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Photochemical Formation of Tetrahydro-2-furyl Ether in Alcohol-Tetrahydrofuran-Iron(III) Chloride System

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Synopsis. Primary and secondary alcohols are converted into the corresponding tetrahydro-2-furyl ethers upon UV- and solar irradiation of alcohol and tetrahydrofuran in the presence of iron(III) chloride.

Preparative organic chemists have expressed increasing interest in the photoreactions which can occur in the presence of metal ions. As for the catalysis of iron(III) under illumination, methoxylation of styrene[1] and coupling of toluene[2] have been reported. Kochi reported the formation of 2-(4-chlorobutoxy)tetrahydrofuran in the photolysis of tetrahydrofuran–copper(II) system.[3] We report here the photochemical formation of tetrahydro-2-furyl ether catalyzed by iron(III) chloride. Several interesting photosubstitution reactions of tetrahydrofuran by sulfur dioxide[4] and 1,2,4,5,-tetracyanobenzene[5] have also been reported. As the method for the preparation of tetrahydro-2-furyl ethers, the reaction of alcohol with 2,3-dihydrofuran,[6] the reaction of alcohol, tetrahydrofuran, and *t*-butyl perbenzoate in the presence of copper(I) chloride[7] and the reaction of 4-formyloxybutyraldehyde with trialkyl orthoformate[8] have been reported.

Experimental

Materials. Tetrahydrofuran(THF) was purified according to Zweifel.[9] When THF was not treated with $LiAlH_4$, a small amount of tetrahydrofuryl ether was formed without irradiation. This is probably due to the reaction induced by peroxides contained in the non-purified THF, similar to the reaction induced by *t*-butyl perbenzoate in the presence of copper(I) chloride.[7] Commercially available alcohols were used after the purification by distillation or by recrystallization.

Irradiation. The general procedure is as follows. A solution containing alcohol(1.0 mmol) and iron(III) chloride (1.0 mmol) in 40 cm^3 of THF is irradiated with a low or a high pressure mercury lamp or with sunlight under nitrogen at room temperature. Quartz and glass vessels were employed in UV and sunlight irradiation, respectively.

Products. After irradiation, the reaction mixture was washed with sodium hydrogencarbonate solution and extracted with diethyl ether. The products were separated by means of thin layer chromatography. Tetrahydro-2-furyl ethers were identified on the basis of IR, NMR, and mass spectra.

Cinnamyl tetrahydro-2-furyl ether (liquid): IR 3030 (aromatic C–H), 2940, 2880 (aliphatic C–H), 1180, 1080 cm^{-1} (ether C–O) No absorption which can be assigned to O–H was observed. NMR(CCl_4) δ=1.84(4H, m, $C\underline{H}_2$ in THF moiety), 3.81(2H, t, J=3 Hz $C\underline{H}_2$ in THF moiety), 4.14 (2H, d, J=6 Hz, $C\underline{H}_2$–O in alcohol moiety), 5.06(1H, t, J=4.5 Hz, O–C$\underline{H}$–O), 6.28(2H, m, olefinic), 7.20(5H, m, phenyl). The NMR spectra are very similar to those of cinnamyl tetrahydro-2-pyranyl ether prepared from 3,4-dihydro-2*H*-pyran and cinnamyl alcohol. MS (70 eV), *m/e*(relative intensity), 204(2), 160(3), 132(4), 131(5), 118(11), 117(23, $[C_6H_5CH{=}CH_2]^+$),116(3), 115(3), 106(7), 105(7), 77(4), 72(5), 71(100, [tetrahydrofuryl]$^+$), 70(3), 57(3), 43(12). Found: C, 75.57; H, 7.94%; M^+, 204. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%; M, 204. By refluxing the ether with hydrochloric acid, cinnamyl alcohol was obtained.

