CATALYTIC ALKYLATION OF TETRALIN

6. ALKYLATION OF TETRALIN WITH SECONDARY ALCOHOLS

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In the study of the alkylation of tetralin (1,2,3,4-tetrahydronaphthalene) with primary alcohols [1,2] we found conditions under which we obtained 6-isoalkyltetralins in about 50% yield calculated on the amount of reactants taken, and about 70% calculated on the amount of tetralin that reacted. The present work was carried out with the object of preparing 6-isoalkyltetralins by the alkylation of tetralin with secondary alcohols. We showed that secondary alcohols react with tetralin at a lower temperature than primary do. In the alkylation of tetralin with 2-nonanol, 3-nonanol, 5-undecanol, and 7-tetradecanol, 6-isoalkyltetralins were formed in yields of, respectively, 49.5%, 45.0%, 33.6%, and 17.6%, calculated on the reactants taken, and about 75% calculated on the tetralin that reacted.

EXPERIMENTAL

The secondary alcohols were synthesized by the Grignard method [3]. 2-Nonanol was obtained from heptylmagnesium bromide and acetaldehyde:

$$CH_3(CH_2)_5CH_2MgBr + CH_3CHO \rightarrow CH_3(CH_2)_5CH_2\underset{\underset{OMgBr}{|}}{C}HCH_3 \xrightarrow{H_2O} CH_3(CH_2)_5CH_2\underset{\underset{OH}{|}}{C}HCH_3.$$

3-Nonanol was obtained from ethylmagnesium bromide and heptanal:

$$CH_3CH_2MgBr + CH_3(CH_2)_5CHO \rightarrow CH_3(CH_2)_5\underset{\underset{OMgBr}{|}}{C}HCH_2CH_3 \xrightarrow{H_2O} CH_3(CH_2)_5\underset{\underset{OH}{|}}{C}HCH_2CH_3.$$

5-Undecanol was obtained from butylmagnesium bromide and heptanal:

$$CH_3(CH_2)_2CH_2MgBr + CH_3(CH_2)_5CHO \rightarrow CH_3(CH_2)_2CH_2\underset{\underset{OMgBr}{|}}{C}H(CH_2)_5CH_3 \xrightarrow{H_2O}$$
$$\rightarrow CH_3(CH_2)_2CH_2CHOH(CH_2)_5CH_3.$$

7-Tetradecanol was obtained from heptylmagnesium bromide and heptanal:

$$CH_3(CH_2)_5CH_2MgBr + CH_3(CH_2)_5CHO \rightarrow CH_3(CH_2)_5CH_2\underset{\underset{OMgBr}{|}}{C}H(CH_2)_5CH_3 \xrightarrow{H_2O}$$
$$\rightarrow CH_3(CH_2)_5CH_2CHOH(CH_2)_5CH_3.$$

The yields of 2-nonanol, 3-nonanol, 5-undecanol, and 7-tetradecanol were 65.5%, 67.3%, 40.5%, and 51.5%, respectively. The properties of the alcohols obtained are given in Table 1.

For the constants of 2-nonanol, 3-nonanol, and 5-undecanol see [4]. We synthesized 7-tetradecanol for the first time. Found: C 77.94, 78.03; H 13.61, 13.80%. $C_{14}H_{30}O$. Calculated: C 78.50; H 14.02%.

TABLE 1

Alcohol	Empirical formula	B.p. in °C (p in mm)	$n^{20}D$	d^{20}_4	MR	
					found	calculated
2-Nonanol	$C_9H_{20}O$	194-195 (747)	1.4270	0.8210	45.02	45.28
3-Nonanol	$C_9H_{20}O$	96-98 (8)	1.4295	0.8244	45.24	45.28
5-Undecanol	$C_{11}H_{24}O$	139-140 (17)	1.4248	0.8275	53.43	53.53
7-Tetradecanol	$C_{14}H_{30}O$	138-140 (6)	After recrystallization from hexane: m.p. 42.0°; f.p. 41.6°			

TABLE 2. Results on the Alkylation of Tetralin by Alcohols in Presence of Zinc Chloride

