show that veratraldehyde is converted to vanillin in at least 30% yield by nitrobenzene and 2 N alkali at 160°, and this reaction therefore competes with the Cannizzaro oxidation–reduction change known to be produced by alkali alone.[6] This observation is not inconsistent with the view that the *p*-hydroxyl group in vanillin may be present as an ether in the lignin precursor, and that cleavage of a 3-carbon side chain in the precursor may produce a para-substituted vanillin by the reverse of an aldol condensation.[5]

Experimental

The directions of Stone and Blundell[7] were followed. Pure veratraldehyde, 10.0 mg., nitrobenzene, 0.06 cc., and 1.0 cc. of 2 N aqueous sodium hydroxide were heated together in a stainless steel micro-bomb for three hours at 160°. This bomb had a metal to metal seal with no gasket. After isolation, 0.01-cc. aliquots of the centrifuged liquor were spotted on filter paper for chromatography, the spots were made acidic with the vapor of glacial acetic acid and were then dried in the air. *n*-Butyl ether saturated with water was the developing agent, and the ascending chromatographic technique was used for 11 to 12 hr., since the descending method was inconveniently rapid. After having been located with a 2,4-dinitrophenylhydrazine spray, aldehydes were extracted with ethanol from the proper parts of the chromatogram.

The content of vanillin in the ethanol extract, 25 cc., was determined according to Lemon[8] by adding 4 cc. of 0.2% ethanolic potassium hydroxide, diluting to 50 cc. with absolute ethanol, and examining the absorption of the solution at wave length 354 mμ. A Beckman Model DU spectrophotometer with a tungsten tube light source was used; plots were made at 5 mμ intervals over the range 320 to 400 mμ against the logarithm of the % transmission, and were assessed against calibration plots for pure vanillin at three different, known concentrations. Other control experiments showed that the recovery of vanillin by the chromatographic technique used was about 87%. Duplicate experiments gave 29.7 and 34.2% recoveries (uncorrected for the chromatographic loss) of vanillin from veratraldehyde.

The above oxidation of veratraldehyde with alkaline nitrobenzene was repeated on a 100-fold scale in another bomb. After being centrifuged, the alkaline liquors were extracted with ether to remove impurities, were acidified, and again extracted with ether to remove phenolic and acidic substances. Phenolic aldehydes were recovered from this extract in a saturated solution of sodium bisulfite, which was then acidified and extracted with ether. The residue left on evaporation of the ether was dissolved in ethanol and was used to prepare a crystalline 2,4-dinitrophenylhydrazone.[9] After recrystallization (yield 0.276 g. or 14%), the product had the correct m.p. 270–271°, not depressed by admixture with a sample of the same m.p. made from pure vanillin.

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(6) H. Decker and R. Pschorr, *Ber.*, **37**, 3403 (1904).

(7) J. E. Stone and M. J. Blundell, *Anal. Chem.*, **23**, 771 (1951).

(8) H. W. Lemon, *ibid.*, **19**, 846 (1947).

(9) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

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Reaction of Acetoin and Hydroxyacetaldehyde with Cyclohexylamine[1]

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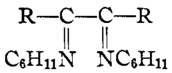
The non-enzymatic browning of vegetables which is generally attributed to reaction of amino groups of amino acids or proteins with reducing sugars is being investigated by the use of simple α-hydroxycarbonyl compounds and aliphatic amines as models for sugars and amino acids. In particular the reactions of acetoin and hydroxyacetaldehyde with primary aliphatic amines have been studied with the idea that α-hydroxyimino compounds might be isolated which would be analogous to the open chain formulas of the 1-amino-1-desoxy sugars.[2]

When acetoin is dissolved in anhydrous primary aliphatic amines at room temperature in the absence of air and allowed to stand several days, removal of excess amine by distillation yields colorless oils generally soluble in hydrocarbons. Short exposure to dry air produces darkening and precipitation of resin. With cyclohexylamine, however, two oxidative products could be isolated, crystalline cyclohexylamine salt of acetic acid and the new crystalline diimine, diacetyldicyclohexylimine I (R = CH_3). The mechanism whereby the primary condensation product of acetoin and amine is split to acetic acid and also oxidized to a derivative of diacetyl has not been investigated. Hydroxyacetaldehyde and cyclohexylamine in a similar way yield small quantities of the crystalline glyoxaldicyclohexylimine II (R = H). No acid has been isolated from this reaction.



$$\underset{C_6H_{11}N}{\overset{\|}{\text{R—C}}}\text{—}\underset{NC_6H_{11}}{\overset{\|}{\text{C—R}}}$$

I, R = CH_3 II, R = H

The structures of the two diimines were established by ultimate analysis and by acid hydrolysis to yield diacetyl or glyoxal and cyclohexylamine. The diimines, on catalytic hydrogenation with platinum oxide, each absorb two moles of hydrogen to yield oily diamines. In the ultraviolet in methanol solution, diacetyldicyclohexylimine shows a strong absorption maximum at 213 mμ and a weak, broad inflection in the range 245–260 mμ. Glyoxaldicyclohexylimine has a maximum at 218 mμ and a second weak maximum at 267 mμ. The principal maxima are near the range where conjugated dienes absorb.

Reaction of diacetyl with cyclohexylamine yields only small quantities of the diimine, the bulk of product being of a different nature.[3] Glyoxaldicyclohexylimine, however, could be prepared in good yield by reaction of 30% aqueous glyoxal solution with cyclohexylamine in alcoholic or aqueous solution.[4] Simple crystalline aliphatic 1,2-diimines have not heretofore been described.

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(1) Presented at 123rd National Meeting of American Chemical Society, Los Angeles, March, 1953.

(2) The importance of 1-amino-1-desoxy sugars as possible intermediates in Maillard browning reactions has been emphasized by J. Hodge and C. Rist (This Journal, **74**, 1494 (1952); **7** , 316 (1952)) and A. Gottschalk and S. M. Partridge (*Nature*, **165**, 684 (1950)).

(3) J. F. Carson, This Journal, **75**, 4300 (1953).

(4) K. Maurer and E. H. Woltersdorf (*Z. physiol. Chem.*, **254**, 18 (1938)) have shown that the reaction of glyoxal bisulfite with aliphatic amines in alcohol yields the corresponding N-alkyl-α-amino acid-N-alkylamide. In our experience, the diimine is obtained in quantity only with free glyoxal. Reaction of glyoxal bisulfite with cyclohexylamine in refluxing ethanol yielded only traces of the diimine and resinous material; no amide was isolated.

Experimental

Reaction of Acetoin and Cyclohexylamine.—Ten grams of crystalline dimer[5] 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 $C_8H_{17}NO_2$: 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 diacetyldicyclohexylimine 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 $C_{16}H_{28}N_2$: 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 Diacetyldicyclohexylimine.—A solution of 710 mg. of diacetyldicyclohexylimine 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 cyclohexylamine[6] 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 $C_{13}H_{19}NSO_2$: 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 glyoxaldicyclohexylimine. 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 glyoxaldicyclohexylimine 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.

Anal. Calcd. for $C_{14}H_{24}N_2$: 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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[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.

Dichlorofumaric Acid

BY NELSON R. ELDRED AND DONALD M. YOUNG

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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 $C_4Cl_2N_2$: 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-

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[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).