Synthesis of Ketones from Aliphatic Nitriles and Phenylmagnesium Bromide

By Charles R. Hauser, Wilbert J. Humphlett and Martin J. Weiss

Shriner and Turner[1] have shown that, in the synthesis of acetophenone from acetonitrile and phenylmagnesium bromide, the best result is obtained with a 300% excess of the Grignard reagent. Accordingly these workers employed this large excess of the reagent in corresponding reactions with higher homologs of acetonitrile. Apparently on this basis the statement has been made in texts[2] that, with the higher aliphatic nitriles, as well as acetonitrile, the large excess of the Grignard reagent is necessary for satisfactory yields of ketones. However, Bary[3] had reported previously that a 90% yield of butyrophenone is obtained from butyronitrile with a 50% excess of phenylmagnesium bromide.

In the present investigation, high yields of ketones have been obtained from propionitrile and higher homologs through *n*-capronitrile with only a 10% excess of phenylmagnesium bromide. These results, and also the corresponding cases reported by Shriner and Turner,[1] are given in Table I. With the three higher nitriles, our results appear even slightly better than those from the large excess of the Grignard reagent.

It should be pointed out that, with ethylmagnesium bromide and propionitrile, we have obtained only a 23% yield of diethyl ketone (b. p. 101–105°) using a 10% excess of the reagent. Earlier workers[4] have similarly reported only fair yields of ketones with this aliphatic Grignard reagent and propionitrile or butyronitrile.

TABLE I

YIELDS OF KETONES FROM ALIPHATIC NITRILES AND PHENYLMAGNESIUM BROMIDE

Nitrile	Ketones, 10% excess Grignard B. p. °C.	Mm.	Yield, %	$n^{20}D$	Ketones, 300% excess Grig.[e] B. p. °C.	Mm.	Yield, %
Aceto	201–205		33	1.5344[a]	202–205		70
Propio	105–106	17	83	1.5270[b]	115–120	21	91
n-Butyro	121–123	20	82	1.5203[c]	125–130	21	77
n-Valero	139–141	24	83	1.5146[d]	135–140	25	79
n-Capro	137–138	13	89	1.5116	145–150	19	83

[a] "International Critical Tables," Vol. VII (compiled by C. J. West, National Research Council, McGraw-Hill Book Co., New York, N. Y., 1930, p. 43) gives 1.53427 at 19.1°. [b] Wallach, *Ann.*, **332**, 317 (1904). [c] "Handbook of Chemistry and Physics" (Chemical Rubber Publishing Co., 28th edition, 1944, p. 680) gives 1.52016 at 18.25°. [d] Layraud [*Bull. soc. chim.*, (3) **35**, 223 (1906)] gives 1.5152 at 19°. [e] Ref. 1.

Procedure.—In a 1-liter three-necked round-bottomed flask equipped through ground-glass joints with a mercury-sealed stirrer, dropping funnel, and a reflux condenser (having a drying tube) was placed 300 ml. of an ether solution containing 0.275 mole of phenylmagnesium bromide. To the stirred refluxing solution was added, during fifteen to twenty minutes, 0.250 mole of the nitrile in 125 ml. of dry ether. The stirring and refluxing was continued for one to six hours[5]; during the first hour a precipitate formed. The cooled mixture was decomposed with ice and acid and the ether removed on the steam-bath under an ether still. After heating for an hour longer to ensure hydrolysis of the ketimine, the ketone was extracted with four 150-ml. portions of ether. The solvent was distilled from the dried combined ether solutions and the residue distilled through a 15 cm. Vigreux column.

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[1] Shriner and Turner. This Journal. **52**, 1267 (1930).

[2] Hickinbottom. "Reactions of Organic Compounds." Longmans. Green and Co.. New York. N. Y.. 1936. p. 258: Fuson and Snyder. "Organic Chemistry." John Wiley and Sons. Inc.. New York. N. Y., 1942. p. 270.

