# A Practical Synthesis of Rosefuran. Furans from Acetylenes and Allyl Alcohols

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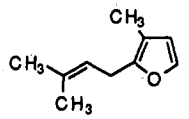
A new atom-economical synthetic strategy for the synthesis of furans emerges from β,γ-unsaturated ketones which are readily available from acetylenes and allyl alcohols by simple additions in the presence of a ruthenium catalyst. Dihydroxylation using catalytic osmium tetraoxide creates a diol that is remarkably prone to cyclize to furans in the presence of an acid catalyst. The novelty of this synthesis lies in the overall strategy whereby furans are available in two steps from allyl alcohols and acetylenes with only water as the byproduct. A straightforward synthesis of the prized fragrance of oil of rose, rosefuran, from propargyl bromide, acetone, and 1-buten-3-ol in 23% overall yield illustrates the utility of this new strategy.

The significance of furans as key structural units as well as useful building blocks draws interest to their syntheses.[1-6] The challenge posed can be illustrated by even very simple furans exemplified by rosefuran (1), the essence of one of the most prized fragrances, oil of rose.[7] Since its first reported synthesis in 1968 by Büchi et al.,[8j] there have been 10 recorded syntheses.[8] A patented



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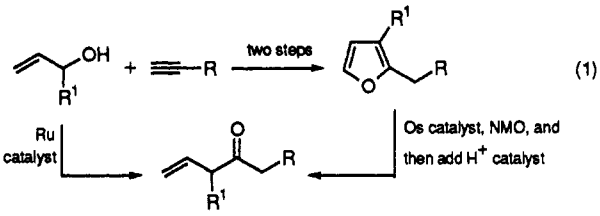
synthesis of Tsukasa published in 1989 delivers rosefuran from methyl 3-formylpropionate and crotonaldehyde in four steps with a 10% overall yield.[8c] Iriye described in 1990 a seven-step synthesis from citral in 4% overall yield.[8d] In 1993, Marshall, utilizing a new furan synthesis, described a novel five-step synthesis in approximately 40% yield from (*Z*)-3-methyl-2-penten-4-yn-1-ol whose synthesis requires at least three steps from commercially available materials.[8a]

Opportunities for new synthetic strategies develop from the invention of new reactions. Those that minimize formation of any byproducts represent the most efficient.[9] We wish to report a two-step method whereby furans arise from simple acetylenes and allyl alcohols with only water as a byproduct (vide infra) that emerges from our recently discovered ruthenium-catalyzed addition of these two building blocks (see eq 1)[10] and the culmination of this




(1)

effort in a practical synthesis of rosefuran.

In our initial work, the β,γ-unsaturated ketone **3** from the reconstitutive addition of 1-dodecyne and 1-buten-3-ol catalyzed by $CpRu(Ph_3P)_2Cl$ (**2**) was hydroxylated using catalytic osmium tetraoxide[11] in aqueous acetone to the diol **4** (eq 2) which proved to be acid sensitive. Simply standing in deuteriochloroform converted it quantitatively to the furan **6**. Its acid lability was revealed by the formation of the furan **6** upon attempts to effect silylation with silyl chlorides or acylation with acid chlorides even in the presence of imidazole or pyridine. The lability of **4** appears associated with an equilibrium to the lactol **5** which loses two moles of water in the presence of a mild acid to give the furan **6**. Evidence in support of this conjecture emanates from the chemoselective acylation with the *N*-acylthiazolinethione 8[12] to give an 86% yield of monoester **7** which is quite stable to acid.

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(1) For some recent reviews, see Dean, F. M. in *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1982; Vol. 31, pp 237–433. Dean, F. M.; Sargent, M. V. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4, Part 3, pp 531–656. Donnelly, D. M. X.; Meegan, M. J. *Ibid.*, pp 657–712.

(2) *The Chemistry of Heterocyclic Flavoring and Aroma Compounds*; Vernin, G., Ed.; Ellis Horwood: Chichester, 1981. Wierenga, W. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981; Vol. 4, p 263.

(3) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795.

(4) For an excellent listing of recent efforts as well as a novel approach using allenyl silanes, see Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407.

(5) For other recent approaches, see Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1991**, *56*, 1685. *J. Am. Chem. Soc.* **1992**, *114*, 1450. *J. Org. Chem.* **1993**, *58*, 3435.

