CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN, B. L. LEBEDEV, and N. A. POZDNYAK

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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SYNTHESIS OF 6-ALKYLTETRALINS

In connection with our investigation of the reaction of catalytic alkylation of tetralin, it became necessary to synthesize certain standard 6-alkyltetralins required for the analysis of catalyzates by the method of infrared spectroscopy.

Fig. 1

Obtaining 6-alkyltetralins in pure form by the interaction of tetralin with alkyl bromides in the presence of $AlCl_3$ is practically impossible, since under these conditions, along with the β-isomer, up to 30% of the α-isomer is formed ([1]), which is extremely difficult to separate. From the works of Schroeter ([2]) and Levy ([3]) it was known that, upon hydrogenation of 2-alkylnaphthalenes in the presence of a nickel catalyst, 6-alkyltetralins are formed predominantly. However, in a later study by Bailey and coauthors ([4]) it was found that, upon hydrogenation of 2-alkylnaphthalenes, a mixture of 2-alkyl- and 6-alkyltetralins is formed in a ratio of 1 : 2.

Therefore it was decided to carry out the synthesis of 6-alkyltetralins according to the following schemes:

$$\text{I}\quad \text{naphthalene} \xrightarrow[(AlCl_3)]{RCOCl} \text{acyl naphthalene (COR)} \longrightarrow \text{naphthalene-}CH_2R \quad (n\text{-alkyltetralins})$$

$$\text{II}\quad \text{tetralin} \xrightarrow[(AlCl_3)]{RCOCl} \text{acyltetralin (COR)} \xrightarrow{R'MgX} \text{tertiary alcohol } (-C(OH)(R)(R')) \xrightarrow[CuO-Cr_2O_3]{H_2} \text{tetralin-CHR}$$

The acylation of tetralin was carried out by the Friedel–Crafts method in nitrobenzene medium, since there are indications in the literature that, when tetralin is acylated in carbon disulfide medium, 2% of the α-isomer is obtained ([1]), whereas in nitrobenzene medium substitution occurs only in the β-position ([5]).

Fig. 2

Figure 2: Fig. 2

In the reaction of tetralin with the acid chlorides of the corresponding acids in nitrobenzene in the presence of $AlCl_3$ at 0°, we obtained 1, 2, 3, 4-tetrahydro-6-naphthylbutyl, -*n*-amyl, -*n*-heptyl, and -*n*-nonyl ketones, whose properties are given in Table 1.

Table 1

Properties of the synthesized alkyl-6-tetralyl ketones

Ketones	b.p., °C/mm	d_4^{20}	n_D^{20}	C, % calculated	C, % found	H, % calculated	H, % found	Yield, %
tetralyl–COC_4H_9	201/15	1.0090	1.5406	83.28	83.01	82.89	9.32	9.24	9.28	60.6
tetralyl–COC_5H_{11}	167–168/2	0.9986	1.5358	83.42	83.28	83.20	9.61	9.77	9.91	66.0
tetralyl–COC_6H_{13}	183–185/4	0.9844	1.5319	83.55	83.15	83.20	9.90	9.82	9.97	61.6
tetralyl–COC_7H_{15}	191–192/4	0.9789	1.5282	83.66	83.63	83.61	10.14	10.18	10.36	81.6
tetralyl–COC_9H_{19}	199–200.5/3	0.9655	1.5218	83.86	83.45	83.40	10.56	10.70	10.43	60.7

Tertiary alcohols were synthesized by the Grignard method. On treatment of 6-tetralylheptyl ketone with CH_3MgJ, 8-(6-tetralyl)nonanol-8 was obtained, with b.p. 180.5–182.5 (3 mm), n_D^{20} 1.5219 and d_4^{20} 0.9728.

Found, %: C 82.84; 82.88; H 10.71; 10.71
$C_{19}H_{30}O$. Calculated, %: C 83.14; H 11.02

Fig. 2

On treatment of 6-tetralyl-*n*-amyl ketone with *n*-C_3H_7Br, 6-(6-tetralyl)nonanol-6 was obtained, with b.p. 162–163°(1), n_D^{20} 1.5268 and d_4^{20} 0.9764.

Found, %: C 83.25; 83.05; H 10.50; 10.30
$C_{19}H_{30}O$. Calculated, %: C 83.14; H 11.02

Figures 1 and 2 show the IR spectra of the synthesized alcohols.* The tertiary alcohols were reduced with hydrogen in an autoclave in the presence of copper chromite ([6]) at 120 atm and 240°. Under these conditions, their

* The IR spectra were recorded by E. D. Lubuzh, to whom the authors express their gratitude.

partial dehydration occurred; therefore the resulting hydrogenation product was subjected to additional hydrogenation in contact with Raney Ni at 50° and a hydrogen pressure of 70 atm. The properties of the resulting 6-(1-methyloctyl)tetralin and 6-(1-*n*-propylhexyl)tetralin are given in Table 2.

Table 2

Properties of 6-alkyltetralins

Alkyltetralins	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found	C, %, calc.	C, %, found	H, %, calc.	H, %, found
6-C_5H_{11}-tetralin	124–125.5/3	1.5184	0.9236	65.67	66.42	89.02	88.63; 88.70	10.98	10.87; 10.97
6-C_7H_{15}-tetralin	162–163/4	1.5128	0.9142	74.91	75.74	88.62	87.97; 87.91	11.38	11.75; 11.89
6-$C_{10}H_{21}$-tetralin	185.5 – 186.5/4	1.5060	0.9045	88.76	89.21	88.15	88.36; 88.20	11.85	11.47; 11.40
6-$CH(CH_3)C_7H_{15}$-tetralin	157/4	1.5079	0.9077	84.14	84.80	88.29	88.30	11.71	11.71
6-$CH(C_3H_7)C_6H_{11}$-tetralin	145–145.5/4	1.5110	0.9112	84.14	84.87	88.29	88.40	11.71	11.51

Normal 6-amyltetralin, 6-heptyltetralin, and 6-decyltetralin were obtained by reduction of the corresponding ketones by the modified Kishner–Wolff method ([7]): decomposition of the hydrazones with sodium in diethylene glycol.

The properties of the synthesized hydrocarbons are given in Table 2. 6-(1-Methyloctyl)tetralin, 6-(1-*n*-propylhexyl)tetralin, 8-(6-tetralyl)-*n*-nonanol-8, and 6-(6-tetralyl)-*n*-nonanol-6 were obtained by us for the first time. The constants of the normal alkyltetralins agree well with the literature data ([8,9]).

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