[3] Bary. *Bull. soc. chim. Belg.*. **31**, 397 (1922).

[4] See ref. 3 and Baerts. *ibid.*, **31**, 184 (1922).

[5] The yields given in Table I were obtained on six-hour runs but an equally good yield (85%) has been obtained in a one-hour run with butyronitrile.

Some Azeotropes of Alkylacetylenes and Ethyl Alcohol[1]

By G. F. Hennion and J. J. Groebner

Azeotropic distillation is a well-known means for the separation and purification of various hydrocarbons and data are available for many hydrocarbon-carrier systems. Particular attention has been given to the azeotropes of paraffins, naphthenes, olefins, diolefins and aromatics. Since there is no information on constant boiling mixtures of higher acetylenes, we have investigated four acetylene–ethyl alcohol binaries. The data are given in Table I. When the boiling points of the azeotropes are plotted against their compositions a smooth curve is obtained, similar to, but appreciably above, the one for paraffins.[2]

The lowering of the hydrocarbon boiling point achieved by azeotropic distillation is greatest for paraffins and least for aromatics; the other hydrocarbons are intermediate and usually in the order cited above.[3] When the data for the acetylenes are compared with those of the other hydrocarbons it appears that the acetylenes fall between the aromatics and the others. Thus the

TABLE I

BINARY AZEOTROPES OF ALKYLACETYLENES AND ETHYL ALCOHOL

Acetylene[a]	Properties of azeotropes B. p., °C.	$n^{25}D$	d^{25}	Acetylene Mole %	Acetylene Wt. %
n-Butyl	62.8	1.3880	0.7264	65.0	76.8
Diethyl	67.5	1.3922	.7399	51.7	65.6
Isoamyl	71.0	1.3857	.7490	42.0	60.2
n-Amyl	74.2	1.3818	.7586	28.5	45.4

[a] The boiling points of the pure hydrocarbons were: *n*-butylacetylene, 70.2°; diethyl-, 80.5°; isoamyl-, 90.8°; *n*-amyl-, 99.5°. Other physical properties are cited by Hennion and Banigan, This Journal, **68**, 1381 (1946).

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[1] Paper LI on the chemistry of substituted acetylenes; previous paper, This Journal, **68**, 1381 (1946).

[2] Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **27**, 47 (1941).

[3] Rossini, Mair and Glasgow, *Oil Gas J.*, **158**, Nov. 14 (1940).

acetylene–alcohol mixtures boil slightly higher than those of the other classes of aliphatic hydrocarbons. This may prove to be significant should the problem of separating acetylenes from hydrocarbon mixtures ever present itself.

Analysis of the constant boiling acetylene–alcohol mixtures was accomplished both by refractive index and density. A sufficient number of mixtures was prepared in each case to establish both isotherms. All distillations were done at atmospheric pressure when the barometer read 745 ± 5 mm.

The acetylenes form ternary alcohol–water heteroazeotropes also. These were not analyzed although some of the data for them were recorded (Table II).

TABLE II

TERNARY HETEROAZEOTROPES OF ALKYLACETYLENES WITH ETHYL ALCOHOL AND WATER

Acetylene	Constant b. p., °C.	Vol. % lower layer[a]	Upper layer $n^{25}D$	Upper layer d^{25}	Lower layer $n^{25}D$	Lower layer d^{25}
n-Butyl	59.9	5.6	1.3921	0.7202	1.3598	0.8597
Diethyl	64.4	14.8	1.4025	.7290	1.3674	.8539
Isoamyl	69.0	17.4	1.3955	.7371	1.3672	.9519
n-Amyl	71.0	28.6	1.3970	.7436	1.3680	.8329

[a] These values are approximate and were measured at 25°.

Experimental

The acetylenes were prepared in the usual way from the alkyl bromides and sodium acetylide in liquid ammonia.[4] Absolute ethyl alcohol (Commercial Solvents Corp.) was redried with magnesium ethoxide immediately before use; d^{25} 0.7852, $n^{25}D$ 1.3594.

