plied to evaporate the liquid, the throttle valve was controlled to remove the vapor isothermally. A nickel resistance thermometer, wound on the tube between the calorimeter and the valve, served to sense the temperature of the vapor as it was removed. The shield temperature was controlled manually.

The International Temperature Scale[5] was used. The temperature in degrees Kelvin was obtained from the relation °K. = 273.16° + °C.

Material.—The highly purified chlorotrifluoroethylene sample, inhibited with terpene-B hydrocarbon, was received from E. I. du Pont de Nemours and Company. The material was degassed by slow freezing and pumping, and about 90% was distilled into the calorimeter. Most of the inhibitor remained behind. The liquid-soluble solid-insoluble impurities in the sample transferred into the calorimeter were found from the equilibrium melting curve[6] to be 0.08 mole per cent.

Results.—The heat of vaporization measurements were made at the normal boiling point, 244.80°K., reported by Oliver, *et al.*[2] The experimentally observed quantity, γ, the energy input per unit mass of sample collected,[7] is related to the heat of vaporization l by the expression

$$l = \gamma - \beta$$

where

$$\beta = Tv(dp/dT)$$

In the quantity β, v is the specific volume of the liquid, T the absolute temperature and p the vapor pressure. The results of the measurements and the subsequent computations are summarized in Table I.

TABLE I

HEAT OF VAPORIZATION OF CHLOROTRIFLUOROETHYLENE AT 244.80°K.

C_2F_3Cl mol. wt. = 116.477; 1 cal. = 4.1840 abs. j.

γ, abs. j. g.$^{-1}$	β, abs. j. g.$^{-1}$	l, abs. j. g.$^{-1}$	L, abs.j.mole^{-1}
180.16	0.74	179.42	20898
179.89	.74	179.15	20867
179.96	.74	179.22	20875
179.97	.74	179.23	20876
		Mean	20879
		Standard deviation of the mean	±6

The quantity β was evaluated using the density of chlorotrifluoroethylene as given by E. I. du Pont de Nemours and Company[8] and the vapor pressure reported by Oliver, *et al.*[2] In terms of the thermochemical calorie (1 cal. = 4.1840 abs. j.), the heat of vaporization becomes 4990 cal. mole^{-1}. Considering the precision (Table I) and the various possible sources of error, the total uncertainty in the value given is believed to be ±4 cal. mole^{-1}. The value (4965 cal. mole^{-1}) calculated by Oliver, *et al.*,[2] is in fairly good agreement with the experimental value obtained.

Combining this experimental value for the heat of vaporization with the low temperature heat capacity work of Oliver, *et al.*,[2] the entropy of chlorotrifluoroethylene in the ideal gaseous state at 244.80°K. and 1 atm. becomes 73.28 ± 0.10 cal. deg.$^{-1}$ mole^{-1}. The uncertainty of the entropy was obtained by statistically combining the uncertainty (±0.10 cal. deg.$^{-1}$ mole^{-1}) assigned by Oliver, *et al.*,[2] to their value of entropy (52.74 cal. deg.$^{-1}$ mole^{-1}) for the liquid chlorotrifluoroethylene at 244.80°K., and the uncertainty (±0.02 cal. deg.$^{-1}$ mole^{-1}) assigned for the entropy of vaporization (20.38 cal. deg.$^{-1}$ mole^{-1}) in this work. The correction (+0.16 cal. deg.$^{-1}$ mole^{-1}) for gas imperfection was computed on assumption that the gas can be represented by a Berthelot equation of state, and the uncertainty of this correction is considered to be negligible.

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The Conversion of Codeinone to Codeine

BY MARSHALL GATES

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No satisfactory method for the potentially important reduction of codeinone to codeine has yet been described,[1] primarily because of the ease with which the oxide ring is opened by the usual methods, both chemical and catalytic. We have found that this reduction can be effected easily and nearly quantitatively by means of sodium borohydride.[2]

We are indebted to Merck and Co., Inc., for generous gifts of thebaine and codeine.

