

Experimental

Reaction of Acetoin and Cyclohexylamine.—Ten grams of crystalline dimer⁵ and 30 g. of anhydrous cyclohexylamine were shaken together in a flask, from which the air was displaced by nitrogen, until the acetoin had dissolved (one hour) and then allowed to stand protected from oxygen for three days. Removal of excess cyclohexylamine *in vacuo* < 30° yielded an almost colorless viscous oil. A solution of the oil in 100 ml. of benzene was exposed to dry oxygen for several minutes and allowed to stand three days during which time 1.5 g. of cyclohexylamine acetate crystallized out. The mother liquor upon dilution with 100 ml. of hexane followed by standing a week deposited an additional 2 g. of faintly colored salt. The salt was recrystallized by solution in 150 parts of boiling benzene followed by slow cooling to yield cyclohexylamine acetate as large colorless needles, m.p. 143.5–145° (dec.).

Anal. Calcd. for C₈H₁₇NO₂: C, 60.34; H, 10.76; N, 8.86. Found: C, 60.5; H, 10.7; N, 8.75.

The identity of the compound as cyclohexylamine acetate was confirmed by microscopic comparison with an authentic sample.

The amber mother liquor was concentrated *in vacuo* to a deeply colored oil, dissolved in 30 ml. of methanol and kept at –20° overnight. Filtration in the cold yielded 9.7 g. (32%) of pink platy crystals. Recrystallization from 30 ml. of methanol at –20° yielded 7 g. (23%) of pure diacetyldicyclohexylamine as large, lustrous, colorless micaceous plates, m.p. 81.5–82.5; ultraviolet absorption in methanol, λ_{max} 213 mμ, log ε 4.075.

Anal. Calcd. for C₁₆H₂₈N₂: C, 77.36; H, 11.36; N, 11.28. Found: C, 77.1; H, 11.3; N, 11.2.

Attempts to improve the yields of oxidation products by bubbling air through hydrocarbon or alcohol solutions of the initial oily condensation product yielded only dark resinous products. On the other hand, neither the cyclohexylamine acetate nor the diimine could be obtained until the oil was exposed to air. Similarly, the reaction of acetoin with aniline under the same conditions yielded the diacetyldianil in small quantities only on exposure to air.

Acid Hydrolysis of Diacetyldicyclohexylamine.—A solution of 710 mg. of diacetyldicyclohexylamine in 100 ml. of 95% ethanol and 15 ml. of 6 N hydrochloric acid was distilled until 100 ml. of distillate was collected. From the distillate, diacetyl bis-2,4-dinitrophenylhydrazone was prepared in the usual manner and recrystallized from nitrobenzene in an 86% yield, identified by microscopic crystallographic comparison with an authentic sample. The distillation residue was converted to the *p*-toluenesulfonamide of cyclohexylamine⁶ in a 78% yield.

The derivative was recrystallized from 20 parts of methanol-water (1:1) as colorless, fibrous needles, m.p. 85.7–86.4°.

Anal. Calcd. for C₁₃H₁₉NSO₂: C, 61.62; H, 7.56; N, 5.53. Found: C, 61.8; H, 7.57; N, 5.54.

Reaction of Glycolaldehyde and Cyclohexylamine.—Crystalline glycolaldehyde dimer (1.4 g.) was shaken with 10 g. of anhydrous cyclohexylamine in the absence of air for eight hours and allowed to stand overnight. Removal of excess amine by vacuum distillation yielded a pasty white solid which was dissolved in hexane and filtered from resinous material. The hexane solution at –20° yielded 1.6 g. (31%) of glyoxaldicyclohexylamine. No crystalline product could be obtained if air was rigidly excluded. Recrystallization from 25 parts of methanol or 15 parts of ethyl acetate yielded the pure glyoxaldicyclohexylamine as colorless lustrous micaceous plates, similar in appearance to the corresponding diacetyl compound, m.p. 149–150° (sl. dec.); ultraviolet absorption in methanol: λ_{max} 217 mμ, log ε 4.340; λ_{max} 267 mμ, log ε 2.532. Hydrolysis of the compound to glyoxal and cyclohexylamine was performed as with the diacetyl derivative.

(5) Low melting crystalline dimer was obtained by inoculation of a commercial sample of liquid monomeric acetoin with a granule of zinc according to the procedure of W. Dirscherl and E. Braun, *Ber.*, **63**, 417 (1930). Similar results were obtained when the higher melting dimeric modification was used.

(6) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Second Ed., 1940, p. 48.

