1690, 1610 cm^{-1}; UV (MeOH) 385 nm (ϵ 27000); ^1H NMR (Me_2SO-d_6) (see Table I); mass spectrum, *m/e* (%) 320/318 (80), 192 (90), 191 (100), 163 (65), 155 (35), 149 (70); high-resolution mass spectrum, found 320.006/318.009 ($C_{13}H_{11}N_4OBr$ requires 320.009/318.011).

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Registry No. 1, 63153-56-0; 2, 72479-07-3; 3, 72479-08-4; 5, 34293-24-8; 6, 72479-09-5; 7, 60-27-5; 8 (*E* isomer), 72479-10-8; 8 (*Z* isomer), 72479-11-9; indole-3-carboxaldehyde, 487-89-8; 5-bromoindole-3-carboxaldehyde, 877-03-2.

Synthesis of Triacontanol via Metathesis-Hydroboration-Isomerization-Oxidation

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In 1977, triacontanol was reported to be a new naturally occurring plant-growth regulator.[1] This prompted us to investigate a general and practical procedure for the synthesis of fatty alcohols with extremely long chain lengths. We here report such an approach via (i) metathesis (Met) of olefins,[2] (ii) hydrometalation-isomerization (HI), and (iii) oxidation (Ox) (eq 1). Generally, the metathesis of

$$CH_3(CH_2)_{13}CH{=}CH_2 \xrightarrow{\text{Met}} CH_3(CH_2)_{13}CH{=}CH(CH_2)_{13}CH_3 \xrightarrow{\text{HI}} CH_3(CH_2)_{27}CH_2CH_2M \xrightarrow{\text{Ox}} \underset{\text{1-triacontanol}}{CH_3(CH_2)_{28}CH_2OH} \quad (1)$$

terminal olefins is more difficult than that of internal olefins.[3] Although we initially employed Ichikawa and Fukuzumi's procedure[4] for 1-hexadecene, the result was unsatisfactory. Therefore, detailed investigations were performed on 1-heptene and soon revealed that the highest yield and selectivity were achieved by using the following reaction conditions: olefin (1.5 mmol), WCl_6 (0.072 mmol), $Cl_2C{=}CClH$ (1.5 mL), CH_3CN (0.048 mmol), Bu_4Sn (0.14 mmol), 80 °C, 5 h (Table I). This procedure was applied to 1-hexadecene, and 15-triacontene was isolated in 40–60% yields. The structure of the olefin was confirmed by ozonolysis (eq 2). The ozonolysis of the recovered

$$CH_3(CH_2)_{13}CH{=}CH(CH_2)_{13}CH_3 \xrightarrow{O_3} CH_3(CH_2)_{13}CH\underset{O\text{-}O}{\overset{O}{<}}CH(CH_2)_{13}CH_3 \xrightarrow{NaBH_4} CH_3(CH_2)_{13}CH_2OH \quad (2)$$

hexadecene gave 1-pentadecanol, indicating no isomerization occurred during the metathesis.

The conversion of internal olefins into terminal metal derivatives is realized by the following procedures: (i) hydroboration-isomerization,[5] (ii) hydroalumination-isomerization,[6] (iii) hydrozirconation-isomerization,[7] (iv) hydrosilylation-isomerization.[8] Previous literature indicates that these procedures are equally effective for olefins with short to medium chain lengths such as 3-hexene, 2-octene, and 5-decene. No data are available on olefins with extremely long chain lengths, apparently because they lack solubility in organic solvents.[9] We first examined the hydroalumination procedure, but only 15-triacontene was recovered.[10] Next we tried the hydrozirconation procedure and again only recovered the olefin. It should be noted that even the hydrometalation itself does not proceed in these two procedures. Finally, allowable yields of 1-triacontanol were obtained by the hydroboration procedure (Table II).

Table I. Systematic Investigation of the Metathesis of 1-Heptene[a]

reactn conditns		product yield, %[b]					selectivity, %[c]
reagent	amt, mmol	C_7	C_9	C_{10}	C_{11}	C_{12}	
WCl_6[d]	0.024	~90					0
	0.072	27	1	2	4	47	64
	0.12	22	3	4	8	23	29
CH_3CN[e]	0	7	12	11	8	4	4
	0.024	54	1	2	3	5	11
	0.048	27	1	2	4	47	64
	0.096	64				2	5
Bu_4Sn[f]	0	98				<1	~0
	0.024	94				5	83
	0.048	27	1	2	4	47	64
	0.096	35	1	1	3	43	66
	0.14	29			3	64	90
	0.24	*g*			1	11	*g*

