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Methods of Arylation

METHODS OF ARYLATION

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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Introduction

The present investigation is an attempt to use the aryl esters of p-toluene sulfuric acid as arylating agents. As there are many cases in which the known methods of phenylation are not applicable, the study of new phenylating agents is of interest. The methyl and ethyl esters of p-toluene sulfuric acid are good alkylating agents, and it was thought that the phenyl ester might act in a similar manner. The action of the phenyl ester on the sodium salts of alcohols and phenol was investigated.

HISTORICAL

In this section existing methods of phenylation will be described, and references given so that the interested reader will be enabled to find readily in the literature what work has been done on the various methods. This discussion will be followed by a summary of the work which has been done on p-toluene sulfone chloride, the substance from which the arylating agents were prepared.

Methods of Phenylation.

Whereas methyl and ethyl groups are readily introduced into almost any compound, the introduction of a phenyl group is in many cases not so readily accomplished. Most phenyl compounds are made by syntheses which do not involve the direct introduction of a phenyl group.

Several standard methods of phenylation of rather wide application are known, and numerous other methods for special cases. There remain many cases in which none of the existing methods of phenylation are applicable, so that work on new methods is of interest.

The Friedel-Crafts reaction, in which AlCl_3 is used to split out halogen acid between benzene and a halogen compound, thereby introducing the phenyl group into the compound which contained the halogen, is one of the best-known methods of phenylation. (See Cohen, Organic Chemistry, I, 195.) It can be carried out on a wide variety of compounds, the use of AlCl_3 not being limited to the splitting out of halogen acid (77-90.) ZnCl_2 or P_2O_5 are sometimes substituted for AlCl_3 .

The Grignard reaction, using phenyl magnesium halide, is another widely used method for introducing the phenyl group (91-94.) PhMgBr adds to a

double bond as Ph- and -MgBr. Hydrolysis of the resulting addition product substitutes a hydrogen atom in place of the -MgBr group. Calcium may sometimes be used in place of magnesium for making the phenyl metallic halide (95,96.)

Ullmann's method (97-116) is one of the most frequently used methods of phenylation. Finely divided copper or copper bronze is used for removing halogen from the benzene nucleus. Benzene derivatives containing halogen in the ring may be condensed with other halogen compounds by this method. They may also be condensed with amines, with a splitting out of HX between the amine group and the benzene derivative. In some cases metallic halide may be split out between a metallic derivative of an organic compound and the halogenated benzene derivative. The function of the copper in many cases has been found to be purely catalytic. Copper salts can be used in place of copper in some substances.

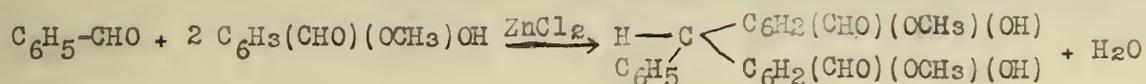
In Fittig's synthesis (117-123) metallic sodium is used to split out halogen between a halogen substituted benzene molecule and another halogen-containing molecule. This method is applicable in some cases of phenylation.

Benzene diazonium chloride, or substituted benzene diazonium chlorides, sometimes in the presence of cuprous chloride in hydrochloric acid solution, are much used as arylating agents (124-136.)

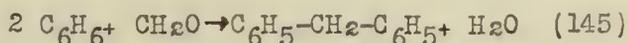
In a few cases the introduction of a phenyl group into a substance can be accomplished by passing the vapor of the substance, together with benzene vapor, through a hot tube (137-141.) Ethylene and benzene give cinnamene by this method. Benzene vapor passed alone thru a hot tube yields diphenyl, along with some more complex products.

Dehydrating agents are sometimes used as a means of carrying out a

phenylation(143-145.) $ZnCl_2$ pulls out water between benzaldehyde and vanillin according to the following equation:



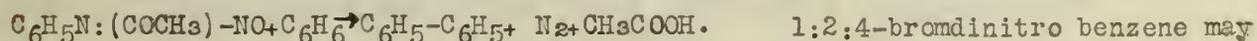
(143). Phenol heated with $ZnCl_2$ or $AlCl_3$ yields phenyl ether (144). Benzene condenses with formaldehyde under the influence of dehydrating agents according to the following equation:



Phenyl groups may be introduced not only on carbon, oxygen, nitrogen, and sulfur (146, 150, 151, 160), but also by various special methods on selenium (147, 148), tellurium (149), boron (152), phosphorus (153-155), arsenic (155-156), antimony (155), mercury (157-160), zinc (157-160), aluminium, cadmium and bismuth (157).

