the thiocyanate reagent also show an increase, probably being dependent on the amount of hydrocarbons present.

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Analysis of Certain Alkylated Phenol Mixtures by Bromination

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By taking advantage of the different number of ortho or para positions available for bromination in nonalkylated and alkylated phenols, it has been possible to apply the acid bromate-bromide method to the analysis of certain phenol mixtures. Attention to the percentage of excess bromine and the reaction time is necessary, the best conditions being determined by a study of known mixtures before applying the method to unknowns.

THE quantitative bromination of phenols by acid bromatebromide solution has been reviewed and examined thoroughly by Ruderman (4). The effect of acid concentration, bromination time, temperature, and substituents was investigated. In particular, Ruderman showed that an appreciable excess of bromine and long reaction times very often resulted in overbromination-i.e., bromination in excess of the number of unsubstituted ortho and para positions. But in certain cases-for cited above, it has been found that the bromate-bromide technique can give satisfactory results, provided one uses a limited excess of bromine and short bromination times. The conditions must be carefully established with known mixtures. This paper describes the application of the bromate-bromide method to mixtures of certain alkylated phenols.

SOLUTIONS AND REAGENTS

Sodium Thiosulfate, 0.1N, standardized against a weighed sample of potassium iodate using standard analytical procedure. Bromide-Bromate Solution, 0.1N, prepared following the direc-

tions of Ruderman (4). Hydrochloric Acid, concentrated acid, specific gravity 1.19. Potassium Iodide, 10% aqueous solution. Methanol. Merck & Co. absolute methanol, c.p., acetone-free,

was used without further purification.

Phenol. C.P. grade phenol was triply distilled, the final distillation being carried out in a nitrogen atmosphere, boiling point

179° to 180° C. o-Cresol. Water-white, c.P. grade o-cresol (Fisher Scientific Co.) was used without further purification.

p-Cresol. Practical grade p-cresol was triply distilled to give

example, m-cresol and phenols with tert-alkyl substituentsexcellent results were obtained regardless of the percentage of excess bromine. Others-for example, p-cresol-gave good results when a reasonable (say 10 to 30%) excess of bromine was used. The most critical variable with most phenols appeared to be the percentage of excess bromine.

To study the kinetics of the alkylation of several phenols with α -phenyl ethyl chloride (2), it became necessary to analyze mixtures of phenols and their alkylated homologs. One possible method would take advantage of the different number of ortho or para positions available for bromination in the nonalkylated and alkylated phenols. Despite the limitations

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Table I. Analysis by Bromination of Phenol, $o-(\alpha-Phenylethyl)$ phenol, p-(α-Phenylethyl)phenol, and Mixtures of These