(6) Also see Tani, K.; Sato, Y.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* **1993**, *34*, 4975. Maruoka, K.; Concepcion, A. B.; Murase, N.; Oishi, M.; Hirayama, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 3943. Ji, J.; Lu, X. *Chem. Commun.* **1993**, 164. Arcadi, A.; Cacchi, S.; Larock, R. C.; Marinelli; F. *Tetrahedron Lett.* **1993**, *34*, 2813. Obrecht, D. *Helv. Chim. Acta* **1989**, *72*, 447. Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343. Sato, S.; Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1987**, *28*, 6657. Hiroi, K.; Sato, H. *Synthesis* **1987**, 811. McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1987**, *28*, 4123. Jansen, B. J. M.; Peperzak, R. M.; de Groot, A. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 549. Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225. Takano, S.; Morimoto, M.; Satoh, S.; Ogasawara, K. *Chem. Lett.* **1984**, 1261. Hagiwara, H.; Uda, H.; Kodama, T. *J. Chem. Soc. Perkin Trans. 1* **1980**, 963.

(7) Guenther, E. *The Essential Oils*; D. VanNostrand Inc.: New York, 1949; Vol. 5, p 1.

(8) (a) Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1993**, *58*, 3602. (b) Iriye, R.; Uno, T.; Ohwa, I.; Konishi, A. *Agr. Biol. Chem.* **1990**, *54*, 1841. (c) Tsukasa, H. *Agr. Biol. Chem.* **1989**, *53*, 3091. (d) Meier, L.; Scharf, H.-D. *Annalen* **1986**, 731. (e) Takano, S.; Morimoto, M.; Satoh, S.; Ogasawara, K. *Chem. Lett.* **1984**, 1261. (f) Okazaki, R.; Negishi, Y.; Inanoto, N. *J. Org. Chem.* **1984**, *49*, 3819. (g) Gedge, D. R.; Pattenden, G. *Tetrahedron Lett.* **1977**, 4443. (h) Birch, A. J.; Stobbe, J. *Tetrahedron Lett.* **1976**, 2079. (i) Vig, O. P.; Vig, A. K.; Handa, V. K.; Sharma, S. D. *J. Indian Chem. Soc.* **1974**, 900. (j) Büchi, G.; Kovats, E.; Enggist, P.; Uhde, G. *J. Org. Chem.* **1968**, *33*, 1227.

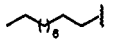
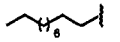
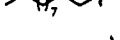
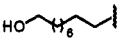
(9) Trost, B. M. *Science* **199**, *254*, 1471.

(10) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809.

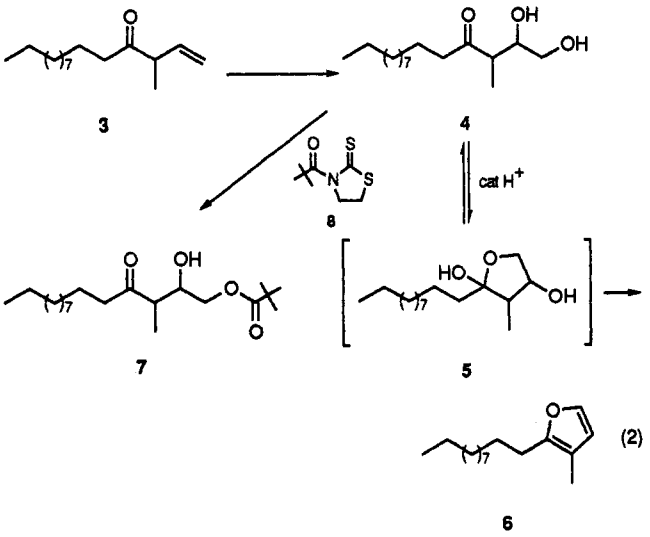
(11) Van Rheenan, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *23*, 1973.

0022-3263/94/1959-1078$04.50/0 

**Table 1. A Practical Furan Synthesis[a]**

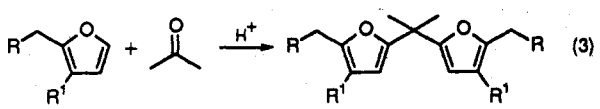
| entry | R | $R^1$ | % yield | % yield |
|---|---|---|---|---|
| 1 |  | $CH_3$ | 74[b] | 88 |
| 2 |  |  | 58 | 91 |
| 3 |  |  | 57 | 84 |
| 4 |  | $CH_3$ | 30[c] | 84 |
| 5 |  | $CH_3$ | 64 | 84 |
| 6 | Ph | $CH_3$ | 68 | 90 |

[a] All compounds have been characterized spectroscopically and new compounds by combustion analysis and/or high-resolution mass spectra. [b] The catalyst in this case was CpRu(COD)Cl and $Ph_3P$. [c] In this case, 22–38% of 1-buten-3-yl ether of the product alcohol was also obtained for a 52–65% yield of the reconstitutive addition product.