The introduction of aldehyde, nitrile, and carboxyl groups into the benzene nucleus may be regarded as phenylation of the carbon atom of one of these groups. The aldehyde group may be introduced into an aromatic hydrocarbon by means of CO and HCl, using $AlCl_3$ or $CuCl$ as a condensing agent (161). HCl and HCN together can be used for putting an aldehyde group into phenols and phenolic ethers (162, 163). The cyanogen group may be introduced by treating the halogen derivative of an aromatic hydrocarbon with a metallic cyanide, by treating the hydrocarbon with cyanogen (164) or by treating the hydrocarbon with $BrCN$ and $AlCl_3$ (188). Carbon dioxide and sodium convert the bromo derivative of an aromatic hydrocarbon into the sodium salt of the corresponding carboxy acid (165).

Nitrosoacetanilide has been used as a phenylating agent (166), e.g.



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act as an arylating agent (167). $p\text{-CH}_3\text{-C}_6\text{H}_4\text{-OK} + 1:2:4\text{-Br-C}_6\text{H}_3(\text{NO}_2)_2 \rightarrow \text{MeC}_6\text{H}_4\text{O-C}_6\text{H}_3(\text{NO}_2)_2$.

Phenyl ethers and substituted phenyl ethers may be made by heating phenols or their alkali salts with a halogen-substituted aromatic compound (170-173). Two molecules of salicylic acid heated to 220° will condense to give phenyl salicylate, splitting out CO_2 and water (168). Aryl ethers can be formed from the corresponding phenols by heating with ThO_2 as a catalytic agent (169).

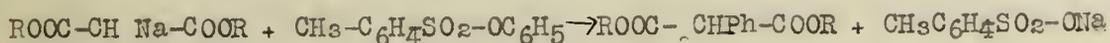
One case is known in which phenol, instead of forming a phenyl ether, substitutes the $-\text{C}_6\text{H}_4\text{OH}$ group for a Br atom in a compound (174). Molten KOH oxidizes phenol to diphenol, $\text{OH-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{OH}$ (187).

Carbonates and acetates sometimes act as condensing agents in phenylations by splitting out a molecule of acid between the two molecules which it is desired to condense (175-180).

In certain rather rare classes of compounds a phenyl group migrates from one part of the molecule to another (181-184.)

Under certain conditions benzene forms additive compounds with unsaturated hydrocarbons, thus introducing a phenyl group (185). Diphenyl adds to phthalic anhydride to form phenyl-benzoyl-o-benzoic acid, $\text{C}_6\text{H}_4\text{-}\begin{matrix} \text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5 \\ \text{COOH} \end{matrix}$ (186).

No direct method has been found for introducing the phenyl radical into active methylene groups, such as the methylene group in malonic ester or acetoacetic ester. It was thought that if phenyl p-toluene sulfonate proved to be a good phenylating agent it might be useful in phenylating active methylene groups. The following type of reaction might be expected to take place:



If such reactions did take place, they would provide a new use for p-toluene

sulfone chloride, from which phenyl p-toluene sulfonate is made.

p-Toluene Sulfone Chloride.

p-Toluene sulfone chloride occurs as a by-product in the manufacture of saccharin, in which it is formed simultaneously with o-toluene sulfone chloride. It is therefore plentiful, and, as but few uses have been found for it, cheap. A patent has been taken out on its use as an insecticide, when mixed with certain other substances (17). It has also been used in the manufacture of p-nitro-phenol and o-nitro-toluene sulfonic acid (1) ~~(See Theoretical)~~. The commercial applications have not been sufficient, however, for the utilization of the amount of p-toluene sulfone chloride made. Any application of the compound to organic synthesis, which might lead to its commercial use, would be of economic value.

