Studies of Photochemical Reaction. VI. The Synthesis of Methylethyl-α-tetrahydrofurylcarbinol and Ethyl-α-tetrahydrofurylcarbinol

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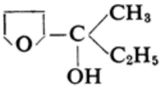
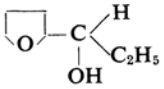
In preceding papers[1,2] we have reported the synthesis of *t*-alcohols by means of the photochemical reaction of acetone in tetralin, dioxane and tetrahydrofuran. By these photoreactions, dimethyl-α-tetralylcarbinol, dimethyldioxanylcarbinol and dimethyl-α-tetrahydrofurylcarbinol were easily synthesized. In this paper, we wish to report the synthesis of methylethyl-α-tetrahydrofurylcarbinol (I) and ethyl-α-tetrahydrofurylcarbinol (II) by means of the photochemical reaction of ethyl methyl ketone and propionaldehyde in tetrahydrofuran.


(I)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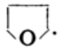

(III)

In the photochemical reaction of ethyl methyl ketone in tetrahdrofuran, *s*-butyl alcohol, methylethyl-α-tetrahydrofurylcarbinol (I) and di-α-tetrahydrofuryl were obtained, as in the photoreaction of acetone in tetrahydrofuran. The new substance, methylethyl-α-tetrahydrofurylcarbinol (I), which can be prepared by other methods only with difficulty, was easily produced.

The photochemical reactions of aldehydes in a liquid phase have been widely studied. Leuschner and Pfordte[3] stated that α-diketones were formed when aldehydes were irradiated. Mayo et al.[4] reported that ethyl cyclohexyl ketone and ethyl-3-cyclohexenylcarbinol were obtained by the reaction of photoactivated propionaldehyde in cyclohexene. It may be predicted that the reactions of photoactivated aldehydes in hydrogen-donor solvents are more complex than those of photo-activated ketones because of the presence of active hydrogen in the aldehyde group. When propionaldehyde was irradiated in tetrahydrofuran, *n*-propyl alcohol and ethyl-α-tetrahydrofurylcarbinol were obtained, and di-α-tetrahydrofuryl was not produced. It was also confirmed that dioxanyldioxane was not produced in the photochemical reaction of propionaldehyde in dioxane. It is assumed that the α-tetrahydrofuryl radical (III), formed by the dehydrogenation of tetrahydrofuran by the photoactivated propionaldehyde, would abstract the hydrogen atom from propionaldehyde without dimerization. Ethyl-α-tetrahydrofurylcarbinol was identified by comparing it with an authentic sample which had been prepared by the following procedure:

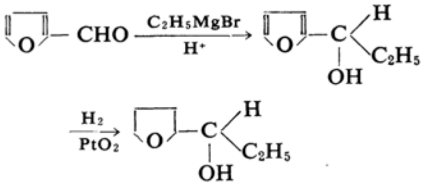
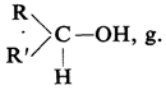
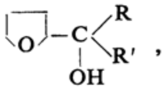
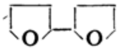


TABLE I. THE REACTION CONDITIONS AND THE YIELDS OF PRODUCTS

Light absorbing reagent (A)	Ethyl methyl ketone	Propionaldehyde
Reaction time, hr.	10	10
A used, g.	48.7	41.7
Tetrahydrofuran used, g.	194.8	203.6
Tetrahydrofuran/(A), mol. ratio	4	4
A consumed, g.	41.7	31.2
Tetrahydrofuran consumed, g.	25.3	22.3
 $\mathrm{RR'CH{-}OH}$, g.	16.1	4.3
(B)  , g.	14.8	10.6
 , g.	10.0	—
High boiling residue, g.	18.9	18.3
Unidentified product, g.	6.0	12.3
Wt. % of B in the products	22.3	23.3
Ultimated yield of B based on A consumed, mol. %	18.3	15.4
Ultimated yield of B based on tetrahydrofuran consumed, mol. %	30.2	26.4

$R=C_2H_5$, $R'=CH_3$ or H

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[1] K. Shima, Y. Shigemitsu and S. Tsutsumi, This Bulletin, 35, 1728 (1962).

