166.0984.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.00; H, 8.74.

Bis-1,1'-[1-hydroxy-1-(2-methyl-3-furyl)]pentane **11**.

This compound was obtained as a viscous oil; ^{1}H nmr: δ 0.85 (t, 3H, J = 7.1 Hz), 0.99-1.38 (m, 4H), 1.75 (dt, 1H, J = 4.2 Hz, J = 12.8 Hz), 1.91 (dt, 1H, J = 4.2 Hz, J = 12.8 Hz), 2.23 (s, 3H), 5.96 (d, 1H, J = 1.7 Hz), 7.17 (d, 1H, J = 1.7 Hz); ^{13}C nmr: δ 13.9 (q), 14.1 (q), 23.6 (t), 25.8 (t), 34.9 (t), 80.6 (s), 112.6 (d), 120.0 (s), 138.8 (d), 172.2 (s). hrms: Calcd. for $C_{20}H_{28}O_3$: (M$^+$-H$_2$O) 316.2038. Found: m/z 316.2060.

3-(1-Hydroxypentyl)-2-methylfuran **12**.

This compound was obtained as an oil, bp 145-146°/5 mmHg; ir (neat): 3350, 1035, 965 cm^{-1}; ^{1}H nmr: δ 0.89 (t, 3H, J = 7.0 Hz), 1.20 (m, 2H), 1.33 (m, 2H), 1.64 (m, 2H), 2.28 (s, 3H), 4.59 (t, 1H, J = 7.0 Hz), 6.34 (d, 1H, J = 1.8 Hz), 7.25 (d, 1H, J = 1.8 Hz); ^{13}C nmr: δ 11.8 (q), 14.0 (q), 22.5 (t), 28.0 (t), 37.5 (t), 66.8 (d), 108.5 (d), 122.2 (s), 140.5 (d), 148.5 (s). hrms: Calcd. for $C_{10}H_{16}O_2$: (M$^+$) 168.1150. Found: m/z 168.1134.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.54. Found: C, 71.35; H, 10.04.

Bis-3,3'-[2-methyl-3-pentanoyl-2,3-dihydrofuran] **13**.

This compound was obtained as a viscous oil; ^{1}H nmr: δ 0.92 (t, 3H, J = 7.2 Hz), 1.24 (d, 3H, J = 7.0 Hz), 1.34 (m, 2H), 1.58 (m, 2H), 2.56 (t, 2H, J = 7.0 Hz), 4.49 (q, 1H, J = 7.0 Hz), 4.99 (d, 1H, J = 2.7 Hz), 6.75 (d, 1H, J = 2.7 Hz); ^{13}C nmr: δ 13.8 (q), 14.8 (q), 22.3 (t), 25.7 (t), 29.1 (t), 87.7 (d), 89.5 (s), 104.9 (d), 152.3 (d), 211.6 (s); ms: m/z (%) 334 (12, M$^+$), 333 (20, [M-1]$^+$), 239 (75), 167 (100); hrms: Calcd. for $C_{20}H_{29}O_4$ (M$^+$-H) 333.2066. Found: m/z 333.2059.

2-Methyl-2,3-dihydro-3-pentanoylfuran **14**.

This compound was obtained as an oil, bp 72-73°/3 mm Hg; ir (neat): 1700, 1210 cm^{-1}; ^{1}H nmr: δ 0.91 (t, 3H, J = 5.5 Hz), 1.31 (m, 2H), 1.33 (d, 3H, J = 4.8 Hz), 1.57 (quint, 2H, J = 5.7 Hz), 2.47 (m, 2H), 3.34 (dt, 1H, J = 1.8 Hz, J = 4.6 Hz), 4.92 (t, 1H, J = 2.0 Hz), 4.95 (quint, 1H, J = 4.6 Hz, J = 4.8 Hz), 6.35 (t, 1H, J = 2.0 Hz); ^{13}C nmr: δ 13.8 (q), 21.4 (q), 22.3 (t), 25.6 (t), 40.2 (t), 62.1 (d), 78.5 (d), 97.7 (d), 147.0 (d), 208.9 (s). hrms: Calcd. for $C_{10}H_{16}O_2$: (M$^+$) 168.1150. Found: m/z 168.1154.

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