has been found very satisfactory. By this method three new phenolic esters have been prepared on a one to three mole scale.

Ethyl 4-Phenylphenyl Carbonate.—To a solution of 510 g. (3 moles) of 4-phenylphenol in 720 ml. of pyridine (dried over potassium hydroxide pellets) in a 2-liter reaction flask, carrying a reflux condenser, dropping funnel and mercury-sealed "Hershberg" stirrer, there was added, with stirring at 0°, over a period of 30 minutes, 365 g. (3.4 moles) of ethyl chlorocarbonate. A bulky precipitate formed. Stirring was continued for thirty minutes after addition was complete. The reaction mixture was stirred to a paste with 500 ml. of water and filtered under suction; the precipitate was washed with three 200-ml. portions of ice-water prior to fusion *in vacuo*. The fused material was recrystallized from 800 ml. of 95% ethanol. There was obtained 430 g. (60%) of ethyl 4-phenylphenyl carbonate, m. p. 73.2–74.3°. A sample, recrystallized repeatedly from methanol, melted at 73.9–75.0°.

Anal.[6] Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 73.90; H, 5.88.

4-Phenylphenyl Isobutyrate.—The acylation of 255 g. (1.5 moles) of 4-phenylphenol in 360 ml. of pyridine by means of 180 g. (1.7 moles) of isobutyryl chloride as described for ethyl 4-phenylphenyl carbonate gave 294 g. (82%) of 4-phenylphenyl isobutyrate, m. p. 73.2–74.8°. A sample, recrystallized repeatedly from methanol, melted at 74.2–74.8°.

Anal.[6] Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.53; H, 6.80.

Phenyl Isobutyrate.—A solution of 94 g. (1 mole) of phenol in 240 ml. of pyridine was acylated by means of 128 g. (1.2 moles) of isobutyryl chloride essentially as described above. After reaction was complete, the mixture was diluted with water and ether to produce two clear phases. The aqueous phase was extracted with ether and the combined ether phases were dried over anhydrous sodium sulfate followed by "Drierite." After removal of the solvent at atmospheric pressure, the residue was distilled through an eight-inch Vigreux column. Fractions boiling at 60–110° (55 g.) and 110–112° (131 g.) were obtained. The lower boiling fraction was distilled up to 105° at 25 mm. and the residue combined with the fraction boiling at 110–112°. Distillation of the mixture gave 4 g. of a fore-run, b. p. 105–111° at 25.5 mm., and 144 g. (87%) of phenyl isobutyrate, b. p. 111–112.2° at 25.5 mm. A mid-fraction (b. p. 112° at 25.5 mm., const.) was analyzed.

Anal.[6] Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.84; H, 7.32.

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(6) Analysis by T. S. Ma, University of Chicago, Chicago, Illinois.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA

RECEIVED DECEMBER 6, 1943

The Preparation of 1- and 2-Phenylpyrrole

BY F. F. BLICKE AND J. L. POWERS

Recently we have been able to synthesize relatively large quantities of 1- and 2-phenylpyrrole by means of the procedures reported below.[1]

The apparatus used for the preparation of 1-phenylpyrrole consisted of two round, cast-iron shells with flanges which were clamped together by means of eight short bolts fitted with wing nuts (only two bolts are shown in the drawing); several "cranite" asbestos gaskets placed between the shells prevented leakage.[2] Each of the shells was sixteen inches in diameter and three inches high at the point at which the pipe was attached. Two iron pipes, one inch in diameter, were screwed into the shells as shown in the diagram. The upper, outlet pipe was attached by rubber tubing to a Pyrex glass tube (combustion type) about six feet long which served as a condenser. At the beginning of the process it was found necessary to cool the condenser with wet cloths, but during the end of the operation it was essential, in some instances, to warm the glass tube with a flame to prevent the condensed material from clogging the tube.

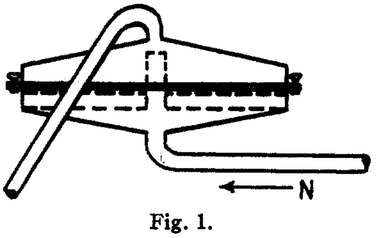

Fig. 1.

The mucic acid salt was placed in a shallow galvanized iron tray. A short, metal tube had been inserted through the center of the tray in order that a stream of nitrogen could be passed through the apparatus.

The apparatus was supported on a tripod, and heated from below with eight Meker burners. Since it was found that rubber tubing attached to the burners melted in a short time, due to the intense heat, it was necessary to unscrew the side arms from the burners and replace them with threaded iron pipes about eighteen inches long.

The upper shell of the apparatus was covered with several removable layers of heavy asbestos, and the whole apparatus was surrounded with a large sheet of the same material.