Anal. Calcd. for C₁₄H₂₄N₂: C, 76.36; H, 10.98; N, 12.71. Found: C, 76.4; H, 11.0; N, 12.7.

Reaction of Glyoxal with Cyclohexylamine.—Twelve grams of a 33% aqueous solution of glyoxal was added to a precooled (0°) solution of 20 g. of cyclohexylamine in 200 ml. of ethanol. After standing overnight, the amber solution, containing crystalline material, was cooled to –20° and filtered to yield 10 g. of product. An additional 1.9 g. was obtained from the mother liquor (77% yield). Recrystallization from methanol yielded the pure colorless compound identical with the product obtained with glycolaldehyde. Reaction of glyoxal with *n*-butylamine or isopropylamine yielded only dark oils from which no pure product could be isolated by crystallization or distillation.

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Dichlorofumaric Acid

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The preparation and properties of dichlorofumaric acid have apparently never been reported. (Reaction of chlorine with acetylenedicarboxylic acid or its sodium salt has been reported to result in splitting of the acid with formation of hydrogen chloride, carbon dioxide and unidentified products.¹) Since no clear-cut results were obtained by the authors in attempts to prepare dichlorofumaric acid or its ester by isomerization of dimethyl dichloromaleate (readily obtained from dichloromaleic anhydride) with mineral acids or amines, a less direct method of synthesis was used.

Chlorination of succinonitrile to yield a mixture of dichloromaleonitrile and dichlorofumaronitrile,² followed by separation of the isomers and acid hydrolysis of the dichlorofumaronitrile, gave the desired dichlorofumaric acid.

The structures of dichlorofumaronitrile, dichlorofumaric acid, dichloromaleic anhydride, and both related dimethyl esters were confirmed by their infrared spectra. The melting point of dichlorofumaric acid (180–182°) is much higher than that of dichloromaleic acid (118–120°) or of dichloromaleic anhydride which is also reported to melt at 118–119°.³

Experimental

Dichlorofumaronitrile.—Succinonitrile (145 g., 1.81 moles) was heated at 130–140° under illumination of a sun lamp, and chlorine was introduced until, after 18 hours, absorption stopped. The product was flash distilled and then fractionated using a 30-plate column. The first 30% of the distillate (b.p. 159° at 745 mm.) was a white solid which, after recrystallization from petroleum ether, weighed 53 g. (20% yield) and melted at 54–55°. (Its infrared absorption spectrum showed peaks at 4.5 μ corresponding to the nitrile group and at 11.9 μ corresponding to the *trans* configuration.)

Anal. Calcd. for C₄Cl₂N₂: C, 32.68; H, 0.00; N, 19.05. Found: C, 32.80; H, 0.02; N, 19.01.

The higher boiling material, which contained the dichloromaleonitrile, was not purified. Both dichloronitriles are powerful lachrymators and are very volatile.

Dichlorofumaric Acid.—Dichlorofumaronitrile (56 g., 0.38 mole) and 750 g. of 60% sulfuric acid were heated under reflux for 14 hours. The solution was then cooled and filtered. The white, crystalline product was combined with additional material obtained by extracting the filtrate with ether and recrystallized from a mixture of xylene and ace-

(1) W. Lossen and W. Bergau, *Ann.*, **348**, 341 (1906).

(2) O. W. Cass, U. S. Patent 2,443,494.

(3) P. Karrer and E. Testa, *Helv. Chim. Acta*, **32**, 1025 (1949).

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_D^{20} 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 $C_6H_8O_4Cl_2$: 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_D^{20} 1.4830, d_4^{20} 1.3993, d_4^{25} 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 $C_6H_8O_4Cl_2$: C, 33.83; H, 2.84; Cl, 33.29. Found: C, 33.94; H, 2.88; Cl, 33.42.

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

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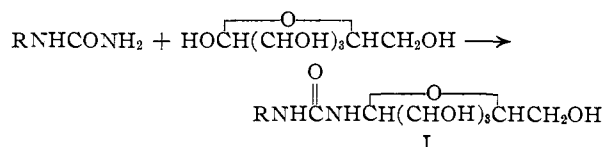
Long-Chain Alkylurea N-Glycosides¹

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Schoorl² 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 Kosche³ 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.



(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 $C_{19}H_{35}N_2O_6$: 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 $C_{25}H_{51}N_2O_6$: C, 63.26; H, 10.62; N, 5.90. Found: C, 63.20; H, 10.42; N, 6.16.

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A Note on the Heat of Vaporization of Chlorotrifluoroethylene (C_2F_3Cl)¹

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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*, **29**, 453 (1947); (b) J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, *THIS JOURNAL*, **73**, 1939 (1951).