dium or potassium. Coulter[7] has reported some density measurements for lithium solutions, which are in quite good agreement with the above data. He gives a value of 0.4920 for the density of the saturated solution at −35°, and a ΔV value of 41.4 cc. for the most dilute solution studied.

It is believed the density data given in the present study are reliable to about 0.5%. The density of pure ammonia is well known.[6] For the density of metallic lithium, the value of 0.53 at 20°, given by Richards and Brink,[8] was used. The error in the ΔV calculation caused by the difference in the density of lithium between 20 and −33° is not serious. On the other hand, an error of 0.5% in the density of the lithium solutions causes an uncertainty as great as 10% in the ΔV value in dilute solutions.

In the present investigation the temperature and concentration range was such as to avoid the appearance of a two liquid phase system.

Sodium and Potassium Solutions

Recently Stosick and Hunt[2] have repeated some of the experiments of Ogg[1] on the determination of the density of solutions of sodium in liquid ammonia at low temperatures, and the subsequent calculation of the apparent molar volume of sodium. They were unable to confirm the unusually large apparent molar volumes reported by Ogg.[1] In this study a question arose regarding the density–temperature coefficient of sodium solutions and lacking data of this type, they assumed the solutions to have the same coefficient of expansion as ammonia.

A number of years ago we made some measurements on the density of saturated solutions of sodium and potassium in liquid ammonia at temperatures ranging from about −32 to −51°, and found the density in each case to be essentially a linear function of the temperature over this relatively small temperature range.

The data are given in Table II.

TABLE II

DENSITY OF SATURATED SOLUTIONS OF SODIUM AND POTASSIUM IN LIQUID AMMONIA AT DIFFERENT TEMPERATURES

Sodium solutions				Potassium solutions	
Temp., °C.	Den.	Temp., °C.	Den.	Temp., °C.	Den.
−31.6	0.576	−45.0	0.584	−32.2	0.628
−33.0	.578	−46.1	.585	−33.3	.625
−33.3	.578	−47.0	.585	−39.0	.627
−40.7	.581	−47.8	.586	−40.5	.629
−41.6	.582	−48.5	.586	−41.0	.629
−43.0	.583	−50.0	.587	−43.0	.634
−44.5	.584	−51.0	.587	−46.4	.636
				−49.6	.638

Due to difficulties in temperature control, by reducing the pressure of ammonia vapor above the liquid and then allowing time for equilibrium to be established, the data are probably not reliable to better than 1%. However, they show the trend of the change in density with temperature, and are sufficiently accurate for general purposes. The change in density with the temperature in each case is approximately 0.1% per degree. The density increases with decreasing temperature, as is to be expected. There is no abrupt change in the density–temperature plot revealing the appearance of a two liquid phase system or an unusually large change in volume. Since the solutions in this study were saturated with metal and, as a consequence, are not comparable to those employed by Ogg and by Stosick and Hunt, who worked with solutions at a concentration of about 0.003 *M*, it is not possible to make any direct comparisons. It is sufficient to say that our experience with these solutions is such that we have never observed the large volume changes that have been reported.

GEORGE HERBERT JONES LABORATORY
THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
RECEIVED AUGUST 11, 1949

---

[7] Coulter, *The Northwest Science*, **16**, 80 (1942).

[8] Richards and Brink, THIS JOURNAL, **29**, 117 (1907).

A Catalytic Synthesis of Triphenylmethyl Mercaptan

BY NORMAN KHARASCH AND HOMER R. WILLIAMS

Vorländer and Mittag[1] reported 60–90% yields of triphenylmethyl mercaptan *via* the reaction of triphenylmethyl chloride with sodium hydrosulfide in ethanol. In many repetitions of this procedure, we obtained only 50–60% of the product; and frequently much lower yields resulted. Blicke[2] made similar observations. In an attempt to reduce the competitive alcoholysis which occurs in this reaction, Gleason[3] substituted isopropyl alcohol for ethanol, and was able to obtain 70–75% conversion to the mercaptan.