Probably the best method of manufacture of o-and p-toluene sulfone chlorides (4, 5) is by treatment of toluene with $\text{SO}_2(\text{OH})\text{Cl}$ at a low temperature. The sulfone chlorides are formed directly, the ortho compound in greater yield than the para. An alternative method of manufacture (4, 6, 7, 8) is to sulfonate toluene, make the sodium salt of the sulfonic acid thus formed, and convert the sodium salt to the chloride by means of PCl_5 . The separation of p- from o-toluene sulfone chloride (9, 10) depends upon the fact that at ordinary temperatures the p-compound is a solid, m. 69° , while the o-compound is a liquid. The chloride may also be prepared from the potassium salt and PCl_5 (11, 12); from the sodium salt and $\text{SO}_2(\text{OH})\text{Cl}$ (13); or by chlorinating p-thio-cresol in glacial acetic acid (14). The properties of p-toluene sulfone chloride are described in several places in the literature (7, 11, 12, 15, 16).

Various studies have been made on the reduction of p-toluene sulfone chloride. The reagents used have been carbon and steam (15), H₂S (18), As₂O₃, Na₂SO₃ and NaOH (19), Zn and H₂SO₄ (6, 7, 12). For reduction of the sulfone chloride to toluene sulfhydrylate, it is recommended (20) that the chloride be converted to the sodium salt by treatment with sodium amalgam in benzene, and the sodium salt reduced by Zn and H₂SO₄. $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-ONa} \xrightarrow{\text{Zn, H}_2\text{SO}_4} \text{CH}_3\text{-C}_6\text{H}_4\text{-SH}$

Chlorination of p-toluene sulfone chloride gives different products under different conditions (21-23). SbCl₃, I₂, FeCl₃, Fe, and phosphorus compounds have been used as catalytic agents. Chlorine may enter the side-chain, the ring, or both. After chlorination the sulfone chloride group may be hydrolyzed off by boiling with 80% H₂SO₄, leaving chloro-toluenes, e.g., $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} \xrightarrow{\text{Cl}_2} \text{ClCH}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} \xrightarrow{\text{H}_2\text{SO}_4} \text{ClCH}_2\text{-C}_6\text{H}_5$.

With ammonia, p-toluene sulfone chloride gives the amide (7, 8, 27). With amino compounds it gives corresponding products (27). $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{NH}_3 \rightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-NH}_2$. The oxidation of these amino condensation products has been studied (27).

Potassium hydroxide with the chloride gives the potassium salt (8). $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{KOH} \rightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{OK}$. Alkali sulfides or hydrosulfides may give the p-toluene sulfinato or the thiosulfonate (28-30).

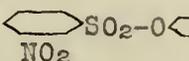
The action of the chloride on thiocarbamides (31) and on the sodium derivatives of certain ketonic esters (32) has been studied. p-Toluene sulfone chloride with the sodium salt of a carboxy acid (33) gives either the chloride or the anhydride of the carboxy acid, depending upon the amount of sodium salt used. $\text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{Cl} + \text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COCl} + \text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{ONa}$. $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + 2\text{CH}_3\text{COONa} \rightarrow (\text{CH}_3\text{CO})_2\text{O} + \text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{ONa} + \text{NaCl}$.

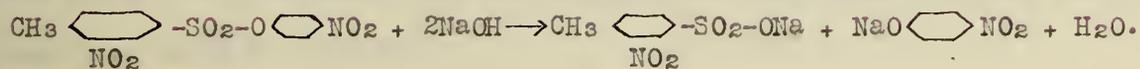
Distilled under ordinary pressure p-toluene sulfone chloride gives SO_2 and $\text{p-CH}_3\text{-C}_6\text{H}_4\text{Cl}$ at about 250° (34). The reaction runs more smoothly and at a lower temperature if a stream of dry chlorine is passed in, but in this case the product is chlorinated.

Toluene may be regenerated from the sulfone chloride if the latter is mixed with carbon and treated under pressure with superheated steam (35). H_2SO_4 and HCl are formed at the same time.

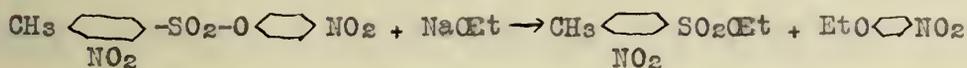
Many derivatives of p-toluene sulfone chloride are known and a large number of condensation products of the chloride with other aromatic substances (36-66,73). Some of the condensation products are used in the dye industry (62-66). The nitration of certain condensation products and the electrolytic reduction of the nitrated products have been studied (24-26.)

