

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

## The Effect of Temperature on the Nitration of *p*-Cymene The Synthesis of 6-Nitrocarvacrylamine and Certain Derivatives

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Recently a considerable quantity of 6-nitrocarvacrylamine was needed for certain studies which were in progress in this Laboratory. Much difficulty was experienced in obtaining good yields of pure 2,6-dinitro-*p*-cymene when the methods of Aschan<sup>2</sup> and of Wheeler and Harris<sup>3</sup> were followed.

Since *p*-cymene upon nitration yields 2,6-dinitro-*p*-cymene,<sup>2,4</sup> 2,4-dinitrotoluene,<sup>5</sup> *p*-nitrotoluene,<sup>3</sup> and various oxidation products, it seemed desirable to observe the reaction at carefully controlled, lower temperatures and to employ chemical methods for the separation of the nitrated products.

Early in this study it was noticed that small changes in the reaction temperature resulted in reaction products which were quite different in quality and quantity. The reaction temperature, previously defined as "below 0°C.,"<sup>3</sup> was herein studied at -3 to -5°, -5 to -7°, and -10 to -12°. With decreasing temperature, the quantity of solid product, its melting point, the ratio of 2,6-dinitro-*p*-cymene to nitrated toluene derivatives, and the reaction time were increased. Likewise, the degree of oxidation, color of product, and the quantity of oils decreased. Contrary to previous work,<sup>3</sup> the reaction product yielded no oil but in every case solidified when washed, dried, and refrigerated at 0°. Oils were obtained from the mother liquor when the product was crystallized.

The separation of 2,6-dinitro-*p*-cymene in pure form was improved by crystallization from a pure solvent instead of mixed solvents.<sup>3</sup> In the selection of a solvent, the following were tried: dioxane, ethyl ether, dichlorodiethyl ether, isopropyl ether, petroleum ether, heptane, toluene, carbon disulfide, chloroform, carbon tetrachloride, methyl alcohol, and ethyl alcohol. Methyl alcohol was the superior solvent both for yield and purity of product. After the third crystallization with

methyl alcohol the 2,6-dinitro-*p*-cymene melted at 51-53° whereas it melted at 40-42° after the sixth crystallization with ethyl alcohol.<sup>3</sup> For use in this study, the purification of 2,6-dinitro-*p*-cymene by one crystallization from methyl alcohol followed by a chemical separation, as described below, proved to save both time and material. The results of the nitration studies are given in Table I.

TABLE I  
THE DINITRATION OF 500 g. OF *p*-CYMENE

Number of runs	2	3	2
Temperature of reaction, °C.	-3 to -5	-5 to -7	-10 to -12
Time of reaction, hrs.	12	20	33
Product, g.	670	750	785
Color, yellow	Brown	Deep	Light
Physical state at 0°	Semi-solid	Solid	Cryst.
Cryst. from MeOH, g.	230	346	420
M. p., °C.	30-32	34-36	38-40
Oil from mother liquor, g.	435	400	360

The reduction of impure 2,6-dinitrocymene with ammonium sulfide gave a reaction product from which 6-nitrocarvacrylamine was separated in pure form after one or two crystallizations. The reduction product was crystallized from dilute hydrochloric acid which yielded 6-nitrocarvacrylamine hydrochloride, m. p., 209°. The free base melted at 52° and the acetyl derivative at 114-115°. These constants confirm those reported by Wheeler and Harris<sup>3</sup> but in the case of the free base and of the acetyl derivative they disagree with those reported by Aschan<sup>2</sup> as 80-82 and 111°, respectively. When an excess of ammonia was added to the mother liquor, 2-nitro-*p*-toluidine separated and after repeated purifications with dilute alcohol it melted at 81°<sup>6</sup>; its benzoyl derivative melted at 174°.<sup>7,8</sup> This formation and identification of 2-nitro-*p*-toluidine confirm the positions of the nitro groups in the dinitrotoluene as proved by Alfthan,<sup>5</sup> who obtained 2,4-toluylenediamine by reduction of both nitro groups. The selective reduction of the para nitro group and not the ortho group agrees

(1) This paper is an abstract of part of the dissertation submitted by Granvil C. Kyker to the Graduate Faculty of the University of North Carolina in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1938.

(2) Aschan, *Finska Kemistsamfundets Medd.*, **25**, 122 (1916).

(3) Wheeler and Harris, *THIS JOURNAL*, **40**, 404 (1927).

(4) Kraut, *Ann.*, **92**, 67 (1854).

(5) Alfthan, *Ber.*, **53**, 78 (1920).

(6) Haibach, *J. prakt. Chem.*, [2] **65**, 246 (1902).

(7) Bell, *Ber.*, **7**, 1504 (1874).

(8) Bernthsen, *ibid.*, **15**, 3017 (1852).

with the work of Beilstein and Kuhlberg<sup>9</sup> on 2,4-dinitrotoluene.

By using the nitration product of *p*-cymene obtained at  $-10$  to  $-12^\circ$ , 6-nitrocarvacrylamine was prepared from *p*-cymene in a higher yield than that which has been reported previously for the nitration alone. The results of the studies on the reduction of impure 2,6-dinitrocymene with ammonium sulfide are listed in Table II.

