

present function, p, and v to represent the present function, L, the values of these coordinates are inserted in the above formulas to determine the values of the a's, b's, and c's, as follows: $a_1 = 0$, $a_2 = -2$, $b_1 = 1/6$, $b_2 = 2^{5}/6$, $a_3 = 0$, $a_4 = 1/3$, $b_3 = 3/4$, $b_4 = -1/{12}$, $c_2 = -1/3$, and $c_4 = 1/4$. Then $r_y = 1/2$ and $r_x = -4/7$. The negative sign of r_x indicates merely that positive values of pare to be located in the negative region of the scale, and vice versa, since $p/(p + r) \equiv -p/(-p - r)$. The nomograph is constructed using these values of r_x and r_y . From a preliminary plot it is apparent that an angle of 30° between the X and Y axes will convert the parallelogram to a rectangle and that the length-to-width ratio desired may be achieved by setting the length (or modulus) of the X axis approximately twice as great as that of the Y axis. The nomograph thus constructed and rotated to place the scales in vertical position is shown in Figure 6.

DERIVATION OF THE METHOD

It may be shown that, like the X axis, every line in the hyperbolic plane may be described as having a hyperbolic subdivision such that the distance from the Y axis of any point on that line is given by $x' = p_x/(p_x + r_x')$, where p_x is the hyperbolic abscissa of the point and r_x' has the value $r_x' = (p'_y + r_y)/(p'_z + r_z)$. In this expression p'_y and p'- are the y and \overline{z} intercepts of the line, while r_y and r_z are the hyperbolic constants of the Y and \overline{Z} axes, respectively. The length of the line segment bounded by the Y and \overline{Z} axes is taken as unit length for any line in the plane.

It may also be shown that the necessary and sufficient condition that two lines (a) and (b) be parallel is that $r_{x'}(a) = r_{x'}(b)$ i.e., that their hyperbolic constants be equal. It is this principle which is applied in determining the values of r_y and r^- (and, in turn, r_x) which must be employed to render the opposite sides of a quadrilateral parallel.

The above value of r_x' is given in terms of its y and \overline{z} intercepts. These, however, are known if any two points on the line are known. It is a simple matter to substitute for these intercepts in the expression for r_x' their values in terms of the coordinates of the four given points. There is a pair of such substitutions for each side of the quadrilateral, resulting in a separate expression for r_x' for each side. The values of r_x' for opposite sides of the quadrilateral are then equated, and the equations thus obtained are solved for r_y and $r_{\overline{z}}$; r_x is given by the expression $r_x = r_y/r_{\overline{z}}$. It is the resulting expressions for r_x and r_y which are evaluated by the above steps involving the a's, b's, and c's.

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l-CARVONE FROM *d*-LIMONENE

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d-Limonene, which constitutes about 95% of orange and grapefruit oils, is potentially available in large quantities as a by-product of the citrus industry. To date, industrial utilization of limonene has been limited. This paper presents the results of a study of the conversion of *d*-limonene to *l*-carvone to provide a substitute or partial replacement for natural oil of spearmint in which *l*-carvone occurs to the extent of about 65%.

The conversion of d-limonene was effected by treatment with nitrosyl chloride, using sulfur dioxide as a solvent to yield the nitrosochloride, which upon treatment with urea yielded carvone oxime. Hydrolysis of the oxime under controlled pH conditions produced *l*-carvone. The over-all yield of *l*-carvone from *d*-limonene was 35%.

l-Carvone produced by this process has high optical activity and organoleptic properties which make it suitable as a flavor or flavor adjunct.

S A by-product of the citrus industry *d*-limonene, which makes up about 95% of orange and grapefruit oils, is potentially available in large quantities. To date, industrial utilization of limonene has been limited to its use as a solvent.

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This paper presents the results of part of a study which had as its object the conversion of *d*-limonene into useful and valuable products.

Since *d*-limonene possesses optical activity, it seemed plausible to investigate processes that were capable of producing products, the optical properties of which were of some significance. A survey of the literature revealed that *d*-limonene is structurally related to *l*-carvone and could be converted into it by the following sequence of reactions:



l-Carvone occurs to the extent of approximately 65% in natural oil of spearmint and possesses the characteristic flavor of this oil. As the availability of spearmint oil has been somewhat variable over the past years, this investigation was undertaken in an effort to provide a substitute for the natural product or a partial replacement of it.