1-Phenylpyrrole.—In order to prepare the required aniline salt of mucic acid, an intimate mixture of 1116 g. of aniline and 1260 g. of mucic acid was placed in a large evaporating dish, 60 cc. of water added, and the mixture stirred and heated on a steam-bath until it became solid. The material was then pulverized and air-dried.

The salt (396 g.) was placed in the apparatus and the distillate was collected in a 2-liter, round-bottomed flask which contained 110 cc. of concd. hydrochloric acid and 400 cc. of water. The aniline dissolved and the insoluble pyrrole was obtained as a brown, crystalline material. After one-half hour the reaction was complete. The crude material was subjected to steam distillation. The phenylpyrrole separated in the distillate in the form of colorless crystals while a tarry residue remained in the distillation flask. The average yield was 60 g. (42%). The product melted at 58°,[3] and boiled at 230–234°.

2-Phenylpyrrole.—A five-foot length of Pyrex combustion tubing was bent, twenty inches from one end, at a 75° angle, and placed in a combustion furnace. To facilitate the flow of the product through the tube, one end of the furnace was raised about two inches above the level of the laboratory table. Fifty grams of 1-phenylpyrrole were put into a 125-cc. distillation flask in which the usual side arm had been replaced by another 10 cm. long and 9 mm. in thickness, sealed close to the bulb and fitted to the tube by a cork. The tube was heated to a dull red heat, and the pyrrole was distilled through the tube at such a rate that about thirty minutes were required to empty the distillation flask. Since the rearrangement was not complete, the product was distilled through the hot tube two more times.

The material was fractionated, and the recovered 1-phenylpyrrole was subjected to the rearrangement process. From 200 g. of 1-phenylpyrrole there was produced 127 g. (63%) of 2-phenylpyrrole; b. p. 272–278°.[4] A completely colorless product could be obtained only by distillation under reduced pressure; b. p. 151–154° (5 mm.).

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(1) Other methods described during the last few years are those of Allen, Gilbert and Young (*J. Org. Chem.*, **2**, 230 (1937)) and of Adkins and Coonradt (THIS JOURNAL, **63**, 1566 (1941)).

(2) When new gaskets are used, the bolts must be tightened again after the apparatus has become hot.

(3) Köttnitz (*J. prakt. Chem.*, [2] **6**, 148 (1873)) found 62°.

(4) Pictet and Crépieux (*Ber.*, **28**, 1905 (1895)) found 271–272°.

But even this material soon turned pink when exposed to air. However, after several recrystallizations of the vacuum-distilled product from 70% alcohol the pyrrole was obtained in a form which remained colorless; m. p. 128–129°.[5]

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[5] The melting point has been reported to be 129° (ref. 4).

COLLEGE OF PHARMACY
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RECEIVED SEPTEMBER 30, 1943

Reactions of *t*-Butyl Cinnamate and *t*-Butyl Benzoate with Phenylmagnesium Bromide[1]

BY FRED FROSTICK, ERWIN BAUMGARTEN AND CHARLES R. HAUSER

Kohler and Heritage[2] showed that methyl cinnamate undergoes both 1,2- and 1,4-addition with phenylmagnesium bromide yielding a mixture of products. We have found that *t*-butyl cinnamate (in which the carbonyl group is relatively hindered) undergoes apparently only 1,4-addition yielding *t*-butyl β,β-diphenylpropionate.

$$C_6H_5CH{=}CHCOOC(CH_3)_3 \xrightarrow{C_6H_5MgBr} (C_6H_5)_2CHCH_2COOC(CH_3)_3$$

To a stirred solution of phenylmagnesium bromide, prepared from 5.6 g. (0.23 mole) of magnesium and 46.1 g. (0.23 mole) of bromobenzene in 100 ml. of dry ether, was added during twenty minutes 23.5 g. (0.115 mole) of *t*-butyl cinnamate.[3] The reaction mixture refluxed gently and a precipitate formed. After refluxing for three hours, the mixture was poured into an ice-cold saturated ammonium chloride solution. The ether layer was shaken with cold 10% sulfuric acid, and then with cold 5% potassium hydroxide solution. After drying with anhydrous sodium sulfate followed by "Drierite," the solvent was distilled, finally using the water aspirator. The solid residue (29.5 g.) was recrystallized from petroleum ether (b. p. 30–60°), yielding 15 g. (44%) of essentially pure *t*-butyl β,β-diphenylpropionate. Four recrystallizations yielded a product melting at 55.5–55.6°.

Anal.[4] Calcd. for $C_{19}H_{22}O_2$: C, 80.85; H, 7.86. Found: C, 80.93; H, 7.60.