We have now found that 75–80% yields of pure triphenylmethyl mercaptan may be readily obtained by the direct interaction of triphenylmethyl chloride with hydrogen sulfide, in dry dioxane as a reaction medium. For this purpose, activated alumina is an essential and very effective catalyst.

Experimental

Commercial dioxane was refluxed with 4% of its weight of sodium for four hours. To 400 ml. of this solvent there was added 100 g. of activated alumina (Alcoa F-20) and 100 g. of triphenylmethyl chloride. Dry hydrogen sulfide was then passed into the mixture, through a 6–8 mm. inlet tube which dipped below the surface of the alumina, at such a rate as to agitate the suspended alumina gently and to keep the solution saturated with the gas. After fifteen hours, the alumina was collected on the suction filter plate and washed with two 50-ml. portions of dioxane. The combined washings and filtrate were then poured into two liters of ice-water, and the mixture was stirred until a granular product precipitated. This was collected by suction filtration, dried between sheets of filter paper, and dissolved in 500 ml. of boiling isopropyl alcohol. On slow cooling of the solution, pale-yellow crystals of tri-

---

[1] D. Vorländer and E. Mittag, *Ber.*, **46**, 3450 (1913).

[2] F. F. Blicke, THIS JOURNAL, **45**, 1967 (1923).

[3] G. I. Gleason, private communication, May 14, 1948.

phenylmethyl mercaptan (m. p. 106–107°) separated; yield 75–80 g. (75–80%). Some triphenylcarbinol, but no appreciable amount of mercaptan, was obtained from the mother liquor.

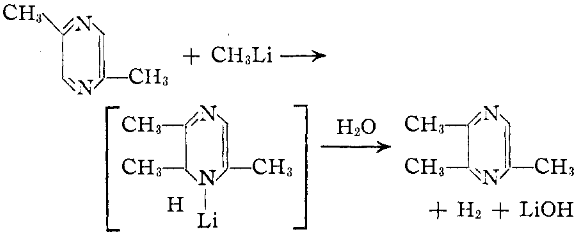
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA

RECEIVED SEPTEMBER 24, 1949

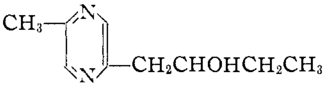
The Action of Organolithium Compounds on 2,5-Dimethylpyrazine

BY BERNARD KLEIN AND PAUL E. SPOERRI

The ease of metalation with alkyllithium of the methyl group in 2-picoline[1] prompted us to attempt a similar reaction with 2,5-dimethylpyrazine. It was hoped thereby to introduce reactive functional groups into the side chain. When 2,5-dimethylpyrazine was treated with one equivalent of methyllithium, 2,5,6-trimethylpyrazine was formed instead. This reaction could take place by the 1,2 addition of the methyllithium across the azomethine linkage of the dimethylpyrazine



To determine whether side chain metalation had occurred, the product of the reaction between methyllithium and 2,5-dimethylpyrazine was treated with propionaldehyde. None of the expected 4-(5-methylpyrazyl)-butan-3-ol was obtained.



Addition reactions, in other heterocyclic series, similar to the one described are well known. For example, phenyllithium will add to pyridine to form 2-phenylpyridine.[2] Organolithium compounds add readily to quinoline[3] to form 2-substituted quinolines in good yield. On the other hand, treating 4-methylpyridine with *n*-butyllithium, 2-butyl-4-methylpyridine is formed by 1,2 addition of the reagent across the azomethine linkage.[4] In a similar manner, Tarbell and his students[5] have reported that addition of lepidine to phenyllithium produced 2-phenyllepidine.

In another experiment, treating 2,5-dimethylpyrazine with phenyllithium produced the corresponding 2,5-dimethyl-6-phenylpyrazine.

Further examples of this reaction are being studied.