NITROSOCHLORINATION OF LIMONENE

The first step in the synthesis of carvone from limonene involves the formation of limonene nitrosochloride. This intermediate was first prepared by Tilden (8) by the action of gaseous nitrosyl chloride on limonene. Wallach (9, 11) later claimed an improvement in the process through the use of amyl or ethyl nitrite in the presence of hydrochloric acid. More recently, Rupe (6) claimed to have obtained good yields through the use of a mixture of hydrogen chloride and nitrogen trioxide.



Figure 1. Hydrolysis of Carvoxime

As nitrosyl chloride is commercially available at a relatively low cost, an investigation was made involving the use of this reagent. A study made of nitrosochlorinating conditions (1, 2)revealed that when sulfur dioxide was used as a solvent at temperatures below -60 ° C., yields as high as 67% could be obtained by successive re-use of the solvent.

EXPERIMENTAL. A solution of 91.6 grams of d-limonene (obtained from orange oil: $[\alpha]_{5}^{\infty} = +122^{\circ}$; boiling point, 64° to 65°/15 mm.) in 200 cc. of liquid sulfur dioxide was maintained in the temperature range of -60° to -70° C., with stirring, while 40 grams of nitrosyl chloride were bubbled in over a period of 0.5 hour. The low temperature was maintained for an additional 0.5 hour while the mixture was maintained. The white solid was separated by vacuum filtration, and the filtrate was kept cold. The solid *d*-limonene nitrosochloride was washed with 200 cc. of cold (at least -60° C.) ether and airdired. The weight of the nitrosochloride was 64 grams, representing a 47% yield.

The filtrate, which was kept cold, was combined with 83 grams of *d*-limonene and again 40 grams of nitrosyl chloride were bubbled in under the conditions described above. The solid, separated, washed, and dried as before, weighed 89 grams, representing a 72% yield.

Again the filtrate was combined with 83 grams of *d*-limonene and the process was repeated. The dry, solid nitrosochloride weighed 105 grams, representing an 86% yield. The over-all yield was 67.5%.

Table I. Ef	FECT OF	TEMPERATURE	IN N	ITROSOCHLORINATION
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	Temp	Yields, %					
Expt. No. ^a	° C.	Run 1	Run 2	Run 3	Av.		
$101 - 169 \\ 101 - 174$	$-60 \\ -60$	$\begin{array}{c} 46.7 \\ 48.2 \end{array}$	$\begin{array}{c} 69.5\\ 69.0 \end{array}$	$64.0 \\ 66.0$	$\substack{60.1\\61.1}$		
101–180 101–183	40 40	$\begin{array}{c} 43.0\\ 37.7\end{array}$	$\begin{array}{c} 59.1\\ 66.5 \end{array}$	57.6 56.8	$\begin{array}{c} 53.1\\ 53.7\end{array}$		
101 - 177 101 - 188	$-20 \\ -20$	20.6 21.6	$\begin{array}{c} 55.1\\ 53.6 \end{array}$	$58.1 \\ 55.5$	$\begin{array}{c} 44.7 \\ 43.6 \end{array}$		
^a In this study	washings we	ere made wi	th acetone	instead of e	ther.		

A study made of the effect of temperature on the yield of nitrosochlorination product using sulfur dioxide as a solvent revealed that substantially lower yields were obtained at higher temperatures. Table I shows the results obtained from three consecutive runs (as described above) made at -20° , -40° , and 60°C.

In an effort to account for the difference in yields in the first and subsequent runs, a study was made of the solubility of dlimonene nitrosochloride in acetone and liquid sulfur dioxide. Table II gives the results of this study which showed that the difference in yield may not be attributed entirely to the factor of solubility.

