Studies of the Photochemical Reactions. V. The Synthesis of Dimethyldioxanylcarbinol and Dimethyl-α-tetrahydrofurylcarbinol[1]

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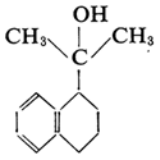
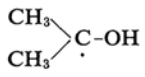
In a previous paper[2], it was reported that dimethyl-α-tetralylcarbinol (I) was easily produced by the reaction of photoactivated acetone in tetralin. In order to use the intermediate radical (II) formed from photoactivated acetone for synthetic purposes, dioxane and tetrahydrofuran were chosen as the hydrogen donor solvents in this experiment. New substances, dimethyldioxanylcarbinol (III) and dimethyl-α-tetrahydrofurylcarbinol (IV), were synthesized in fairly high yields.



(I)



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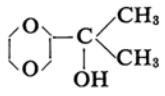
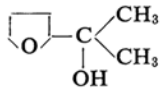


(III)

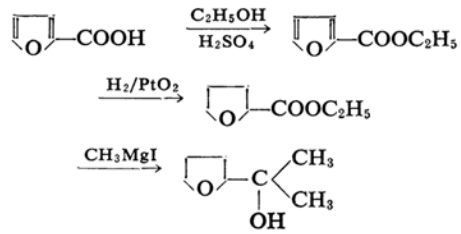


(IV)

A mixture of acetone and dioxane or tetrahydrofuran (mole ratio: 1:4) was irradiated in an atmosphere of nitrogen at room temperature for 10 hr. using a high pressure mercury lamp. The reaction products were then fractionated and analyzed by gas chromatography.

In the photochemical reaction of acetone in dioxane, isopropyl alcohol, dioxanyldioxane and dimethyldioxanylcarbinol (III) were obtained as the reaction products. The new substance, dimethyldioxanylcarbinol (III), which can only with difficulty be prepared by other methods, was easily synthesized.

When acetone was irradiated in tetrahydrofuran, isopropyl alcohol, dimethyl-α-tetrahydrofurylcarbinol (IV) and di-α-tetrahydrofuryl were isolated as the reaction products. The new substance, dimethyl-α-tetrahydrofurylcarbinol (IV), was also easily obtainable by this method. Dimethyl-α-tetrahydrofurylcarbinol was identified by comparison with an authentic sample which had been prepared by the following procedure:



(IV)

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

TABLE I. THE REACTION CONDITIONS AND THE YIELDS OF PRODUCTS

Hydrogen donor solvent	Dioxane	Tetrahydrofuran
Reaction time, hr.	10	10
Acetone used, g.	39.1	40.8
Solvent used, g.	237.2	203.0
Solvent/Acetone, mol. ratio	4	4
Acetone consumed, g.	30.6	31.9
Solvent consumed, g.	29.2	19.8
Isopropyl alcohol, g.	6.8	5.1
R-COH$(CH_3)_2$ g. (A)	12.4	17.8
R—R g.	4.8	7.3
High boiling residue, g.	22.3	12.6
Unidentified product, g.	10.9	8.0
Ultimated yield of (A) based on acetone consumed, mol. %	16.0	24.9
Ultimated yield of (A) based on solvent consumed, mol. %	25.6	49.8

Experimental[3]

Materials.—Dioxane was purified by the following method. The mixture of 900 cc. of commercial dioxane, 11.7 cc. of 37% hydrochloric acid, and 90 cc. of water was refluxed for 10 hr. while nitrogen was bubbled. After the mixture had been cooled, solid potassium hydroxide was added and the separated dioxane layer was fractionated over metallic sodium: b. p., 100~101°C, n_D^{20} 1.4222. Tetrahydrofuran was purified by the fractional distillation over sodium: b. p., 66~67°C, n_D^{20} 1.4052. Acetone was purified by the ordinary method[4]: b. p., 56.5~57°C, n_D^{20} 1.3598.

The Photochemical Reaction of Acetone in Dioxane.—The reaction apparatus used was described in the previous paper[2]. A mixture of

1) Reported at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.
2) K. Shima, Y. Shigemitsu and S. Tsutsumi, This Bulletin, 35, 1728 (1962).
3) The boiling and melting points are uncorrected.
4) A. Bramley *J.Chem Soc.*, 59, 10 (1916).