The methyl and ethyl esters of p-toluene sulfonic acid are made by treating the chloride with methyl or ethyl alcohol (7, 11, 67). $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{-OC}_2\text{H}_5 + \text{HCl}$. They are used as methylating and ethylating agents (67-72). The methyl ester is found to be as good a methylating agent as dimethyl sulfate (67). The methyl and ethyl esters have been used particularly for alkylating aromatic bases (68-71). $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-OC}_2\text{H}_5 + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-OH} + \text{C}_6\text{H}_5\text{-NHC}_2\text{H}_5$. This method of alkylation is sometimes used in the dye industry.

Phenyl p-toluene sulfonate can be prepared from the chloride and sodium phenolate (74,1, 2) or from the chloride and phenol in pyridine (73). $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{C}_6\text{H}_5\text{ONa} \rightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-OC}_6\text{H}_5 + \text{Na Cl}$. The phenyl ester can be nitrated (1) to give a product, CH_3  NO_2 , melting at 115°C . When the di-nitro ester is suspended in NaOH solution and warmed to complete solution, it was split to give sodium p-nitrophenolate and sodium o-nitro toluene p-sulfonate.



In 1918 (2) it was reported that the dinitro ester when treated with sodium ethylate in absolute alcohol gave sodium nitrotoluene sulfonate and p-nitrophenetole, the latter in 98% yield.



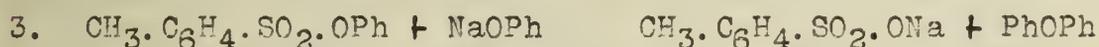
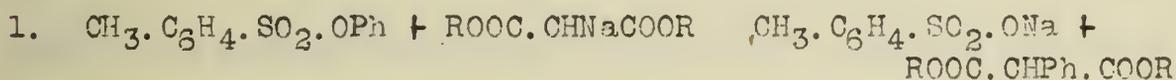
THEORETICAL

The methyl and ethyl esters of p-toluene sulfonic acid are very good methylating and ethylating agents, and as such are used in the dye industry.



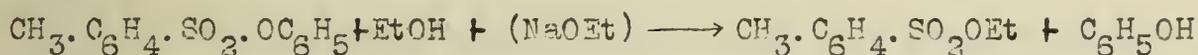
The methyl ester has been found to be as good a methylating agent as dimethyl sulfate, but is not as easily prepared unless p-toluene sulfone chloride is available for its preparation. Even if this substance is not available, ethyl p-toluene sulfonate is more easily prepared than diethyl sulfate.

By analogy with the aliphyl esters, the phenyl ester of p-toluene sulfonic acid might, it was thought, prove to be a valuable phenylating agent. Its use might be easier than some of the methods of phenylation already existing, and it might be applicable in some cases where other methods fail to work. Reactions such as the following might be expected:

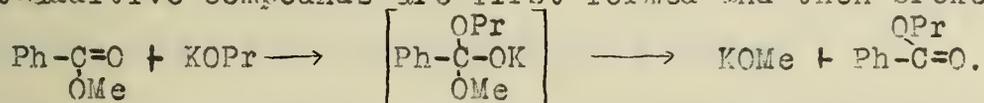


Some work reported in the literature made it seem especially probable that such reactions as those indicated above would take place. The investigation was begun by attempting to carry out the reaction between the phenyl ester and sodium ethylate. It was found to take place; corresponding reactions occurred when phenyl-p-toluene sulfonate was treated with sodium methylate and with sodium butylate, anisole and butyl-phenol ether being formed. Moreover, when the p-bromo-, 2:4-dibromo-, and p-nitro-phenyl esters

were treated with sodium ethylate, p-bromophenetole, 2:4-dibromophenetole, and p-nitrophenetole were formed. When NaOPh is used in place of sodium ethylate, no diphenyl ether is obtained, but alkylphenyl ethers depending upon the nature of the alcohol used as solvent. When ethyl, methyl, and butyl alcohols were used, the sodium phenolate and phenyl p-toluene sulfonate gave phenetole, anisole, and butyl-phenyl ether. Similar results were obtained with the substituted phenyl esters. When phenol was used as solvent for sodium phenolate and phenyl p-toluenesulfonate, no ethers were formed. Probably an exchange of radicals was taking place between the ester and the solvent, in the case of the phenyl ester in ethyl alcohol according to the equation:



