MONONITRATION OF *p***-CYMENE**

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p-Cymene has been successfully nitrated with yields of over 90 per cent of mononitrated products, consisting of 2-nitro-p-cymene and about 8 per cent p-nitrotoluene. The particular features of this process are (a) the maintenance of a good emulsion throughout the nitration, enabling the utilization of all of the p-cymene with a minimum of oxidation at -10° C., and (b) a very decreased nitration time due to effective means of heat removal by means of solid carbon dioxide in alcohol for the cooling bath.

To an emulsion consisting of 500 grams of technical *p*-cymene (boiling at 174–178 °C.), 1,000 grams of sulfuric acid (density, 1.84), and 300 ml. of glacial acetic acid are added at -10 °C. a mixture of 369 grams of nitric acid (density, 1.42) and 1,000 grams of sulfuric acid (density, 1.84) with the cooling bath at -30 ° to -35 °C. In spite of the extreme exothermic nature of the reaction, the total nitration time is only 2 hours.

A technical *p*-cymene, obtained from sulfite turpentine, has been used. It possesses certain emulsifying properties which make it more advantageous than pure *p*-cymene, besides being far more economical. Pure *p*-cymene may be successfully nitrated provided an appropriate emulsifying agent is added. Oxidation products are formed along with the nitration products in the absence of the emulsion.

The importance of a good emulsion and temperature control are stressed for the nitration of other easily oxidized compounds.

HEN easily oxidized substances are nitrated, difficulty is usually encountered, especially when certain labile groups are present which cannot be protected by interaction with a suitable reagent. The problem assumes considerable magnitude when the desired product is obtainable only under very narrow reaction conditions. Besides experiencing difficulty in executing these reactions smoothly and safely, the yield of desired product is low because of the formation of oxidation and side products. Hence, this contamination sometimes makes the purification so tedious and time consuming that the process becomes valueless.

p-Cymene has long been regarded as a compound easily oxidized during nitration. Some oxidation products reported in the nitration of this substance are p-tolyl methyl ketone (18, 19, 23, 25), p-toluic acid (10, 19), 2-nitro-p-toluic acid (5, 9, 15), and a deleterious tarry material of unknown composition, obtainable in surprisingly high yields under the more usual nitrating conditions. Besides these, p-nitrotoluene (19)is also found to complicate the problem further.

The chief constituent of sulfite turpentine, a by-product in the pulping of resinous spruce by the sulfite process, is pcymene. Mann, Montonna, and Larian (19) recently discussed sulfite turpentine, especially its composition. The mononitration of p-cymene has been carried out by many investigators; however, much of the work has been in the nature of an attempt to duplicate the results of others. Three essential types of reagents have been used for this nitration: (a) nitric acid alone, (b) a mixture of nitric and sulfuric acids, and (c) a mixture of nitric, sulfuric, and acetic acids.

Nitric acid alone was first used by Barlow (5); he added the *p*-cymene to the acid, cooled by salt and ice, and the yield was only a small amount of mononitro-*p*-cymene. Essentially the same method was used by Landolph (15) at 40-50 ° C. and Fittica (9) at room temperature. The last two investigators claimed to have obtained a solid isomeric mononitro-*p*-cymene; however, Gerichten (10) proved this to be *p*-toluic acid. Widman and Bladin (25) obtained very little nitro-*p*-cymene by Fittica's method but considerable *p*-tolyl methyl ketone and unchanged *p*-cymene. Aschan, Teräsvuori, and Ekwall (3) found that adding *p*-cymene to nitric acid (density, 1.52) yielded products other than 2nitro-*p*-cymene.

A mixture of nitric and sulfuric acids was first used by Widman and Bladin (25), and more successfully by Söderbaum and Widman (23). The latter method consisted in adding the p-cymene to the calculated amount of nitric acid (density, 1.4) in sulfuric acid at 20° to 25° C., and finally warming to 40° C.; considerable amounts of unchanged pcymene as well as *p*-tolyl methyl ketone were obtained. A recent French patent (16) provided for the addition of the nitric acid-sulfuric acid mixture to the cymene at -5° C. Andrews (1) added a mixture of 50 grams of nitric acid (density, 1.42) and 105 grams of sulfuric acid (density, 1.84) during 4 hours to a mixture of 67 grams of p-cymene and 105 grams of sulfuric acid at 0° C.; yields as high as 85 per cent of the theoretical amount of 2-nitro-p-cymene were obtained. The isomeric 3-nitro-p-cymene was found not to be a product of the nitration. This method was patented in the United States and Great Britain (2). Another British patent (4) gives essentially the same conditions for nitrating p-cymene obtained by heating monocyclic terpenes with sulfur in the presence of substituted urea or guanidine derivatives. Many investigators have been unsuccessful in duplicating Andrews' results. Demonbreun and Kremers (?) found Andrews' method to give poor yields, ending with a copious evolution of nitrogen oxides; they accordingly varied many factors and obtained a method similar to that of Andrews, which resulted in a maximum yield of 65 per cent. Hixson and Cauwenberg (11) obtained a 54.6 per cent yield by the latter method. Using Andrews' method, Kimura (13) obtained 46 per cent, Kuan (14) 60 per cent, and Inoue and Horiguchi (12) 80.7 per cent of nitro-p-cymene; the last two investigators used slightly more sulfuric acid. Phillips (20) used slightly less sulfuric acid with a yield of 45 to 50 per cent; this process was patented in the United States (21). A British patent (22) provides for the addition of alkyl or acyl nitric acids, particularly diacetyl nitric acid, to a mixture of equal weights of *p*-cymene and sulfuric acid.

