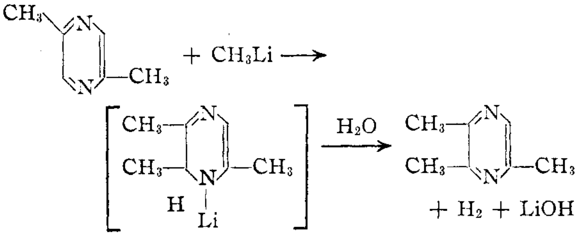
phenylmethyl mercaptan (m. p. 106–107°) separated; yield 75–80 g. (75–80%). Some triphenylcarbinol, but no appreciable amount of mercaptan, was obtained from the mother liquor.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA
RECEIVED SEPTEMBER 24, 1949

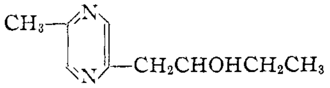
The Action of Organolithium Compounds on 2,5-Dimethylpyrazine

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)