monium chloride. The organic layer was separated and washed with dilute hydrochloric acid, sodium carbonate and water, then dried over calcium chloride. The major portion of ether was rapidly distilled off through a small column.

Method B.—The directions described by Hennion[3] were closely followed.

Method C.—To a solution of the halide in 100 cc. of dry ether was added an ether solution of lithium aluminum hydride (1.6 molar) at a rate to maintain refluxing. The clear solution was stirred under reflux for an additional 2 hours, and hydrolyzed with a concentrated solution of ammonium chloride at the reflux temperature of ether. The ether solution was decanted, washed with dilute hydrochloric acid, and dried over calcium chloride. Most of the ether was removed by a rapid distillation through a small column. The residue was fractionally distilled.

Fractional Distillation and Analysis.—A two-foot column packed with nickel saddles (column 1) or a one-foot semimicro column (column 2)[20] was used. There was a little difference in the efficiency of these two columns as evident from the infrared spectrum analysis. Cumene was used as a "chaser." The boiling point of collected fractions is listed in Table I. Fractions boiling below the listed boiling range consisted almost entirely of ether (methods A and C) or of alcohol (method B). There was a steep rise in temperature after the product exceeded the upper limit of the listed boiling range. Although boiling points showed a very good separation of isomers refractive indices and the intensities of bands in the infrared spectrum, showed a constant variation in composition. With the exception of experiment 3, refractive indices of individual fractions showed a gradual variation within the values of pure acetylenic and allenic products. The infrared analyses were usually performed within 48 hours after distillation. The refractive index of the lower boiling fraction in experiment 3, was outside the limit of the pure hydrocarbons. This was due to incomplete removal of ether (column 1 was used), found in rather high molar concentration by the infrared analysis. No other unexpected absorption bands were found in any experiment or fraction.

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[20] Manufactured by the Glass Engineering Laboratories of Belmont, Cal. Claimed efficiency by 75 theoretical plates. The author wishes to thank Drs. Orchin and Wender of the U. S. Bureau of Mines, Bruceton, Pa., for the use of this column.

[Contribution from the Department of Chemistry of De Paul University]

Preparation of Some 2-Picolyl Ketones Using Phenyllithium

BY ROBERT P. ZELINSKI AND MARY BENILDA[1]

2-Picoline has been acylated in the presence of phenyllithium with ethyl benzoate, ethyl 2-furancarboxylate and ethyl 2-thiophenecarboxylate to yield the corresponding 2-picolyl ketones. These have been characterized and then reduced by Wolff–Kishner reduction to give substituted 2-pyridylethanes.

Acylations of 2-picoline and similar methyl ammono ketones by means of basic reagents and acid halides, anhydrides and esters have been briefly reviewed elsewhere.[2]

The present investigation describes the preparation of three 2-picolyl ketones by acylation of 2-picoline in the presence of phenyllithium with ethyl benzoate, ethyl 2-furancarboxylate[3] and ethyl 2-thiophenecarboxylate. In agreement with the results reported for the acylation of 2-picoline by alkali amide and ethyl benzoate,[2] it has been found that altering the mole ratio of phenyllithium to 2-picoline materially changed the yield of ketone. 2-Picolyl phenyl ketone (2-phenacylpyridine) decomposed slowly on standing, but 2-picolyl 2-furyl ketone and 2-picolyl 2-thienyl ketone were stable.

In agreement with a recent report,[7] these 2-picolyl ketones have been found to manifest ketonic reactions. Treatment with 2,4-dinitrophenylhydrazine gave good yields of the hydrazones. However, while reaction with 2-picolyl 2-furyl ketone was successful in the presence of acetic acid, hydrochloric acid catalyzed the formation of a distinctly different product. Presumably, this was furyldinitropyridylindole formed in a particularly rapid indole synthesis.[4,5]

Reduction of the 2-picolyl ketones by a Wolff–Kishner reaction gave the expected hydrocarbons, all of which rapidly resinified at room temperature. However, the picrates of these were stable. With excess picric acid the dipicrates appear to form, but these are converted to monopicrates by recrystallization.

Experimental[6]

2-Picolyl Phenyl Ketone.—A solution of 0.63 mole of ethyl benzoate in 100 ml. of anhydrous ether was rapidly added with stirring to 200 ml. of an ethereal solution of 2-picolyllithium prepared from 1.4 g. atoms of lithium sand, 0.71 mole of bromobenzene and 1.4 moles of 2-picoline. After the initial vigorous reaction the mixture was stirred under reflux for 1 hour. It was then poured onto 200 g. of ice and water, and the aqueous layer was saturated with salt and extracted with ether. After having been dried over anhydrous sodium sulfate, the combined ether solution was distilled through a heated column, 1.2 × 20 cm., packed with glass helices. The 2-picolyl phenyl ketone, b.p. 158–170° (1 mm.), weighed 34 g. (27% yield, 87% based on ester not recovered). Recrystallization from petroleum ether (b.p. 30–60°, Skellysolve F) gave yellow needles, m.p. 52.5–54°, literature[7] 54°. When the mole ratio of ethyl benzoate 2-picoline and phenyllithium was 1:1:1, the yield was 20% based on the total amount of ester employed.