A mixture of nitric, sulfuric, and acetic acids was first used by Wheeler and Smithey (24), who used Andrews' method modified by the addition of 10 ml. of acetic acid per mole of *p*-cymene. The function of the acetic acid is to prevent the solidification of the reaction products during the nitration. Bert and Dorier (6) obtained a 50 per cent yield of nitro-p-cymene by this method; LeFevre (18) obtained 70 per cent, using more sulfuric and acetic acids. Ershov and Fedotova (8) employed nitric acid with a density of 1.38 instead of 1.42. Recently Mann, Montonna, and Larian (19) nitrated p-cymene by Wheeler and Smithey's modified method and obtained a maximum yield of 55 to 60 per cent as well as a large amount of side products; they further found no apparent explanation for their results as compared with yields of certain investigators of as high as 80 per cent, and finally stated that a much closer definition of conditions is necessary.

This paper is an attempt to define clearly the conditions for the successful mononitration of p-cymene, and to summarize the effect of variations in conditions upon the course of the reaction.

Preliminary Observations

In nitrating *p*-cymene according to Andrews' method (1)as well as by the modified method of Wheeler and Smithey (24), considerable difficulty was encountered in attempting to obtain satisfactory yields. This is consistent with previous investigations. The reaction product consisted of much tarry matter and unchanged *p*-cymene, making purification of the nitro-*p*-cymene difficult. The evolution of nitrogen oxides, the large amount of reaction heat, the splashing of the *p*-cymene by stirring during the early part of the nitration, and the difficulty of stirring the viscous mixture during the latter part were characteristics of this nitration, according to the previously cited methods. To overcome some of these difficulties, special means of stirring as well as heat removal were necessary. Finally, to obtain the proper conditions for nitration, considerable study was made of the reaction under widely varying conditions.

Apparatus and Materials

The apparatus used for the nitration is illustrated in Figure 1:

A 5-quart (4.75-liter) enamel pail, c, is the container in which the nitration is carried out when 0.5 kg. of *p*-cymene is used, whereas a 12-quart (11.4-liter) pail is employed for 1.0 and 2.0 kg, of p-cymene. The pail is immersed to a third of its depth in an alcohol bath, g, containing 3 liters of alcohol. The pail is better of $d_{2,0}$ whereas $d_{2,0}$ is the second sec is kept an inch (2.5 cm.) from the bottom of the bath by supports, f. Solid carbon dioxide is used as the cooling agent and is added to the alcohol bath at a rate sufficient to maintain the desired temperature. To nitrate 500 grams of p-cymene, 8.5 pounds (3.86 kg.) of solid carbon dioxide are used. The alcohol desired temperature. To nitrate 500 grams of a pounds (3.86 kg.) of solid carbon dioxide are used. bath consists of a square sheet metal can surrounded by insulating material, a, enclosed in a fiberboard box. Both the cooling bath and the nitration pail are equipped with thermometers, b, with a temperature range of -50° to $+50^{\circ}$ C. To regulate accurately the rate of addition of nitrating acid, a 500-ml. dispensing buret, e, is used, equipped at the tip with a short piece of glass tubing which dips into the emulsion in the pail. Owing to the viscous nature of the nitration mixture and the necessity to the viscous nature of the mitration mixture and one metassay for vigorous agitation, a heavy-duty stirrer is used.¹ It con-sists of a 3/s-inch (0.95-cm.) diameter, stainless-steel shaft, d, and propeller of two blades, 5.5 inches (14 cm.) long and 0.9 inch (2.29 cm.) wide, at right angles to each other. The 5,000 r. p. m. motor of 0.1 horsepower is connected to the shaft by a worm-gear drive of 20 to 1 reduction.

¹ A. H. Thomas, No. 9241, heavy-duty stirring apparatus.



NITRATOR CONTROL ROOM IN THE DU PONT INTERMEDIATE PLANT AT DEEPWATER POINT, N. J. Courtesy. E. I. du Pont de Nemours & Co., Inc. The *p*-cymene, a product of the West Virginia Pulp and Paper Company, obtained through the Industrial Chemical Sales Company, Inc., as a technical grade, was used throughout this work. With the exception of the technical sulfuric acid, all chemicals were of reagent quality.

