Anal. Calcd. for $C_{15}H_{21}O_5N_2Na$: Na, 6.92. Found: Na, 6.99.

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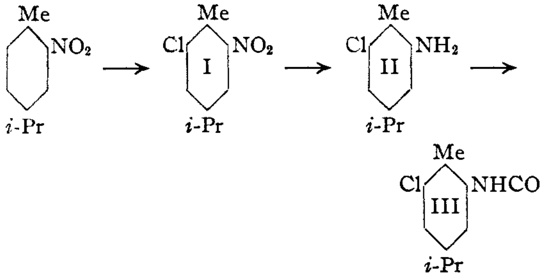
The Chlorination of 2-Nitro-*p*-cymene. I. Monosubstitution[1]

BY ALVIN S. WHEELER, J. M. EARLY AND JOSEPH N. LECONTE



The chlorination of 2-nitro-*p*-cymene yielded 2-nitro-6-chloro-*p*-cymene (I). There was evidence of the formation of 2-chloro-*p*-toluic acid, m. p. 195°, and an aldehyde fraction, b. p. 110–120°. The 2-nitro-6-chloro-*p*-cymene was reduced to 2-amino-6-chloro-*p*-cymene (II), and its acetate (III) and hydrochloride were prepared and studied. The structure of the chlorinated product was proved by reduction, diazotization to remove the amino group, and subsequent oxidation to 2-chloro-*p*-toluic acid.

TABLE I

Compound	Formula	M. p., °C.	B. p., °C.	Sp. g. 20°C.	Refractive index 26°	% Chlorine Calcd.	% Chlorine Found
2-Nitro-6-chloro-*p*-cymene (I)	$C_{10}H_{12}O_2NCl$	....	152–153 (26 mm.)	1.1965	1.4934	16.61	16.42
2-Amino-6-chloro-*p*-cymene (II)	$C_{10}H_{14}NCl$	....	137–138 (27 mm.)	1.0968	1.5583	19.32	19.88
Derivatives of II							
Acetate	$C_{12}H_{16}ONCl$	59–60	....	....	....	15.74	15.66
Hydrochloride	$C_{10}H_{16}NCl_2$	206–208 dec.	....	....	....	32.24	32.10

Experimental

Preparation of 2-Nitro-6-chloro-*p*-cymene.—Dry chlorine gas was led into 100 g. of redistilled nitrocymene and 0.5 g. of aluminum–mercury couple until the system had gained the necessary weight for mono-substitution. The mixture was poured into water, washed first with sodium hydroxide solution, and then with sodium bisulfite solution, and finally with water. It was extracted with ether and the ethereal solution dried over calcium chloride. The ether was evaporated and the residual oil distilled under diminished pressure. That portion boiling between 152 and 153° at 26 mm. pressure was the nitrochlorocymene; yield 45.5 g. of a pale yellow, sweet aromatic odored oil.

Preparation of 2-Amino-6-chloro-*p*-cymene.—Forty-five grams of mossy tin, 39.5 g. of nitrochlorocymene, and 25 cc. of 95% ethanol were placed in a 500-cc. balloon flask, attached to a reflux condenser, and 150 cc. of concentrated hydrochloric acid was added in 10-cc. portions, precautions being taken to prevent overheating. When the initial reaction subsided, the mixture was heated on a steam-bath for four hours. The reaction mixture was then distilled with steam and the unreacted nitro compound retrieved. The mixture was now made basic with sodium hydroxide, the amine steam distilled, extracted with ether, dried over solid sodium hydroxide, the ether evaporated and the residual oil distilled under diminished pressure. The water white oil which distilled at 137–138° at 27 mm. pressure was saved; yield was 25.2 g.

Derivatives. (1) **Hydrochloride.**—Dry hydrogen chloride was passed into an ethereal solution of the amine. The precipitate was dried in a desiccator. The white solid melted 200–205° dec. It was soluble in acetone, hydrolyzed by cold water, and was insoluble in concentrated hydrochloric acid.

(2) **2-Acetamino-6-chloro-*p*-cymene.**—The compound was prepared in the usual way. Four parts of acetic anhydride, one part of the amine and pyridine (2% of the anhydride) were heated for a period of two hours, poured into water, excess anhydride destroyed by heating and the acetamino compound purified by recrystallization from ethanol; m. p. 59–60°; white needles from alcohol and from acetic acid.

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[1] This paper is an abstract of a thesis submitted by J. M. Early in partial fulfilment of the requirements for the degree of Master of Science at the University of North Carolina, with completion of work by J. N. LeConte now of the University of Georgia. Alvin S. Wheeler is now deceased.