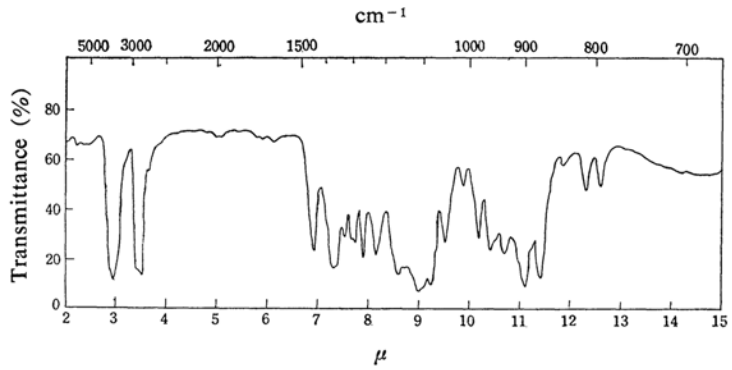


Fig. 1. Infrared spectrum of dimethyldioxanylcarbinol.

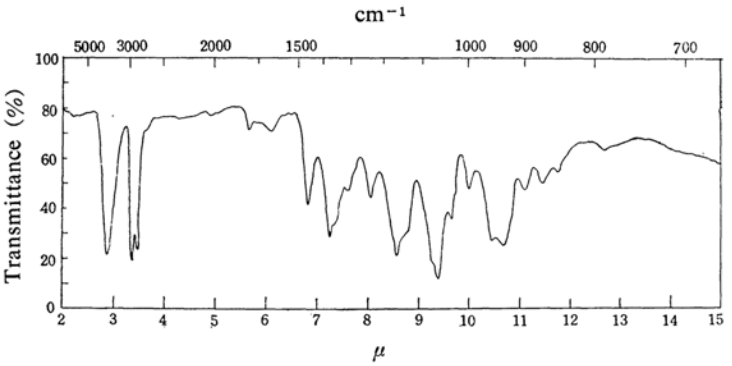


Fig. 2. Infrared spectrum of dimethyl-α-tetrahydrofurylcarbinol.

acetone (39.1 g., 0.675 mol.) and dioxane (237.2 g., 2.69 mol.) was placed in a 300 cc. reaction vessel and irradiated at 11°C in a nitrogen atmosphere for 10 hr. After the irradiation, the reaction product was fractionally distilled to give the following fractions:

	b. p., °C	Weight, g.	n_D^{20}
(1)	56～ 63	5.8	1.3572
(2)	63～ 82	4.7	1.3681
(3)	82～ 95	3.4	1.3807
(4)	95～101	13.2	1.4143
(5)	101～103	195.2	1.4199
	Residue	53.0	

The presence of isopropyl alcohol was assumed by gas chromatography. 3, 5-Dinitrobenzoate was synthesized from fraction 3 and was identified as the 3, 5-dinitrobenzoate of isopropyl alcohol by the mixed-melting point test. The amounts of acetone, dioxane and isopropyl alcohol were estimated by gas chromatography: column, D. N. P. 3 m.; carrier gas, H_2, 0.32 kg./cm²; bridge current, 160 m amp.; column temp. 50°C; retention time, acetone: 4 min., isopropyl alcohol: 7 min., dioxane: 9.5 min. After the residue had been cooled, the crystalline substance precipitated was filtered and washed with a small amount of cold methanol to give 4.8 g. of dioxanyldioxane, m. p. 155～155.5°C (recrystallized from methanol) (lit[5]. m. p. 157°C). (Found: C, 55.16; H, 7.95. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10%.)

The filtrate was distilled under reduced pressure to give the following fractions:

	b. p., °C/11 mmHg.	Weight, g.	n_D^{20}
(1)	～ 72	1.3	1.4312
(2)	72～ 81	15.1	1.4445
(3)	81～ 87	4.1	1.4497
(4)	87～100	2.2	1.4521
	Residue	22.3	

Fractions 2 and 3 were shown by gas chromatography to consist of almost only one component and were purified by using preparative gas chromatography: column, Si D. C. 550; column temp., 150°C; carrier gas, N_2; gas pressure, 1 kg./cm²; b. p. 86～87°C/11 mmHg, n_D^{20} 1.4533. The Denigés test[6] gave a positive result for this fraction. The infrared spectrum is shown in Fig. 1.