Method of Nitration

A necessary feature of this nitration is the maintenance of a good emulsion throughout the nitration mixture during the entire nitrating process. The conditions are quite exacting; however, when adhered to, the results are easily capable of duplication. It was found useful to record the thermometer temperatures and the dispensing buret volume at 5-minute intervals during all runs. Typical nitration data for the recommended conditions are given in Table I. Owing to difficulties encountered in emulsifying well-purified *p*-cymene, the technical *p*-cymene is recommended. It is fractionated



FIGURE 1. APPARATUS FOR NITRATING *p*-Cymene

through a rod and disk column, and the small initial and final fractions are rejected. The remaining liquid with a boiling range of 174.0° to 178.0° C. (corrected) is used. The initial emulsifying acid consists of a mixture of 1,000 grams of sulfuric acid (density, 1.84) and 300 ml. of glacial acetic acid. The nitrating acid consists of a mixture of 1,000 grams of sulfuric acid (density, 1.84) and 369 grams (4.10 moles) of nitric acid (density 1.42). Both the initial emulsifying acid and the nitrating acid are previously cooled with ice and water.

The initial emulsifying acid mixture is placed in the 5quart enamel pail and further cooled to -10° C. by means of the solid carbon dioxide-alcohol bath. Five hundred grams (3.73 moles) of the technical *p*-cymene are slowly added from the dispensing buret into the initial emulsifying acid at -10° C. with vigorous stirring. During this addition the cooling bath is held only a few degrees below -10° C., owing to the small amount of heat evolved. This operation, requiring about 15 minutes, completely emulsifies the *p*cymene. The cooling bath is now lowered to -30° C. and the previously cooled nitrating acid mixture is added from the dispensing buret into the emulsified mixture at the rate of about 5 ml. per minute with continued vigorous stirring. The solid carbon dioxide is added to the alcohol at such a rate that the temperature of the cooling bath remains at -30° to -35° C. The carbon dioxide gas evolved during the sublimation of the solid carbon dioxide keeps the cooling bath effectively mixed. The reaction mixture may easily be held at -10° C. throughout the nitrat-



ing period, after which stirring is continued for 10 minutes. The total nitrating time is about 2 hours.

It is now poured slowly with efficient stirring into a mixture of about 1 kg. of crushed ice and 1 kg. of ice water. Upon standing for several hours the crude nitration products will be found as a yellow liquid on the surface of the aqueous acids: the latter may be conveniently removed by siphoning from below. The aqueous acids are now extracted with two 50-ml. portions of petroleum ether, the extract is washed with water, and the ether is evaporated, yielding a further quantity of the nitration products. The crude nitration products are washed free of nitric acid with six 300-ml. portions of water. Sometimes a loose emulsion is encountered with the wash water which may be broken by the addition of a few milliliters of concentrated sulfuric acid upon shaking. The combined washings are extracted with 50 ml. of petroleum ether, the extract is washed with water, and the ether is evaporated, the residue being added to the nitration products. After the nitration products are dried partially on the steam bath and finally with calcium chloride, the weight should be 615-630 grams.

Isolation and Identification of Nitrated Products

To facilitate the distillation of the nitration products, it was found desirable to remove the small quantity of unchanged p-cymene from the washed nitration products by steam distilling until the distillate, which at first was less dense than water, continued to pass over denser than water.

	Т	ABLE I.	TYPICA				
Tim Min	Re- action e Temp. . ° C.	Bath Temp. ° C.	Ni- trating Acid Added <i>Ml</i> .	Time Min.	Re- action Temp. ° C.	Bath Temp. $^{\circ}C.$	Ni- trating Acid Added <i>Ml</i> .
$\begin{array}{c} 0 \\ 5 \\ 10 \\ 15 \\ 25 \\ 30 \\ 35 \\ 40 \\ 50 \\ 56 \\ a \end{array}$	$ \begin{array}{r} -10 \\ -9 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \\ -11 \\ -10 \\ \end{array} $ Pup 57: 50	-30 -31 -31 -32 -31 -32 -32 -32 -32 -32 -32 -32 -32 -32 -32	0 25 45 75 100 125 153 153 210 245 275 305 335	$ \begin{array}{c} 65\\ 70\\ 75\\ 80\\ 95\\ 90\\ 95\\ 100\\ 105\\ 110\\ 114_{b}\\ 124_{c} \end{array} $	$ \begin{array}{r} -10 \\ -11 \\ -11 \\ -11 \\ -11 \\ -11 \\ -10 \\ -10 \\ -11 \\ -12 \end{array} $	- 33 - 33 - 33 - 33 - 32 - 32 - 31 - 32 - 30 - 30 - 30	370 405 445 525 590 625 670 720 756
b c	All nitrating On ice.	g acid add	ed.	abie II.			