The product was further identified by hydrolysis in the presence of concentrated hydrochloric acid to β,β-diphenylpropionic acid, which, after recrystallization from acetone–water mixture, melted at 152–154° (reported, 155°).[5]

Analogous to methyl or ethyl benzoate, *t*-butyl benzoate has been found to undergo the "normal" carbonyl addition reaction with phenylmagnesium bromide, yielding triphenylcarbinol. Some benzoic acid (which might have resulted from hydrolysis of the ester) was also isolated. Neither isobutene nor *t*-butylbenzene was found; these products would have resulted had the elimination or substitution reaction occurred.

To a stirred solution of phenylmagnesium bromide (prepared from 0.5 mole each of magnesium and bromobenzene in 150 ml. of ether), contained in a reaction flask equipped with a U-tube immersed in a dry ice-bath, was added during one-half hour 0.3 mole of *t*-butyl benzoate[6] in 100 ml. of ether. After standing overnight the reaction mixture was refluxed for five hours. The liquid condensed in the U-tube did not absorb an appreciable amount of bromine in carbon tetrachloride solution, indicating that no significant amount of isobutene was formed. After decomposition of the reaction mixture with ammonium chloride, the ether solution was shaken with bicarbonate (from which was isolated a 10% yield of benzoic acid), dried and the solvent distilled. The residue was subjected to steam distillation until oily material (containing diphenyl but apparently no *t*-butylbenzene) ceased to pass over, and then recrystallized from alcohol, yielding triphenylcarbinol (41%), m. p. 159–162°.

In a similar experiment, carried out with *t*-butyl benzoate and methylmagnesium iodide, no isobutene appeared to be formed.

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[1] This work was supported by a grant from the Duke University Research Council.

[2] Kohler and Heritage, *Am. Chem. J.*, **33**, 21 (1905); see also Allen and Blatt in "Organic Chemistry," Gilman, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 681.

[3] Abramovitch, Shivers, Hudson and Hauser, THIS JOURNAL, **65**, 986 (1943).

[4] Analysis by T. S. Ma, University of Chicago, Chicago, Illinois.

[5] Bacon, *Am. Chem. J.*, **33**, 84 (1905).

[6] Norris and Rigby, THIS JOURNAL, **54**, 2097 (1932).

DEPARTMENT OF CHEMISTRY
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RECEIVED DECEMBER 6, 1943

Nature of Carotenes in Alfalfa

BY A. R. KEMMERER AND G. S. FRAPS

According to Beadle and Zscheile,[1] spinach and some other plants contain appreciable amounts of "neo-β-carotene," stereoisomer of β-carotene, which can be produced by heating β-carotene in petroleum ether. This pigment is the same as that termed pseudo-α-carotene by Gillam and El Ridi,[2] and neo-β-carotene B, by Polgár and Zechmeister.[3] Kemmerer and Fraps,[4] by chromatographic analysis with calcium hydroxide, found, besides β-carotene and this "neo-β-carotene" in plants, another pigment which they termed "carotenoid X." "Carotenoid X" did not possess vitamin A potency, while "neo-β-carotene" had one-half the potency of β-carotene. Polgár and Zechmeister,[4] by various treatments of β-carotene, secured about twelve neo-β-carotenes including neo-β-carotenes B and U. Since the identification of the carotenes in plants is of both practical and scientific importance, both the "neo-β-carotene" and "carotenoid X" in alfalfa were studied.

Neo-β-carotene B was prepared by refluxing a solution of 20 mg. of crystalline carotene in 100 ml. of hexane for one hour.[4] The solution was chromatographed on calcium hydroxide and the neo-β-carotene B was separated and extracted. Then it was purified by another chromatographic treatment. This pigment is just below the β-carotene band in the chromatogram. Neo-β-carotene U was prepared by dissolving about 10 mg. of crystalline carotene in petroleum naphtha (Skellysolve F), adding a small crystal of iodine, and allowing the solution to stand an hour.[4] The neo-β-carotene U was separated and purified by absorption on calcium hydroxide. The neo-β-carotene U is just above the β-carotene in the chromatogram.

"Carotenoid X" and "neo-β-carotene" were prepared from alfalfa leaf meal by extraction with alcholic potassium hydroxide and petroleum naphtha (Skellysolve F) and chromatographic separation on calcium hydroxide.[3]

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[1] B. W. Beadle and F. P. Zscheile, *J. Biol. Chem.*, **144**, 21 (1942).

[2] A. E. Gillam and M. S. El Ridi, *Biochem. J.*, **30**, 1735 (1936).

[3] A. Polgár and L. Zechmeister, THIS JOURNAL, **64**, 1856 (1942).

[4] A. R. Kemmerer and G. S. Fraps, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 714 (1943).