tone. The purified product weighed 59 g. (84% yield) and melted at 180–182°. (The spectrum showed absorption peaks at 5.79 μ (carbonyl group), and 11.62 μ associated with the *trans* configuration.)

*Anal.* Calcd. for $C_4H_2Cl_2O_4$: C, 25.97; H, 1.09; Cl, 38.33; neut. equiv., 92.5. Found: C, 26.06; H, 1.16; Cl, 38.79; neut. equiv., 91.6.

**Dimethyl Dichlorofumarate.**—The dimethyl ester of dichlorofumaric acid was prepared by treating the acid with methanol and sulfuric acid. It boiled at 125° at 20 mm., $n^{20}D$ 1.4820. (The spectrum had absorption peaks at 6.13 μ (conjugated double bond), 7.9 μ (C–O–C), 5.75 μ (carbonyl group), and 11.1 and 11.75 μ (*trans* configuration).)

*Anal.* Calcd. for $C_6H_6O_4Cl_2$: C, 33.83; H, 2.84; Cl, 33.29. Found: C, 34.28; H, 2.93; Cl, 33.31.

**Dimethyl Dichloromaleate.**—Dichloromaleic anhydride was prepared in 7.5% yield by chlorinating maleic anhydride at 180° using $FeCl_3$–$CaCl_2$ catalyst.[4] The yield can be increased by further chlorination of the recovered intermediate chloromaleic anhydride. The dichloromaleic anhydride, after recrystallization from isopropyl ether and from carbon tetrachloride, was treated with methanolic hydrogen chloride. The dimethyl dichloromaleate obtained boiled at 121° at 20 mm., $n^{20}D$ 1.4830, $d^{20}{}_4$ 1.3993, $d^{25}{}_4$ 1.3943. (The spectrum of this ester, like that of the dimethyl dichlorofumarate, showed absorption peaks at 6.13, 7.9 and 5.75 μ. The bands at 11.1 and 11.75 μ were replaced, however, by a strong band at 14.6 μ, associated with the *cis* configuration. Both esters, dichlorofumaronitrile, and dichloromaleic anhydride (but not dichlorofumaric acid) had an unassigned absorption peak varying between 9.8–9.9 μ.)

*Anal.* Calcd. for $C_6H_6O_4Cl_2$: C, 33.83; H, 2.84; Cl, 33.29. Found: C, 33.94; H, 2.88; Cl, 33.42.

**Acknowledgments.**—The authors wish to thank Mr. Harry Vineyard for technical assistance, Mr. C. M. Lovell for determination and interpretation of the infrared spectra, and Mr. Quentin Quick and his staff for the microanalyses.

(4) C. R. Milone, U. S. Patent 2,391,261; F. Johnston and L. W. Newton, private communication.

RESEARCH AND DEVELOPMENT DEPARTMENT
CARBIDE AND CARBON CHEMICALS COMPANY
SOUTH CHARLESTON 3, WEST VIRGINIA

## Long-Chain Alkylurea N-Glycosides[1]

By JOHN G. ERICKSON AND JOAN S. KEPS

Schoorl[2] found that aldose sugars react with urea, methylurea, dimethylurea, phenylurea, benzylurea, thiourea, biuret and urethan. Dilute aqueous sulfuric acid was used to catalyze the reaction. Helferich and Kosche[3] did closely similar work. No one seems to have used any alkylureas higher than methylurea.

We have found that the long-chain alkylureas react with aldohexoses in warm dilute alcoholic hydrochloric acid. The products presumably have structure I. The reactions fail in the absence of acid.

$$RNHCONH_2 + HOCH(CHOH)_3CHCH_2OH \longrightarrow$$
$$\underset{I}{RNHCNHCH(CHOH)_3CHCH_2OH}$$
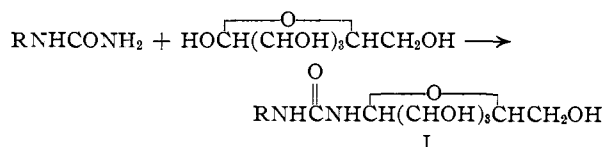
(1) Paper No. 147, Journal Series. General Mills, Inc., Research Dept.

(2) M. N. Schoorl, *Rec. trav. chim.*, **22**, 31 (1903).

(3) S. B. Helferich and W. Kosche, *Ber.*, **59**, 69 (1926).

