on the quantity of phenylmagnesium bromide present, was approximately equal to that obtained when a liberal excess of ether was used under corresponding conditions. These experiments emphasize the drawbacks to the use of ether even in minimal quantities.

By-Products.—From the oxidation of one mole of phenylmagnesium bromide, 3% of diphenyl and 18% of phenylmethyl carbinol were obtained. The carbinol was characterized by the urethan prepared with phenylisocyanate. Under corresponding conditions, one molecular equivalent of *p*-tolylmagnesium bromide gave 15.3% of *p*-cresol, 16% of *p*-ditolyl, 11% of toluene and 11% of *p*-tolylmethyl carbinol. No study was made of other by-products.

Phenylmagnesium Bromide and Metallic Oxides.—Yellow mercuric oxide was refluxed with an ether-toluene solution of phenylmagnesium bromide at 108° for 19 hours; the yield of phenol was 15.1%. Silver oxide refluxed with an ether solution for ten hours gave 18% phenol, and sodium peroxide refluxed with an ether solution for five hours gave 14.5% of phenol. The extent of oxidation due directly to these metallic oxides is probably less than the percentages of phenol indicate, because other experiments (see above under **Time**) show that some phenol is formed by merely protracted digestion when air is not excluded.

Summary

In a study of the optimal conditions for the preparation of phenols by the oxidation of arylmagnesium halides it is shown that the yields are strictly limited by the oxidation of ethyl ether. The ether peroxide so formed reacts with unaltered RMgX compound to give a secondary alcohol.

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[Contribution from the Drug Control Laboratory in Coöperation with the Color Laboratory, Bureau of Chemistry, United States Department of Agriculture]

IDENTIFICATION OF PHENOLS BY MEANS OF THE SPECTROSCOPE. II

By H. Wales and S. Palkin

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In a previous paper[1] absorption-spectra data were given for the azo dye derivatives of a number of simple phenols. A method was there outlined for the identification of those phenols based on coupling them with *p*-nitrobenzene diazonium chloride, extracting the dye acid with a suitable solvent and measuring the absorption spectra of the potassium salts in three different solvents. In another publication[2] a further applica-

[1] This Journal, **46**, 1488 (1924).

[2] *Ibid.*, **47**, 2005 (1925).

tion of this principle for the identification of certain alkaloids from ipecac was described.

In this paper the investigation has been extended to cover a large number of phenolic compounds and the data obtained are recorded. To permit ready reference and to correct several typographical errors the data previously recorded are included in the table accompanying this report. Not infrequently different dyes exhibit absorption maxima, in a given solvent, so nearly the same as to be practically indistinguishable. In these cases the value of examination in more than one solvent is apparent. We have found that with one possible exception similar maxima in one solvent are shifted by various degrees by using another solvent.

All of the phenols used were chemically pure as far as could be ascertained. Many of the rarer derivatives were obtained from the Eastman stock of pure organic chemicals.

In preparing the dye solutions for examination the same precautions were observed as in our previous work. It was found that most dyes made from phenols having more than one hydroxyl group and from those having a carboxyl group required relatively more alkali to produce the color. Thus the dye from resorcinol when dissolved in our alkaline acetone gave an absorption maximum at 547.5 $\mu\mu$. On adding another drop of alkali two maxima were found, one at 605 and the other at 547.5 $\mu\mu$. Increasing the amount of alkali resulted in the disappearance of the maximum at the lower wave length. The influence on the acetone solution spectrum of a small amount of alcohol (1%), introduced as the solvent for the potassium hydroxide, is quite apparent in this case as the maximum found when the dye was dissolved in acetone saturated with potassium hydroxide was 620 $\mu\mu$, a variation of 15 millimicrons.

Fourteen of the phenols used were derivatives in which the position *para* to the phenol hydroxyl group was occupied. Of these, six did not couple with *p*-nitrobenzene-diazonium chloride at ice temperature but coupled readily at room temperature. There is no apparent relationship between their constitution and ease of coupling. The figures given for phenol-*p*-sulfonic acid (sulfocarbolate) in our first paper, which were obtained by coupling in the cold, have been found to be due to an impurity, probably the *ortho* derivative. This dye was produced in minute amounts from all available samples of phenol-*p*-sulfonic acid when treated with the diazo reagent in the cold.