Cholesteryl tetrahydro-2-furyl ether(liquid): IR 2940, 2900, 2860(aliphatic C–H), 1090, and 1040 cm^{-1}(ether C–O); NMR(CCl_4) δ=0.7—2.3, 3.30(O–C$\underline{H}$ of cholesteryl moiety), 3.73($C\underline{H}_2$–O of THF moiety), 5.10(O–C$\underline{H}$–O), and 5.22(olefinic); Found: C, 81.03; H, 12.07%, Calcd for $C_{31}H_{54}O_2$: C, 81.16; H, 11.86%. Reflux of the ether (0.2 mmol) in aqueous ethanol in the presence of *p*-toluenesulfonic acid gave cholesterol (yield by TLC, 62%).

Other tetrahydro-2-furyl ethers were identified by the comparison of their IR and NMR spectra with those of tetrahydro-2-pyranyl ethers prepared by 3,4-dihydro-2*H*-pyran with alcohols. NMR spectra of tetrahydro-2-furyl ethers have a good correspondence with those of methyl and ethyl tetrahydro-2-furyl ether reported by Frehel and Delongchamps.[8] Hexyl,[7] cyclohexyl,[6] and benzyl[6] tetrahydro-2-furyl ethers are described in the literature.

Butyl tetrahydro-2-furyl ether (liquid): IR 2990, 2950, 2870 (aliphatic C–H), 1460, 1440 (CH_2 and CH_3), 1195, and 1040 cm^{-1} (ether C–O); NMR(CCl_4) δ=0.87(3H, t, J=6.8 Hz, $C\underline{H}_3$), 1.36(4H, m, $C\underline{H}_2$ of alcohol moiety), 1.80 (4H, m, $C\underline{H}_2$ of THF moiety), 3.1—3.9 (4H, m, $C\underline{H}_2$–O of alcohol and THF moieties), 4.92 (1H, t, J=4 Hz, O–C$\underline{H}$–O).

s-Butyl tetrahydro-2-furyl ether(liquid): IR 2950, 2900 (aliphatic C–H), 1090, and 1030 cm^{-1} (ether C–O); NMR (CCl_4) δ=0.9—1.6 (8H, ethyl and methyl of alcohol moiety), 1.80 (4H, $C\underline{H}_2$ of THF moiety), 3.5—3.7(3H, m, O–$C\underline{H}_2$ of THF moiety and O–C$\underline{H}$ of alcohol moiety), 5.08 (1H, t, J=4 Hz, O–C$\underline{H}$–O).

Hexyl tetrahydro-2-furyl ether (liquid): IR 2950, 2920, 2850 (aliphatic C–H), 1450 (CH_2 and CH_3) 1100. 1090, and 1040 cm^{-1} (ether C–O); NMR(CCl_4) δ=0.88 (3H, t, J=5.7, CH_3), 1.32 (8H, m, CH_2 of alcohol moiety), 1.80-(4H, m, $C\underline{H}_2$ of THF moiety), 3.61 (4H, m, $C\underline{H}_2$–O of alcohol and THF moieties), 4.94 (1H, t, J=4 Hz, O–C$\underline{H}$–O).

Cyclohexyl tetrahydro-2-furyl ether (liquid): IR 2930, 2850 (aliphatic C–H), 1450(CH_2), 1090, and 1040 cm^{-1} (ether C–O); NMR(CCl_4) δ=1.2—1.8 (14H, CH_2 in cyclohexyl and THF moieties), 3.2—3.8(3H, m, C$\underline{H}$–O of cyclohexyl moiety and $C\underline{H}_2$–O of THF moiety), 5.10(1H, t, J=4.5 Hz, O–C$\underline{H}$–O).