Experimental[3]

Codeine from Codeinone.—A solution of 194 mg. of codeinone, m.p. 185–187°, in 10 cc. of methanol was treated with 0.5 g. of sodium borohydride which had just been suspended in 12 cc. of methanol. The mixture was allowed to stand for 1.5 hours, concentrated to about half the original volume and diluted with 10 cc. of 10% sodium hydroxide. The clear colorless solution was heated momentarily to boiling, diluted with water and extracted four times with chloroform. The washed, dried and filtered chloroform extract on concentration left 196 mg. of codeine as a colorless glass which crystallized readily on scratching, m.p. 153–157°. Recrystallization from quite dilute methanol gave 173 mg. (83.4%) of pure codeine hydrate, m.p. 157–158.5°, $[\alpha]^{25}D$ −136° (*c* 2.80, alc.), whose mixed m.p. with authentic codeine hydrate was undepressed.

Its **hydrobromide**, colorless needles from water, melted at 151–160° with effervescence, resolidified and remelted with extensive decomposition at 273–278°,[4] as did both the hydrobromide of authentic codeine and a mixture of the two.

Anal. Calcd. for $C_{18}H_{21}NO_3 \cdot HBr \cdot 2H_2O$: C, 51.93; H,

(1) C. Schöpf and H. Hirsch, *Ann.*, **489**, 242 (1931), have reported this transformation in poor yield by the action of stannous chloride and hydrochloric acid. For further comments on this reduction see S. P. Findlay and L. F. Small, THIS JOURNAL, **72**, 3247 (1950).

(2) The stereospecificity of this reduction seems worthy of comment. In the two cases described in the experimental section, this stereospecificity was complete. However, with both *cis*- and *trans*-dihydrothebainone (oxide ring open) both sodium borohydride and lithium aluminum hydride give mixtures of the epimeric C_6 alcohols.

(3) All melting points are corrected.

(4) Dott, *Pharm. J. Trans.*, [3] **14**, 917, 973 (1884), has reported the m.p. of codeine hydrobromide dihydrate as 190–192°. It has been prepared by us a number of times from several different samples of codeine and has always exhibited the behavior described above.

6.30; Br, 19.20; H_2O, 8.65. Found: C, 52.07; H, 6.24; Br, 18.82, 19.64; H_2O, 8.83.

1-Bromocodeine from 1-Bromocodeinone.—Under similar conditions, 101 mg. of 1-bromocodeinone[5] yielded 101 mg. of crude 1-bromocodeine, m.p. 158–160.5°, which on crystallization from ethyl acetate gave 72 mg. (71%) of pure 1-bromocodeine, m.p. 161–163°, whose mixed m.p. with authentic 1-bromocodeine[6] was undepressed.

Its **methiodide** melted at 262.5–264°[7] with decomposition, and did not depress the melting point of the methiodide obtained from authentic 1-bromocodeine.

Anal. Calcd. for $C_{19}H_{23}NO_3BrI$: C, 43.86; H, 4.46. Found: C, 43.89; H, 4.43.

(5) M. Gates and G. Tschudi, THIS JOURNAL, **74**, 1109 (1952).

(6) E. Speyer and H. Rosenfeld, *Ber.*, **58**, 1110 (1925).

(7) E. Vongerichten, *Ann.*, **297**, 204 (1897), has reported the melting point of this methiodide to be 242–244°.

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4-Alkyldiphenylketimine Hydrochlorides and Related Ketones

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RECEIVED MAY 19, 1953

In connection with another investigation which has since been discontinued, the ultraviolet absorption spectra of a series of 4-alkyldiphenylketimine hydrochlorides and the related ketones were determined. Of the compounds examined, four appear to be new. Ketimines were prepared by the method adopted by Pickard and Vaughan.[1] The hydrochlorides were precipitated from ethereal solution with dry hydrogen chloride, repeatedly recrystallized from chloroform solution and washed well with ether. Of the alkyl-substituted benzophenones, the methyl compound was prepared by the Friedel–Crafts reaction and the others were obtained by hydrolysis of the ketime hydrochlorides with 6 *N* hydrochloric acid. Spectral data were obtained with a Hilger "Uvispek" spectrophotometer and the range covered was 2100–3200 Å. Approximately 1×10^{-4} *M* solutions in methanol were used for all compounds. Absorption curves of the alkylated compounds have the simple shape shown by the parent bodies (*e.g.*, see Culbertson[2]).

