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.

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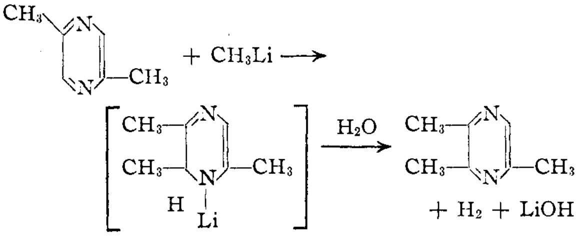
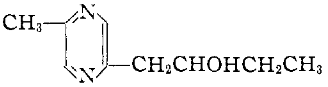
The Action of Organolithium Compounds on 2,5-Dimethylpyrazine

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.

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(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.

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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.

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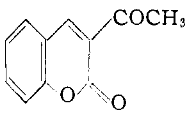
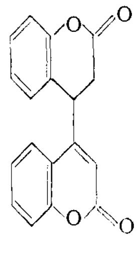
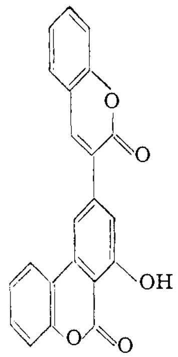
(1) From the Ph.D. Thesis of Sherman A. Sundet, June, 1948.

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


I

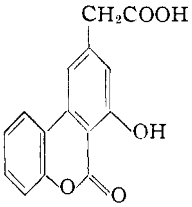

II

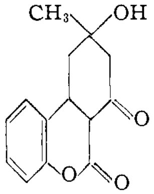

III

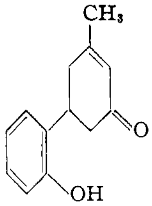
The presence of an hydroxyl group is indicated by the formation of an acetate with acetic anhydride. The presence of two coumarin nuclei and a phenolic ring are indicated by the formation of salicylic acid and a phenolic acid, $C_{15}H_{10}O_5$ (IV), when the substance is fused with alkali.

The formation of III involves a Michael condensation in which one molecule of 3-acetocoumarin acts as an acceptor and another as an addendum. The phenolic ring of III is then formed by spontaneous intramolecular aldolization, dehydration and dehydrogenation.

When 3-acetocoumarin is heated with piperidine in acetone, a similar initial reaction takes place, but a molecule of acetone, rather than a second molecule of 3-acetocoumarin, acts as the addendum in the Michael condensation. The product is best formulated as the lactone of a β-keto acid (V), for it loses carbon dioxide (and water) when it is boiled with sodium carbonate, forming a phenolic ketone (VI).


IV


V


VI

Experimental

2-(3-Coumarinyl)-4-benzo[c]coumarinol, III.—Three 2.5-g. portions of piperidine were added at intervals during twenty-one hours to a boiling solution of 100 g. of 3-acetocoumarin in 300 ml. of absolute alcohol. The crystalline product (16.7 g.) was removed from the hot mixture, washed with alcohol and crystallized from pyridine; m. p. 298°.

Anal. Calcd. for $C_{22}H_{12}O_5$: C, 74.1; H, 3.4. Found: C, 74.1; H, 3.5.

No pure substance other than unchanged acetocoumarin (11 g.) could be isolated from the dark oil comprising the rest of the reaction product.

The acetate of III, faintly yellow crystals from benzene, m. p. 234–236°, was obtained by boiling III with acetic anhydride containing a little sulfuric acid for twenty-five minutes.

Anal. Calcd. for $C_{24}H_{14}O_6$: C, 72.4; H, 3.5. Found: C, 72.1; H, 3.9.

One gram of III was heated at 200–225° for thirty minutes with 10 g. of sodium hydroxide and 1 ml. of water. The acidic products were separated by extraction with hot water into 0.1 g. of salicylic acid and 0.23 g. of an insoluble acid. The latter, **4-hydroxybenzo[c]coumarin-2-acetic acid (IV)** formed colorless needles from acetone, m. p. 209–210°. It gave a red ferric chloride test.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.7; H, 3.7. Found: C, 66.4; H, 3.9.

1,2,3,4,4a,10b-Hexahydro-2-hydroxy-2-methyl-4-benzo[c]coumarinone, V.—A solution of 8.8 g. of 3-acetocoumarin and 2 ml. of piperidine in 250 ml. of acetone was boiled for ten hours. The excess acetone was then distilled, and the residue was crystallized from alcohol, giving 2.5 g. of unchanged 3-acetocoumarin and 2.5 g. of V. The latter formed colorless needles from acetone, m. p. 231–231.5°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.2; H, 6.1.

One gram of V dissolved rapidly when it was boiled with 10 g. of sodium carbonate in 100 ml. of water, but during ninety minutes of continued boiling, the solution deposited 0.9 g. of **5-(*o*-hydroxyphenyl)-3-methyl-2-cyclohexen-1-one, VI**, colorless needles from dilute alcohol, m. p. 132.5°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.3; H, 6.9. Found: C, 77.6; H, 7.3.

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Vapor Density of Bromine Near 100°

By James A. Lasater, Stone D. Cooley and Robbin C. Anderson

In order to calibrate a flowmeter for use with bromine vapor, it became necessary to have data on the density of bromine vapor at temperatures close to 100°, and on its deviation from the perfect gas laws. Perman[1] measured the density at several temperatures including 78.4 and 132.2° but his results were such that values could not well be determined for 100° by interpolation (*cf.* Fig. 1). Accordingly experimental determinations have been made of the bromine vapor density in the region from 87 to 112°.

Experimental

The density of bromine vapor was determined by weighing a bulb of known volume filled with vapor at atmospheric pressure and at constant temperature. A mineral oil-bath was used as the heating medium for the gas bulb. To minimize any effect of residual gases, the bulb was evacuated with an oil pump and refilled with helium several times before it was finally evacuated and weighed. A small amount of liquid bromine was introduced into the bulb. It was then placed in the oil-bath and brought to the desired temperature. Excess bromine vapor was permitted to escape until the pressure in the bulb was equal to that of the atmosphere. When the bulb had reached bath temperature and the pressure was equalized, the stopcock on the bulb was closed and it was removed from the bath. The bulb was washed with benzene and rinsed with acetone and allowed to reach atmospheric temperature before each weighing.

The volume of the bulb was determined by calibration with distilled water at room temperature. Correction for the buoyancy of air and for the expansion of the bulb and stem corrections for the thermometer were applied. Temperatures were measured with a thermometer calibrated against a U. S. Bureau of Standards thermometer. Pressures were measured with a mercury barometer corrected

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[1] Perman, *Proc. Roy. Soc.* (*London*), **48**, 45 (1890); **66**, 10 (1900).