The distillate was separated from the water, diluted with petroleum ether, dried with calcium chloride, and fractionated. The unchanged *p*-cymene could also be obtained from the nitration products more completely by fractionation in a Vigreux flask *in vacuo;* the small fraction (30 ml.) of wide boiling range (160° to 165° C.) was collected and refractionated at atmospheric pressure (4 to 6 grams). This unchanged *p*-cymene consisted mostly of terpenic impurities associated with the original *p*-cymene.

1

			Initial Emulsifying $Aoid^a$			Nitrating Acid ^b		Emul- sify-	Un-		Nitro- cymene		
Run No.	Reaction Temp. °C.	Bath Temp. °C.	Time <i>Hr</i> .	HOA0 Ml.	H₂SO₄ Grams	HNO₃ Grams	H ₂ SO ₄ Grams	Agent Ml.	Cymene Grams	Grams	p-Nitro- toluene Grams	Remarksd	
123456789	$ \begin{array}{r} -10 \\ -10 \\ -5 \\ -5 \\ -5 \\ -5 \\ -5 \\ -5 \\ -5 \\ -5$	$\begin{array}{rrrrr} -30 & {\rm to} & -50 \\ -30 & {\rm to} & -50 \end{array}$	5332331 33	$250 \\ 250 \\ 250 \\ 0 \\ 400 \\ $	2000 2000 3000 3000 1000 2000 2000 2000	738 676 738 811 811 811 811 738 738	2000 2000 1000 1000 3000 2000 2000 2000	0 0 0 0 0 0 0 0 0	68 142 103 160 10 137 104	$125 \\ 150 \\ 255 \\ 400 \\ 600 \\ 175 \\ 204 \\ \dots$	994 900 840 570 502 865 1061 1080	N₂ oxides: crystals Stirring difficult; N₂ oxides Like run 1 Impossible to stir well N₂ oxides; too fast rate N₀ emulsion at first N₂ oxides; fair emulsion Fair emulsion Fair emulsion	
$ \begin{array}{r} 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ \end{array} $	- 8 - 8 - 8 - 8 - 8 - 10 - 10 - 10 - 10 to - 15	$\begin{array}{rrrrr} -30 & {\rm to} & -50 \\ -30 & {\rm to} & -40 \end{array}$	$ \begin{array}{c} 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 8 \\ 1 \\ $	200 200 200 200 200 200 200 200 200	$ \begin{array}{r} 1000\\ 1000\\ 1000\\ 1000\\ 1000\\ 1000\\ 1000\\ 1000\\ 1000 \end{array} $	369 369 369 369 369 369 369 369 369 369	$ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 $	0 0 0 0 0 0 0 0	$62 \\ 59 \\ 55 \\ 78 \\ 72 \\ 4 \\ 115 \\ 48 \\ 10$	$\begin{array}{r} 41 \\ 72 \\ 60 \\ 85 \\ 110 \\ 18 \\ 103 \\ 60 \\ 20 \end{array}$	$513 \\ 418 \\ 450 \\ 401 \\ 394 \\ 581 \\ 385 \\ 460 \\ 560$	Poor emulsion at first Like run 10 N ₂ oxides; crystals N ₂ oxides; poor emulsion Like run 13 Good emulsion; tech. cymene N ₂ oxides; crystals Like run 16 Emulsion broke (107 ml.), formed (335 ml.)g	
19	-10	-26 to -38	1.8	200	1000	369	1000	0	7	11	576	Emulsion broke (65 ml.), formed (310 ml.)g	
20 21 22 23	-10 -10 -20 - 8 to -18	$\begin{array}{r} -31 \text{ to } -42 \\ -25 \text{ to } -35 \\ -38 \text{ to } -40 \\ -29 \text{ to } -44 \end{array}$	2 2 2 2	200 200 200 200	1000 1000 1000 1000	369 369 369 369 369	1000 1000 1000 1000	40h 20h 5h 0h	6 8 7 6	$20 \\ 25 \\ 21 \\ 20$	591 590 584 590	Emulsion loosened (80 ml.)g Emulsion loosened (175 ml.)g Much crystal formation Emulsion broke (70 ml.), formed (315 ml.)g	
$24 \\ 25$	$-10 \\ -3$	-29 to -39 -26 to -36	$\begin{array}{c} 1.5\\ 1.8\end{array}$	200 200	$\begin{array}{c} 1000 \\ 1000 \end{array}$	369 369	$\begin{array}{c} 1000 \\ 1000 \end{array}$	10h 10h	5 	51 	522 	Crystal formation (200 ml.)g Tech. cymene; much crystal forma- tion	
$\frac{26}{27}$	-10 - 10	-26 to $-40-30 to -40$	$\substack{1.7\\1.7}$	$\begin{array}{c} 200\\ 200 \end{array}$	$\begin{array}{c} 1000 \\ 1000 \end{array}$	$369 \\ 369$	$\begin{array}{c} 1000 \\ 1000 \end{array}$	$10h \\ 15h$	8 5	46 14	$\begin{array}{c} 533\\ 550\end{array}$	Tech. cymene; good emulsion Tech. cymene; good emulsion	