TABLE II. SOLUBILITY	OF <i>d</i> -LIMONENE NITH	ROSOCHLORIDE
Solvent	Temp., °C.	Grams/100 Cc. Solvent
Acetone Sulfur dioxide Sulfur dioxide	-60 -55 to -60 -30	$\begin{array}{c} 1.7\\5.0\\15.5\end{array}$

DEHYDROCHLORINATION OF LIMONENE NITROSOCHLORIDE

Dehvdrochlorination of limonene nitrosochloride leads to the formation of carvone oxime from which carvone can be prepared by acid hydrolysis. In the initial stages of this work, the oxime was isolated and purified, but later work revealed the expediency of proceeding directly to carvone without the purification step. The yield of distilled carvone from the nitrosochloride was about 54%.

Reagents reported as effective in splitting out hydrogen chloride from the nitrosochloride include alcohol (4), alcoholic solutions of sodium and potassium hydroxide (10, 12), sodium methylate (3), and pyridine (14). A preliminary study revealed that a 91% yield of the oxime could be obtained using pyridine in acetone solution. Further study revealed the feasibility of using urea as the dehydrohalogenating agent. When absolute isopropyl alcohol was used as the solvent, yields of 99% were obtained. The use of 90% isopropyl alcohol gave somewhat lower yields.

DEHYDROCHLORINATION OF LIMONENE NITROSOCHLORIDE USING PYRIDINE. A mixture of 40 grams of d-limonene nitroso-chloride, 160 cc. of acetone, and 30 cc. of denaturing grade pyridine was refluxed for 1 hour. The mixture was poured into by the was related for 1 both. The initiate was pointed into an excess of water whereby the oxime separated first as an oil and then crystallized on standing. The mixture was filtered and the oxime washed with water and dried. The oxime weighed 30 grams (91% yield) and had a melting range of 65° to 73° C.

DEHYDROCHLORINATION OF LIMONENE NITROSOCHLORIDE USING UREA. A mixture of 50 grams of *d*-limonene nitroso-chloride and 20 grams of urea in 250 cc. of absolute isopropyl alcohol was refluxed for 1 hour. The oxime, recovered as described above, weighed 40.7 grams (99% yield) and had a melting range of 65° to 72° C.

HYDROLYSIS OF CARVONE OXIME

Hydrolysis of *l*-carvoxime to *l*-carvone with a minimum of racemization presented some difficulty. In addition to racemization there was also the possibility of isomerization of the oxime in the presence of acids to yield *p*-aminothymol (13).

A study of hydrolysis conditions revealed that if a pH of 0.7 was maintained during the hydrolysis of the oxime, carvone could be produced satisfactorily. The carvone, removed as formed from the reaction mixture by steam and purified by distillation, could be obtained in 60% yields.

Figure 1 shows the effect of pH during the hydrolysis on the rotation of the carvone obtained. In addition to having a lower rotation, the carvone obtained at a pH less than 0.5 had a decided "off" odor which was probably due to the presence of decomposition products. The oil distillate obtained by the use of pH values above 0.7 contained increasing quantities of carvoxime. To ensure the production of a high quality product, therefore, hydrolysis was generally carried out at a pH of 0.9 ± 0.1 . Fractional distillation of the crude carvone yielded a product having a rotation $[\alpha]_D^{27^\circ} = -60^\circ$. Table III summarizes the properties of the carvone obtained by this process as compared to those reported for carvone obtained from natural sources.

TABLE III. COMP	ARISON OF NATURAL AND	Synthetic Carvone
	This Work	Natural (7)
Boiling point	44-44.5° C./2 mm. 91-92° C./10 mm. 239.5-240° C./745 mm	230-231° C./763 mm. 97-98° C./9 mm. (5)
Melting point Refractive index Specific gravity Optical rotation [a	$\begin{array}{rcl} -25.2^{\circ} & \text{C.} & n_{D}^{27} & = 1.4973 \\ & 0.9555 & (27^{\circ}/4^{\circ}) \\ \text{d} & \text{D} & -60^{\circ} & (27^{\circ} & \text{C.}) \end{array}$	$n_{\rm D}^{20^{\circ}} = 1.4988$ 0.9652 (15°/15°) -62.4° (20° C.)

DETERMINATION OF OPTIMUM pH FOR HYDROLYSIS

The hydrolysis was carried out in a flask equipped with high temperature glass (Beckman 8990 TA) and calomel (Beckman 8970 TA) electrodes. Measurement of the pH was made using a Macbeth pH meter with the above electrodes.