Millimole									
Phenol	o- (α-Phenyl- ethyl)- phenol	p- (α-Phenyl- ethyl)- phenol	Re- action Time, Sec.	Meq. BrO3 ⁻ - Br ⁻	Meq. S2O3	$egin{array}{c} { m Net} & \ { m Meq.} & \ { m Br}_2 & \ { m Absorbed} \end{array}$	R ^a	Phen Found	ol, % Calcd.
$\begin{array}{c} 0.402 \\ 0.402 \\ 0.402 \\ 0.402 \\ 0.402 \\ 0.402 \\ 0.402 \\ 0.402 \end{array}$			$120 \\ 120 \\ 240 \\ 20 \\ 25-30$	$\begin{array}{c} 2.7160 \\ 2.7160 \\ 2.7160 \\ 2.7160 \\ 2.7160 \\ 2.7160 \\ 2.7160 \\ 2.7160 \end{array}$	$\begin{array}{c} 0.3726\\ 0.3575\\ 0.3575\\ 0.3520\\ 0.3320\\ 0.3320\\ 0.3370 \end{array}$	$\begin{array}{c} 2.3434\\ 2.3585\\ 2.3585\\ 2.3640\\ 2.3840\\ 2.3840\\ 2.3790\end{array}$	2.92 2.93 2.93 2.95 2.97 2.96		
	0.384 0.384 0.384		20 20 30	$1,6490 \\ 1,6490 \\ 1,6390$	$\begin{array}{c} 0.1913 \\ 0.1913 \\ 0.1720 \end{array}$	$\substack{1.4577\\1.4577\\1.4770}$	$1.92 \\ 1.92 \\ 1.95$		
		$0.1656 \\ 0.1656 \\ 0.1656 \\ 0.1656 \\ 0.1656 \\ 0.3312$	$\begin{array}{r} 60 \\ 10-15 \\ 10-15 \\ 5 \\ 25-30 \end{array}$	$\begin{array}{c} 0.7760 \\ 0.7760 \\ 0.7760 \\ 0.7760 \\ 0.7760 \\ 1.4550 \end{array}$	$\begin{array}{c} 0.0504 \\ 0.0957 \\ 0.0856 \\ 0.1007 \\ 0.0705 \end{array}$	$\begin{array}{c} 0.7256 \\ 0.6803 \\ 0.6904 \\ 0.6753 \\ 1.3845 \end{array}$	$2.20 \\ 2.06 \\ 2.09 \\ 2.05 \\ 2.09 \\ 2.05 \\ 2.09 \\ 2.00 \\ $		
0.396 0.396 0.396	$\begin{array}{c} 0.0212 \\ 0.0212 \\ 0.0212 \end{array}$	0.0229 0.0229 0.0229	20 25–30 25–30	$2.7160 \\ 2.7160 \\ 2.7160 \\ 2.7160$	$\begin{array}{c} 0.206 \\ 0.156 \\ 0.156 \end{array}$	$2.510 \\ 2.550 \\ 2.550$		85.3 89.8 89.8	90.0 90.0 90.0
0.396 0.396 0.396	$\begin{array}{c} 0.0772 \\ 0.0772 \\ 0.0772 \end{array}$	0.0557 0.0557 0.0557	$30-35\ 25\ 25\ 25$	3,100 3,100 3,100	${ \begin{smallmatrix} 0.216 \\ 0.201 \\ 0.212 \end{smallmatrix} }$	$2.884 \\ 2.899 \\ 2.888$		$72.6 \\ 73.9 \\ 73.0$	$74.9 \\ 74.9 \\ 74.9 \\ 74.9$
0.396 0.396 0.396 0.396 0.396	0.193 0.193 0.193 0.193 0.193	0.209 0.209 0.209 0.209 0.209	20 25–30 25–30 25–30	$\begin{array}{c} 4.171 \\ 4.171 \\ 4.171 \\ 4.171 \\ 4.171 \end{array}$	$\begin{array}{c} 0.236 \\ 0.201 \\ 0.201 \\ 0.201 \\ 0.201 \end{array}$	3.935 3.970 3.970 3.970 3.970		$46.4 \\ 48.7 \\ 48.7 \\ 48.7 \\ 48.7 $	$\begin{array}{r} 49.7 \\ 49.7 \\ 49.7 \\ 49.7 \\ 49.7 \\ 49.7 \end{array}$
0.158 ^a Numb	0.278 per of reactive	0.201 positions per :	20-25 molecule—i	3.100 i.e., for pher	0.246 nol, $R = 3$.	2.854		24.0	24.8

a water-white product, boiling point 199-200° C.; recrystallized from petroleum ether gave a melting point 36-37° C. $2-\alpha$ -Phenylethylphenol. A sample obtained from Chemical Division, Koppers Co., Pittsburgh, Pa., was distilled through a Podbielniak column; boiling point 127-127.5° C. at 0.9 mm. of mercure $\alpha^{29} = 1.502$ mercury, $n_{\rm D}^{20} = 1.5923$.

4-a-Phenylethylphenol. A sample obtained from Koppers, was recrystallized from petroleum ether, melting point 56.0-56.3° C.
 4-a-Phenylethyl-2-methylphenol. This compound was pre-

pared by the alkylation of σ -cresol with α -phenyl ethyl chloride (3). The crude $4 - \alpha$ -phenethyl-2-methylphenol was doubly distilled and collected as a water-white viscous liquid, boiling point $158-159^{\circ}$ C. at 6 mm. of mercury. The reported boiling point is 179° C. at 13 mm. (1).