Alcohol	Reaction temp. (°C)	Alcohol taken (g)	Alkyltetralins obtained	
			g	% on amount of reactants taken
1-Nonanol	185	18	8.0	24.8
1-Nonanol	175	18	None	None
3-Nonanol	175	18	11.0	34.0
3-Nonanol	165	18	11.8	36.8
3-Nonanol	155	18	14.5	45.0
3-Nonanol	185	18	10.5	32.6
2-Nonanol	165	18	12.0	37.2
2-Nonanol	155	18	16.0	49.5
5-Undecanol	185	21.5	12.0	33.6
7-Tetradecanol	185	16.7	7.0	17.1

TABLE 3. Properties of Alkyltetralins

Alkyltetralin	B.p. (°C at 6 mm)	$n^{20}D$	MR	
			found	calculated
Nonyltetralin	168-175	1.5130	84.33	84.14
Undecyltetralin	212-214	1.5113	95.06	94.38
Tetradecyltetralin	223-224	1.5150	107.21	103.23

Alkylation of Tetralin with Secondary Alcohols. The alkylation of tetralin with secondary alcohols was carried out in presence of zinc chloride at atmospheric pressure in a flask fitted with a mechanical stirrer. The experiments lasted for 5 hr with equimolecular amounts of tetralin and the alcohol. Taking the alkylation of tetralin with 3-nonanol as example, we showed that the optimum temperature for the alkylation of tetralin with nonanols is 155°; at this temperature reaction begins and is accompanied by the separation of the reaction mixture into layers. Experiments with other alcohols were carried out at the temperature at which reaction began. The results of the experiments are given in Table 2.

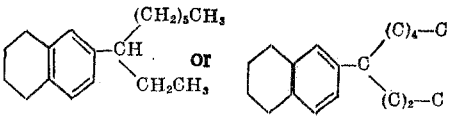
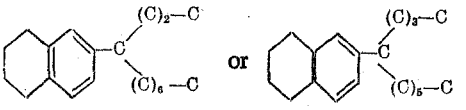
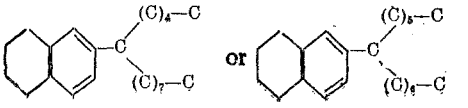
For the alkylation, 16.5 g (0.125 mole) of tetralin was taken in all experiments. The yield on the amount of tetralin that reacted was about 75%. The properties of the alkyltetralins obtained are given in Table 3.

We give the results of elementary analysis on undecyltetralin. Found: C 87.98, 88.14; H 11.90, 11.75%. $C_{21}H_{34}$. Calculated: C 88.11; H 11.89%. For tetradecyltetralin. Found: C 87.91, 87.90; H 11.73, 11.70%. $C_{24}H_{40}$. Calculated: C 87.20; H 12.20%.

The structures of the alkyltetralins were determined with the aid of infrared spectroscopy. Spectra were determined with an IKS-12 instrument in the regions 700-900, 1600-2000, and 2800-3000 cm^{-1}. In the spectra we found bands at 720, 725, 750 w, 810 s, 830 s, 1612, 1750 s, 1850, 1885, and 2000 cm^{-1}, which are characteristic for 6-alkyltetralins.

In the 2800-3000 cm^{-1} region for the bands at 2926 and 2956 cm^{-1} (unsymmetrical C – H vibrations for the CH_2 and CH_3 groups, respectively) we determined the absorption coefficients ϵ_1 and ϵ_2 [5], and from these we calculated the numbers of CH_2 and CH_3 groups (Table 4).

TABLE 4. Results of Spectrum Investigations on Isoalkyltetralins

Isoalkyltetralin	ε_1	Number of CH_2 groups	ε_2	Number of CH_3 groups	Structural formula
6-Isononyl-tetralin	624	10	197	2	
6-Isoundecyltetralin	730	12	177	2	
6-Isotetradecyltetralin	1024	15	209	2	

It was thus shown that the alkyltetralins obtained were 6-isoalkyltetralins. As in our previous investigations, from the reaction products, apart from alkyltetralins we isolated unchanged tetralin, alkenes corresponding to the alcohols taken for reaction and, in the case of the undecanol and tetradecanol, unchanged alcohols.

The infrared spectra were determined by I. N. Lifanova, to whom the authors express their thanks.

SUMMARY

1. Secondary alcohols react with tetralin in presence of zinc chloride at a lower temperature than primary alcohols do.

2. With rise in the molecular weight of the alcohol, the yield of alkyltetralins falls.

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