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CERTAIN 1-NAPHTHYL KETONES[1]

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In the past, preparation of 1-naphthyl ketones has presented a number of difficulties. The single most important method for their synthesis has been the Friedel-Crafts reaction.

In 1886, Pampel and Schmidt (1) prepared methyl 1-naphthyl ketone by the reaction of naphthalene in petroleum ether with acetyl chloride in the presence of anhydrous aluminum chloride. Later in this same year, Claus and Feist (2) used carbon disulfide as the diluent in another preparation of this ketone. Then Rousset (3) found that the addition of an equivalent amount of the acyl chloride in small portions to a boiling carbon disulfide solution of naphthalene and aluminum chloride gave a mixture of 1- and 2-naphthyl ketones. He prepared thus the following 1- and 2-naphthyl alkyl isomers: methyl, ethyl, *n*-propyl, isopropyl, and isobutyl. Separation of the pairs of isomers was effected by conversion into picrates and recrystallization of the latter; this procedure is long and laborious and seldom gives wholly satisfactory results.

Stobbe and Lenzer (4) published in 1911 a somewhat improved method for the preparation of methyl 1- and 2-naphthyl ketones through initial formation of an aluminum chloride complex with acetyl chloride in carbon disulfide and interaction with naphthalene below 15°. About this time Caille (5) described a procedure whereby freshly sublimed aluminum chloride was added in small portions to a carbon disulfide solution of naphthalene and acyl chloride cooled to 0°. He claimed high yields of ketones requiring only a single crystallization (or distillation) to produce pure alkyl 1-naphthyl ketones, specifically, methyl, ethyl, *n*-propyl, and isopropyl. However, more recently Samuelsson (6) has stated that regardless of the temperature of reaction, when using this procedure in no case is the pure alkyl 1-naphthyl ketone obtained. And Fieser (7) has pointed out that through Caille's procedure a small amount of 2-naphthyl ketone is formed, but does not appear in the final product because the complex is soluble in the carbon disulfide used.

By alkylation of methyl 1-naphthyl ketone, through treatment with the theoretical quantity of sodamide and subsequent addition of the appropriate alkyl halide, the ethyl, *t*-butyl, and *t*-amyl ketones have been prepared by Volmar (8). He, too, found that it was necessary to form and recrystallize the picrates to secure separation from the starting material.

1-Naphthyl phenyl ketone and di-1-naphthyl ketone have been prepared by means of the Grignard reaction. Thus in 1913, Tschitschibabin (9) allowed

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1-naphthylmagnesium bromide to react with 1-naphthonitrile. The reaction product was hydrolyzed with ammonium chloride to give the ketimine which, in turn, was decomposed by boiling with sulfuric acid. Grignard (10) prepared both ketones by action of 1-naphthylmagnesium bromide on cyanogen chloride, to give the nitrile, and subsequent addition of a second equivalent of the arylmagnesium halide. In each case the product was hydrolyzed by chipped ice yielding the ketimine which was separated as the hydrochloride; this salt was decomposed by boiling in water. Wilmart (11) modified Grignard's method by the addition of cyanogen chloride to the Grignard reagent, to form the nitrile, and by isolation of the ketimine as the sulfate.

TABLE I

1-NAPHTHYL KETONES, $C_{10}H_7COR$

—R	YIELD, %	B.P., °C/MM.	B.P., °C/MM.	d^{20}_4	n^{20}_D	MOLEC. REFRACT.		C		H	
						Calc'd	Found	Calc'd	Found	Calc'd	Found
Methyl	52	148–150/8[a]		1.1203[a]	1.6257[b]	53.59	53.76				
Ethyl	37	169–170/11[c]		1.0971[c]	1.6108[d]	58.21	55.51				
n-Propyl	63	178–179/12		1.0722[e]	1.5988[f]	62.83	62.83				
Isopropyl	39	159/20[g]		1.0666	1.5948	62.83	62.66				
n-Butyl	46	184–186/10	331–333/745	1.0562	1.5894	67.45	67.45	84.86	84.93	7.60	7.75
Isobutyl	48	178–180/10[h]		1.0500[h]	1.5848[i]	67.45	67.42				
n-Amyl	44	199–201/12	346–348/744	1.0394	1.5808	72.16	72.22	84.91	84.62	8.02	8.11
Isoamyl	51	183–185/8	339–341/745	1.0395	1.5795	72.16	72.08	84.91	84.48	8.02	8.12
n-Hexyl	35	196–198/7	355–357/745	1.0251	1.5728	76.78	76.91	84.95	84.86	8.39	8.34
Cyclohexyl	37	206–208/8	[j]					85.67	85.20	7.61	7.71
Phenyl	55		74.5–75.5[k]								