Found: C, 57.34; H, 9.42. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.65%.

3, 5-Dinitrobenzoate was synthesized and recrystallized from ethanol; m. p., 158.5～159.4°C.

Found: C, 49.34; H, 4.67. Calcd. for $C_{14}H_{16}O_8N_2$: C, 49.41; H, 4.74%.

From the above results, this fraction was confirmed to be dimethyldioxanylcarbinol.

The Photochemical Reaction of Acetone in Tetrahydrofuran.—A mixture of acetone (40.8 g.,

5) G. Leuschner and K. Pfordt, *Ann.*, **625**, 30 (1959).

6) G. Denigés, *Compt. rend.*, **126**, 1048, 1277 (1898).

0.705 mol.) and tetrahydrofuran (203.0 g., 2.82 mol.) was irradiated at 10～15°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)	58～62	11.0	1.3859
(2)	62～66	34.3	1.3980
(3)	66～75	171.6	1.4051
(4)	～30/15 mmHg	5.1	1.3863
(5)	30～57/15 mmHg	2.1	1.4374
(6)	57～78/15 mmHg	21.6	1.4468
(7)	78～85/15 mmHg	9.0	1.4502
	Residue	12.6	

Fraction 4 was assumed to be isopropyl alcohol, and the amounts of acetone, tetrahydrofuran and isopropyl alcohol were estimated by gas chromatography: column, D. N. P. 3 m.; carrier gas, H_2, 0.5 kg./cm²; bridge current, 160 m amp.; column temp. 46°C; retention time, acetone: 3 min., tetrahydrofuran: 7 min.

It was established that fractions 5, 6 and 7 were mainly composed of two components and were separated by preparative gas chromatography.

(A) B. p. 57～59.5°C/10 mmHg, n_D^{20} 1.4468.

Found: C, 64.64; H, 10.83. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84%.

The infrared spectrum is shown in Fig. 2. 3, 5-Dinitrobenzoate was synthesized and recrystallized from ethanol (m. p., 81～82°C), and no depression was observed in the mixed-melting point test with an authentic sample.

Found: C, 51.95; H, 5.03. Calcd. for $C_{14}H_{16}O_8N_2$: C, 51.85; H, 4.97%.

From the above results, fraction (A) was identified as dimethyl-α-tetrahydrofurylcarbinol.

(B) B. p. 71°C/10 mmHg, n_D^{20} 1.4594

Fraction B was confirmed to be di-α-tetrahydrofuryl from the infrared spectrum and from the elementary analysis described below. Infrared absorption spectrum data: 1070 cm^{-1} (tetrahydrofuran ring), no hydroxy absorption.

Found: C, 67.33, H, 9.66. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93%.

Synthesis of Dimethyl-α-tetrahydrofurylcarbinol. —Ethyl furan-2-carboxylate[7] was prepared by the reaction of furan-2-carboxlic acid with ethanol in the presence of concentrated sulfuric acid under reflux conditions. B. p. 193～195°C; m. p., 35～36°C (lit[7]. m. p. 34～35°C). Ethyl tetrahydrofuran-2-carboxylate[8] was prepared by the hydrogenation of ethyl furan-2-carboxylate in the presence of an Adams catalyst[9]; b. p., 76～86°C/10 mmHg, n_D^{20} 1.4484 (lit[8]. 82°C/11 mmHg, n_D^{18} 1.4455). Dimethyl-α-tetrahydrofurylcarbinol was prepared by the reaction of methylmagnesium iodide with ethyl tetrahydrofuran-2-carboxylate; b. p., 66～73°C/15 mmHg, n_D^{22} 1.4455, 3,5-dinitrobenzoate; m. p., 82～83°C (from ethanol).

Summary

The photochemical reaction of acetone in dioxane or tetrahydrofuran has been studied, and two new compounds, dimethyldioxanylcarbinol (III) and dimethyl-α-tetrahydrofurylcarbinol (IV), were easily produced by this photoreaction.

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7) H. B. Hill and L. L. Jackson, *Am. Chem. J.*, **12**, 24 (1890).
8) W. Kaufmann and R. Adams, *J. Am. Chem. Soc.*, **45**, 3041 (1923).
9) R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Col. Vol. I. 2nd Ed., (1948) p. 463.