28 29 30 31 31A 31B 31C 32 33 34	$ \begin{array}{c} -10 \\ -10 \\ -10 \\ \cdots \\ -10 \\ \cdots \\ -10 \\ -10 \\ -10 \\ -10 \end{array} $	$\begin{array}{c} -22 \ {\rm to} \ -33 \\ -28 \ {\rm to} \ -35 \\ -26 \ {\rm to} \ -35 \\ -27 \ {\rm to} \ -32 \\ & \ddots \\ -24 \ {\rm to} \ -33 \\ -11 \ {\rm to} \ -30 \\ -19 \ {\rm to} \ -23 \end{array}$	2 2 2 1.5 1.7 2	200 200 200 200 200 200 200 200 200 200	$1000 \\ 1000 \\ 1000 \\ 200 \\ 500 \\ 750 \\ 1000 \\ 0 \\ 1000 \\ 0 \\ 1000 \\ 0 \\ 0 \\$	369 369 369 369 369 369 369 369 369 369	$1000 \\ 1000 \\ 200 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 0 \\ 1000$	$egin{array}{ccc} 10i & 5i & 5i & 10i & 5ii & 5ii & 5ii & 10ii & 10iii & 10ii$	$ \begin{array}{c} 10 \\ 8 \\ 14 \\ 35 \\ \dots \\ 94 \\ 112 \\ 20 \\ \end{array} $	$21 \\ 16 \\ 23 \\ 13 \\ \dots \\ 14 \\ 42 \\ 35$	552 581 574 558 472 385 534	Emulsion loosened (235 ml.)g Good emulsion Good emulsion No HsSO,-cymene emulsion Same as run 31A Fair emulsion, loosened (200 ml.) No emulsion at first Good emulsion	
35 36 37 38 39	$\begin{array}{r} 0 \text{ to } -7 \\ 0 \text{ to } -5 \\ -10 \\ -10 \\ -10 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$3,5 \\ 4 \\ 1.8 \\ 1.8 \\ 2.7 $	$75 \\ 0 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ $	$500 \\ 600 \\ 1000 \\ 1000 \\ 1000 \\ 1000 $	374 336 374 672 374	$780 \\ 600 \\ 10$	0 10i 5i 5i 5	$90 \\ 51 \\ 25 \\ 4 \\ 5$	$46 \\ 33 \\ 35 \\ 61 \\ 45$	$391 \\ 484 \\ 362 \\ 510 \\ 557$	No emulsion until 500 ml.ø Emulsion broke (40 ml.)ø Added emulsified cymene to HNOs Considerable dinitrated product 20 grams Hg(NOs)2 added; some solid formed	
40 41	$-10 \\ -10$	-27 to $-35-28$ to -34	$\substack{2.3\\1.8}$	$\begin{array}{c} 200\\ 200 \end{array}$	$\begin{array}{c} 1000 \\ 1000 \end{array}$	$\begin{array}{c} 163 \\ 375 \end{array}$	$\begin{array}{c} 1000 \\ 1000 \end{array}$	10i 10i	62 87	$\begin{smallmatrix}156\\10\end{smallmatrix}$	$380 \\ 395$	N_2 oxides (55 ml.)g 200 ml. H_2O added to nitrating acid	
42 43	10 10	-23 to -30 -10 to -15	1.5	$\begin{array}{c} 200 \\ 200 \end{array}$	$\begin{array}{c} 1000 \\ 1000 \end{array}$	$375 \\ 375$	$500 \\ 500$	$10i \\ 10i$	155	9 	345	Same as run 41 Used pure 2-nitro-p-cymene; one third dipitrated	
44	-10	-20 to -38	1,5	200	1000	375	500	10i	258	4	246	Very pure cymene; very poor emulsion	
45	-10	-29 to -38	2	200	1000	375	500	10i		10	4 26	Loose emulsion throughout	
46 47 48 49 50 51	$ \begin{array}{r} -10 \text{ to } +50 \\ -10 \text{ to } +50 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \end{array} $	$\begin{array}{r} -18 \text{ to } +50 \\ -18 \text{ to } +50 \\ -26 \text{ to } -30 \\ -20 \text{ to } -29 \\ -20 \text{ to } -30 \\ -22 \text{ to } -30 \end{array}$	$ \begin{array}{c} 3 \\ 2 \\ 2 \\ 3 \end{array} $	400 <i>i</i> 200 200 200 200 200 200	0 1000 <i>t</i> 1000 1000 1000 1000	258/ 258/ 369 369 369 369 369	$\begin{array}{c} 250k \\ 1000l \\ 1000 \\ 1000 \\ 1000 \\ 1000 \\ 1000 \end{array}$	0 5i 10i 10m 25i	$19 \\ 20 \\ 27 \\ 21$	30 30 28	$560 \\ 520 \\ 515 \\ 530$	Scarcely any reaction Like run 46 N ₂ oxides (285 ml.)g Good emulsion N ₂ oxides (180 ml.)g Emulsion loosened (100 ml.), ox- ides (192 ml.)g	
52	-10	-20 to -35	2.5	200	1000	369	1000	10i	11	49	549	Tech. cymene; good emulsion	
53 54 55 56 57 58	-10 -10 -10 -10 -10 -10 -10	$\begin{array}{rrrrr} -25 & {\rm to} & -35 \\ -20 & {\rm to} & -35 \\ -22 & {\rm to} & -36 \\ -20 & {\rm to} & -30 \\ -30 & {\rm to} & -35 \\ -30 & {\rm to} & -35 \end{array}$	$2.5 \\ 2.7 \\ 2.5 \\ \\ 2$	200 100 200 200 300 300	$1000 \\ $	369 369 369 369 369 369 369	1000 1000 1000 1000 1000 1000	$0\\0\\20n\\0\\0\\0$	4 4 4	36 34 35	555 574 574	Like run 52 Tech. cymene; some crystals Tech. cymene; good emulsion Emulsion broke (175 ml.)ø Very good emulsion; tech. cymene Very good emulsion; tech. cymene	