Benzyl tetrahydro-2-furyl ether(liquid) : IR 3030(aromatic C–H), 2970, 2940, 2880,(aliphatic C–H) 720, and 690 cm^{-1} (monosubstituted benzene); NMR(CCl_4) δ=1.89 (4H, m, $C\underline{H}_2$ in THF moiety), 3.82(2H, $C\underline{H}_2$–O in THF moiety), 4.55 (2H, CH_2–O of alcohol moiety), 5.10 (1H, t, J=4.5 Hz,

Table 1. Photochemical formation of tetrahydro-2-furyl ether in alcohol–tetrahydrofuran–iron(III) chloride system

Alcohol	Light source[a)]	Irradiation time (h)	Yield of ether (%)	Recovered starting material (%)
Butyl alcohol[b)]	LP	24	86	
	HP	24	97	
	Solar	6	46	
Hexyl alcohol[b)]	LP	24	40	
	HP	16	70	
	Solar	6	46	
s-Butyl alcohol[b)]	LP	24	66	
	HP	24	43	
	Solar	6	26	
Cyclohexanol[b)]	LP	24	51	
	HP	24	43	
	Solar	6	37	
Benzyl alcohol[c)]	LP	16	48	
	HP	16	46	
	Solar	6	24	
Cinnamyl alcohol[c)]	LP	24	36	
	HP	24	27	
	Solar	6	18	
Cholesterol[c)]	LP	24	15	53
	HP	24	14	39
	Solar	6	14	61

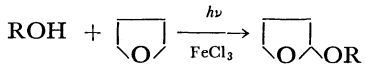
a) LP=low pressure mercury lamp, HP=high pressure mercury lamp. b) Yield was determined gas-chromatographically. c) Yield was determined by means of thin layer chromatography.

O–CH–O), 7.28 (5H, phenyl). Found: C, 73.18; H, 7.37%.

Gas-Chromatographic Analysis. Gas-chromatographic analysis was performed with a Shimadzu GC-6A equipped with 2 m column of Carbowax 20M at about 100 °C.

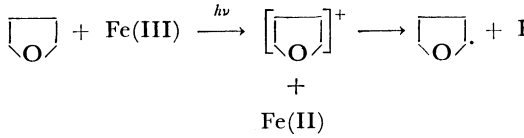
Results and Discussion

Primary and secondary alcohols react with tetrahydrofuran (THF) under irradiation in the presence of iron(III) chloride to give the corresponding tetrahydro-2-furyl ether of alcohols.

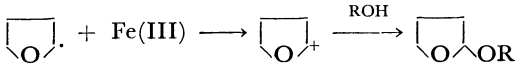


The results are shown in Table 1. Both aliphatic and aromatic alcohols give photochemically tetrahydrofuryl ether, but *t*-butyl alcohol does not undergo the photoetherification. Tetrahydro-2-furyl ethers are formed upon irradiation not only with a low or a high pressure mercury lamp, but also with sunlight. The presence of iron(III) chloride as the catalyzer in the reaction is essential, since no reaction took place in the absence of iron(III) chloride. These facts suggest that the photoreaction has a possibility for synthetic utilization of sunlight catalyzed by metal ions.[10)]

The formation of tetrahydro-2-furyl ether is accompanied by that of iron(II). In the initial stage, the consumption of iron(III) is nearly twice as much as the formation of tetrahydro-2-furyl ether : in hexyl alcohol–THF–$FeCl_3$ system(hexyl alcohol : $FeCl_3$=1 : 1) the ratio of iron(II) to hexyl tetrahydro-2-furyl ether at 1 and 2 hours' irradiation were 2.5 and 1.8, respectively. The formation of $CH_3\dot{C}HOCH_2CH_3$ was reported in the UV-irradiation of the diethyl ether–iron(III) system.[11)] One mole of iron(III) is consumed for the generation of tetrahydro-2-furyl radicals, probably *via* the electron transfer from THF to iron(III).



The second step in which iron(III) participates would be the oxidation of tetrahydro-2-furyl radicals to give tetrahydro-2-furyl cations, which react with alcohol in the following scheme.



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10) Tetrahydro-2-furyl ether is easily hydrolyzed by refluxing with acid to give the starting alcohol. Like tetrahydro-2-pyranyl ether, tetrahydro-2-furyl ether can be used for the protection of the hydroxyl group.
11) S. A. Ivanitskaya, A. N. Korol, and A. I. Kryukov, *Ukr. Khim. Zh.*, **39**, 1248 (1973).