

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

## The Preparation of Some Alkyl Substituted Phenylacetoneitriles in Liquid Ammonia

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Recent work in these laboratories with phenylacetoneitrile, sodium and alkyl halides in liquid ammonia suggested that the reactions would be of value in synthesizing an homologous series of nitriles from which the corresponding acids could be prepared by hydrolysis. It was desired to obtain these acids in order to determine their relative bactericidal values, work to be reported elsewhere.

Sodium ethylate,<sup>1</sup> sodium hydroxide,<sup>2</sup> sodamide,<sup>3</sup> and sodium<sup>4</sup> have been used to prepare the alkali salt of phenylacetoneitrile as a preliminary step in the formation of substituted nitriles. Phenylacetoneitrile in excess, methyl alcohol, toluene and anhydrous ether have been used as reacting media. Attempts by Bodroux and Taboury to prepare di-alkyl derivatives by treating the parent nitrile with two moles of sodamide and alkyl halide gave such low yields that they advised the formation of these compounds to be carried out in two steps. It was noted in our work that only one mole of sodium will react at one time with one mole of nitrile, which fact coincides with the findings of these workers.

In our method of preparing the nitriles, using liquid ammonia as a reacting medium, yields of 35 to 50% were obtained. These are low as compared with those obtained by using sodamide in anhydrous ether. These losses are partially accounted for by the sweeping away of some of the nitrile by ammonia vapor and by the reduction of some of the sodium salt by sodium in liquid ammonia with the formation of toluene. Investigations by other workers of the properties of sodium phenylacetoneitrile<sup>5</sup> showed that toluene and sodium cyanide were formed by a reduction of the sodium salt in ether. The formation of toluene in our experiments was similarly shown. Presumably sodium cyanide was also formed. The liquid ammonia method affords a quick means of making a substituted nitrile practically free from the parent nitrile. Liquid ammonia has been used recently as a medium for similar reactions,<sup>6</sup> with sodamide as the condensing agent.

(1) Oliveri, *Gazz. chim. ital.*, **18**, 754 (1883).

(2) Meyer, *Ann.*, **250**, 123 (1889); Neure, *ibid.*, **250**, 153 (1889); Rossolimo, *Ber.*, **22**, 1237 (1889); Pickard and Yates, *J. Chem. Soc.*, **95**, 1017 (1909).

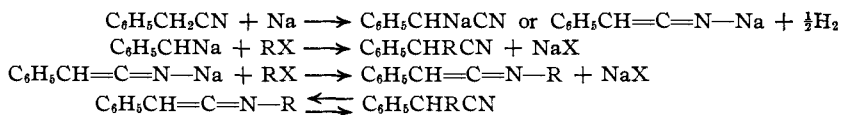
(3) Hintikka, *Ann. Acad. Sci. Fennicae*, **19A**, No. 1, 4 pp. (1923); Bodroux and Taboury, *Compt. rend.*, **150**, 531, 1241 (1910); *Bull. soc. chim.*, **7**, 666, 670, 732 (1910); Rising and Zee, *THIS JOURNAL*, **49**, 541 (1927); Blondeau, *Compt. rend.*, **174**, 1424 (1922).

(4) Rising, *THIS JOURNAL*, **42**, 128 (1920).

(5) Upson, Maxwell and Parmelee, *ibid.*, **52**, 1971 (1930); Rising and Braun, *ibid.*, **52**, 1069 (1930).

(6) Cloke, Anderson, Lachmann and Smith, *ibid.*, **53**, 2791 (1931).

In view of the tautomerism of the alkali phenylacetone nitrile as proposed by numerous workers,<sup>5a,7</sup> it is probable that the nitriles are formed according to the equations



It was observed that the alkyl chlorides reacted more smoothly than the iodides or bromides. There was, however, no noticeable difference in percentage of yield.

### Experimental Part

**Materials.**—Commercial anhydrous liquid ammonia was used without purification. The phenylacetone nitrile, b. p. 98–100° (8 mm.), methyl iodide, b. p. 41–43°, and ethyl bromide, b. p. 38–40°, were obtained from the Eastman Kodak Co. The *n*-propyl, *n*-butyl and *n*-amyl chlorides were prepared in these laboratories. Only fractions boiling over a 2 to 3° range were used.