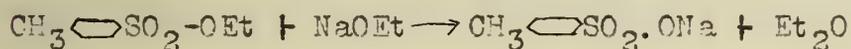
J. C. Irvine, in the Annual Reports of the Chemical Society, XV, 57, remarks that "reactions involving metallic alkyl oxides, alcohols and esters are always complicated by an interchange of groups between the dissolved ester and the solvent". Many instances of this phenomenon are reported in the literature (189-198). It is thought that additive compounds are first formed and then broken down; e.g.



Several facts came out during the investigation which further support the view that an exchange of radicals takes place in the cases under consideration in this thesis. It was found that considerable quantities of phenol could be isolated from the reaction products. That it did not come from a splitting up of phenetole by the sodium ethylate used was proved by treating phenetole with sodium ethylate under the same conditions as prevailed during

the experiments with the phenyl ester and sodium ethylate. No phenol was formed in this manner. It is therefore highly probable that the phenol was formed by an interchange of radicals between phenyl-p-toluene sulfonate and ethyl alcohol. The use of sodium phenolate in place of sodium ethylate with the phenyl ester increased the yield of phenetol. Moreover, an increase in the amount of sodium ethylate used decreased the yield of phenetole, whereas an increase in the amount of sodium phenolate used increased the yield of phenetole. These facts make it appear that the phenetole formed comes from the ethyl ester, formed by exchange of groups, acting on sodium phenolate, either added or formed during the reaction, rather than from phenyl ester and sodium ethylate.

The yield of phenetole obtained by refluxing phenyl ester with sodium ethylate in alcohol was never higher than 33%; the yields of sodium p-toluene sulfonate, on the other hand, were nearly theoretical. The large excess in the yield of sodium p-toluene sulfonate over the yield of phenetole could be accounted for by a reaction between the ethyl ester formed in the above reaction and sodium ethylate:



No ethyl p-toluene sulfonate could be isolated from the reaction products when the phenyl ester was refluxed in ethyl alcohol containing a trace of sodium ethylate. In order, therefore, to verify the conclusion that the ethyl ester is formed during the experiments described above and that this ethyl ester, and not the phenyl ester, is involved in the formation of phenetole, some ethyl ester was prepared and refluxed with sodium phenolate in ethyl alcohol. Phene-

tole was formed in the same amount as was formed from the phenyl ester and sodium ethylate under the same conditions.

In order to determine whether the conclusion drawn above concerning the high yield of sodium p-toluene sulfonate was justified, ethyl ester was refluxed with sodium ethylate in ethyl alcohol. About a 60% yield of sodium p-toluene sulfonate was obtained.

p-Nitrophenyl o-nitrotoluene sulfonate, described in reference (1) as giving a 28% yield of p-nitrophenetole, was prepared and refluxed with sodium ethylate in ethyl alcohol, but no p-nitrophenetole was obtained.

The p-bromophenyl, 3:4-dibromophenyl, and p-nitrophenyl esters of p-toluene sulfonic acid were prepared, and with sodium ethylate gave results similar to those obtained with the phenyl ester. They gave respectively p-bromophenetole, 3:4-dibromophenetole, and p-nitrophenetole. The bromophenyl esters gave higher yields of the respective ethers than did the phenyl ester; the nitro ester gave a lower yield.

In spite of the fact that phenyl p-toluene sulfonate does not act directly as a phenylating agent, in some cases it acts indirectly as such, and therefore may be of some value in phenylation.