[a] The same procedures as described in the Experimental Section were used. [b] Yield of olefins detected after the reaction, determined by GLC. C_7 = heptene, C_8 = octene, etc. Yield C_7 = [C_7 recovered (mmol)/C_7 used (mmol)] × 100. Yields for C_9-C_{12} = [C_9-C_{12} recovered (mmol)/C_7 used (mmol)] × 2 × 100. [c] [C_{12} recovered (mmol)/C_7 consumed (mmol)] × 2 × 100. [d] 1-Heptene (1.5 mmol), CH_3CN (0.048 mmol), Bu_4Sn (0.048 mmol), 80 °C, 5 h. [e] 1-Heptene (1.5 mmol), WCl_6 (0.072 mmol), Bu_4Sn (0.048 mmol), 80 °C, 5 h. [f] 1-Heptene (1.5 mmol), WCl_6 (0.072 mmol), CH_3CN (0.048 mmol), 80 °C, 5 h. [g] Not determined.

The yield of 1-triacontanol was improved by the addition of other 1-olefins at the monohydroboration stage (eq 3).

$$CH_3(CH_2)_{13}CH{=}CH(CH_2)_{13}CH_3 + BH_3 \xrightarrow{\text{DG}} (C_{30}\text{-}BH_2) \xrightarrow{2RCH=CH_2} (C_{30}\text{-}BR'_2) \xrightarrow[\text{160 °C, 12 h}]{} \xrightarrow[\text{NaOH}]{H_2O_2}$$

$$\underset{\substack{66\%,\ R^1\\ 63\%,\ R^2}}{\text{1-triacontanol}} + \underset{\substack{13\%,\ R^1\\ 27\%,\ R^2}}{\textit{sec}\text{-}C_{30}H_{61}OH} + \underset{\substack{21\%,\ R^1\\ 7\%,\ R^2}}{C_{30}H_{60}} \quad (3)$$

$$R^1 = n\text{-}C_{14}H_{29};\ R^2 = n\text{-}C_6H_{13}$$

This may be due to more facile hydroboration of the 1-

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(9) Solubility of 15-triacontene in ether, THF, diglyme, or triglyme, in which hydroboration and hydroalumination are carried out, is quite low, while that in hydrocarbon solvents is moderate.
(10) Our own examination revealed that this procedure was unsatisfactory even for 2-octene; 1-octanol was obtained in ~10% yield.

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Table II. Hydroboration-Isomerization-Oxidation of 15-Triacontene[a]

solvent (amt, mL)	reagent (amt, mmol)	t_H, h[c]	T,[d] °C (t_R,[d] h)	product yield, %[b] $C_{30}H_{60}$	sec-$C_{30}H_{61}OH$	1-$C_{30}H_{61}OH$
diglyme (30)	BH_3 (0.37)	4	160 (9)	45	36	15
diglyme (20)	BH_3 (0.5)	4	160 (9)	36	34	30
diglyme (30)	BH_3 (0.5)	5	160 (13)	20	32	47
diglyme (20)	BH_3 (0.6)	4	160 (12)	32	17	51
triglyme (20)	BH_3 (1.5)	12	216 (19)	44	39	17
diglyme (100)	Sia_2BH (2.5)	6	160 (5)	13	56	31
diglyme (1)	9-BBN (2)		160 (16)	45	55	

[a] 15-Triacontene (1 mmol). [b] By GLC analysis. [c] Time for hydroboration. [d] Reflux temperature (T) and time (t_R).

olefins at the second stage than that of 15-triacontene, which leads to the $C_{30}BR'_2$ instead of the $(C_{30})_3B$ compound. However, the problem of this improved procedure is contamination of the alcohols arising from the 1-olefins added, making the separation of the desired product difficult. The hydrosilylation method was not examined, since the addition of the Si–H bond to olefins requires high temperature and long reaction times. In conclusion, it is now clear that the metathesis of 1-olefins–hydroboration–isomerization–oxidation procedure is generally applicable to the synthesis of fatty alcohols with extremely long chain lengths.

Experimental Section

^1H NMR spectra were recorded on a JEOL JNM-MH-100 instrument; chemical shifts (δ) are expressed in parts per million relative to Me_4Si. IR spectra were recorded on a JASCO IRA-1 spectrophotometer. All temperatures are uncorrected. Reagent-grade solvents were purified by standard techniques and kept over a drying agent. The chemicals, such as WCl_6 and Bu_4Sn, were purchased from Nakarai Chemical Co. Ltd. and purified by standard procedures.