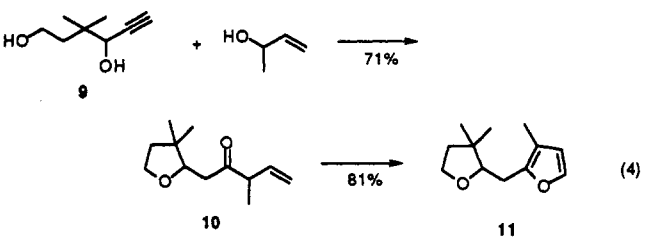

(2)

For synthetic purposes, acidification of the hydroxylation reaction with 3 equiv of *p*-toluenesulfonic acid permits direct cyclization to the furan in 88% isolated yield. Under these conditions, the hydroxylation cannot be performed in acetone since the furan may undergo condensation as in eq 3. THF-*tert*-butyl alcohol-water



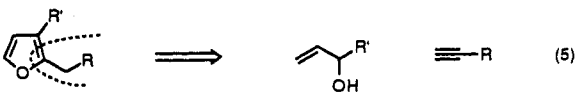

(3)

proved generally satisfactory. Only 10% of the acid is required if the hydroxylation reaction is worked up in normal fashion, the crude diol dissolved in methylene chloride and then the acid added. Obviously, the buffering effect of *N*-methylmorpholine in the hydroxylation reaction mixture mandates the use of excess acid to perform the one-pot procedure. Its convenience, however, led us to adopt the one-pot protocol as our standard one. The facility of this two-step furan synthesis led us to briefly examine variation of the substituents on the allyl alcohol (see Table 1, entries 1-3) and the acetylene (see Table 1, entries 4-6). We have also demonstrated the ability of ruthenium to catalyze the simultaneous cyclization–reconstitutive addition of ω-hydroxypropargyl alcohols such as **9** (eq 4) via an allenylidene ruthenium intermediate.[13] These β,γ-unsaturated ketones (eq 10) participate with equal facility in the hydroxylation–cyclization sequence. β-Elimination of the tetrahydrofuran ring was not a problem. Thus, the two-step sequence of eq 4 involves formation of both a tetrahydrofuran and a furan ring with the byproduct being only 1 equiv of water for each step (vide infra).



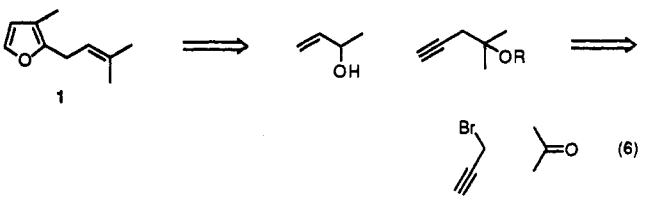

(4)

The simplicity of this two-step protocol and the significance of rosefuran drew our attention to the feasibility of a practical synthesis from inexpensive commercially available starting materials. Conceptually, our protocol dissects the furan as outlined in eq 5. For rosefuran, this



(5)

dissection translates into propargyl bromide and acetone as the primordial building blocks (eq 6).




(6)

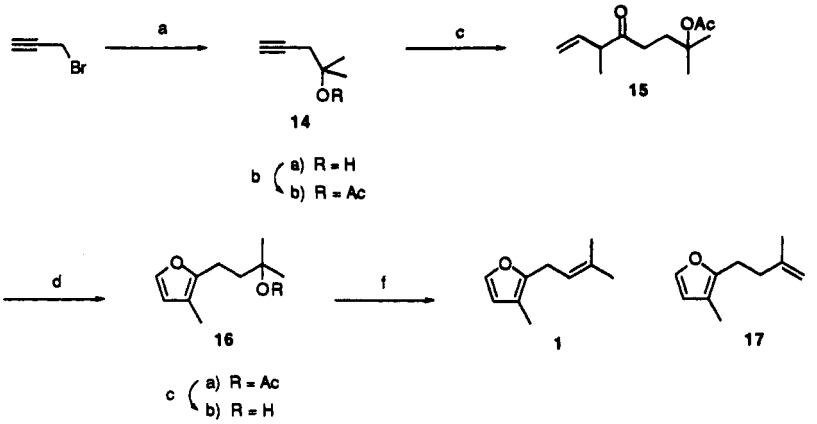
Since alcohols normally participate in reconstitutive addition (Table 1, entries 4 and 5), the known homopropargylic alcohol **14a**[14,15] (see Scheme 1) was reacted with 1-buten-3-ol in the presence of 10% **2** and 20% ammonium hexafluorophosphate. Only starting materials were recovered. Bruce and co-workers reported the formation of a stable ruthenium complex from 1-butyn-4-ol and **2** in methanol solution (eq 7).[16] It is possible that an analogous intramolecular addition leads to complex **12** irreversibly which ties up the catalyst. If this explanation is correct, it is obvious that ring size is critical since entry 5 of Table 1 could have produced the corresponding seven-membered ring complex **13**; nevertheless, this alcohol participates quite normally in the reconstitutive addition.

