The rate is seen to be distinctly less at these lower pressures, as has been found for other first-order reactions, such as the decomposition of ethyl ether.[4] The rate is, however, definitely not lowered sufficiently to suggest a second-order reaction. These results suggest the desirability of carrying out similar measurements over a wide pressure range between a few millimeters and 1 atmosphere. We plan to study this aspect of the problem further.

Summary

Further investigation of the thermal dissociations of propane and the butane has confirmed the earlier conclusion that these are fundamentally first-order, homogeneous gas reactions. Due probably to such secondary reactions as re-hydrogenation, the first-order constants fall rather rapidly as reaction proceeds. Dilution with nitrogen has the effect of increasing the rate constants somewhat. At pressures of a few millimeters the constants are distinctly less than at 1 atmosphere, but the difference is not sufficient to indicate a reaction order higher than the first.

The temperature coefficient of rate is about 2.75 per 25°, and the heat of activation is about 65,000 cal. for all three substances, and appears to be of the same order of magnitude for the alternative modes of dissociation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF NITRILES. PREPARATION OF ALKYL PHENYL KETONES

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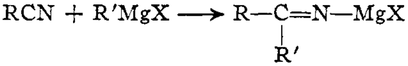
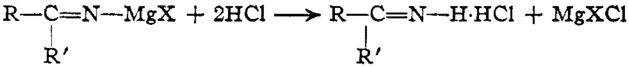
RECEIVED NOVEMBER 29, 1929 PUBLISHED MARCH 6, 1930

Nitriles are usually identified by hydrolyzing them to acids and identifying the latter. When the acid so obtained is aromatic no great difficulty is experienced but in the case of aliphatic acids from alkyl cyanides the isolation and preparation of a solid derivative is more difficult. In an attempt to find an easier means of identifying alkyl cyanides, the reaction with the Grignard reagent was studied.

The following main reactions, involving addition of the Grignard reagent with subsequent decomposition and hydrolysis, were studied by Blaise[1] but no yields were recorded.

(a)


$$RCN + R'MgX \longrightarrow R-\underset{\displaystyle R'}{\underset{|}{C}}=N-MgX$$

(b)


$$R-\underset{\displaystyle R'}{\underset{|}{C}}=N-MgX + 2HCl \longrightarrow R-\underset{\displaystyle R'}{\underset{|}{C}}=N-H\cdot HCl + MgXCl$$

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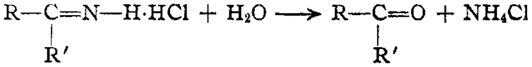
[4] Hinshelwood, *Proc. Roy. Soc. London*, **114A**, 84 (1927).

[1] Blaise, *Compt. rend.*, **132**, 38 (1901).

(c) 

$$R{-}\underset{R'}{C}{=}N{-}H{\cdot}HCl + H_2O \longrightarrow R{-}\underset{R'}{C}{=}O + NH_4Cl$$

Baerts[2] obtained four products as the result of the action of ethyl magnesium bromide on propionitrile: diethyl ketone, tri-ethyl carbinol and di- and trimolecular cyano-ethane $(C_2H_5CN)_2$, $(C_2H_5CN)_3$. The yield of ketone was very low.

It was found that by using an excess of the aryl Grignard reagent, phenylmagnesium bromide, the alkyl cyanides could be converted into the corresponding ketones in good yields and the formation of by-products could be avoided. The ketones can be easily converted into solid semicarbazones, hydrazones or oximes and thus identified. This reaction is not only of value for identification but it also furnishes an additional method for the synthesis of the higher alkyl-phenyl ketones. These ketones are usually prepared by the Friedel–Crafts reaction between benzene and the acid chloride or anhydride.[3] However, the alkyl cyanides are much more readily available as starting materials than the higher acid chlorides or anhydrides.

A series of experiments was run with phenylmagnesium bromide and acetonitrile in order to determine the optimum concentrations for the production of the ketone. It was found that a ratio of four moles of the Grignard reagent to one of the nitrile was necessary to give the best results. The use of a larger proportion of phenylmagnesium bromide gave a lower yield of ketone, due probably to conversion of some of the ketone to the carbinol noted by Baerts.[2]

It is not exactly clear why such a large excess of the Grignard reagent is necessary but it seems probable that the excess used converts the nitrile completely to the addition product and hence there is less chance for the polymerization products mentioned by Baerts[2] to form.

Experimental

A typical procedure for carrying out the reaction between phenylmagnesium bromide and a nitrile is as follows.