Metathesis of 1-Hexadecene. Into a 50-mL flask, equipped with a magnetic stirrer and a reflux condenser and maintained under Ar, were injected 1-hexadecene (30 mmol, 8.6 mL), a trichloroethylene solution of WCl_6 (22 mL, 1.4 mmol), CH_3CN (0.96 mmol, 0.05 mL), and a trichloroethylene solution of Bu_4Sn (6 mL, 2.8 mmol) in this order by means of hypodermic syringes. The mixture was heated at 80 °C for 5 h and filtered through a short column of alumina to remove tungsten derivatives. Distillation of the filtrate gave 2.5–3.8 g of 15-triacontene [40–60%, bp 172–174 °C (0.015 mmHg)] and hexadecene [bp 81 °C (0.015 mmHg)]. Recrystallization of 15-triacontene from benzene gave white crystals: mp 53–55 °C; IR (KBr) 960 cm^{-1}; NMR ($CDCl_3$) δ 5.24 (t, 3 H), 1.92 (m, 4 H), 1.24 (m, 48 H), 0.87 (t, 3 H); mass spectrum, m/e 420 (parent) (calcd 420). Anal. Calcd for $C_{30}H_{60}$: C, 85.63; H, 14.37. Found: C, 85.65; H, 14.47. Ozonolysis of 15-triacontene was carried out by the known procedure,[11] and the alcohol thus obtained was identified by comparison with an authentic sample (Tokyo Kasei Co. Ltd.) as 1-pentadecanol by various spectroscopic methods.

Conversion of 15-Triacontene into 1-Triacontanol. Into a 100-mL flask, equipped with a magnetic stirrer and reflux condenser and maintained under Ar, were placed 15-triacontene (10 mmol, 4.21 g) and diglyme (60 mL). A BH_3–THF solution (5 mmol, 2.2 mL) was added at room temperature. The mixture was stirred at this temperature for 1 h and then maintained at 70 °C for 3 h. The resulting mixture was refluxed for 11 h and cooled to room temperature. Oxidation was accomplished with large excess amounts of H_2O_2–NaOH. Since separation of secondary alcohol $C_{30}H_{61}OH$ and primary alcohol $C_{30}H_{61}OH$ is quite difficult, the reaction products were acetylated with acetic anhydride in pyridine. Separation by column chromatography on silica gel with benzene–hexane as an eluent gave the primary acetate. Treatment with KOH in EtOH–H_2O produced 1-triacontanol in 47% overall yield: mp 87–88.5 °C (lit.[12] 86.5 °C); IR (KBr) 3300, 1068 cm^{-1}; NMR ($CDCl_3$) δ 3.62 (m, 2 H), 1.24 (m, 56 H), 0.88 (t, 3 H).

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Registry No. 1-Hexadecene, 629-73-2; 15-triacontene, 72443-19-7; 1-triacontanol, 593-50-0; 1-heptene, 592-76-7; 1-nonene, 124-11-8; 1-decene, 872-05-9; 1-undecene, 821-95-4; 1-dodecene, 112-41-4; 6-dodecene, 29493-00-3; 8-hexadecene, 18899-20-2; 9-octadecene, 5557-31-3; 10-eicosene, 66587-45-9; 11-docosene, 62978-77-2; sec-triacontanol, 28351-05-5.

Synthetic Furocoumarins. 10. Synthesis of α-Methylbenzo[*b*]furano Compounds[1]

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Phenols can be converted to α-methylbenzofurans by a five-step process which involves O-allylation, Claisen rearrangement to an *o*-allylphenol, acetylation of the phenolic hydroxyl group, addition of halogen to the allylic double bond, and cyclization in an alkaline alcoholic medium.[2] That approach has been successfully utilized to convert 7-hydroxycoumarins to α-methylfurocoumarins,[3] including 4,5′,8-trimethylpsoralene (**5**) which was obtained from 4,8-dimethyl-7-hydroxycoumarin (**1a**) in 28% overall yield. Trimethylpsoralen, under the generic name Trioxsalen, has been extensively used with ultraviolet radiation in the treatment of vitiligo[4] and has been recommended[5] in psoriasis therapy. Recently, its 4′-aminomethyl derivative has been recommended for the study of nucleic acids because it can form cross-linking diadducts[6] or, with short-pulse laser radiation, monoadducts.[7] Thus, a convenient and efficient synthesis of α-methylfurocoumarins is of contemporary practical interest.

Such a synthesis was sought through the conversion of hydroxycoumarins (**1**) to β-haloallyl ethers (**2**) which, it was hoped, would undergo Claisen rearrangement to *o*-(β-haloallyl)umbelliferones (**3** or **4**) that could subsequently

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