A carefully purified sample of each acetylene was mixed with an excess of amount of absolute alcohol and slowly distilled through a helix packed column having an efficiency of 15 plates as determined with an ethylene bromide–benzene mixture. The distillate was collected in fractions and those of nearly the same boiling point, density and refractive index were combined and redistilled. The process was repeated until successive fractions of the distillate showed practically the same composition, not altered by redistillation.

The ternary mixtures were obtained in substantially the same way, except that water was added to the still charge and the column was provided with a special head to prevent premature phase separation. The material which distilled at constant temperature was collected separately but was not redistilled since analysis was not intended.

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(4) Vaughn, Vogt, Hennion and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

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Relative Association of Hydrogen and Deuterium Fluorides in the Liquid State

BY JOEL H. HILDEBRAND AND ALLEN GEE

Claussen and Hildebrand[1] found that the vapor pressure of deuterium fluoride is greater than that of hydrogen fluoride, the ratio, P_{DF}/P_{HF} varying from 1.150 at 240° K. to 1.049 at 290° K. The vapor pressure of the deuterium compound is greater than that of the hydrogen compound also in the case of the acetic acids, but it is less in the case of the two kinds of water and ammonia and with deuterium and hydrogen chloride. It was pointed out that the first two pairs are alike in being highly associated in the gaseous phase while the last three are not.

Long, Hildebrand and Morrell[2] determined the variation in the association factors of gaseous hydrogen fluoride and deuterium fluoride with pressure and temperature, showing deuterium fluoride to be more associated. They confirmed the earlier results of Simons and Hildebrand[3], who found that the association of hydrogen fluoride could be reproduced over a wide range by assuming the single equilibrium, $6HF = (HF)_6$, with evidence for smaller polymers below a degree of association represented by the association factor, 1.3. It has been recognized that polymers other than $(HF)_6$ may be present also in the range of higher association, and that the single equilibrium that has been assumed may represent only an average of a more complex scheme of association. The only reason for a preponderance of a hexamer would appear to be a closed ring with its additional hydrogen bond and with corresponding preferred bond angles.[4] However, no independent evidence for ring structure has yet been discovered, and the recent measurements of dielectric constant by Benesi and Smyth indicate linear polymers.[5]

This does not interfere with the purpose of this communication, which is to calculate the partial pressures of the monomers, p_{HF} and p_{DF}, in the saturated vapors in order to learn whether, in the liquid state, the hydrogen compound is less strongly associated than the deuterium compound, as in the cases of water and ammonia.

The following table gives the total pressures at saturation according to Claussen and Hildebrand together with the corresponding partial pressures of the monomers, calculated by the aid of the equations of Long, Hildebrand and Morrell. The ratio, p_{HF}/p_{DF}, is greater than unity, indicating stronger association of the deuterium compound in the liquid, and bringing these com-

TABLE I

T, °K.	Total pressure P_{HF}	Total pressure P_{DF}	Monomer pressure p_{HF}	Monomer pressure p_{DF}	Ratios P_{HF}/P_{DF}	Ratios p_{HF}/p_{DF}
270	314.0	340.1	140.7	133.0	0.923	1.057
280	468.9	499.5	232.8	220.5	.939	1.056
290	681.1	714.2	371.1	351.8	.953	1.055

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(1) Wm. M. Claussen and J. H. Hildebrand, THIS JOURNAL, **56**, 1820 (1934).

(2) R. W. Long, J. H. Hildebrand and W. E. Morrell, *ibid.*, **65**, 182 (1943).

(3) J. H. Simons and J. H. Hildebrand, *ibid.*, **46**, 2138 (1924).

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 298.

(5) H. A. Benesi and C. P. Smyth, *J. Chem. Phys.*, **15**, 337 (1947).