$(C_8H_8)_{17}OH$: C, 87.75; H, 7.31; Br, 4.11. Found: C, 87.77; H, 7.24; Br, 4.2.[6]

Since no polystyrene was formed in a parallel experiment in which the diazonium salt was omitted, it appears that the p-bromophenyl radicals from the decomposition of p-bromobenzenediazonium hydroxide are capable of initiating the polymerization of styrene and are thereby incorporated in the polymer.

(6) This analysis was carried out by wet oxidation with silver and potassium dichromate in sulfuric acid. The halogen was absorbed in alkaline hydrogen peroxide according to Zacherl and Krainick (*Mikrochemie*, **11**, 61 (1932)) but analysis by titration of excess alkali was entirely unsatisfactory, evidently due to volatilization of organic acids. Volhard titration for bromide ion in the alkaline peroxide, however, proved very convenient and accurate.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS   RECEIVED AUGUST 10, 1942

The Composition of Alkylmagnesium Chloride Solutions in Ethyl Ether

BY C. R. NOLLER AND A. J. CASTRO

In previous work on the composition of n-butylmagnesium chloride solutions in ethyl ether,[1] it was thought that the values obtained were true equilibrium values expressing the relation between the amounts of n-butylmagnesium chloride, di-n-butylmagnesium and magnesium chloride as etherates in ether solution. On attempting to repeat, refine and extend this work, we have found that other factors seem to be involved. For example, in the original experiments it appeared that equilibrium was reached after fifty to one hundred and fifty hours. In the new series of experiments, at least in the higher concentrations, much less magnesium chloride had precipitated after seventy days than had been precipitated after 150 hours in the first series and did not reach the latter value until after 300 days. The only difference in procedure of which we are aware is that in the second series the solutions were kept in sealed glass tubes whereas in the first series the tubes were closed by stopcocks. It is possible, too, that in the second series somewhat more care may have been given to avoiding contact with air.

That exposure to air may be the cause of the discrepancy was indicated by a third series in which extreme care was taken to avoid contact with air by preparing the reagent and carrying out all transfers in an atmosphere of purified nitrogen. After 160 days practically no magnesium chloride had precipitated. In fact the chloride concentra-

(1) Noller and Raney, THIS JOURNAL, **62**, 1749 (1940).

tion of the solution was still greater than the alkylmagnesium concentration, a condition which had never been observed previously even in freshly prepared solutions of Grignard reagent. If no magnesium chloride precipitates, one should, of course, have an excess of chloride over alkylmagnesium because of side reactions which do not result in the formation of Grignard reagent. Similar but even more marked results were obtained with Grignard solutions from tertiary butyl chloride which after 150 days contained over 2.5 equivalents of chloride for each two equivalents of alkylmagnesium.

When increasing amounts of oxygen reacted with a 0.5 N solution of n-butylmagnesium chloride, the ratio of halogen to basic magnesium in the precipitate was about three to one for one-fourth oxidation, about one to one for the next fourth while complete oxidation caused removal of all of the halogen from the solution and all but a trace of basic magnesium. This indicates that if ROMgCl is the product of oxidation, it is capable of bringing down with it additional magnesium chloride, presumably by using the unshared electrons of the oxygen atom to form a complex with magnesium chloride much in the same way as dioxane forms an insoluble complex or as ether forms a soluble complex. If this is the case one might expect the precipitate to have ultimately the composition $ROMgCl \cdot 2MgCl_2$ in which the ratio of chloride to basic magnesium would be 5:1. To explain the behavior of the Grignard solutions on standing one might assume that, in the absence of oxygen, magnesium chloride is soluble in the Grignard solution either because the reagent is entirely in the form RMgCl or because the Grignard solution is a much better solvent for magnesium chloride than pure ether.[2] If oxygen is present, ROMgX, which itself is relatively insoluble, would be precipitated fairly rapidly, carrying down some magnesium chloride with it. This precipitate would then slowly go over to the still less soluble $ROMgCl \cdot 2MgCl_2$, causing slow precipitation of more magnesium chloride.

This picture, however, is incomplete because in the case of Grignard solutions from benzyl chloride, magnesium chloride precipitates fairly rapidly in spite of all precautions we have taken

(2) At present the latter seems to be the better explanation since we have obtained Grignard solutions from tertiary butyl chloride which contained as much as 0.3 mole of magnesium chloride per 1000 g. of solution above the 1:1 ratio while the solubility of magnesium chloride etherate in pure ether is of the order of 0.001 mole.

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 $ROMgCl \cdot 2MgCl_2$. 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.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIV., CALIF.   RECEIVED JULY 6, 1942

Preparation of Phenylpropiolic Acid

BY MARIE REIMER

Preparation of phenylpropiolic 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 phenylpropiolic acid in small amounts, a less elaborate procedure can be used than that recommended[2] 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 phenylpropiolic 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).

DEPARTMENT OF CHEMISTRY
BARNARD COLLEGE
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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