Ketohexoses do not react, even in the presence of acid. Neither the alkylureas nor the sugars used are very soluble in alcohol and rather long reaction times are therefore necessary.

### Experimental

**Dodecylurea N-Galactoside.**—A mixture of dodecylurea (22.8 g., 0.10 mole), galactose (19.8 g., 0.11 mole), concd. hydrochloric acid (2.5 g.), and 95% ethanol (200 ml.) was stirred and heated at 50° for 100 hours, then cooled and filtered. Washing with water and hot benzene gave 15.6 g. (40%) of white solid, m.p. 165–188° (dec.).

*Anal.* Calcd. for $C_{19}H_{38}N_2O_6$: C, 58.44; H, 9.81; N, 7.18. Found: C, 58.31; H, 9.64; N, 7.05.

**Octadecylurea N-Glucoside.**—A mixture of octadecylurea (6.2 g., 0.02 mole), glucose (4.0 g., 0.022 mole), concd. hydrochloric acid (0.5 g.) and 95% ethanol (100 ml.) was stirred and heated at 50° for 147.5 hours, cooled and filtered. Washing with hot benzene left 1.5 g. (27%), m.p. 175–188° (dec.); m.p., after further washing with water and hot benzene, 181–189° (dec.).

*Anal.* Calcd. for $C_{25}H_{50}N_2O_6$: C, 63.26; H, 10.62; N, 5.90. Found: C, 63.20; H, 10.42; N, 6.16.

CHEMICAL LABORATORIES
GENERAL MILLS, INC.
MINNEAPOLIS, MINN.

## A Note on the Heat of Vaporization of Chlorotrifluoroethylene $(C_2F_3Cl)$[1]

By GEORGE T. FURUKAWA, ROBERT E. McCOSKEY AND MARTIN L. REILLY

Oliver, *et al.*,[2] recently reported the entropy of chlorotrifluoroethylene in the ideal gaseous state at 244.80°K. (normal boiling point) and 1 atm. as 73.18 cal. deg.$^{-1}$ mole$^{-1}$ from the results of their low temperature calorimetric measurements. These workers computed the entropy of vaporization from their vapor pressure data and the Clapeyron equation. In many calculations of this sort large uncertainties arise on account of the inaccuracies in the density data and the derivative of the vapor pressure. In connection with the program at the National Bureau of Standards involving the spectral assignments for a series of compounds related to chlorotrifluoroethylene, it was felt desirable to determine the heat of vaporization of chlorotrifluoroethylene directly to eliminate any uncertainty that may exist in this quantity. As this molecule is considered to be a "key" member of the series, an accurate value for the entropy was especially desirable to verify the spectral assignment.[3] This note deals with the measurement of the heat of vaporization of chlorotrifluoroethylene.

### Experimental

**Apparatus.**—The vaporization experiments were made in an adiabatic calorimeter similar in design to that described by Osborne and Ginnings[4a] and by Aston, *et al.*,[4b] in which a throttle valve is contained within the space enclosed by the adiabatic shield. Briefly, as electrical energy was sup-

(1) This investigation was conducted under research sponsored by the Ordnance Corps, Department of the Army.

(2) G. D. Oliver, J. W. Grisard and C. W. Cunningham, THIS JOURNAL, **73**, 5719 (1951).

(3) D. E. Mann, N. Acquista and E. K. Plyler, *J. Chem. Phys.*, submitted for publication.

(4) (a) N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947); (b) J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, THIS JOURNAL, **73**, 1939 (1951).

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, $\gamma$, 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 $\beta$, $v$ 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.

| $\gamma$, abs. j. g.$^{-1}$ | $\beta$, 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 $\beta$ 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

(5) H. F. Stimson, J. Research Natl. Bur. Standards, 42, 209 (1949).

(6) G. T. Furukawa, D. C. Ginnings, R. E. McCoskey and R. A. Nelson, ibid., 46, 195 (1951).

(7) N. S. Osborne, ibid., 4, 609 (1930).

(8) "Kinetic" Technical Bulletin B-6, E. I. du Pont de Nemours and Company, 1952.

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.

**Acknowledgment.**—The authors are indebted to R. C. Downing and D. E. Kvalnes of E. I. du Pont de Nemours and Company for the highly purified sample.

THERMODYNAMICS SECTION
HEAT AND POWER DIVISION
NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

## The Conversion of Codeinone to Codeine

BY MARSHALL GATES

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-dihydro-thebainone (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.