The Oxidation of Acetic Acid with Selenium Dioxide

BY R. B. THOMPSON AND J. A. CHENICEK

The oxidation of compounds that contain an activated hydrogen with selenium dioxide is now a standard preparative method.[1] The reaction is usually carried out by heating the material to be oxidized under reflux with selenium dioxide while employing a suitable inert solvent. Under these conditions acetic acid is frequently used as the inert solvent. However, it has been found that under more drastic conditions acetic acid undergoes an unexpected reaction with selenium dioxide, namely, oxidation in a small yield to succinic acid. Thus selenium dioxide (14 g.), acetic acid (75 cc.), and water (2.2 cc.), were sealed in a rotating autoclave and heated in an atmosphere of nitrogen at 200° for twelve hours. Selenium (9.7 g.) was separated by filtration. The liquid product was evaporated *in vacuo* and deposited 2 g. of solid material which was identified as succinic acid by mixed melting point with an authentic sample. Conversion to the anhydride gave a product which did not depress the melting point of an authentic sample of succinic anhydride. The only other oxidized material which could be identified was carbon di-

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[1] G. R. Waitkins and C. W. Clark, *Chem. Rev.*, **36**, 235 (1945).

oxide; presumably the formation of carbon dioxide must also be accompanied by the formation of water. By approximate measurement the amount of carbon dioxide was that which should be expected from the amount of selenium dioxide used in excess of that required for the condensation reaction.

This reaction resembles those which Kharasch[2] has carried out with peroxides and it appears likely that it proceeds by a similar mechanism

$$CH_3CO_2H \xrightarrow{[O]} {}^*CH_2CO_2H$$
$$2\,{}^*CH_2CO_2H \longrightarrow HO_2CCH_2CH_2CO_2H$$

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(2) M. S. Kharasch and M. T. Gladstone. THIS JOURNAL, 65, 15 (1943).

COMMUNICATIONS TO THE EDITOR

A RAPID METHOD OF PREPARING NaC^{14}N FROM BaC^{14}O$_3$

Sir:

Studies on the exchange of radiocyanide ion with cyanide complexes have been initiated recently in this Laboratory. Since radiocarbon is presently available only in the form of barium carbonate, it was necessary to investigate various means of converting it into a soluble cyanide.

A possible procedure is that of Cramer and Kistiakowsky.[1,2] This makes use of the reaction of gaseous ammonia and carbon dioxide with a potassium mirror. The procedure is somewhat elaborate and requires the use of a vacuum apparatus. For this reason, some simpler method of accomplishing the conversion would be highly desirable.

Several exploratory experiments were carried out on the use of electro-positive metals as reductants.[3] It was found that insignificant yields of cyanide resulted on heating zinc, aluminum, magnesium or sodium with barium carbonate, in a nitrogen atmosphere. This is in agreement with Loftfield's report.[2]

Preliminary results indicate, however, that yields of 75–80% can be obtained by heating sodium azide and barium carbonate in a nitrogen atmosphere. The method has the advantage of requiring only about thirty minutes and not necessitating the use of any special apparatus.

The procedure is: 0.1 g. of barium carbonate is mixed with 1 g. of sodium azide (Amend Drug and Chemical Co., N. Y.) in a six-inch test-tube, and a slow stream of nitrogen is directed into the mouth of the tube. The mixture is then heated carefully so as to maintain a steady but not too rapid decomposition of the azide. The fumes of sodium oxide may be drawn off into a hood or through a funnel connected to an aspirator. When the decomposition is complete, the test-tube is heated at a dull red heat for ten minutes. After cooling, water is added dropwise until all of the sodium present has reacted. The solution is then diluted, acidified with sulfuric acid, and the hydrogen cyanide distilled over into a slight excess of sodium hydroxide solution.

Four experiments were made with inactive barium carbonate. The resulting cyanide was determined by adding ammonia and potassium iodide and titrating with silver nitrate solution. The average yield was 78 ± 2%. In addition, two runs were made with added BaC^{14}O$_3$.[4] The specific gravity of the radiocyanide, counted as silver cyanide, was within experimental error of the calculated value, indicating that the radiochemical yield is the same as the analytical yield.

Much of the cyanide is formed during the final heating when no sodium azide is present. This suggests that the actual reaction may involve not the sodium azide, but the sodium nitride formed by its decomposition.

Support of this investigation by a grant-in-aid from The Research Corporation is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
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RECEIVED SEPTEMBER 10, 1947

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(1) Cramer and Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

(2) Loftfield, "The Preparation of Carbon-fourteen Labelled Hydrogen Cyanide, Alanine and Glycine," Circular C-3, Isotopes Branch, United States Atomic Energy Commission, June, 1947.

(3) A portion of these experiments was carried out by Mr. M. Volpe.

(4) Supplied by the U. S. Atomic Energy Commission.

POLY-LYSINE

Sir:

On extending experiments concerning polymerization of amino acids[1] to basic amino acids, we succeeded in preparing poly-lysine. This polymer represents the first synthetic basic α-poly-amide and as it is water soluble, it may serve as a useful model in protein research.

A suitable monomer was found in ϵ-carbobenzoxy-α-carboxyl-l-lysine anhydride (I)[2] which

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(1) Frankel and Katchalski, THIS JOURNAL, **64**, 2264 (1942); **64**, 2268 (1942).

(2) Bergmann, Zervas and Ross, *J. Biol. Chem.*, **111**, 245 (1935).