TABLE I

	Ketone			Ketimine hydrochloride		
4-Substituent	M.p. or b.p., °C.	$\lambda_{max.}$ (Å.)	$\epsilon_{max.} \times 10^{-4}$	M.p.,[a] °C.	$\lambda_{max.}$ (Å.)	$\epsilon_{max.} \times 10^{-4}$
H	M. 48	2520	1.750	310	2755	1.665
Methyl	M. 58	2590	1.745	244	2855	1.570
Ethyl	B. 318–320	2535	1.555	264[b]	2820	1.660
Isopropyl	B. 338–340 (774 mm.)	2570	1.660	260[c]	2875	1.715
t-Butyl[d]	B. 198 (13 mm.)	2585	1.755	280–282[e]	2875	1.680

[a] Visible sublimation occurred to a greater or less extent with each salt, beginning 20–30° below recorded m.p. [b] *Anal.* Calcd. for $C_{15}H_{16}NCl$: N, 5.71; Cl, 14.47. Found: N, 5.58; Cl, 14.30. [c] Calcd. for $C_{16}H_{18}NCl$: N, 5.40; Cl, 13.66. Found: N, 5.44; Cl, 13.55. [d] Calcd. for $C_{17}H_{18}O$: C, 85.70; H, 7.56. Found: C, 85.86; H, 7.86; n^{19} 1.5762. [e] Calcd. for $C_{17}H_{20}NCl$: N, 5.13; Cl, 12.96. Found: N, 5.15; Cl, 12.88.

Analysis of the 4-*t*-butylbenzophenone was carried out by Dr. A. D. Campbell of Otago University.

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(1) P. L. Pickard and D. J. Vaughan, THIS JOURNAL, **72**, 876 (1950).

(2) J. B. Culbertson, *ibid.*, **73**, 4818 (1951).

Pipecolic Acid in *Phaseolus vulgaris:* Evidence on its Derivation from Lysine

BY N. GROBBELAAR[1] AND F. C. STEWARD

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After the discovery of pipecolic acid as a prominent constituent of the green bean (*Phaseolus vulgaris*) and of other plants, the question of its origin and metabolic relationships arises. Advantage has been taken of the availability of lysine containing radioactive carbon to test the possibility that it may arise from, or be interconvertible with, lysine by a process of ring closure and loss of ammonia. The lysine used in this experiment was prepared synthetically by Dr. R. W. Helmkamp of the University of Rochester and was made available to us through the courtesy of Dr. Leon Miller, also of the University of Rochester.

The lysine was labelled in the ϵ-position and was made available to us dissolved in dilute salt solution. The specific activity of the lysine was 0.85 microcurie per milligram and 10 mg. of L-lysine was dissolved in 0.65 ml. of 0.9% sodium chloride solution.

The plants selected for the experiments were grown in pots and had fruits approximately 10 cm. in length. The morphology of the specimen selected for the first experiment is shown in Fig. 1. It will be noted that there were two developing fruits in the axil of the same leaf which was removed (X in Fig. 1). The main branch bearing the fruits was also decapitated (Y in Fig. 1). The method was to inject with a hypodermic needle, 0.25 ml. of the autoclaved lysine solution into the cavities surrounding the two lower ovules of fruit A (Fig. 1).

After the elapse of an appropriate period (55 hours) the tissue of the injected fruit was dissected and sampled and also the tissue of the adjacent fruit in the same leaf axil (B in Fig. 1).

In sampling the material for analysis, the ovules and carpel walls were treated separately and all the rest of the tissue of the plant examined as a whole. The weights of the organs analyzed are given in Table I.

TABLE I

FRESH WEIGHTS OF TISSUES EXTRACTED

Material	Weight, g.
First Experiment	
Injected fruit	2.468
carpel wall	2.229
ovules	0.239
Uninjected fruit	4.501
carpel wall	3.530
ovules	0.971
Rest of shoot	15.521
Second Experiment	
Stem tissue (F–F)	0.446
Fruit	8.098
carpel wall	5.395
ovules	2.703
Rest of shoot	37.600

(1) Predoctoral Rockefeller Foundation Fellow at Cornell University.