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).

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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).

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Nature of Carotenes in Alfalfa

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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).