

Anal. Calcd. for $C_{15}H_{21}O_2N_2Na$: Na, 6.92. Found: Na, 6.99.

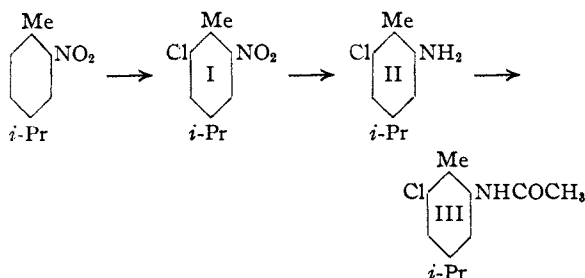
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The Chlorination of 2-Nitro-*p*-cymene. I. Monosubstitution¹

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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.

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-Acetamido-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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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

TABLE I

Compound	Formula	M. p., °C.	B. p., °C.	Sp. g. 20°C.	Refractive index 26°		% Chlorine	
					Calcd.	Found	Calcd.	Found
2-Nitro-6-chloro- <i>p</i> -cymene (I)	$C_{10}H_{12}O_2NCl$	152–153 (26 mm.)	1.1965	1.4934	16.61	16.42	
2-Amino-6-chloro- <i>p</i> -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,

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-

(1) This paper is an abstract of a thesis submitted by J. M. Early in partial fulfillment 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.

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