Derivatizing the alcohol to prevent cyclization provides a further test of this suggestion. Gratifyingly, the tertiary acetate **14b**[15] participates quite normally to provide the β,γ-unsaturated ketone **15**. Hydroxylation–cyclization proceeds without incident to the furan **16a** whose hydrolysis produces the alcohol **16b** which has been the

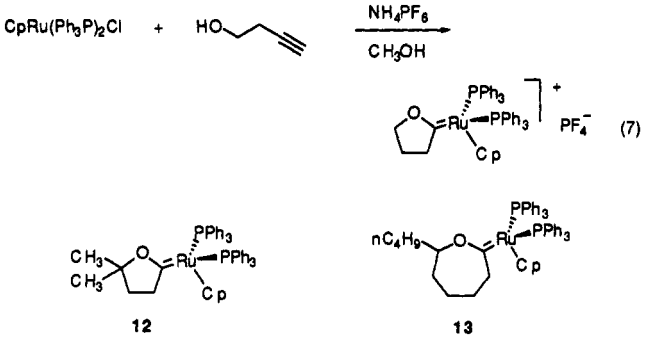
(12) Yamada, S. *Tetrahedron Lett.* **1992**, *33*, 2171.

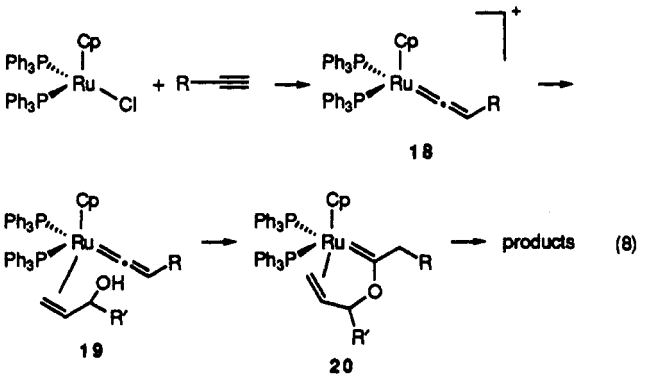
(13) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476.
(14) Barrelle, M.; Plouin, D.; Glenat, R. *Bull. Soc. Chim. Fr.* **1967**, 449.
(15) Viola, A.; Mac Millan, J. M.; Proverb, R. J.; Yates, B. L. *J. Am. Chem. Soc.* **1971**, *93*, 6967.
(16) Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605.

**Scheme 1. A Practical Synthesis of Rosefuran[a]**




[a] (a) Mg, acetone, ether, rt 89%; (b) $Ac_2O$, DMAP, $(C_2H_5)_3N$, $CH_2Cl_2$, rt, 94%; (c) 10% **2**, 20% $NH_4PF_6$, $CH_3CH(OH)CH{=}CH_2$, 100 °C, 69%; (d) $OsO_4$, NMO, THF, $tC_4H_9OH$, $H_2O$, rt, and then TsOH, rt, 83%; (e) LiOH, $H_2O$, $CH_3OH$, rt, 88%; (f) DMSO, 160 °C, 54% **1**, 13% **17**.




penultimate intermediate in many previous syntheses.[8] Dehydration of this alcohol has typically generated nearly equimolar mixtures of rosefuran **1** and isorosefuran **17**. A significant improvement in regioselectivity occurs effecting dehydration by simply heating in DMSO[17] whereby rosefuran is isolated in 54% yield and isorosefuran in 13% yield. This synthesis produces rosefuran in six steps and 23% overall yield from propargyl bromide, acetone, and 1-buten-3-ol.