[2] K. Shima and S. Tsutsumi, ibid, 36, 121 (1963).

[3] G. Leuschner and K. Pfordte, *Ann.*, **622**, 6 (1959).

[4] P. de Mayo, J. B. Stothers and W. Templeton, *Proc. Chem. Soc.* (*London*), **1960**, **72**; *Can. J. Chem.*, **39**, 488 (1961).

The reaction conditions and yields of the products are summarized in Table I.

Experimental

Materials.—Ethyl methyl ketone and propionaldehyde were purified by fractional distillation: ethyl methyl ketone, b. p., 79~80°C, n_D^{20} 1.3772; propionaldehyde, b. p., 49~50°C, n_D^{20}, 1.3733. Tetrahydrofuran was also purified by distillation over sodium: b. p., 66~67°C, n_D^{20}, 1.4052.

The Photochemical Reaction of Ethyl Methyl Ketone in Tetrahydrofuran.—A mixture of ethyl methyl ketone (48.7g., 0.676mol.) and tetrahydrofuran (194.8 g., 2.706 mol.) was placed in a 300 cc. reaction vessel and irradiated at 11°C in a nitrogen atmosphere for 10 hr. After this irradiation, the reaction product was fractionated to give the following fractions:

	B. p., °C	Weight, g.	n_D^{20}
(1)	64~68	144.5	1.4041
(2)	68~70	19.6	1.4029
(3)	70~81	11.2	1.3862
(4)	~35/13 mmHg	15.8	1.3943
(5)	35~59/13 mmHg	1.8	1.4223
(6)	60~84/13 mmHg	23.6	1.4512
(7)	85~87/13 mmHg	3.4	1.4530
(8)	87~97/13 mmHg	1.9	1.4504
(9)	Residue	18.9	

Fraction 4 was suspected to be *s*-butyl alcohol on the basis of gas chromatography, and it was identified as such by comparing its infrared spectrum with that of an authentic sample. The amounts of ethyl methyl ketone, tetrahydrofuran and *s*-butyl alcohol were estimated by gas chromatography: column, D. N. P. and Si DC 550; carrier gas, H_2, 0.32 kg./cm^2; bridge current, 160 mamp.; column temp., 47°C; retention time: ethyl methyl ketone, 8.5 min. (Si DC 550), 9.5 min. (D.N.P.); tetrahydrofuran, 10 min. (Si DC 550), *s*-butanol: 14 min. (D.N.P.).

It was established that fractions 6 and 7 were mainly composed of two components; they were separated by preparative gas chromatography. Fraction 1, n_D^{20}, 1.4518.

Found: C, 66.54; H, 11.12. Calcd. for $C_8H_{14}O_2$: C, 66.63; H, 11.18%.

The infrared spectrum is shown in Fig. 1. This fraction was confirmed to be methylethyl-α-tetrahydrofurylcarbinol by elemental analysis, study of its infrared spectrum, and comparison of it with the findings of a previous report[2].

The other fraction was di-α-tetrahydrofuryl.

The amounts of methylethyl-α-tetrahydrofurylcarbinol and di-α-tetrahydrofuryl were estimated by gas chromatography: column, Si DC 550, 3 m.; carrier gas, H_2, 0.3 kg./cm^2; bridge current, 160 mamp; column temp., 155°C; retention time: methylethyl-α-tetrahydrofurylcarbinol, 8.2 min.; di-α-tetrahydrofuryl, 11.4 min.