 $2-\alpha$ -Phenylethyl-4-methylphenol. This was prepared in a manner identical to that described for $4-\alpha$ -phenylethyl-2-methylphenol using *p*-cresol instead of *o*-cresol. It was obtained after double distillation as a water-white, viscous liquid, boiling point 165° to 170° C. at 9 mm. of mercury. The reported boiling point is 175° to 177° C. at 13 mm. (1).

PROCEDURE

The procedure was essentially a modification of the method of Ruderman (4). Stock solutions of phenol, *p*-cresol, and *o*-cresol and their respective α -phenylethyl substituted derivatives were prepared by dissolving a weighed sample of the phenol in meth-anol and diluting the solution to volume with 60% aqueous methanol. These solutions were usually about 0.04*M*. It was shown that 60% aqueous methanol solutions could be used safely without bromine consumption by the methanol, since dilution with acetone-free methanol instead of water in standardization of the bromate-bromide solution did not alter the titer of sodium thiosulfate required.

An appropriate aliquot of the stock solution (or solutions in the case of mixtures) was pipetted into a 250-ml. iodine flask. The calculated excess of standard bromate-bromide solution was added together with sufficient distilled water or methanol to make the combined volume about 40 to 50 ml. Five milliliters of concentrated hydrochloric acid was then added, and the flask was quickly stoppered, and swirled for the desired reaction time, as measured by a stop watch. The excess bromine was then de-stroyed with 10 ml. of a 10% potassium iodide solution. The iodine liberated was titrated within 30 seconds with standard sodium thiosulfate solution to the disappearance of the iodine color, or to a starch end point. The results are tabulated in Tables I, II, and III.

The amount of bromine consumed is a measure of the relative amount of the phenol and its α -phenylethyl derivative present in a mixture, while the total amount of both phenols is known from the composition of the original mixture. Thus, the percentage of phenol or alkylated phenol found by the bromination technique may be calculated from a pair of simultaneous equations. For example, in the case of mixtures of phenol and o- or p- α -phenylethylphenol, the following equations were used:

> x + y = total moles of phenols present 6x + 4y = equivalents of bromine consumed

where x = moles of phenol present and y = moles of α -phenylethylphenol present.

 \mathbf{E} valuation of x and y in the above equation permitted the determination of the percentages of each phenol as given in Tables I, II, and III. Similar equations were used for mixtures of o- and p-cresol and their alkylated derivatives. The number of reactive positions, R, for the cases in which

only one phenol was present, was found by dividing the milli-

equivalents of bromine consumed by twice the millimoles of phenol present (as 2 moles of bromine were required per position brominated).

DISCUSSION

Table II. Analysis by Bromination of p-Cresol,2-(α-phenylethyl)-4methylphenol, and Mixtures of These