## Discussion

The novelty of this furan synthesis stems from the overall synthetic strategy whereby furans are available in only two steps from terminal acetylenes and allyl alcohols. The high chemoselectivity exhibited by both the ruthenium- and osmium-catalyzed reactions assures a broad applicability. However, two restrictions can be identified. The ruthenium-catalyzed reaction involves the generation of a vinylidene complex **18** (eq 8) which subsequently undergoes nucleophilic addition of the hydroxyl group of the allyl alcohol facilitated by initial precoordination of the olefin as in **19** → **20**. If the **R** group of the acetylene possesses a hydroxyl group whose juxtaposition particularly favors an intramolecular addition to form a stable alkoxyalkylidene complex as in eq 7, then such a substrate may fail to participate. Other groups that may function similarly (e.g., amino) may also fail for the same reason. The osmium-catalyzed process will not allow the presence of other carbon–carbon unsaturation that is more nucleophilic than the $\beta,\gamma$-double bond of these substrates.

A major benefit of this process is the fact that the first step is a simple addition, and the second step involves only the loss of water with all reagents being used catalytically except for NMO. The fact that NMO derives from oxidation of *N*-methylmorpholine allows it to be recycled in principle, thus making this furan synthesis highly atom-economical, an increasingly important goal for chemical processing. The practicality of the sequence is highlighted by the simplicity of the synthesis of rosefuran, the major olefactory ingredient of Bulgarian rose oil, from inexpensive and readily available starting materials.

## Experimental Section

**Preparation of 3-Cyclohexylpentadec-1-en-4-one.** 1-Cyclohexyl-2-propen-1-ol (1.5 mL) followed by 1-dodecyne (200 mg, 1.20 mmol) were added to a mixture of ruthenium catalyst **2**[18] (87 mg, 0.12 mmol) and ammonium hexafluorophosphate (40 mg, 0.24 mmol). After heating the resulting solution to 100 °C for 5 h, it was directly chromatographed (10% ether/hexane) to produce 213 mg (58%) of the titled product as a colorless oil: IR (neat) 3078, 2925, 2953, 1715, 1634, 1450, 1367, 1084, 997, 917 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.67 (dt, $J$ = 16.9, 9.9 Hz, 1H), 5.12 (d, $J$ = 9.9 Hz, 1H), 5.10 (d, $J$ = 17 Hz, 1H), 2.88 (t, $J$ = 9.3 Hz, 1H), 2.31–2.49 (m, 2H), 1.45–1.80 (m, 11H), 1.04–1.44 (m, 18H), 0.88 (t, $J$ = 6.6 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 211.9, 136.2, 118.1, 64.6, 42.7, 39.0, 31.7, 31.5, 30.1, 29.4, 29.3, 29.2, 29.13, 29.05, 26.2, 26.0, 23.2, 22.5, 13.8. HRMS calcd for $C_{21}H_{38}O$ 306.2924, found 306.2934.

**Preparation of 9-Hydroxy-3-methyltridec-1-en-4-one.** Following the above protocol, 200 mg (1.30 mmol) of 6-hydroxy-1-

(17) Traynelis, V. J.; Hergenrother, W. L.; Hanson, H. T.; Valicenti, J. A. *J. Org. Chem.* **1964**, *29*, 123. For related work in HMPA, see Monson, R. S. *Tetrahedron Lett.* **1971**, 567.

(18) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Syn.* **1982**, *21*, 78.

**Table 2. Experimental Details for Furan Formation[a]**

| entry | substrate (mg, mmol) | NMO, mg, mmol | $OsO_4$, mL of 0.06 M, mmol | $TsOH \cdot H_2O$, mg, mmol | product,[b] mg, % yield |
|---|---|---|---|---|---|
| 1 | 3-cyclohexylpentadec-1-en-4-one (100, 0.33) | 44, 0.37 | 0.052, 0.0031 | 186, 1.00 | 90, 91 |
| 2 | 3-isopropylhexadec-1-en-4-one[d] (100, 0.38) | 53, 0.45 | 0.062, 0.0037 | 215, 1.35 | 83, 84 |
| 3 | 14-hydroxy-3-methyltetradec-1-en-4-one[d] (100, 0.39) | 56, 0.48 | 0.065, 0.0039 | 225, 1.18 | 83, 84 |
| 4 | 9-hydroxy-3-methyltridec-1-en-4-one (100, 0.45) | 63, 0.54 | 0.074, 0.0044 | 254, 1.34 | 83, 84 |
| 5 | 3-methyl-5-phenylpent-1-en-4-one (80, 0.46) | 65, 0.55 | 0.075, 0.0045 | 262, 1.38 | 71, 90 |
| 6[c] | **10**[e] (100, 0.77) | 108, 0.92 | 0.127, 0.0077 | 437, 2.30 | 123, 83 |

[a] All reactions were run in a solvent mixture consisting of 2.0 mL of THF, 0.5 mL of *tert*-butyl alcohol, and 0.5 mL of water unless otherwise noted. [b] All products were isolated by column chromatography on silica gel eluting with hexane. [c] Solvent mixture consisted of 3.0 mL of THF, 0.5 mL of *tert*-butyl alcohol, and 0.5 mL of water. [d] See ref 10. [e] See ref 13.