Anal. Calcd. for $C_{13}H_{11}NO$: N, 7.11. Found: N, 7.51.

The **picrate**[8] melted at 180–181° after recrystallization from 95% alcohol. It darkened on exposure to light.

Anal. Calcd. for $C_{19}H_{14}N_4O_4$: N, 13.14. Found: N, 13.35.

The 2,4-dinitrophenylhydrazone[9] of 2-picolyl phenyl ketone was obtained in 63% yield after recrystallization from alcohol, m.p. 193–194°.

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[1] Abstracted from the thesis submitted by Sr. Mary Benilda Nadzieja, Fel., O.S.F., in partial fulfillment of the requirements for the degree of Master of Science.

[2] Weiss and Hauser, THIS JOURNAL, **71**, 2023 (1949).

[3] This ester has been previously used for the acylation of 2-quinaldine with alkali amide as the basic reagent: Bergstrom and Moffat, THIS JOURNAL, **59**, 1494 (1937).

[4] Fischer, *Ber.*, **19**, 1563 (1886).

[5] Robinson and Robinson, *J. Chem. Soc.*, **113**, 639 (1918).

[6] All analyses are by the Micro-Tech Laboratories, Skokie, Illinois.

[7] Kloppenburg and Wibaut, *Rec. trav. chim.*, **65**, 393 (1946).

[8] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 180.

[9] *Ibid.*, p. 171.

Anal. Calcd. for $C_{19}H_{15}N_5O_4$: N, 18.57. Found: N, 18.35.

2-Picolyl 2-Furyl Ketone.—From 0.40 mole of ethyl 2-furancarboxylate and the 2-picolyllithium prepared from 0.40 g. atom of lithium, 0.21 mole of bromobenzene and 0.40 mole of 2-picoline, there was obtained 10.3 g. (27.4% yield, 42% based on ester not recovered) of product, b.p. 141–143° (1 mm.). Two recrystallizations from petroleum ether (b.p. 30–60°, Skellysolve F) gave yellow needles, m.p. 49–51°, stable at room temperature. With two moles of 2-picoline per mole of ester the yield was 23%.

Anal. Calcd. for $C_{11}H_9NO_2$: N, 7.48. Found: N, 7.70.

The **picrate**[8] melted at 149–150° after recrystallization from alcohol and slowly darkened on exposure to light.

Anal. Calcd. for $C_{17}H_{12}N_4O_4$: N, 13.45. Found: N, 13.59.

The **2,4-dinitrophenylhydrazone**, m.p. 166–167.5°, was prepared with acetic acid as a catalyst in 68% yield. Two crystallizations from 95% alcohol gave the purified hydrazone, m.p. 170–172°.

Anal. Calcd. for $C_{17}H_{13}N_5O_5$: N, 19.07. Found: N, 19.44.

When 2-picolyl 2-furyl ketone was treated with 2,4-dinitrophenylhydrazone in the presence of hydrochloric acid,[9] a product decomposing at 248–252° resulted. This seemed to be a mixture of the hydrazone and furyldinitropyridylindole since warming the hydrazone with a little dilute hydrochloric acid converted it to the high-melting material.

2-Picolyl 2-Thienyl Ketone.—When 0.40 mole of ethyl 2-thiophenecarboxylate was heated under reflux with 0.20 mole of picolyllithium, prepared from 0.40 g. atom of lithium, 0.20 mole of bromobenzene and 0.40 mole of 2-picoline, the yield of 2-picolyl 2-thienyl ketone was 10.6 g. (26% yield, 43% based on ester not recovered), of yellow sirup, b.p. 167–172° (1 mm.). Recrystallization at 5° from petroleum ether (b.p. 30–60°, Skellysolve F) gave pale yellow needles, m.p. 28.5–29.5°.

Anal. Calcd. for $C_{11}H_9NOS$: N, 6.89. Found: N, 6.92.

The **picrate**[8] was obtained as yellow needles, m.p. 154–155°, after recrystallization from alcohol.

Anal. Calcd. for $C_{17}H_{12}N_4O_8S$: N, 12.96. Found: N, 13.00.

The **2,4-dinitrophenylhydrazone**[9] was obtained as dark red needles, m.p. 194.5–195.5° (43% yield), after recrystallization from alcohol.