TABLE II. SUMMARIZED DATA AND RESULTS

^a Cymene emulsified in this mixture. ^b Mixture added to the emulsion. ^c Residue on distillation at 10- to 20-mm. pressure. ^d Only those remarks which seem most important are tabulated—i. e.. factors relating to the emulsion; unless otherwise indicated, 500 grams of cymene purified by method A given under "Effect of Purity of p-Cymene" was used. ^e 1,000 grams cymene used. ^f Density, 1.51.

volume of nitrating acid added.
"Sulfatate."
"Aquasol," 90 per cent.
Acetic anhydride.
Glacial acetic acid.
Phosphoric acid (density, 1.83).
m Oil of turpentine.
Borneol.

Simple distillation of the nitration products in vacuo, after the removal of the unchanged p-cymene fraction, was carried out in a Claisen flask. The crude product was always found to distill over a large range—boiling point at 17 mm., $132-145^{\circ}$ C. (565–575 grams); however, most of it distills at approximately 137–138° C. A wide boiling range has been noted in the reported results of all other investigators. The tarry matter remaining in the flask varied from 25 to 35 grams.

Crude nitro-p-cymene (1,155 grams) from which the small amount of unchanged *p*-cymene and tarry matter had been removed was fractionally distilled in vacuo in well-lagged Vigreux columns. Fractions were taken every 2° C. until a constant refractive index was obtained. Refractive indices were taken by the Abbe refractometer when there were large differences; however, as their values became approximately constant, the dipping refractometer was used. By one fractionation, approximately 50 per cent of the crude nitro-pcymene had to be distilled before a constant refractive index was obtained. The impure 50 per cent was refractionated repeatedly, starting with the lowest boiling fractions. After several refractionations, the lowest fraction formed crystals in the receiver. To obtain all of the crystalline fraction, repeated fractionation was continued for about a week and resulted in the separation of the crude nitro-*p*-cymene into two fractions: (a) 90 grams with a boiling point at 17 mm. of 115-116° C. (corrected) and (b) 1,015 grams with a boiling point at 17 mm. of 137-139° C. (corrected). Thus, the solid (fraction 1) was 8.1 per cent of the crude nitrop-cymene.

Fraction 1 was crystallized from alcohol to the constant melting point of $51.6-51.8^{\circ}$ C.; the mixed melting point with *p*-nitrotoluene was the same. Mann, Montonna, and Larian (19) found only 1 to 2 per cent of *p*-nitrotoluene; Andrews (1) found none, although from his boiling range of $115-120^{\circ}$ C.



Courtesy, Pacific Pulp and Paper Industry DIGESTER BUILDING, SHOWING VERTICAL PIPE CONVEYOR FOR CHIPS, ACID TOWERS, AND CHEMIPULP ACCUMULATOR

at 3-5 mm. it is apparent that his product did not consist only of 2-nitro-p-cymene. Run 35, using the conditions of Andrews (as modified by Wheeler and Smithey), showed approximately 10 per cent p-nitrotoluene. By refractive indices, using the dipping refractometer and the refractive index-composition curve (Figure 2), the amount of p-



nitrotoluene has been found to be approximately 10 per cent of the 2-nitro-*p*-cymene-*p*-nitrotoluene mixture, as the result of many separate nitrations under varying conditions. The removal of the isopropyl group in the nitration and bromination of *p*-cymene derivatives has been reported by various investigators; work is now being carried on to reveal the mechanism of its removal.