Experimental

2,5,6-Trimethylpyrazine.—To 125 ml. of an ethereal solution of methyllithium[6] (0.2 mole), cooled in ice water, was added dropwise and with good stirring, 25 ml. of a dry ether solution containing 21.6 g. (0.2 mole) of dry, freshly distilled, 2,5-dimethylpyrazine. A dark red precipitate soon formed. No gas was evolved and reflux was held to a minimum. When the addition was complete, the mixture was stirred in the cold for an additional ten minutes, refluxed for fifteen minutes and cooled in ice. The mixture was cautiously decomposed with 25 ml. of ice water, containing a few drops of concentrated hydrochloric acid. Gas was evolved and the red precipitate dissolved to form a yellow solution. The layers were separated, the aqueous layer extracted with ether, the extracts combined, washed once with water and dried over sodium sulfate. After removal of the solvent, the 20-g. residue was fractionated through a jacketed, modified Widmer column,[7] collecting 10.8 g. (44.4%) of material, b. p. 89–94° (62 mm.), n^{24}_D 1.4958–1.4960. For analysis, a portion was redistilled, b. p. 86–88.5° (35 mm.), n^{25}_D 1.4968.

Anal.[8] Calcd. for $C_7H_{10}N_2$: C, 68.82; H, 8.25. Found: C, 69.01; H, 8.42.

The picrate melted 138–138.5° (lit.[9] 138–139°).

Anal.[10] Calcd. for $C_{19}H_{16}O_{14}N_8$: N, 19.31. Found: N, 19.65.

2,5-Dimethyl-6-phenylpyrazine.—To 170 ml. of an ether solution containing 0.16 mole of phenyllithium, 17.3 g. (0.16 mole) of freshly distilled 2,5-dimethylpyrazine in 25 ml. of dry ether was added dropwise with good stirring. A deep red precipitate settled out which made efficient stirring difficult. When the addition was complete, the mixture was refluxed for one hour under nitrogen, chilled in ice water and cautiously decomposed with ice water and enough acid to dissolve all the precipitate. The layers were separated, the aqueous portion extracted with ether, the extracts combined, washed once with water and dried. The residue was fractionally distilled through the modified Widmer column. The main fraction, after a small forerun, weighed 7.4 g. (25.2%), b. p. 137–141° (15 mm.). Redistillation gave 6.4 g. of material b. p. 124–126 (1.4 mm.), n^{19}_D 1.5792.

The compound was analyzed as the picrate, m. p. 154–155°.

Anal.[9] Calcd. for $C_{18}H_{15}O_7N_5$: C, 52.40; H, 3.67; N, 16.99. Found: C, 52.43, 52.44; H, 3.78, 3.89; N, 16.99, 17.04.

---

(1) Ziegler and Zeiser, *Ann.*, **485**, 174 (1931).

(2) Ziegler and Zeiser, *Ber.*, **63**, 1847 (1930).

(3) Gilman and Spatz, THIS JOURNAL, **63**, 1553 (1941).

(4) Gilman and Broadbent, *ibid.*, **70**, 2809 (1948).

(5) Tarbell, Bunnett, Carlin and Wystrach, *ibid.*, **67**, 1584 (1945).

(6) Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933).

(7) Smith and Adkins, *ibid.*, **60**, 663 (1938).

(8) Microanalysis by Dr. Francine Schwartzkopf.

(9) Brandes and Stoehr, *J. prakt. Chem.*, [2] **53**, 509 (1896).

(10) Microanalysis by Mr. Ralph E. Schachat of this Laboratory.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 2, N. Y.

RECEIVED NOVEMBER 23, 1949

Condensation of 3-Acetocoumarin with itself and with Acetone[1]

BY C. F. KOELSCH AND S. A. SUNDET

When an alcoholic solution of 3-acetocoumarin (I) containing a little piperidine is boiled for several hours, there is deposited a pale yellow substance, m. p. 298°. The substance has been formulated as II,[2] but it is now suggested that it is actually III.

---

(1) From the Ph.D. Thesis of Sherman A. Sundet, June, 1948.

(2) Sastry and Seshadri, *Proc. Indian Acad. Sci.*, **16A**, 29 (1942)