decyne, 94 mg (0.13 mmol) of **2**, and 43 mg (0.26 mmol) of ammonium hexafluorophosphate in 1.5 mL of 1-buten-3-ol after 4 h at 100 °C gave 186 mg (64%) of the titled compound as a colorless oil: IR (neat) 3150–3600, 2955, 1714, 1480 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.71–5.88 (m, 1H), 5.10–5.20 (m, 2H), 3.52–3.64 (m, 1H), 3.16–3.26 (m, 1H), 2.38–2.61 (m, 2H), 1.21–1.72 (m, 13H), 1.17 (d, $J$ = 6.9 Hz, 3H), 0.90 (t, $J$ = 7 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 211.6, 137.5, 116.7, 71.6, 51.3, 40.6, 37.18, 37.12, 27.8, 25.2, 23.5, 22.7, 15.7, 14.0; HRMS calcd for $C_{14}H_{24}O$ ($M^+ - H_2O$) 208.1827, found 208.1819.

**Preparation of 3-Methyl-5-phenyl-1-penten-4-one.** Following the above protocol, 100 mg (0.98 mmol) of phenylacetylene, 71 mg (0.098 mmol) of **2**, and 32 mg (0.196 mmol) of ammonium hexafluorophosphate in 1.5 mL of 1-buten-3-ol after 8 h at 100 °C gave 116 mg (68% yield) of the titled compound whose spectral properties agree with that of the known compound.[10]

**Preparation of 7-Acetoxy-3,7-dimethyl-1-octen-4-one (15).** Following the above protocol, 100 mg (0.714 mmol) of 4-acetoxy-4-methyl-1-pentyne, 52 mg (0.071 mmol) of **2**, and 23 mg (0.142 mmol) of ammonium hexafluorophosphate in 1.2 mL of 1-buten-3-ol after 5 h at 100 °C gave 104 mg (69% yield) of the titled compound as a colorless oil: IR (neat) 2980, 1740, 1715, 1360, 1250 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.73–5.88 (m, 1H), 5.11–5.22 (m, 2H), 3.18–3.31 (m, 1H), 2.41–2.63 (m, 2H), 1.88–2.05 (m, 2H), 1.97 (s, 3H), 1.43 (s, 6H), 1.19 (d, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 210.6, 170.2, 137.5, 116.9, 111.4, 81.3, 51.3, 35.2, 34.7, 25.75, 25.70, 22.3, 15.8; HRMS calcd for $C_{10}H_{16}O$ 3152.1201, found 152.1194.

**General Procedure for Furan Synthesis. Preparation of 3-Methyl-2-undecyl-furan.** NMO (118 mg, 1.00 mmol) followed by osmium tetraoxide (0.138 mL of 0.06 M solution in water, 0.008 mmol) were added to a solution of 200 mg (0.840 mmol) of 3-methylpentadec-1-en-4-one[10] in 4 mL of THF, 1 mL of *tert*-butyl alcohol, and 1 mL of water at room temperature. After stirring 12 h, 479 mg (2.52 mmol) of *p*-toluenesulfonic acid hydrate was added and stirring continued an additional 10 h. The reaction was quenched by addition of 100 mg of sodium sulfite and, after 10 min, ether. The ether layer was washed with saturated sodium carbonate, 10% sodium bisulfate, and saturated aqueous sodium chloride. After drying ($Na_2SO_4$) and evaporation in vacuo, chromatography of the residue on silica gel (hexane) gave 174 mg (88% yield) of the titled compound as a colorless oil: IR (neat) 2940, 2850, 1510, 1480, 730 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.20 (d, $J$ = 1.7 Hz, 1H), 6.14 (d, $J$ = 1.7 Hz, 1H), 2.54 (t, $J$ = 7.4 Hz, 2H), 1.94 (s, 3H), 1.51–1.63 (m, 2H), 1.19–1.36 (m, 16H), 0.88 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 151.5, 139.5, 113.4, 112.6, 31.9, 29.7, 29.6, 29.41, 29.36, 29.2, 28.5, 25.9, 22.7, 14.1, 9.8; HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2135.

The experimental details for the remaining examples except for reaction of **14b** are summarized in Table 2.