Fraction 2 (100 grams) was reduced with iron powder and hydrochloric acid to the amine. There were no nonbasic impurities or unreacted material obtained by steam distilla-



FIGURE 2. REFRACTIVE INDEX-COM-POSITION DIAGRAM FOR 2 NITRO-*p*-CY-MENE AND *p*-NITROTOLUENE

tion when the amine was acidified with hydrochloric acid. The conditions and method of reduction in detail are given in the paper by Doumani and Kobe (page 264). Acetylation of the amine by refluxing with the theoretical amount of acetic anhydride for one hour was next carried out. The only product which could be isolated by repeated fractional crystallization from petroleum ether was 2-acetamino-p-cymene with a melting point of 71.3-71.5° C. (Andrews, 1, gives 71° C.). The 2-nitro-*p*-cymene has a refractive index (n_p^{20}) of 1.52872; the boiling point at 10 mm. is 126.0, at 20 mm., 142.1° C. Mann, Montonna, and Larian (19) gave a refractive index (n_p^{20}) of 1.5282, and boiling points of 126.2° at 10 mm. and 141° C. at 20 mm. The discrepancy in the refractive index is probably due to the large dispersion which renders this measurement with the Abbe refractometer quite inaccurate.

Yields

Using the technical p-cymene, the yield of 2-nitrop-cymene plus p-nitrotoluene amounts to 86-88 per cent, of which approximately 8 per cent is p-nitrotoluene; the amount of recovered p-cymene



Courtesy, Pacific Pulp and Paper Industry

BLOW PITS AND VOMIT STACKS OF WOOD STAVE CONSTRUCTION PARALLEL THE DIGESTER BUILDING. THE STACKS, 103 FEET HIGH, ARE REPORTED TO BE THE HIGHEST EVER BUILT

(consisting almost entirely of terpenic impurities associated with the original p-cymene) amounts to less than 1 per cent; and the amount of tarry matter after distillation of the nitration products below 20 mm. pressure averages about 4 to 6 per cent of the total nitration products.

When partially purified p-cymene is used and nitration is carried out with the aid of an added emulsifying agent, the yield of 2-nitro-p-cymene plus p-nitrotoluene has amounted to over 90 per cent, the amount of recovered p-cymene to less than 1 per cent, and the tarry matter to 3-4 per cent.

Factors Affecting Emulsification

During the course of some of the early nitrations carried out with a fairly pure p-cymene (method A), it was found impossible to emulsify the p-cymene in the acetic acid-sulfuric acid mixture; in others it was observed that after the addition of approximately one third of the nitrating acid, the characteristically large amount of heat which had been evolved during the reaction decreased rapidly with further addition of the nitrating acid. Simultaneously, the p-cymene was found to separate partially from the reaction mass as a layer floating above the nitration mixture. The mixture rapidly darkened and nitrogen oxides were evolved. After approximately two thirds of the nitrating acid had been added, the p-cymene layer disappeared, as well as the evolution of nitrogen oxides; the reaction was once more highly exothermic. The reaction products contained much tarry matter and unreacted *p*-cymene. The explanation for the failure in these nitrations is as follows: The decrease in the evolution of heat was due to the marked reduction in the amount of emulsified *p*-cymene available for reaction with the nitrating acid, as a result of the breaking of the *p*-cymene emulsion; consequently, the nitric acid concentration would

increase sufficiently to oxidize the *p*-cymene to deleterious products found in the tarry matter. The reformation of the emulsion after two thirds of the nitrating acid had been added was due in part to the good emulsifying properties of the nitrated products.

In all further runs, considerable study was made of the factors which affect the emulsification of the p-cymene in the nitration mixture. The most important factors were found to be the purity of the p-cymene, the amount of initial emulsifying acid, the temperature, the efficiency of agitation, and the addition of emulsifying agents. The summarized data for the variation of these factors are given in Table II.

Recognition of the extremely important role which emulsification plays in this reaction leads us to suspect that in many other reactions this might easily be a controlling factor.

Effect of Purity of *p*-Cymene

The technical *p*-cymene recommended for nitration was found to possess desirable emulsifying properties, attributable to the impurities associated with the original *p*-cymene. In general, it was found that the more pure the *p*-cymene, the poorer the emulsifying qualities and consequently the poorer the yields of 2-nitro-*p*-cymene.

The technical *p*-cymene elaborately purified by the method of LeFevre, LeFevre, and Robertson (17) gave a product with a boiling point at 759 mm. of 177.2° C., and a refractive index (n_{D}^{25}) of 1.48818–1.48850; the previously cited investigators gave a boiling point at 760 mm. of 177–177.5° C.,

and a refractive index of 1.48878. With this *p*-cymene it was impossible to maintain an emulsion throughout the nitration, even after the addition of 10 ml. of 90 per cent "Aquasol"; consequently, the yield of 2-nitro-*p*-cymene plus *p*-nitrotoluene was low (run 44).