EXPERIMENTAL

Preliminary Experiments

50 g. (0.2 mol) of phenyl p-toluenesulfonate was dissolved in hot absolute alcohol containing a molecular amount of sodium ethylate (4.6 g. sodium) and boiled under a reflux. Water-soluble crystals appeared at the end of a few minutes. When 5 g. of sodium was used and the boiling was continued for 8 or 9 hrs., 34 g. of these crystals of sodium p-toluenesulfonate were formed, as was shown by filtering off the solid, drying, weighing, and dissolving in water to make sure that the crystals were sodium salt and not unchanged ester. 39 g. would have been the theoretical yield. The alcohol was distilled off from the filtrate, water was added to the residue in the flask, and the mixture was extracted with ether. The ether solution was dried on CaCl_2 , filtered, and the ether distilled off. The residue consisted of 8 g. of oil distilling up to 200°C . The theoretical yield of phenetole would be about 25g.

It was thought that much of the phenetole might have been carried over with the alcohol when this was distilled off, inasmuch as about 750 cc. had been necessary to completely dissolve the ester used. It was also thought that an excess of sodium ethylate might help to carry the reaction to completion. In the next run 10 g. of sodium and about 400 cc. of alcohol were used. The boiling was carried on for about 6 hrs. The alcohol was distilled off through a good fractionating column. 40 g. of sodium salt and a small amount of phenetole which was not distilled were obtained. Next the amount of alcohol used was cut down still further. 6 g. of sodium in about 200 cc. of alcohol were boiled for 6 hrs. with 50 g. of ester. 33g. of sodium salt and 12.5 g. of oil boiling at $170\text{--}192^\circ$ were obtained. This was redistilled from a small flask on which a wide asbestos shield was placed to protect the thermometer

from heating by the flame. 11.5 g. of phenetole distilled over at 165-168°C. In all subsequent distillations the asbestos shield was used. The reaction is seen to have run just as well in 200cc. of alcohol as in an amount sufficient to dissolve the ester.

Methyl alcohol was tried as a solvent, with the idea that as it could be distilled off at a lower temperature it would be less likely to carry off phenetole with it. 5 g. of sodium dissolved in ethyl alcohol was added to 50 g. of ester in about 500 cc. of methyl alcohol and refluxed for 12-14 hrs. The sodium salt was rather soluble in methyl alcohol. 14 g. precipitated out on cooling, and by evaporating the water layer after the ether extraction 26.5 g. more of water-soluble material was recovered. 6 g. of oil boiling at 172-202° was obtained.

In order to see whether phenyl p-toluenesulfonate would react with sodium alcoholates other than ethyl, 50 g. of ester and 6 g. of sodium in about 400 cc. of butyl alcohol were refluxed in an oil bath for about two hours. 40 g. of sodium salt was obtained, and 15.5 g. of an oil which boiled at 185-205°.

Since the ester formed phenetole with sodium ethylate and appeared to form some butyl-phenyl ether with sodium butylate, sodium phenolate was used with the expectation of getting phenyl ether. 6 g. of sodium was dissolved in about 350 cc. of dry alcohol and a molecular quantity (24.5 g.) of phenol was added. 50 g. of ester was added and the mixture was refluxed for about 6 hrs. 32 g. of sodium salt was formed, and 23 g. of an oil boiling at 167-173°. An attempt was made to extract this with alkali to remove any phenol which might be present, but a good separation of layers was not obtained. No phenyl ether had been formed; the use of sodium phenolate in place of sodium ethylate had increased the yield of phenetole.

A possible explanation is that the phenyl ester reacts with the alcohol used as solvent to give the ethyl ester, which then reacts with phenol to give

phenetole, and with ethyl alcohol to give ethyl ether. If the reaction could be carried out dry or in a non-alcoholic solvent, the exchange of groups between the ester and the solvent could be prevented. Toluene and acetone were tried as solvents with the phenyl ester and dry sodium phenolate, and a number of fusions and dry distillations of the ester with the dry sodium phenolate were made, but no useful results were obtained.

If the phenyl ester reacts with ethyl alcohol to form ethyl ester, phenol must be formed at the same time. It was possible that the phenetole obtained was contaminated by phenol. Therefore it was decided to extract all ether extracts with concentrated sodium hydroxide solution. This was done in all subsequent experiments.