**Spectral Data for Furans of Table 2. 3-Cyclohexyl-2-undecylfuran:** IR (neat) 3080, 2957, 2926, 2855, 1715, 1635 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.21 (d, $J$ = 1.8 Hz, 1H), 6.21 (d, $J$ = 1.8 Hz, 1H), 2.55 (t, $J$ = 7.4 Hz, 2H), 2.30–2.41 (m, 1H), 1.52–1.84 (m, 8H), 1.18–1.42 (m, 20 H), 0.88 (t, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 150.2, 139.7, 124.8, 109.2, 34.5, 34.3, 31.9, 29.64, 29.59, 29.39, 29.35, 29.21, 28.8, 26.7, 26.10, 26.07, 22.7, 14.1; HRMS calcd for $C_{21}H_{36}O$ 304.2766, found 304.2775.

**3-Isopropyl-2-dodecylfuran:** IR (neat) 2960, 2830, 1450, 1160, 740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.21 (d, $J$ = 1.7 Hz, 1H), 6.23 (d, $J$ = 1.7 Hz, 1H), 2.70–2.85 (m, 1H), 2.55 (t, $J$ = 7.4 Hz, 2H), 1.52–1.65 (m, 2H), 1.19–1.34 (m, 18H), 1.13 (d, $J$ = 6.9 Hz, 6H), 0.79–0.98 (m, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 149.9, 139.8, 125.3, 108.6, 31.9, 29.64, 29.58, 29.39, 29.35, 29.26, 28.8, 26.1, 24.4, 23.9, 22.7, 14.1, HRMS calcd for $C_{19}H_{34}O$ 278.2610, found 278.2606.

**2-(10-Hydroxydecyl)-3-methylfuran:** IR (neat) 3120–3800, 2960, 2840, 1500, 1460, 1050, 720 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.20 (d, $J$ = 1.7 Hz, 1H), 6.21 (d, $J$ = 1.7 Hz, 1H), 3.64 (t, $J$ = 6.3 Hz, 2H), 2.54 (t, $J$ = 7.4 Hz, 2H), 1.95 (s, 3H), 1.21–1.68 (m, 19H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 151.4, 139.5, 113.4, 112.6, 62.9, 32.7, 29.5, 29.37, 29.32, 29.1, 28.4, 25.8, 25.7, 9.7. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18; MW, 252.2089. Found: C, 75.95; H, 10.91; MW, 252.2100.

**3-Methyl-2-(5-hydroxynonyl)furan:** IR (neat) 3100–3500, 2940, 1500, 1150, 740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.20 (d, $J$ = 16 Hz, 1H), 6.14 (d, $J$ = 1.6 Hz, 1H), 3.51–3.62 (m, 1H), 2.56 (t, $J$ = 7.2 Hz, 2H), 1.95 (s, 3H), 1.21–1.69 (m, 13H), 0.90 (t, $J$ = 7 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 151.2, 139.6, 113.5, 112.6, 71.8, 37.1, 28.5, 27.8, 25.8, 25.1, 22.7, 14.0, 9.7. Anal. Calcd: C, 74.95; H, 10.78; MW, 224.1776. Found: C, 75.05; H, 10.75; MW, 224.1788.

**2-Benzyl-3-methylfuran:** IR (neat) 2926, 1510, 1495, 1454, 1149, 1087 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.12–7.33 (m, 6H), 6.18 (d, $J$ = 1.7 Hz, 1H), 3.92 (s, 2H), 2.00 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 149.2, 140.4, 138.8, 128.5, 128.3, 126.2, 114.9, 112.8, 32.1, 9.9; HRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0889.

**3-Methyl-2-[(3′,3′-dimethyltetrahydrofuran-2′-yl)methyl]-furan (11):** IR (neat) 2958, 2872, 1512, 1467, 1150, 1092, 1051, 1029, 892, 726 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.23 (d, $J$ = 1.8 Hz, 1H), 6.16 (d, $J$ = 1.8 Hz, 1H), 3.75–3.95 (m, 2H), 3.66 (dd, $J$ = 8.0, 5.3 Hz, 1H), 2.59–2.76 (m, 2H), 1.98 (s, 3H), 1.68–1.83 (m, 2H), 1.00 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 148.4, 139.9, 114.7, 112.8, 85.1, 65.4, 41.4, 40.3, 27.0, 24.9, 21.2, 9.9. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; MW, 194.1306. Found: C, 73.92; H, 9.58; MW, 194.1301.