A less pure *p*-cymene (method A) was prepared by shaking 2 liters of the technical p-cymene with six to eight 50-ml. portions of concentrated sulfuric acid, washing with water, drying with calcium chloride, and fractionating; a product boiling at 176.5-7.5° C. was formed. Nitration of this product was carried out under widely varying conditions, alone and with the addition of the following substances as emulsifying agents: 90 per cent "Aquasol" (a sulfonated castor oil produced by the Calco Chemical Company, Inc.), "Sulfatate" (Glyco Products Company), oil of turpentine, and borneol. The first two emulsifying agents enabled a good emulsion to be had throughout some of the nitrations, with yields of 2-nitro-p-cymene plus p-nitrotoluene greater than 90 per cent; neither borneol nor turpentine was effective. The emulsifying agent was dissolved in the sulfuric acidacetic acid mixture before the *p*-cymene was added. Owing to the difficulty of maintaining the emulsion throughout some of the nitrations using *p*-cymene from separate purifications, this method is not recommended; instead it is more economical and advantageous to use the technical product after fractionating (boiling point, 174.0-178.0° C.). The much larger amount of terpenic impurities contained in this pcymene as compared with the purified *p*-cymene probably accounts for its excellent emulsifying qualities.

Effect of Time and Temperature

Under the recommended conditions, this reaction has been found to proceed extremely exothermically, quickly,

and smoothly without evolution of nitrogen oxides. A comparison of the nitrating times as employed by Andrews (1), using salt and ice, with the present time of nitration with solid carbon dioxide and alcohol, shows that the present rate is over eighteen times as great.

Theoretically it would be of interest to study this reaction at much lower temperatures; however, owing to the solidification of the acetic acid as well as the products of nitration, this is impossible. As the nitrating temperature is raised above -10° C., the amount of oxidation increases, so that around room temperature and higher, oxidation products are principally obtained. The oxidizing effect of the nitric acid can become quite drastic for this compound even at low temperatures when there is inadequate emulsification, for under these conditions the concentration of nitric acid may become quite large. The considerable amount of *p*-tolyl methyl ketone and tarry matter obtained by Mann, Montonna, and Larian (19) was probably due in part to inadequate emulsification and the higher nitrating temperature.

The cooling bath temperature is very important for proper emulsification; thus, even under good agitating conditions the nitration products will partially freeze out if the bath temperature is lowered much below the optimum temperature. This is due to the fact that the temperature drop through the pail is very small; consequently its inside surface, where crystal formation first takes place, is practically the same temperature as the cooling bath. Early in the nitration when there is a large amount of unreacted *p*-cymene, the partial freezing out of the nitrated products is usually sufficient to break the emulsion. This was the difficulty with many of the runs (as runs 1 to 17) where the bath temperature was too low for the amount of acetic acid added to prevent crystal formation.

Effect of Altering Mixed Acids

The recommended amount of sulfuric acid has been found sufficient to enable the utilization of all of the p-cymene. There is no advantage in varying the relative amount of sulfuric acid in the nitrating acid and in the initial emulsifying acid mixture, respectively, but distinct disadvantages; thus, an appreciable decrease in the amount of sulfuric acid in the latter mixture makes the emulsification of the pcymene impossible, whereas an increase makes efficient agitation of the mixture more difficult.

The recommended amount of acetic acid has been found to be sufficient, at the temperature employed, to prevent the freezing out of any of the nitration products and thus affords at all times a homogeneous emulsion. In the absence of acetic acid it is impossible to maintain the emulsion or stir the mixture effectively.

The use of a fuming nitric acid (density, 1.51) or a large excess of nitric acid (density, 1.42) is disadvantageous, causing considerable oxidation with the former and some polynitration with the latter.

A substitution of phosphoric acid for the sulfuric acid proved to be ineffective. Owing to the solidification of the phosphoric acid a higher temperature was used; however, even at 50° C. there was scarcely any nitration. Similarly, a mixture of acetic anhydride and fuming nitric acid was of little effect.

Effect of Adding p-Cymene to Mixed Acid

Instead of adding the nitrating acid to the emulsified pcymene, an attempt was made to add the p-cymene to the mixed acid. By this means a portion of the *p*-cymene remains unattacked and a considerable amount is dinitrated. By increasing the amount of nitric acid, all of the *p*-cymene may be utilized (however, only with a correspondingly larger amount of dinitrated products). Hence, this method cannot be utilized in the mononitration of p-cymene owing to its high reactivity; this method, however, is advantageous when polynitrated products are desired. When the *p*-cymene is added to the mixed acid, no emulsification



difficulties are encountered; consequently, a p-cymene of any degree of purity is suitable.

Conclusions

1. p-Cymene has been successfully nitrated with yields of over 90 per cent of mononitrated products consisting of 2nitro-p-cymene and p-nitrotoluene-the latter about 8 per cent.

2. The particular features of this process are (a) the maintenance of a good emulsion throughout the nitration, enabling the utilization of all of the p-cymene with a minimum of oxidation at -10° C., and (b) a very decreased nitration time due to effective means of heat removal by means of solid carbon dioxide in alcohol.

3. A technical *p*-cymene obtained from sulfite turpentine has been used which possesses certain emulsifying properties that make it more advantageous than pure *p*-cymene, besides being far more economical.

4. Good emulsification and temperature control are important in the nitration of other easily oxidized compounds.

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