In order to compare the yields of phenetole obtained from the phenyl ester and sodium ethylate and phenolate under the same conditions, the following two experiments were carried out. 9.2 g. of sodium dissolved in 300 cc. of absolute alcohol was refluxed with 50 g. of ester for 22 hrs. 36 g. of sodium salt and 4 g. of phenetole boiling at 166-168° were obtained. 9.2 g. of sodium was dissolved in 300 cc. of ethyl alcohol and 38 g. of phenol was added. This was refluxed for 20 hrs. with 50 g. of ester. 35 g. of sodium salt and 14 g. of phenetole boiling at 167-170° were formed. The yield of phenetole was greater when sodium phenolate was used.

The same amounts of sodium and ester in 300 cc. of dry methyl alcohol were refluxed for a long time. Exact account of the time was not kept. 36 g. of sodium salt and a tiny bit of anisole boiling at 150-157° were formed. The experiment was repeated using half the amount (0.1 mol) of sodium, 14 g. of sodium salt and a very small amount of anisole were obtained.

The first run in which phenol was used was repeated, to see if the apparent high yield of phenetole could be duplicated when the phenol was extracted from the ether extract. 19 g. of sodium salt and 7 1/2 g. of phenetole

were formed.

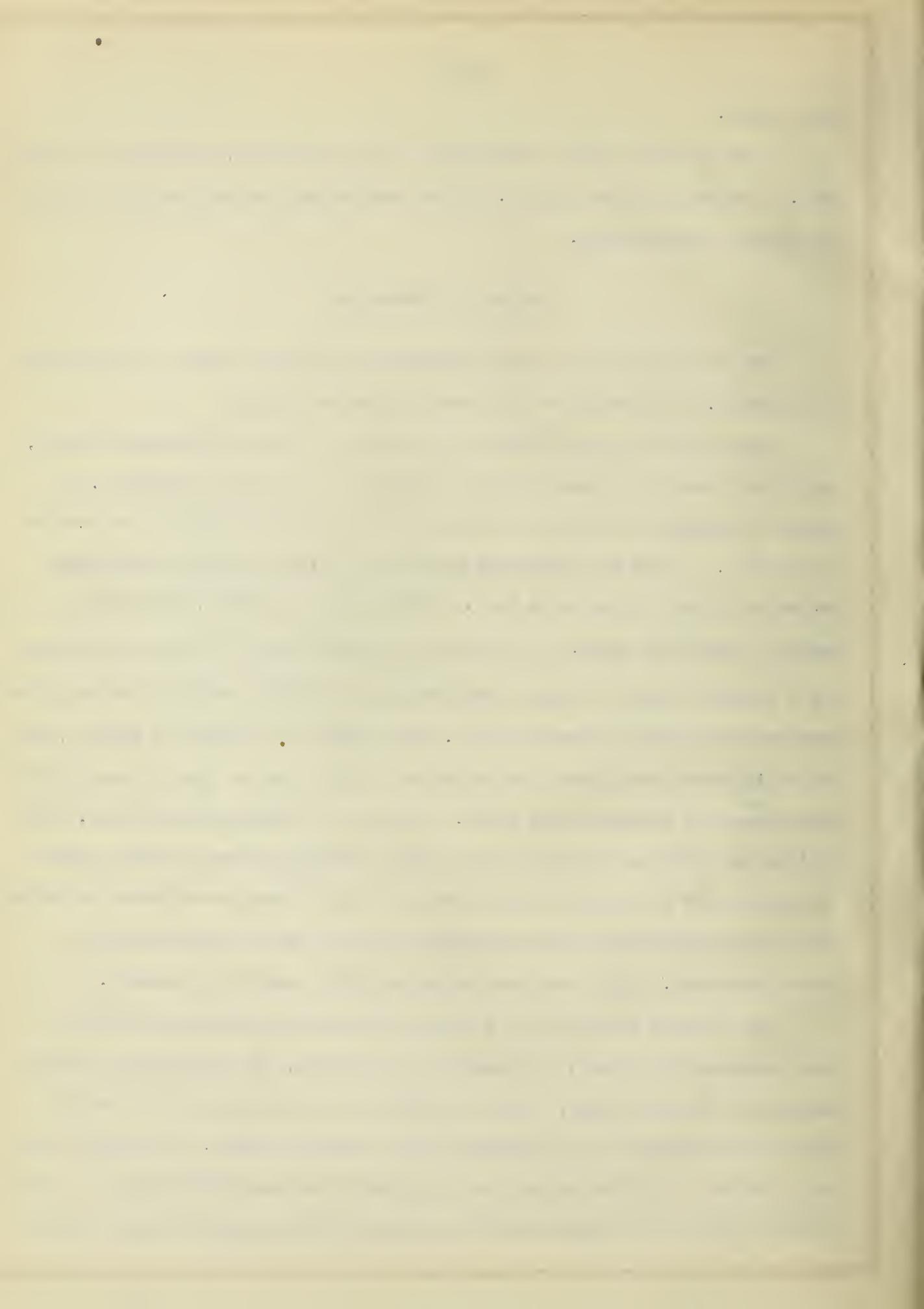
A run was made using p-bromphenol in place of phenol, refluxing for 6 hrs. 36 g. of sodium salt and 8 1/2 g. of what was probably p-bromphenetole, boiling at 182-242° were obtained.