Millimole		Reaction			Net			
p-Cresol	2-(α-Phenylethyl)- 4-methylphenol	Time, Sec.	Meq. BrO3-Br-	$\substack{\mathbf{Meq.}\\ \mathbf{S}_{2}\mathbf{O}_{3}}^{\mathbf{Meq.}}$	Meq. Br ₂ Absorbed	R	$\frac{p-Cre}{Found}$	sol, % Calcd.
0,1930 0.1930 0.1930 0.1930 0.1930		$15 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25$	$1.183 \\ 1.18$	$\begin{array}{c} 0.470 \\ 0.415 \\ 0.405 \\ 0.408 \end{array}$	$0.713 \\ 0.768 \\ 0.778 \\ 0.775$	$1.85 \\ 1.99 \\ 2.02 \\ 2.01$		
	$\begin{array}{c} 0.2165 \\ 0.2165 \\ 0.2165 \\ 0.2165 \\ 0.2165 \\ 0.2165 \end{array}$	25 25 25 25	$\begin{array}{c} 0.592 \\ 0.592 \\ 0.592 \\ 0.592 \\ 0.592 \\ 0.592 \end{array}$	$\begin{array}{c} 0.179 \\ 0.170 \\ 0.159 \\ 0.144 \end{array}$	$\begin{array}{c} 0.413 \\ 0.422 \\ 0.433 \\ 0.448 \end{array}$	0.96 0.98 1.00 1.03		
$\begin{array}{c} 0.1544 \\ 0.1544 \end{array}$	$0.0217 \\ 0.0217$	25 25	0.986 0.986	$0.328 \\ 0.326$	$\begin{array}{c} 0.658 \\ 0.660 \end{array}$		86.9 87.4	$\begin{array}{c} 87.4\\ 87.4\end{array}$
$\begin{array}{c} 0.1544 \\ 0.1544 \\ 0.1544 \\ 0.1544 \\ 0.1544 \\ 0.1544 \end{array}$	$\begin{array}{c} 0.0433\\ 0.0433\\ 0.0433\\ 0.0433\\ 0.0433\\ 0.0433\\ 0.0433\end{array}$	25 20 25 25 25 25	1.085 1.085 1.085 1.085 1.085 1.085	0.382 0.392 0.385 0.387 0.387 0.378	0.703 0.693 0.700 0.698 0.707		77.8 75.3 77.3 76.8 78.8	77.8 77.8 77.8 77.8 77.8 77.8
$\begin{array}{c} 0.1351 \\ 0.1351 \\ 0.1351 \\ 0.1351 \\ 0.1351 \\ 0.1351 \end{array}$	0.0650 0.0650 0.0650 0.0650 0.0650 0.0650	25 25 35 30 30	0.986 0.986 0.986 0.986 0.986 0.986	$\begin{array}{c} 0.322 \\ 0.324 \\ 0.310 \\ 0.316 \\ 0.314 \end{array}$	$\begin{array}{c} 0.664 \\ 0.662 \\ 0.676 \\ 0.670 \\ 0.672 \end{array}$		$\begin{array}{c} 66.0\\ 65.5\\ 69.0\\ 67.5\\ 68.0 \end{array}$	67.5 67.5 67.5 67.5 67.5
$\begin{array}{c} 0.1158 \\ 0.1158 \\ 0.1158 \\ 0.1158 \end{array}$	0.0866 0.0866 0.0866	30 30 35	0.986 0.986 0.986	$\begin{array}{c} 0.352 \\ 0.347 \\ 0.342 \end{array}$	$\begin{array}{c} 0.634 \\ 0.639 \\ 0.644 \end{array}$		$56.9 \\ 57.9 \\ 59.4$	$57.4 \\ 57.4 \\ 57.4 \\ 57.4$

Table III. Analysis by Bromination of o-Cresol, 4-a-phenylethyl-2methylphenol, and Mixtures of These

