

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.

DEPARTMENT OF CHEMISTRY  
STANFORD UNIVERSITY  
STANFORD UNIV., CALIF.

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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.<sup>1</sup> 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 recommended<sup>2</sup> 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).

DEPARTMENT OF CHEMISTRY  
BARNARD COLLEGE  
NEW YORK, N. Y.

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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

a partially *cis*-configuration.<sup>1</sup> This statement refers to flowers which have developed fully under natural conditions on the intact plant. In recent experiments it was found, however, that, if stems with buds were placed in water for several days and exposed only to diffuse light in the laboratory at room temperature, the flowers were noticeably different in tint and paler in color than flowers which developed on the intact plant in the open. Parallel chromatograms of extracts of the two materials established the fact that under these two sets of conditions, the polyene pigment mixtures differed both qualitatively and quantitatively with respect to the components found. The paler flowers contained a greater number of lycopene stereoisomers than the controls. The chromatogram of the paler flowers included considerable quantities of polycopene, C<sub>40</sub>H<sub>56</sub>, and pro- $\gamma$ -carotene, C<sub>40</sub>H<sub>56</sub>. The spectral maxima of these pigment fractions in petroleum ether (b. p. 60–70°) were 467, 440 m $\mu$  and 461, 431 m $\mu$ , respectively. Upon addition of iodine to the solutions, the bands showed the characteristic shift to 500.5, 469.5, 440 m $\mu$  and 494, 461 m $\mu$ . Both pro-carotenoids have been identified by mixed chromatograms with samples from other sources.

In the light of the above observation, it is possible that polycopene and pro- $\gamma$ -carotene are precursors of lycopene and  $\gamma$ -carotene in the biosynthesis of the *Mimulus* pigment.

(1) L. Zechmeister, A. L. LeRosen, F. W. Went and L. Pauling, *Proc. Nat. Acad. Sci.*, **27**, 468 (1941); A. L. LeRosen and L. Zechmeister, *This Journal*, **64**, 1075 (1942); L. Zechmeister and W. A. Schroeder, *ibid.*, p. 1173.

GATES AND CRELLIN LABORATORIES OF CHEMISTRY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
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### Some Physical Constants of N-Octyl-, N-Dodecyl- and N-Cetyl-piperidine

By F. H. STROSS AND R. J. EVANS

There exists little available information on the physical properties of the higher N-alkyl-piperidines. When, in the course of an investigation, it became necessary to prepare N-cetyl-piperidine, only two references<sup>1,2</sup> were found which mentioned this compound. Its ionization constant was found to be surprisingly low in comparison with the known constants of the lower homologs,

(1) P. Karrer, F. W. Kahnt, R. Epstein, W. Jaffe and T. Ishii, *Helv. Chim. Acta*, **21**, 233 (1938).

(2) H. W. Magnusson and E. R. Schierz, *Univ. of Wyoming, Publications VII*, 1–11 (1940).

and, therefore, the N-dodecyl- and N-octyl-piperidines were also prepared and their characteristic properties measured. The results are given in Table I.

TABLE I  
PHYSICAL CONSTANTS OF N-OCTYL, N-DODECYL AND N-CETYL PIPERIDINES

Piperidines	N-Octyl	N-Dodecyl	N-Cetyl
M. p., °C.	..	..	21
B. p. { °C.	89 112 122	141 161	176–177
{ Mm.	1 6 10	1 5	1
$d_{20}^{20}$	0.8324	0.8378	0.8468
$n_D^{20}$	1.4544	1.4588	1.4620
N, % { Calcd.	7.1	5.5	4.5
{ Found	6.9 7.0	5.5	4.4
Mol. wt. { Calcd.	197.4	253.5	309.6
{ Found	197	253	304
$pK_H$ at 27°C.	8.28	5.92	5.8

While the N-cetyl and N-dodecyl compounds are weak bases of a strength close to that of pyridine, N-octylpiperidine occupies a position intermediate between the higher homologs and the N-methyl- to butylpiperidines. The latter are almost as strong bases as the unsubstituted piperidine, which has a  $pK_H$  of 11.1 at 25°.

The bases were prepared by the method described by Magnusson and Schierz.<sup>2</sup> Aqueous piperidine was refluxed with a slight excess of the alkyl iodide, while an excess of potassium hydroxide was gradually added. The upper of the two layers formed during refluxing was fractionally distilled over solid potassium hydroxide at 2 mm. pressure, yielding a clear distillate. The cetyl-piperidine was yellow, the dodecyl compound had a slight yellow tinge, and the octyl-piperidine was colorless. The analyses were made and the constants determined after redistilling these products.

SHELL DEVELOPMENT CO.  
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### Empirical Heat Capacity Equations of Gases

By HUGH M. SPENCER AND GORDON N. FLANNAGAN

Since the publication of empirical heat capacity equations of simple gases,<sup>1</sup> values of thermodynamic functions for many gases have been derived from spectroscopic data.<sup>2</sup> In the case of

(1) Hugh M. Spencer and John L. Justice, *This Journal*, **56**, 2311 (1934). The heat capacities of bromine and equilibrium chlorine are better represented by equations of form (2). The constants  $a$ ,  $b \times 10^3$ ,  $c' \times 10^{-5}$ , maximum and average percentage deviations are 8.911, 0.140, -0.0298, 0.09, 0.02 and 8.764, 0.271, -0.656, 0.24 and -0.11, respectively.

(2) E. B. Wilson, Jr., *Chem. Rev.*, **27**, 17 (1940).