TABLE II  
THE REDUCTION OF 2,6-DINITRO-*p*-CYMENE

Temp., °C., of nitration	6-Nitrocarvacrylamine HCl			2-Nitro- <i>p</i> -toluidine	
	From solid, g.	From oil, g.	Yield from cymene, %	From solid, g.	Yield from cymene, %
- 3 to - 5	126	43	19.7	65	11.4
- 5 to - 7	216	40	29.8	56	9.9
-10 to -12	281	36	36.8	51	9.0

### Experimental

**2,6-Dinitro-*p*-cymene.**—One kilogram of fuming nitric acid (sp. gr., 1.52) and 2 kg. of sulfuric acid (sp. gr., 1.84) were placed in a 3-liter three-necked balloon flask equipped with a dropping funnel, thermometer, and an efficient stirrer. After cooling to  $-15^\circ$  in a well insulated ice-salt mixture, the addition of 500 g. of *p*-cymene (Eastman, terpene-free, fraction boiling at  $176.5^\circ$ ) was regulated so that the temperature did not exceed  $-10^\circ$  and was maintained from  $-12$  to  $-10^\circ$ . It was necessary to arrange the stirrer so as to prevent the collection of a hydrocarbon layer, since this induced localized heating, oxidation, and a lower yield. The addition of *p*-cymene required thirty-three hours and stirring was continued for an additional hour. The reaction product was poured over 8 liters of cracked ice, stirred vigorously for one hour and washed successively with six to eight 3-liter portions of water by working and removing the aqueous layer by a siphon, once with dilute sodium hydroxide, and again with water. The spongy, lemon yellow product melted at  $25^\circ$ ; it was warmed to  $35^\circ$  and separated from the aqueous layer in a separatory funnel. The oil was dried by heating in a distilling flask at  $100^\circ$  and 20–25 mm. The dry oil, when refrigerated at  $0^\circ$ , solidified to a hard crystalline lemon-yellow mass which weighed 785 g. The solid was recrystallized from 750 ml. of methyl alcohol at  $0^\circ$ . Impure 2,6-dinitro-*p*-cymene separated, weighing 420 g., and melted at  $38-40^\circ$ . On evaporation the mother liquor gave 360 g. of heavy, reddish-yellow oil which did not yield a further crop of crystals. Without further purification, the 2,6-dinitro-*p*-cymene was used for the preparation of 6-nitrocarvacrylamine.

**6-Nitrocarvacrylamine Hydrochloride.**—Two hundred and fifty grams of 2,6-dinitro-*p*-cymene (impure, m. p.  $38-40^\circ$ ) in 1 liter of alcohol was placed in a 3-liter flask equipped with an inlet tube and an outlet *via* a reflux condenser. To the flask was added 170 ml. of ammonium

hydroxide (28%). Hydrogen sulfide was passed into the flask at a rapid rate until the contents of the flask were saturated and the hydrogen sulfide was continued another five minutes. The reaction mixture was refluxed for fifteen minutes. The process of cooling, saturating, and refluxing for fifteen minutes was carried out three times. After the saturation with hydrogen sulfide the fourth time, the condenser was turned down and the alcohol was removed until the distillate produced a turbidity when allowed to drop in water. The residue was boiled with 3 liters of dilute hydrochloric acid (containing 375 ml. of concd. hydrochloric acid) in three successive portions of 2000, 500, and 500 ml. and filtered after each extraction. The filtrate was boiled, charcoaled, filtered, and cooled slowly to  $0^\circ$ . Straw colored needles separated which weighed 167.5 g.; m. p.  $208^\circ$ ; yield 65% (from *p*-cymene, 36.8%).

**6-Nitrocarvacrylamine.**—Ten grams of the hydrochloride was suspended in 100 ml. of water and ammonia was added in slight excess. The amine which precipitated was recrystallized from dilute alcohol below  $45^\circ$ ; yellow needles; m. p.  $52^\circ$ ; yield, practically the theoretical.

**N-Acetyl-6-nitrocarvacrylamine.**—Three grams of the free base was dissolved in 2 ml. of pyridine and treated cautiously with 2 ml. of acetyl chloride. After warming the mixture for ten to fifteen minutes on a steam-bath it was cooled, washed with water until it solidified, and then washed successively with dilute sodium hydroxide, water, dilute hydrochloric acid, and water. After recrystallization from dilute alcohol the melting point was  $114-115^\circ$ .

**2-Nitro-*p*-toluidine.**—The acid mother liquor from the crystallization of 6-nitrocarvacrylamine hydrochloride was neutralized with concentrated ammonium hydroxide. Fifty-five grams of impure amine separated. After recrystallizing several times with dilute alcohol it melted at  $81^\circ$ .

**N-Benzoyl-2-nitro-*p*-toluidine.**—Five grams of 2-nitro-*p*-toluidine was dissolved in 3 ml. of pyridine, treated with 5 g. of benzoyl chloride, and warmed on a steam-bath for ten to fifteen minutes. The product was washed with water, dilute alkali, water, dilute acid, and water, respectively. Dilute alcohol was used for crystallization; m. p.  $174-175^\circ$ .

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### Summary

1. The dinitration of *p*-cymene has been studied at  $-3$  to  $-5^\circ$ ,  $-5$  to  $-7^\circ$ , and  $-10$  to  $-12^\circ$ .
2. The preparation of 6-nitrocarvacrylamine from *p*-cymene has been improved.
3. The chemical method of separation of the nitration products of *p*-cymene is far superior to the methods previously used.

(9) Beilstein and Kuhlberg, *Ann.*, **155**, 14 (1870).