Millimole		Reaction	Net						
o-Cresol	4-α-Phenyl- ethyl-o-cresol	Time, Sec.	Meq. BrO:-Br-	$\mathrm{Meq.}_{\mathrm{S_2O_3}}$	Meq. Br ₂ Absorbed	R	o-Cres Found	sol, % Calcd.	
$\begin{array}{c} 0.200 \\ 0.186 \\ 0.186 \\ 0.186 \\ 0.186 \end{array}$		$15 \\ 15 \\ 15 \\ 25$	1.183 1.085 1.085 1.183	$\begin{array}{c} 0.372 \\ 0.338 \\ 0.344 \\ 0.405 \end{array}$	$\begin{array}{c} 0.811 \\ 0.746 \\ 0.741 \\ 0.778 \end{array}$	$2.03 \\ 2.01 \\ 2.00 \\ 2.10$			
	0.204 0.204 0.204 0.204 0.204 0.204	15-20 25 27 15 15	0.6902 0.6902 0.6902 0.5916 0.5916	$\begin{array}{c} 0.2867 \\ 0.2847 \\ 0.2796 \\ 0.1925 \\ 0.2026 \end{array}$	$\begin{array}{c} 0.404 \\ 0.406 \\ 0.411 \\ 0.399 \\ 0.389 \end{array}$	$0.99 \\ 1.00 \\ 1.01 \\ 0.98 \\ 0.96$			
$\begin{array}{c} 0.180\\ 0.360 \end{array}$	$0.0200 \\ 0.0400$	15 15	$\substack{\textbf{1.183}\\\textbf{2.268}}$	$\begin{array}{c} 0.415 \\ 0.729 \end{array}$	$0.768 \\ 1.538$		$91.7 \\ 91.8$	90.0 90.0	
$\begin{array}{c} 0.334 \\ 0.334 \end{array}$	0.081 0.081	$15 \\ 15$	$\substack{\textbf{2.169}\\\textbf{2.169}}$	$0.672 \\ 0.669$	$\substack{1.497\\1.500}$		80.3 80.8	$\frac{80.5}{80.5}$	
$\begin{array}{c} 0.278 \\ 0.278 \\ 0.278 \\ 0.278 \end{array}$	$\begin{array}{c} 0.122 \\ 0.122 \\ 0.122 \\ 0.122 \end{array}$	$15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\$	$1.972 \\ 1.972 \\ 1.972 \\ 1.972$	$0.598 \\ 0.612 \\ 0.598$	$1.374 \\ 1.360 \\ 1.374$		$71.6 \\ 70.0 \\ 71.6$	69.5 69.5 69.5	
0.241 0.241	0.163 0.163	$\begin{smallmatrix}15\\15\end{smallmatrix}$	$\substack{1.873\\1.873}$	0.580 0.573	$\begin{array}{c}1.293\\1.300\end{array}$		$\begin{array}{c} 60.2\\ 60.8 \end{array}$	$59.8 \\ 59.8$	

In order to develop a reproducible method for the analysis of phenol mixtures by a bromination technique, the variables effecting the bromination must be carefully controlled. Analysis of known mixtures must be carried out until reproducibility is obtained before the method can be used with confidence on mixtures of unknown composition. Thus, it becomes necessary to carry out the bromination on known mixtures covering the entire composition range that may be encountered in unknown mixtures.

Probably the two primary factors contributing to overbromination are the bromine excess used and the time of reaction with bromine. In this procedure, the percentage of excess bromine was kept constant for the entire composition range of each mixture-e.g., for all compositions containing phenol, o- α -phenylethylphenol and p- α phenylethylphenol (Table I) the excess bromine was kept at $6 \pm 2\%$. The reaction time was then varied until reproducible results within 1 to 2absolute % of the calculated values were obtained.

ANALYTICAL CHEMISTRY

As shown in Table I, the reaction time, while not critical for phenol itself, must be maintained at 25 to 30 seconds for the o- and p- α -phenylethylphenol and for mixtures of these with phenol. If this is done, results in satisfactory agreement with the calculated values are obtained.

For p-cresol, 2-(α -phenylethyl)-p-cresol and mixtures of these, conditions essentially identical to those employed for phenol and its alkylated derivatives gave very satisfactory results (Table II). However, when o-cresol, 4-(α -phenylethyl-)-o-cresol and mixtures of these were analyzed, it was found that a shorter reaction time was necessary in order to obtain reproducible and accurate results. This rapid overbromination of o-cresol has also been observed by other investigators (4, 5), but may be successfully overcome by careful control of the reaction time. Lower temperatures may also be helpful (4).

This analytical procedure has been successfully applied to analysis of mixtures arising from the alkylation of phenol, o-, and *p*-cresol by α -phenyl ethyl chloride, permitting a kinetic study of that reaction (2). However, in using the bromination technique for the analysis of phenol mixtures, determinations on mixtures of known compositions must first be made before applying this method to unknown mixtures. It is very likely that this technique cannot be adapted to all phenol mixtures successfully, and experimentation must be undertaken to determine its suitability for each specific case.