Anal. Calcd. for $C_{17}H_{13}N_5O_4S$: N, 18.27. Found: N, 18.25.

Wolff–Kishner Reduction—The Huang-Minlon[10] modification of this reduction was used. Solutions of 0.02 mole of the 2-picolyl ketones, 0.06 mole of sodium hydroxide and 3 ml. of 85% hydrazine hydrate in 50 ml. of diethylene glycol were employed. The reduction products were purified by distillation from sodium metal through the helix packed column. All were colorless liquids when first obtained, but at room conditions they rapidly changed to dark brown sirups.

1-Phenyl-2-(2-pyridyl)-ethane was obtained in 83% yield, b.p. 110–112° (1 mm.), n^{25} 1.5197. Preparation of the picrate[8] gave yellow crystals, m.p. 135–135.5° Recrystallization from alcohol gave the *monopicrate*, m.p. 128–129°, mixed m.p. with the picrate of the product obtained by a different method,[11] m.p. 128–129°.

Anal. Calcd. for $C_{19}H_{16}N_4O_7$: N, 13.59. Found: N, 13.67.

1-(2-Furyl)-2-pyridyl)-ethane was prepared in 64% yield, b.p. 100–101° (1 mm.) or 113–117° (8 mm.), n^{25} 1.5132. The initial precipitate obtained in preparation of the picrate was recrystallized from alcohol to give the **monopicrate**, yellow needles, m.p. 112–113.5°.

Anal. Calcd. for $C_{17}H_{14}N_4O_8$: N, 13.93. Found: N, 14.03.

1-(2-Thienyl)-2-(2-pyridyl)-ethane was obtained in 40% yield, b.p. 115–119° (1 mm.), n^{25} 1.5428. The precipitate from the reaction of hydrocarbon with a saturated alcoholic solution of picric acid was the **dipicrate**, yellow needles, m.p. 130.5–132°.

Anal. Calcd. for $C_{23}H_{17}N_7O_{14}S$: N, 15.15. Found: N, 15.04.

Recrystallization from alcohol gave the **monopicrate**, m.p. 99.5–100°.

Anal. Calcd. for $C_{17}H_{14}N_4O_7S$: N, 13.29. Found: N, 13.35.

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(10) Huang-Minlon, This Journal, **68**, 2487 (1946).

(11) Ziegler and Zeiser, *Ann.*, **485**, 192 (1931).

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 14, 1950

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

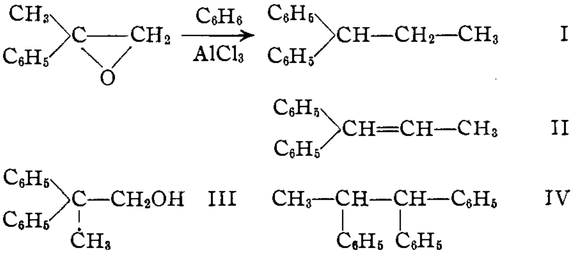
The Friedel–Crafts Reaction with Disubstituted Ethylene Oxides. II. α-Methylsytrene Oxide

BY WILLARD T. SOMERVILLE[1] AND PAUL E. SPOERRI

The Friedel–Crafts reaction of α-methylstyrene oxide in benzene has been found to give the expected alcohol 2,2-diphenylpropanol-1 together with 1,1,2-triphenylpropane, 1,1-diphenylpropene and 1,1-diphenylpropane. The exclusive formation of the rearranged product 1,1,2-triphenylpropane as a product of the secondary condensation is contrasted with the secondary products obtained from the Friedel–Crafts reaction with isobutylene oxide. The above three hydrocarbons are formed as the result of a rearrangement and a mechanism is proposed for this rearrangement.

Previous work on 2,3-butylene oxide and isobutylene oxide[2] has been extended to include α-methylstyrene oxide, in order to determine whether the same type of rearrangements occurred.

α-Methylstyrene oxide was treated with a twenty molar excess of benzene in the presence of two moles of anhydrous aluminum chloride at 5–10°. Under these conditions the reaction proceeded with the formation of 1,1-diphenylpropane (I), 1,1-diphenyl-1-propene (II), 2,2-diphenyl-1-propanol (III) and 1,1,2-triphenylpropane (IV).



The unsaturated hydrocarbon, II, obtained melted at 48° and was at first believed to be the low melting (*cis* ?) form of α-methylstilbene, since this substance has been reported as a dehydration product of 2,2-diphenyl-1-propanol by other

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(1) Taken in part from a dissertation presented by Willard T. Somerville to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

(2) Somerville and Spoerri, This Journal, **72**, 2185 (1950).