[a] Rousset, ref. 3, reported b.p. 154–156°/5 mm.; d_0^0 1.1336.

[b] Caille, ref. 7, recorded n_D^{27} 1.622.

[c] Rousset reported b.p. 166–168°/8 mm., d_0^0 1.1082.

[d] Caille recorded n_D^{27} 1.606.

[e] Rousset reported d_0^0 1.0861.

[f] Caille recorded n_D^{27} 1.596.

[g] Rousset reported b.p. 172–174°/8 mm.; d_0^0 1.0761.

[h] Rousset reported b.p. 180–182°/9 mm.; d_0^0 1.059.

[i] Caille recorded n_D^{27} 1.582.

[j] M.p. 62.5–63.5°.

[k] Fieser, "Experiments in Organic Chemistry," Heath, New York, 1935, p. 193, reported m.p. 76°.

In this study, the Grignard reaction involving 1-naphthonitrile has been found to be entirely satisfactory for the synthesis of eleven 1-naphthyl ketones, five of which have not previously been reported. Since bromine reacts readily with naphthalene to form 1-bromonaphthalene, which subsequently may be converted smoothly into 1-naphthonitrile (12), the structure of the ketones, prepared from the latter by means of the Grignard reaction, is unambiguous.

EXPERIMENTAL

Preparation of alkyl l-naphthyl ketones. A typical preparation was as follows: to a Grignard reagent prepared from magnesium turnings (0.21 gram atom) and an alkyl bromide (0.22 mole) in 250 ml. of anhydrous ether, 1-naphthonitrile (0.20 mole) in 300 ml. of anydrous toluene was added over a period of one hour with continuous stirring. The ether was removed by distillation and the toluene solution was refluxed for five hours. After cooling, the ketimine was obtained by hydrolysis of the toluene solution with 100 ml. of saturated ammonium chloride and chipped ice. The aqueous layer was then separated from the toluene solution and extracted once with ether. The ether and toluene extracts were combined and extracted twice with 100-ml. portions of dilute sulfuric acid. These two acid extracts were combined, extracted once with ether, and heated at reflux temperature for two hours, cooled, and extracted twice with an ether-benzene mixture. The ether-benzene extracts were washed with water, twice with saturated sodium carbonate solution, and twice with saturated sodium chloride solution. The ether-benzene layer was then concentrated and distilled under diminished pressure.

In some of the preparations, a modification of the foregoing procedure was used in that the toluene solution of the nitrile was added to the Grignard reagent in boiling ether. This variation was found to give equally good results and shortened the time interval required for distillation of the ether.

It was found also that in some cases when the removal of ether was incomplete, considerably lower yields were obtained. This point was quite clearly illustrated in the synthesis of *n*-amyl 1-naphthyl ketone. Of the latter, two preparations, using the same molar quantities and essentially the same procedure, were made. In the first experiment, it was evident that the ether had been incompletely removed and a yield of only 11% was obtained; in the second experiment, care was taken to remove the ether completely and a yield of 44% was realized.

Certain physical and analytical data for the eleven 1-naphthyl ketones are listed in Table I.

SUMMARY

By means of the Grignard reaction, involving pure 1-naphthonitrile and appropriate Grignard reagents, eleven 1-naphthyl ketones have been prepared; this represents the initial synthesis of five of these ketones.

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