### General Procedure

Two hundred milliliters of liquid ammonia was run into a 500-ml. Florence flask fitted with a two-holed stopper through which were inserted a dropping funnel and a glass tube connected to a safety bottle, filled with mercury, from which the ammonia vapors were conducted to a vent. The stem of the dropping funnel was surrounded by a small condenser tube filled with liquid ammonia<sup>8</sup> in order to cool the reagents to near reaction temperature. To the ammonia was added 9.8 g. (1 mol) of sodium in fine pieces, care being observed to prevent contamination of the metal by reaction with air or moisture. Some ammonia was lost by evaporation due to heat of solution. This was replaced and the two-holed stopper inserted in the flask. Fifty grams (1 mol) of phenylacetone nitrile was allowed to drop very slowly into the sodium-liquid ammonia solution. The reaction was very vigorous and the flask was shaken constantly. If exact molecular amounts of nitrile and sodium were used, the blue color of the solution faded simultaneously with the addition of the last portion of the nitrile. The sodium salt settled out as a light yellow colored precipitate. A slight excess of alkyl halide was added slowly to the sodium salt in the flask. The reaction mixture was allowed to stand for thirty minutes, and the excess ammonia then evaporated by means of a water-bath. The pasty mass was treated with 150 ml. of slightly acidulated water and extracted four times with 50-ml. portions of ethyl ether. After drying the combined ethereal extracts over calcium chloride, the ether was removed over a water-bath and the nitrile fractionated under reduced pressure.<sup>9</sup>

The physical constants and analytical data of the nitriles are tabulated in Tables I and II. The refractive indices listed in Table I were determined with a Pulfrich refractometer. From these values and the values for the densities in Table II the molecular refractivities were calculated. In calculating the theoretical molecular refractivity the carbide formula

(7) Upson and Thompson, *THIS JOURNAL*, **44**, 181 (1922); Rising and Zee, *ibid.*, **50**, 1699 (1928); Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929).

(8) Vaughn and Pozzi, *J. Chem. Education*, **8**, 2433 (1931).

(9) The nitrile should not be permitted to stand in contact with the aqueous ammonia solution for any length of time after dilution of the reaction mixture, since strong alkaline solutions tend to induce the formation of black tars.

for the nitriles was assumed. If the nitride formula for the nitriles is used, the calculated values for the molecular refractivity are 1.707 higher than the values listed. Presumably the carbide form of the nitrile must predominate under ordinary conditions. The surface tension measurements, listed in Table II, were made by the maximum bubble pressure method of Sugden, and the parachors were calculated according to the formula developed by him. The parachor for phenylacetone nitrile has been previously reported.<sup>10</sup> Since all of the compounds examined have relatively high boiling points, the density ( $d$ ) of the vapor was neglected in calculating the parachors.

TABLE I

$\alpha$ -Phenyl derivative of	Formula	B. p., °C. (corr.)	$n_D^{25}$	MR' <sub>D</sub>		Nitrogen, %	
				Calcd.	Found	Calcd.	Found
<i>n</i> -Propionitrile	C <sub>9</sub> H <sub>9</sub> N	118-120 <sub>19</sub>	1.51146	40.14	39.73	10.68	10.5
<i>n</i> -Butyronitrile	C <sub>10</sub> H <sub>11</sub> N	126-129 <sub>19</sub>	1.50777	44.74	44.46	9.65	9.68
<i>n</i> -Valeronitrile	C <sub>11</sub> H <sub>13</sub> N	120-123 <sub>7</sub>	1.5039	49.53	49.12	8.8	8.67
<i>n</i> -Capronitrile	C <sub>12</sub> H <sub>15</sub> N	152-155 <sub>20</sub>	1.50073	53.95	53.92	8.08	7.95
<i>n</i> -Heptonitrile	C <sub>13</sub> H <sub>17</sub> N	165-168 <sub>22.5</sub>	1.49961	58.56	58.46	7.49	7.39

TABLE II

$\alpha$ -Phenyl derivative of	$\gamma_{25}$	$d_4^{25}$	[ $P_{25}$ ]	$\gamma_{35}$	$d_4^{35}$	[ $P_{35}$ ]	[ $P$ ] <sub>calcd.</sub>
<i>n</i> -Propionitrile	38.57	0.9884	330.3	37.24	0.9808	330.0	331.9
<i>n</i> -Butyronitrile	36.97	.9717	368.0	35.79	.9639	367.9	370.9
<i>n</i> -Valeronitrile	37.33	.9583	410.1	33.55	.9522	406.3	409.9
<i>n</i> -Capronitrile	35.50	.9449	446.9	34.08	.9391	445.1	448.9
<i>n</i> -Heptonitrile	36.62	.9402	489.3	33.89	.9332	483.5	487.9

### Summary

1. Sodium in liquid ammonia reacts vigorously with phenylacetone nitrile to form a sodium salt, which, when treated with alkyl halides, reacts to form alkyl substituted phenylacetone nitriles.

2. An homologous series of these nitriles has been prepared by this method.

3. Some physical constants have been reported for these compounds.

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(10) Sugden, *J. Chem. Soc.*, **125**, 27, 1177 (1924).