Ten grams of *l*-carvoxime and 500 cc. of water were placed in the flask, the pH adjusted to the desired level by the addition of hydrochloric acid and maintained at that level while steam passed in. When oil no longer passed over into the distillate, the distillation was stopped. The oil was separated from the water, weighed, and its rotation determined. (The data from this series are shown in Figure 1.)

HYDROLYSIS OF CARVOXIME (FINAL PROCEDURE)

Eighty-one grams of crude carvoxime (obtained by the procedure described above) were admixed with 500 cc. of water and the mixture adjusted to a pH of 0.9 ± 0.1 using 6 N sulfuric acid. Steam was passed into the mixture and the pH maintained at 0.9 until no more oil was distilled over. About 48 grams (65% yield) of oil having a rotation, $[\alpha]_{D}^{27^{\circ}}$, of -50° to -55° was obtained. Distillation at 10 mm. yielded 40 grams of *l*-carvone (54% yield) boiling 91° to 92° C.

LARGE SCALE PRODUCTION

For the purposes of evaluating the synthetic carvone, a 25pound sample was required. The process was satisfactorily scaled up and was carried out essentially as described above.

Table IV summarizes the results obtained for the nitrosochlorination step from a typical series of runs in which the solvent was replenished and re-used three times before discarding.

TABLE IV. TYPICAL RESULTS OBTAINED FOR THE NITROSOCHLORINATION STEP							
Run No.	Weight Limonene, Lb.	Mole Ratio, Limo- nene: NOCl	SO ₂ Solv % of T Solvent Previous run	rent ^a , Yotal from Fresh	Av. Temp. for Nitroso- chlorina- tion, ° C.	Time for Nitroso- chlorina- tion, Hr.	% Ni- troso- chloride Yield¢
$20 \\ 21 \\ 22 \\ 23$	$9.0 \\ 9.5 \\ 12.7 \\ 6.2$	$1.04 \\ 1.01 \\ 1.03 \\ 1.22$	$100 \\ 42 \\ 75 \\ 100$	$0 \\ 58 \\ 25 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	-50 - 49 - 48 - 48	$\begin{array}{c} {4.5} \\ {4.3} \\ {6.0} \\ {2.6} \end{array}$	$56.2\\46.8\\56.3\\51.7$
^{<i>a</i>} Normal total volume of solvent = 13 liters. ^{<i>b</i>} Based on limonene used.							

Table V summarizes the results of conversion of the limonene nitrosochloride to distilled carvone. Pyridine was used as the dehydrochlorinating agent.

г	ABLE V. Nitro	RESULTS SOCHLORE	of Conv. de to Dist	ersion of filled Ca	r Limoi rvone	NENE
	Nitroso-		Over			
Run Charge	Charge	Crude		Pure		all
No.	Lb.	Wt. Lb.	[<i>α</i>]	Wt. Lb.	%	Yield ^{a, b}
$\frac{20}{21}$	$7.50 \\ 6.60$	$\frac{2.97}{2.84}$	-49.9° -50.0°	$\frac{2.33}{2.28}$	$\frac{42.0}{46.1}$	23.6 21.6
$\overline{2}\overline{2}$	10.50	4.20	-49.0°	3.30	42.2	23.7
23	4.75	2.04	-48.5°	1.59	45.0	23.2
${}^{a}_{b}$ Cal	culated to c ed on limor	arvone $[\alpha]$	$= -62.4^{\circ}.$			

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Next month I&EC will publish the papers that were presented last December at the Annual Christmas Meeting of the ACS Division of Industrial and Engineering Chemistry. The 1950 feature is a symposium on dispersions in gases, and includes studies in generation, particle size analysis, transfer and collection, and filters. Persons working on air pollution control problems will find interesting data in these reports.

The June I&EC pilot plant article is "Control of Particle and Size Distribution in a Spray Dryer," by H. Wallman and H. A. Blynth of American Cyanamid Co. This paper is from the pilot plant symposium of the Division of Industrial and Engineering Chemistry held at Houston, Tex., last Spring.