Studies of the Photochemical Reactions. IV. The Synthesis of Dimethyl-α-tetralylcarbinol by the Photochemical Reaction of Acetone in Tetralin[1]

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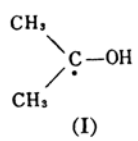
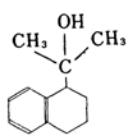
In a previous paper[2], the reactions of photoactivated acetone in cyclohexane or methylcylclohexane was reported on. In these reactions, it was ascertained that photoactivated acetone abstracted hydrogen from the hydrogen donor solvent to form an intermediate radical, the dimethylhydroxymethyl radical (I).

In order to use this radical (I) for synthetic purposes, tetralin, having the reactive α-hydrogen for autoxidation[3] or other radical reactions[4], was chosen as the hydrogen donor solvent. The present paper reports on the synthesis of dimethyl-α-tetralylcarbinol (II), which can only with considerable difficulty be prepared by other methods[5].

In this experiment, an ultraviolet light from a 400 W high pressure mercury lamp was used. A mixture of acetone and tetralin (mole ratio: 1 : 4 and 1 : 2 respectively) was irradiated in a nitrogen atmosphere at 10～15°C for 100, 25 and 10 hr., and then the reaction products were fractionated and analyzed chromatographically.



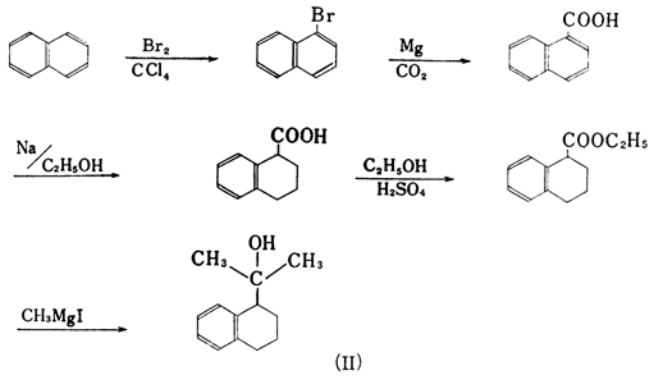
(I)



(II)

From the lower boiling fraction, isopropyl alcohol was obtained, and the fraction (b. p. 124～126°C/4 mmHg) was identified as dimethyl-α-tetralylcarbinol (II), the adduct of the (I) radical and the α-tetralyl radical. The infrared spectrum, shown in Fig. 2, was identical with that of an authentic sample, and the mixed melting point of its phenyl urethane was not depressed. The authentic sample was prepared by the following procedure[5]:

1) Reported at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.
2) K. Shima and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 460 (1961).
3) M. Hartmann and M. Seiberth, *Helv. Chim. Acta*, **15**, 1390 (1932); H. Hock and W. Suemihl, *Ber.*, **66**, 61 (1933).
4) G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, **25**, 899 (1960)
5) F. W. Kay and A. Morton, *J. Chem. Soc.*, **105**, 1571 (1914).



(II)

Table I. The reaction conditions and the yields of products

Reaction number	1	2	3
Reaction time, hr.	100	25	10
Acetone used, g.	43.5	45.0	26.4
Tetralin used, g.	194.5	201.3	240.0
Tetralin/Acetone (mol. ratio)	2	2	4
Unreacted acetone, g.	6.7	30.2	15.6
Unreacted tetralin, g.	116.9	156.4	214.0
Acetone consumed, g.	36.8	14.8	10.8
Tetralin consumed, g.	77.6	44.9	26.0
Isopropyl alcohol, g.	12.6	4.0	1.6
II, g.	35.4	17.9	11.7
High boiling residue, g.	58.3	31.3	16.2
Wt. % of II in the products*	33.3	33.7	39.7
Ultimated yield of II, based on acetone consumed, mol. %	30.2	37.0	33.1
Ultimated yield of II, based on tetralin consumed, mol. %	31.7	27.7	31.4

* Isopropyl alcohol, II, and high boiling residue.

The reaction conditions and the yields of the products are summarized in Table I. The amounts of unreacted acetone and isopropyl-alcohol were estimated by gaschromatographic analysis.

It is of interest to note that dimethyl-α-tetralylcarbinol (II) is easily produced in a fairly high yield by the photochemical reaction of acetone in tetralin.

Experimental[6]

Materials.—Tetralin was purified by fractional distillation over sodium; b.p., 81.5~83°C/14 mmHg, n_D^{20} 1.5380. Acetone was purified by the ordinary method[7]; b. p. 56.5~57°C, n_D^{20} 1.3588.