The phenylmagnesium bromide is prepared in the usual way from 25 g. of magnesium turnings and 160 g. of bromobenzene in 350 cc. of dry ether. A solution of 0.25 mole of the nitrile in 100 cc. of dry ether is run in slowly with stirring during a period of fifteen minutes. The solution is stirred for an hour longer and allowed to stand overnight. The mixture is poured onto 500 g. of ice and 300 cc. of concd. hydrochloric acid. The water layer, which contains the hydrochloride of the ketimide, is separated from the ether layer and refluxed vigorously for one hour. The solution is cooled and extracted with four 200-cc. portions of ether. The ether extract is dried over anhydrous calcium chloride and the ether distilled from a water-bath. The residue is transferred to a small modified Claisen flask and vacuum distilled. The ketones and their properties are recorded in Table I.

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[2] Baerts, *Bull. soc. chim. belg.*, **31**, 184 (1922).

[3] Noller and Adams, This Journal, **46**, 1889 (1924).

Preparation of Semicarbazones.—One cubic centimeter of the ketone was dissolved in 10 cc. of ethyl alcohol in a test-tube. Water was added until the solution was faintly turbid and the turbidity then removed with a few drops of alcohol. Then 1.0 g. of semicarbaizde hydrochloride and 1.50 g. of sodium acetate were added. The solution was vigorously shaken and the test-tube placed in a beaker of boiling water. The water-bath was allowed to cool and at the end of thirty minutes the test-tube was cooled in cold water and scratched with a glass rod. The semicarbazone crystallized out and was filtered. One recrystallization from 50% alcohol gave pure white crystals. Further recrystallization did not change the melting point. They were analyzed for nitrogen by the Kjeldahl method. The properties and analyses are given in Table II.

TABLE I

KETONES OBTAINED BY THE ACTION OF ONE MOLE OF PHENYLMAGNESIUM BROMIDE ON NITRILES

Nitrile	Used (0.25 mole), g.	Ketone	Yield, g.	Yield, %	Properties of ketones B. p., °C. (corr.)	at mm.	d^{20}_{20}	n^{20}_{D}
CH_3CN	10.2	$C_6H_5COCH_3$	21	70	202–205	760	1.020	1.541
C_2H_5CN	13.7	$C_6H_5COC_2H_5$	31	91	115–120	21	1.015	1.534
n-C_3H_7CN	17.2	$C_6H_5COC_3H_7$-*n*	28.5	77	125–130	21	0.989	1.524
n-C_4H_9CN	20.8	$C_6H_5COC_4H_9$-*n*	32	79	135–140	25	.988	1.532
n-$C_5H_{11}CN$	24.3	$C_6H_5COC_5H_{11}$-*n*	36.5	83	145–150	19	.981	1.538
Iso-$C_5H_{11}CN$	24.3	$C_6H_5COC_5H_{11}$-*iso*	22	50	143–148	20	.971	1.533

TABLE II

SEMICARBAZONES FROM PHENYL ALKYL KETONES

Ketone	M. p. (corr.) of semicarbazone, °C.	Nitrogen analysis of semicarbazones, % Calcd.	Found
$C_6H_5COCH_3$	198–199^a	24.02	^{a}
$C_6H_5COC_2H_5$	173–174^b	21.99	21.75
$C_6H_5COC_3H_7$-*n*	184–184.5^c	20.49	20.61
$C_6H_5COC_4H_9$-*n*	157–157.5	19.65	19.67
$C_6H_5COC_5H_{11}$-*n*	127–128	18.02	18.32
$C_6H_5COC_5H_{11}$-*iso*	145–146	18.02	18.37

[a] Melting points previously given, 162°, Clarke "Handbook of Organic Analysis," Arnold and Co., **1928;** Stobbe [*Ann.*, **308,** 123 (1899)] gives 195–198°; Borsche [*Ber.*, **34,** 4301 (1901)] gives 198–199°.

[b] Blaise, *Compt. rend.*, **133,** 1218 (1901), gives 182°; Stobbe and Niedenzuin, *Ann.*, **321,** 103 (1902), give 173–175°.

[c] Sorge, *Ber.*, **35,** 1074 (1902), gives 188°.

Summary

Phenyl alkyl ketones can be obtained in 50 to 90% yields by hydrolysis of the product formed by the action of phenylmagnesium bromide on alkyl cyanides.

The properties of the ketones and their semicarbazones are described.

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