Summary

An improved method for the synthesis of uracil is described.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

LECTURE EXPERIMENTS WITH THE NEW HALOGENOID, AZIDO-CARBONDISULFIDE

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The surprising reactivity of azido-carbondisulfide toward various groups of substances, including acids, alkalies, oxidizing and reducing agents, and its susceptibility to autocatalytic decomposition even at ordinary temperatures, render available a series of instructive experiments suitable for use in lecture-table demonstration. Azido-carbondisulfide, itself a halogenoid, may be considered to contain potentially within its molecular structure three other halogenoids: $(SCN)_2$, $(CN)_2$ and $(N_3)_2$. Of these, thiocyanogen is evolved in the free state during thermal decomposition of the mother substance.

The experiments described in the present article are fairly representative of the large number that have been performed repeatedly by the authors at this University and elsewhere.

1. Demonstration of the Halogenoid Character of Azido-carbondisulfide.—(a) Like the halogens, azido-carbondisulfide reacts with aqueous solutions of potassium, sodium or ammonium hydroxide, yielding salts of the oxy-acid and hydracid corresponding, for example, to hypochlorous and hydrochloric acids. By acidification of the resulting solution, a reprecipitation of the white, crystalline halogenoid is effected.

Drop 0.5 g. of freshly prepared,[1] slightly moist azido-carbondisulfide into 100 cc. of approximately 1 *N* sodium hydroxide solution, either in a large test-tube or small cylinder, at ordinary or, better, at somewhat lower temperature. Acidify the yellow-green solution by gradual addition of 25–50 cc. of dilute (approximately 6 *N*) sulfuric acid. The precipitate may be identified by testing its behavior toward heat as outlined under Section 3.

(b) Despite its very limited solubility in water, azido-carbondisulfide is capable of discharging the iodide ion in aqueous solution to an appreciable extent, although the reaction normally proceeds in the opposite direction, as illustrated in the current method of preparing the halogenoid. In any case the equilibrium concentration of free iodine is sufficiently high to enable its detection by the usual test.

Introduce 0.5 g. of solid azido-carbondisulfide into 1 liter of a 1% aqueous

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[1] Browne, Hoel, Smith and Swezey, THIS JOURNAL, **45**, 2541 (1923).

solution of potassium iodide containing 5 cc. of the usual starch solution. The characteristic deep blue coloration appears after the solution has been stirred for a few moments.

(c) The $SCSN_3^-$ ion reacts instantaneously, in aqueous solution, with the silver ion, forming the explosive, white precipitate, $AgSCSN_3$. Add to 1 liter of water 5 cc. of the concentrated solution of potassium (or sodium) azido-dithiocarbonate used in preparing the halogenoid under investigation. Introduce, drop by drop, a 10% solution of silver nitrate until precipitation is complete. The precipitate should never be filtered off or dried without suitable precautions for the protection of the operator from possible explosion.

2. Demonstration of the Production of Free Thiocyanogen from Azido-carbondisulfide.—Paint upon an ordinary sheet of writing paper, with the aid of a small camel's-hair brush, any desired word or pattern, using a 10% solution of azido-carbondisulfide in acetone. After the paper has dried, attach closely to it a second sheet, which has been previously impregnated with a 10% solution of ferric chloride and dried. When the first sheet of paper is gently warmed by rapidly and repeatedly passing the Bunsen flame over it, the pattern quickly develops as a result of a transformation of the invisible film of azido-carbondisulfide into the dark orange, polymeric thiocyanogen. The ferric chloride paper shows a similar pattern, in the deep red color of ferric thiocyanate, indicating the liberation of thiocyanogen, $(SCN)_2$, in the form of vapor.

3. Demonstration of the Instability of Azido-carbondisulfide.—The new halogenoid undergoes explosive decomposition when subjected (a) to mechanical impact, (b) to heat or (c) to the chemical action of a current of such gases as ammonia, hydrogen chloride or chlorine. The intensity of the explosion may vary from that of a mere puff, in case the sample is appreciably moist, to that of a sharp detonation, if it has been thoroughly dried. The importance of exercising extreme care in the preparation and use of azido-carbondisulfide or its compounds should be borne in mind at all times. It is inadvisable to store the dry halogenoid, even for a brief period, in any apparatus of glass or other material that might undergo fragmentation in the event of an explosion. The approved procedure is to keep the material between two pieces of filter paper, and to remove small samples for use with the aid of a bone spatula.

(a) Place a small sample (0.01 to 0.02 g.) of the halogenoid upon the polished surface of an iron plate or block, and strike it a sharp blow with a hammer.

(b) Heat a sample (0.02 to 0.2 g.) upon a piece of sheet iron with the aid of a Bunsen flame, or let the sample fall upon a metallic plate previously heated to 100° or higher.

Drop a sample (0.05 to 0.5 g.) into an iron water-bath containing water heated to from 80° to 100°. By means of a series of experiments at different temperatures within this range, the influence of temperature in accelerating the velocity of decomposition of the halogenoid may be strikingly demonstrated. In every case the sample may be observed to undergo incipient fusion and partial decomposition with evolution of gas before it explodes. The explosion usually consists of little more than a crackling or sputtering sound. The interval elapsing between the time of contact with the hot water and the time of explosion varies from about 10 to 12 seconds at 80°, to 4 to 6 at 85°, 2 to 3 at 90°, 1.5 to 2.5 at 95° and 1.0 to 1.5 at 100°.

(c) Arrange four portions of azido-carbondisulfide weighing approximately 0.02, 0.05, 0.15 and 0.4 g. about 10 cm. apart in a straight line on a wooden board. Direct a gentle stream of ammonia gas upon the samples in rapid succession, preferably beginning with the smallest. A series of explosions of increasing intensity will ensue.

Summary

The present article contains a brief description of several lecture experiments upon azido-carbondisulfide, $(SCSN_3)_2$, which serve to demonstrate (1) its halogenoid character, on the basis of its reaction with (a) sodium hydroxide, (b) potassium iodide and (c) silver nitrate; (2) its thermal decomposition, with formation of free thiocyanogen; (3) its sensitivity to (a) mechanical impact, (b) heat and (c) the chemical action of ammonia gas.

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OMEGA-CYCLOHEXYL DERIVATIVES OF VARIOUS NORMAL ALIPHATIC ACIDS. IV

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In a recent paper[2d] it was pointed out that the cyclic structure present in chaulmoogric and hydnocarpic acids was, among others, an important factor in the bactericidal effect of these acids on *B. leprae.* As a consequence other acids containing a cyclic structure in the omega position have been studied. The κ-cyclohexyl-undecanoic acid and the μ-cyclohexyltridecanoic acid were described in a previous paper.[2d] This investigation

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[1] This communication is an abstract of a portion of a thesis submitted by G. S. Hiers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] For previous papers in this field see (a) Shriner with Adams, THIS JOURNAL, **47,** 2727 (1925). (b) Noller with Adams, *ibid.*, **48,** 1074; (c) 1080 (1926). (d) Hiers with Adams, *ibid.*, **48,** 1089 (1926).