The Photochemical Reaction of Acetone in Tetralin.—A mixture of acetone (45 g., 0.77 mol.) and tetralin (201.3 g., 1.53 mol.) was placed in a 300 ml. reaction vessel and irradiated at 10~15°C in a nitrogen atmosphere for 25 hr. The reaction apparatus is shown in Fig. 1. After this irradiation, the reaction product was fractionally distilled under atmospheric and reduced pressure to give the following fractions:

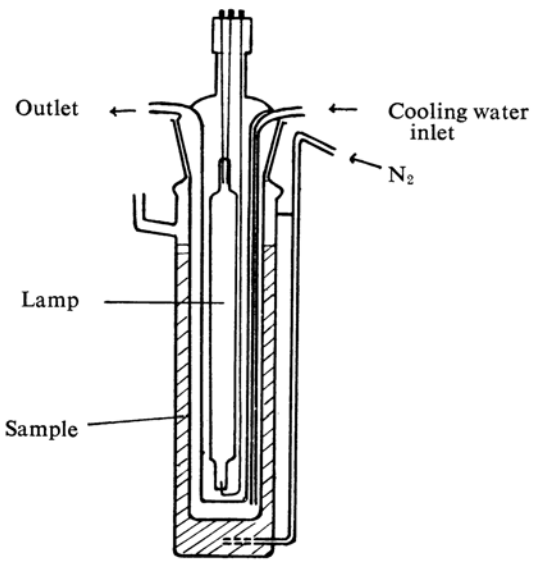


Fig. 1. Reaction apparatus.

	B. p.	Weight g.	n_D^{20}
(1)	57.5~59°C	20.5	1.3588
(2)	59.5~83°C	7.7	1.3645
(3)	~30°C/14 mmHg	6.0	1.3838
(4)	76 ~96.5°C/14 mmHg	156.4	1.5364
(5)	118~129°C/4 mmHg	17.9	1.5452
(6)	Residue	31.3	

By gaschromatographic analysis, it was assumed that 1, 2 and 3 fractions were unreacted acetone, a mixture of acetone and isopropyl alcohol, and isopropyl alcohol respectively. The 3, 5-dinitrobenzoate of fraction 3 (m. p. 120~121°C, recrystallized from ethanol) was confirmed to be the 3, 5-dinitrobenzoate of isopropyl alcohol by the mixed melting point test.

6) The boiling and melting points are uncorrected.
7) A. Bramley, *J. Chem. Soc.*, **59**, 10 (1916).

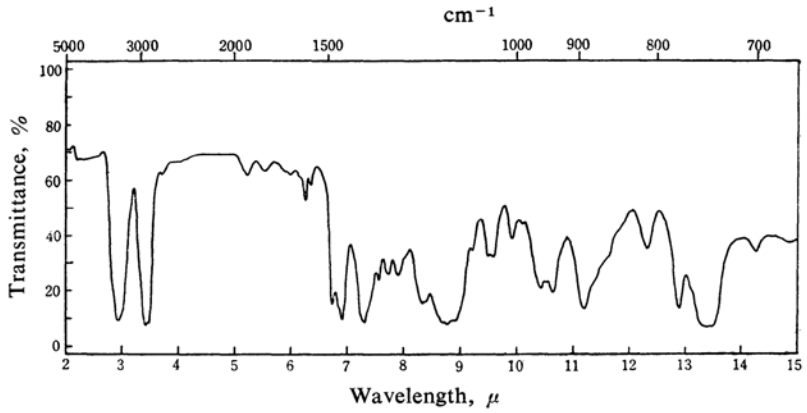


Fig. 2. Infrared spectrum of dimethyl-α-tetralylcarbinol (II).

The amounts of unreacted acetone and isopropyl alcohol were estimated by gaschromatographic analysis: column, D. N. P. 3 m.; carrier gas, H_2, 0.3 kg./cm²; bridge current 160 mA; column temp., 50°C; retention time, acetone: 5 min., isopropyl alcohol: 7 min.

Fraction 4 identified as unreacted tetralin by the gaschromatographic analysis.

Fraction 5 gave positive results to the Denigés test[8] and so was identified as dimethyl-α-tetralylcarbinol.

Found: C, 82.24; H, 9.60. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54%.

Phenyl urethane was synthesized and recrystallized from ligroin; m. p., 84~85°C, and its mixed melting point with an authentic sample showed no depression.

Found: C, 77.63; H, 7.49. Calcd. for $C_{20}H_{23}O_2N$: C, 77.64; H, 7.49%.

Synthesis of Dimethyl-α-tetralylcarbinol.—α-Bromonapthalene was prepared by the reaction of naphthalene with bromine in carbon tetrachloride according to the procedure of Clarke and Brethen[9]; b. p. 130~133°C/11 mmHg.

α-Naphthoic acid[10] was prepared by the carbonation of α-naphthylmagnesium bromide, formed by the action of magnesium on α-bromonaphthalene in ether; m. p. 161~162°C.

Ethyl tetrahydro-α-naphthoate[5] was prepared by the reaction of tetrahydro-α-naphthoic acid with ethanol in the presence of concentrated sulfuric acid under reflux conditions; b. p. 123~125°C/12 mmHg, n_D^{20} 1.5241.

Dimethyl-α-tetralylcarbinol (II)[5] was prepared by the reaction of methylmagnesium iodide with ethyl tetrahydro-α-naphtoate; b. p. 121~123°C/3 mmHg, n_D^{20} 1.5460, phenyl urethane, m. p. 84~85°C.

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

9) H. T. Clarke and M. R. Brethen, "Organic Syntheses", Coll. Vol. I (1948), p. 121.

10) H. Gilman, N. B. St. John and F. Schulze, ibid., Coll. Vol. II (1948), p. 425.