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Displacement of the Nitro Group during Determination of Nitrophenols and Nitroanilines by the Koppeschaar Method

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During a study of the determination of 2,4-dinitrophenol and picric acid in mixtures by the Koppeschaar method, it was found that picric acid consumes bromine under the conditions of the procedure and a displacement of the nitro group may occur, rendering the final titration inaccurate. A procedure has been developed in which both phenols are titrated initially and the Koppeschaar method is applied to the titrated liquid to determine 2,4-dinitrophenol; picric acid is calculated by difference.

THE Koppeschaar procedure (10), though capable of excellent results with compounds that brominate normally (5), is by no means general for the classes named and is subject to errors from several recognized causes. These errors may be due to incomplete bromination because of conflicting directive influences or to the low solubility of the sample or of the partially brominated sample [the latter, in the case of nitrophenols, is the hypobromite compound (11)]; oxidation of the sample by bromine or hypobromous acid, as with aniline (5) and the nitroresorcinols examined in the present study; bromination of side chains (15); displacement of certain nuclear substituents by bromine-e.g., conversion of anthranilic acid and of sulfanilic acid to tribromoaniline (5, 8); and replacement of alcoholic-e.g., hydroxymethylgroups (13). In the course of work on the analysis of mixtures of picric acid and 2,4-dinitrophenol (16) it was observed that picric acid, presumably immune to bromination, consumed measurable amounts of bromine if the period of contact exceeded a few minutes, this result being accompanied by a fugitive end point in the final titration with thiosulfate. A similar displacement under preparative conditions-the conversion of picric acid to 6-bromo-2,4-dinitrophenol-was reported by Armstrong (1) and by Dhar (6). This paper presents the findings of a study of the displacement of the nitro group under the relatively mild conditions of the Koppeschaar analysis.

Of the 18 compounds examined (Table I) all except o-nitroaniline, *m*-nitroaniline, the nitroanisoles, and dinitrophenetole were found to consume bromine in excess of that attributable to normal bromination. The nitrophenolic ethers yielded no significant results because of their insolubility in the Koppeschaar liquid. The nitroanilines formed bulky amorphous precipitates that obstructed action of bromine (5). The nitroresorcinols consumed abnormally large amounts of bromine owing to oxidation.

DETECTION OF NITROUS ACID FOLLOWING DISPLACEMENT OF NITRO GROUP BY BROMINE

Preliminary tests showed that the consumption of more than the calculated bromine is associated with the presence of nitrous acid in the liquid; this is detectable by application of the Griess-Ilosvay test, following alkalization of the mixture and acidification with sufficient formic acid to reduce excess bromine and to leave the liquid at an acidity suitable for the diazotization and subsequent coupling.

Attempts to estimate colorimetrically the amount of nitrous acid formed and to correlate this with the excess bromine consumed revealed that the amount of nitrous acid in some cases increased to a maximum and then decreased slightly.

It appears that the momentary concentration of nitrous acid is not a dependable index of the extent of the displacement reaction. Analysis of the reaction liquid for nitrogen (other than nitro nitrogen) by use of Devarda's alloy (4) proved to be unfeasible, as this yielded ammonia from picric acid and reduced the nitro group to some extent. To exclude the effect of nitrous acid on the end point of the titration several reagents capable of destroying nitrous acid (urea, sulfamic acid, hydrazine sulfate) were tested, but none was completely effective and all consumed bromine. Analogy with the behaviors of anthranilic acid and sulfanilic acid suggests that displacement of the nitro group is followed by introduction of bromine in its place. Thus far, a number of attempts to isolate and identify such a product (bromodinitrophenol from picric acid or tribromophenol from 2.6-dibromo-4-nitrophenol or from 4,6-dibromo-2-nitrophenol) following prolonged action under the conditions of the Koppeschaar analysis have been unsuccessful. The scantiness of the recovered material and its indefinite character (no increase in bromine and small loss of nitrogen) suggest that action was destructive.

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