TABLE I

ABSORPTION SPECTRA MAXIMA $\mu\mu$

	Acetone	Alcohol	Water
Salicylamide	525	480	...
Pyrogallol	528	...	...
Methyl salicylate	530	485	467
Ethyl salicylate	531	490	465

TABLE I (*Concluded*)

	Acetone	Alcohol	Water
Orcinol	539	...	...
p-Bromophenol	550	504	498
2,4-Dibromophenol	555	511	493
Thiocol	555	536	510
n-Butyl salicylate	556	496	480
m-Chlorophenol	556	501	470
o-Bromophenol	559	502	480
Salicylaldehyde	564	500	478
Salicylalcohol (saligenin)	565	509	483
p-Hydroxybenzoic acid	566	505	475
Phenol	566	505	475
Phenolphthalein	568	508	495
Resorcinol-monomethyl ether	574	520	493
2-Chloro-5-hydroxytoluene	580	524	505
m-Hydroxybenzoic acid	583	508	474
m-Cresol	585	520	487
β-Naphthol	587	555	...
p-Cresol	590	542	499
o-Cresol	590	530	490
m-Dimethylaminophenol	596	564	530
2-Hydroxy-1,4-dimethylbenzene	599	544	510
Guaiacol	600	540	510
4-Hydroxy-1,2-dimethylbenzene	600	540	510
Creosol	602	545	512
4-Hydroxy-1,3-dimethylbenzene	605	553	513
Carvacrol	606	545	511
Salicylic acid	609	555	514
Eugenol	610	556	535
Thymol	610	559	515
2-Hydroxy-1,3-dimethylbenzene	610	558	517
α-Naphthol	630	590	568
o-Methylaminophenol	635	573	550
Excess of alkali required			
o-Cresotinic acid	535	530	512
m-Cresotinic acid	544	525	508
Resorcinol	605	570	550
Little or no coupling in the cold Coupling takes place at room temperature			
p-Hydroxybenzaldehyde	547	494	470
Vanillin	572	525	509
Phenol-*p*-sulfonic acid	575	514	...
**p*-Cresotinic acid	579	535	515
Capsaicin	593	550	510
p-Homosalicylaldehyde	595	546	525

* Excess of alkali required.

In Table I the phenols have been classified with a view to convenience for use. They have been separated according to whether coupling takes place at room temperature or in the cold and the amount of alkali required to produce the dye. Classification in each part has been made in accordance with the position of the maximum absorption in acetone solution.

Summary

Azo dye derivatives of 45 phenolic compounds were examined spectrophotometrically. Absorption spectra maxima are reported for solutions of these dyes in water, alcohol and acetone.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA

III. DI- AND TRIPHENYLAMINE

BY FREDERICK K. BELL

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Introduction

In the previous papers of this series[1] of studies, mixed amines of the aryl-alkyl type were selected for investigation. The results obtained revealed the importance of the region of 3.3 μ of the infra-red absorption in the case of these ammonia derivatives.

It will be recalled that the aryl group (the phenyl and naphthyl groups, at least) displays a characteristic absorption at 3.25 μ and that the alkyl group has a characteristic band at 3.43 μ. It is unfortunate that these two bands occur so closely in a region in which the dispersion of rock salt is greatly reduced. The absorption curves previously obtained offer no promise of the possibility of resolving additional bands in this region, if they are present, by means of the experimental method employed.

As a possible alternative, indirect methods might aid in determining whether the alkyl and the aryl groups display their characteristic absorption in this region independently when both of these groups are present in the same compound or, more specifically, when these groups occur independently in the same molecule, the linkage of each group taking place by means of a common nitrogen atom. It appears that information concerning the absorption of pure aryl amines would be of importance in this connection and, therefore, aid in the interpretation of the results previously obtained in the examination of the aryl-alkyl amines.

To this end the phenylamines have been selected for examination. The infra-red absorption of the mono derivative (aniline) having been examined and reported in an earlier communication[2] need not be repeated. The infra-

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[1] THIS JOURNAL, (a) **47**, 2192, (b) 3039 (1925).

[2] Ref. 1 a, p. 2201.