The Photochemical Reaction of Propionaldehyde in Tetrahydrofuran.—A mixture of propionaldehyde (41.0 g., 0.706 mol.) and tetrahydrofuran (203.6 g., 2.83 mol.) was irradiated at 12°C for 10 hr, and the reaction product was fractionally distilled under atmospheric and reduced pressure to give the following fractions:

	B. p., °C	Weight, g.	n_D^{20}
(1)	49~ 52	7.0	1.3710
(2)	52~ 64	5.4	1.3840
(3)	64~ 66	171.5	1.4063
(4)	~ 40/18 mmHg	11.2	1.3852
(5)	40~ 76/18 mmHg	0.7	1.4431
(6)	76~ 92/18 mmHg	20.0	1.4473
(7)	92~100/18 mmHg	2.2	1.4492
(8)	Residue	18.3	

Fraction 4 was assumed to be *n*-propyl alcohol on the basis of gas chromatography, and it was identified as such by means of a mixed melting point test of its 3, 5-dinitrobenzoate with an authentic sample.

Fraction 6 was purified by preparative gas chromatography: b. p., 71~72°C/11 mmHg, n_D^{20}, 1.4483.

The presence of the hydroxyl group was proved by the infrared spectrum. Its 3, 5-dinitrobenzoate was synthesized and recrystallized from ethanol; m. p., 81.2~82.2°C.

Found: C, 51.68; H, 5.10. Calcd. for $C_{14}H_{16}O_8N_2$: C, 51.85; H, 4.97%.

From the above results, this fraction was confirmed to be ethyl-α-tetrahydrofurylcarbinol.

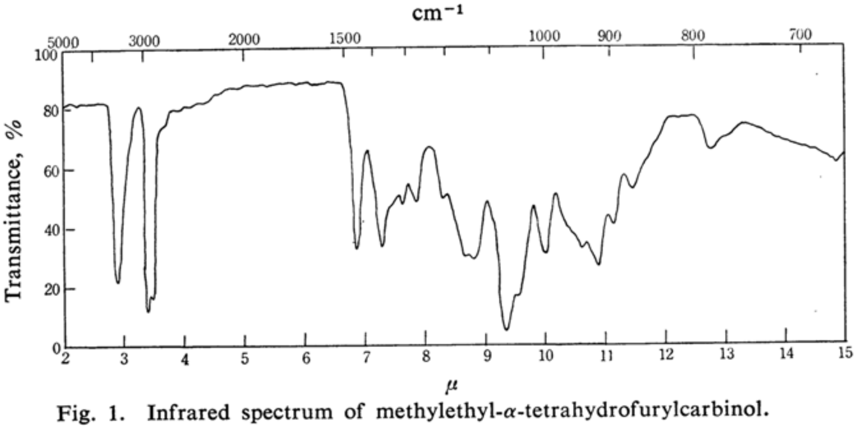

Fig. 1. Infrared spectrum of methylethyl-α-tetrahydrofurylcarbinol.

The Synthesis of Ethyl-α-tetrahydrofurylcarbinol.—Ethyl-α-furylcarbinol was prepared by the reaction of ethylmagnesiumbromide with furfural: b. p., 85~86°C/22 mmHg, n_D^{20}, 1.4763 (lit.,⁵⁾ 87~90°C/25mmHg). Ethyl-α-tetrahydrofurylcarbinol⁶⁾ was prepared by the hydrogenation of ethyl-α-furylcarbinol in the presence of an Adams catalyst: b.p., 85~95°C/19 mmHg, (lit.,⁶⁾ 182~186°C/745 mmHg, n_D^{20}, 1.4485).

Summary

The photochemical reaction of ethyl methyl ketone and propionaldehyde in tetrahydrofuran has been studied. Methylethyl-α-tetrahydrofurylcarbinol and ethyl-α-tetrahydrofurylcarbinol were easily obtained. In the photochemical reaction of propionaldehyde in tetrahydrofuran, di-α-tetrahydrofuryl was not produced, but it was observed to be produced in the photochemical reaction of acetone and ethyl methyl ketone in tetrahydrofuran.

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5) R. Douris, *Compt. rend.*, **157**, 723 (1913).

6) J. S. Pierce and R. Adams, *J. Am. Chem. Soc.*, **47**, 1098 (1925).