

so far to exclude oxygen. Moreover, the precipitate contains as much as ten equivalents of chloride per equivalent of basic magnesium, which is much greater than the 5:1 ratio expected from the formula $\text{ROMgCl} \cdot 2\text{MgCl}_2$. Evidently, the effect of some Grignard solutions on the solubility of magnesium chloride is much less than others and magnesium chloride precipitates in addition to that brought down by the oxidized reagent.

Obviously this problem requires further study. It will be necessary to devise a technique for the preparation and sampling of the Grignard solutions entirely in the absence of oxygen. Moreover, the sampling will have to be done over a period of several years to ensure equilibrium conditions. We hope to initiate such experiments in the near future.

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Preparation of Phenylpropionic Acid

BY MARIE REIMER

Preparation of phenylpropionic acid can be facilitated by a simple improvement in the preparation of cinnamic acid dibromide. The fact that the usual procedure for addition of bromine to the ethylenic linkage, using ice-cold solvents, is discouragingly slow in the case of cinnamic acid has led to the bromination of cinnamic ester.¹ The preparation of the ester can be eliminated, however, and a good grade of commercial cinnamic acid brominated quickly and in excellent yield by use of boiling carbon tetrachloride as solvent. A typical reaction is as follows: 74 g. (0.5 mole) of cinnamic acid and 500 ml. of carbon tetrachloride were placed in a three-necked flask fitted with an efficient stirrer, a reflux condenser and a separatory funnel. The mixture was heated to boiling, the stirrer started and the addition of 79.9 g. (0.5 mole) of bromine in 50 ml. of carbon tetrachloride begun. The color disappeared slowly at first, then so rapidly that all the bromine could be added in the course of forty-five minutes. Heating and stirring were carried on for an additional fifteen minutes and the stirring continued while the mixture cooled. The product, which began to separate from the solution when about two-thirds of the bromine had been added, consisted of fine colorless, shining needles, softening at 195° and melting with decomposition at 199–

(1) *Org. Syntheses*, **12**, 36 (1932).

200°. This is sufficiently pure for subsequent use. The yield was 147 g. (95%) with an additional 2 g. of less pure material obtained by distilling the filtrate to 50-ml. volume. Repeated crystallization of the cinnamic acid dibromide from carbon tetrachloride did not improve the melting point appreciably, but after one crystallization from chloroform the compound separated in brilliantly shining needles, melting at 200–202°.

For obtaining phenylpropionic acid in small amounts, a less elaborate procedure can be used than that recommended² for its preparation in larger quantity from the ester of cinnamic acid dibromide. Twenty-five grams of cinnamic acid dibromide was placed in an evaporating dish, 100 ml. of a 25% solution of potassium hydroxide in methanol added, and the mixture stirred over rapidly boiling water until nearly all the alcohol had evaporated. To the thick, pasty residue, 75 ml. of methanol was added and the procedure repeated to ensure complete reaction. The pale yellow granular product was cooled, subjected to strong suction to rid it of a small amount of residual liquid, washed with a few milliliters of chilled methanol and dissolved in 500 ml. of ice-water. To the solution, iced hydrochloric acid was added to faint acidity. As phenylpropionic acid separates as an oil, the mixture was then seeded and the hydrochloric acid added slowly with vigorous stirring until the mixture was strongly acid. To make sure that all the oil had solidified, the mixture was left standing overnight in the ice-chest. The acid which had separated in 80% yield was pure white and melted at 128–136°. There was but slight loss on recrystallization from boiling carbon tetrachloride from which the acid separates in long, shining needles, melting at 136–138°.

(2) *Ibid.*, **12**, 60 (1932).

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Formation of Pro-carotenoids in "Monkey Flowers" under Some Conditions

BY W. A. SCHROEDER

An unpublished investigation, which has been carried out in these laboratories during the past year, has shown that the flowers of *Mimulus longiflorus* Grant (*Scrophulariaceae*), commonly termed "monkey flowers," contain no representative of the class of pro-carotenoids which possess