**Furan Formation from 15. Method A (dimer formation as in eq 3).** NMO (133 mg, 1.14 mmol) followed by osmium tetraoxide (0.156 mL of 0.06 M solution in water, 0.0094 mmol) were added to a solution of 200 mg (0.94 mmol) of **15** in 6 mL of acetone. After stirring 12 h at room temperature, 538 mg (2.83 mmol) of *p*-toluenesulfonic acid hydrate was added and the mixture heated at reflux for 4 h. Addition of 100 mg of sodium sulfite and ether quenched the reaction. The ether layer was washed with saturated aqueous sodium carbonate, 10% aqueous sodium bisulfate and brine. After drying ($Na_2SO_4$) and evaporation *in vacuo*, flash chromatography on silica gel (hexane) gave 118 mg (60% yield) of 2,2-bis[3′-methyl-5′-(4″-acetoxy-4″-methylbutyl)furan-2′-yl]propane and 30 mg (15%) of furan **16a**: IR (neat) 1734, 1367, 1253, 1222 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.73 (s, 4H), 2.51–2.62 (m, 8H), 1.97 (s, 12H), 1.90 (s, 12H), 1.55 (s, 6H), 1.45 (s, 24H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 170.3, 157.4, 148.7, 113.7, 107.1, 81.7, 39.2, 37.1, 26.3, 25.8, 22.4, 20.7, 9.8; HRMS calcd for $C_{26}H_{40}O_4$ 416.2927, found 416.2938.

**Method B: Synthesis of 16a.** Following the general protocol, 200 mg (0.94 mmol) of **15**, 133 mg (1.10 mmol) of NMO, 0.156 mL of 0.06 M aqueous solution of osmium tetraoxide (0.0094 mmol) in THF (4 mL), *tert*-butyl alcohol (1 mL), and water (1 mL) for 14 h followed by 538 mg (2.83 mmol) of *p*-toluenesulfonic acid for 12 h gave after flash chromatography on silica gel (hexane: ether 9:1) 164 mg (83% yield) of **16a** as a colorless oil: IR (neat) 1368, 1254, 1222, 740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.20 (d, $J$ = 1.7 Hz, 1H), 6.14 (d, $J$ = 1.7 Hz, 1H), 2.54–2.68 (m, 2H), 1.98–2.08 (m, 2H), 1.97 (s, 3H), 1.95 (s, 3H), 1.47 (s, 6H); $^{13}C$

NMR (75 MHz, $CDCl_3$) δ 170.3, 150.4, 139.7, 113.5, 112.7, 81.6, 39.1, 25.8, 22.3, 20.5, 9.7; HRMS calcd for $C_{10}H_{14}O$ 150.1044, found 150.1043.

**Preparation of 16b.** Lithium hydroxide (60 mg, 2.50 mmol) was added to 100 mg (0.48 mmol) of **16a** dissolved in 1 mL of methanol and 1 mL of water. After stirring 18 h at room temperature, the reaction mixture was diluted with ether. The ethereal solution was washed with aqueous sodium carbonate, 10% aqueous sodium bisulfate, and brine. After drying ($Na_2SO_4$) and evaporation *in vacuo*, flash chromatography on silica gel (7:3 hexane:ether) gave 70 mg (88% yield) of the known alcohol whose spectral data agree with that reported:[8c] $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.21 (d, $J$ = 1.7 Hz, 1H), 6.15 (d, $J$ = 1.7 Hz, 1H), 2.61–2.72 (m, 2H), 1.96 (s, 3H), 1.73–1.82 (m, 2H), 1.40–1.50 (m, 1H), 1.25 (s, 6 H).

**Preparation of rosefuran (1).** A solution of 100 mg (0.60 mmol) of alcohol **16b** in 1 mL of DMSO was heated at 160 °C for 24 h. The reaction was diluted with ether and the resultant ethereal solution washed with 10% aqueous sodium bisulfate and brine. After drying ($Na_2SO_4$) and evaporation *in vacuo*, flash chromatography on silica gel (hexane) gave 11 mg (13% yield) of isorosefuran **17** followed by 48 mg (54% yield) of rosefuran whose spectral properties agree with that reported.[8c] **1**: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.22 (d, $J$ = 1.7 Hz, 1H), 6.16 (d, $J$ = 1.7 Hz, 1H), 5.21–5.30 (m, 1H), 3.28 (d, $J$ = 7 Hz, 2H), 1.96 (s, 3H), 1.73 (s, 6H). **17**: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.22 (d, $J$ = 1.7 Hz, 1H), 6.15 (d, $J$ = 1.7 Hz, 1H), 4.69 (br s, 1H), 4.73 (br s, 1H), 2.66–2.73 (m, 2H), 2.24–2.33 (m, 2H), 1.92 (s, 3H), 1.74 (s, 3H).

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**Supplementary Material Available:** Copies of $^{13}C$ NMR spectra of all new compounds for which a combustion analysis is not reported (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.