Method of Procedure

The procedure had now been standardized so that the rest of the runs can be tabulated. The details of the procedure are as follows:

About 200 cc. of dry alcohol was placed in a 1-liter round-bottom flask, which was placed in a steam cone and connected to an upright condenser. The amount of sodium to be used was cut into small pieces and added all at once to the alcohol. After the sodium had dissolved a weighed amount of dry phenol was added in case it was to be used. When this had dissolved, the weighed amount of ester was added. The steam was turned on and the refluxing continued for a definite number of hours, after which the flask was removed from the steam cone and the contents allowed to cool. They were then filtered by suction, and the solid washed with alcohol and dried on a porous plate. When it was dry it was weighed and extracted with water. If any of it remained undissolved, this residue was dried and weighed and the weight subtracted from the first weight in order to get the weight of sodium salt. In some cases the solution of sodium salt was acidified with concentrated HCl to see if any of it consisted of sodium phenolate. In no case was sodium phenolate found to be present.

The filtrate was placed in a 500 cc. round-bottom flask fitted with a good fractionating column, thermometer and condenser, and the alcohol fractionated off on the steam cone. Water was added to the residue in the flask and when this had cooled it was extracted three times with ether. The water layer was discarded. The ether extract was extracted with concentrated NaOH, and then dried on CaCl₂. The NaOH extract was acidified with concentrated HCl, and in



case an oil separated or the solution became turbid it was extracted with ether. This ether extract was also dried on CaCl_2 . The two ether extracts were treated alike but separately. After drying they were filtered into a distilling flask fitted to a condenser, and the ether was distilled off on the steam cone. The residue was transferred to a small flask fitted with an asbestos shield, a thermometer and a small air condenser, and distilled. The pure fraction was collected in a test tube and weighed.

Tabulated Experiments

The runs which followed are numbered consecutively from 1 to 46. In all cases 0.1 mol of ester was used. (See table.)

Experiments with Sodium Ethylate

Runs 1-14 were made in order to determine the effect of the length of time of refluxing and of an excess of sodium ethylate. 25 g. of phenyl p-toluenesulfonate was used in each case. In runs 1-7, 2.3 g. of sodium, or 0.1 mol,

was used. The refluxing was carried on for 2, 5, 6, 8, 10, 12, and 20 hrs. The yields of phenetole ranged irregularly from 2 1/2 to 4 g., or 20-33%. Phenol was formed in each case, the yields running from 1/2 to 1 1/2 g. The length of time of refluxing had very little influence on the yield of either phenetole or phenol.

In runs 8-14, 25 g. of phenyl ester and 4.6 g. (0.2 mol) of sodium in ethyl alcohol were refluxed for 2, 4, 6 1/6, 9 1/3, 10, 12, and 20 hrs. The yields of phenetole ran from 1/2 to 1 1/2 g. or 4-12%. No phenol was isolated. Obviously if any was formed it would be converted to sodium phenolate by the excess of sodium ethylate and so escape extraction with ether. Again the length of time of refluxing had little influence on the yield of phenetole.

In run 15 only a trace of sodium was used, to see if the mere presence of sodium ethylate were sufficient to cause the formation of phenetole or of phenol. The refluxing was carried on for 4 1/12 hrs. No phenetole or phenol was formed.

It was thought possible that the phenol might have been formed from phenetole during the course of the run. Accordingly, 0.1 mol of phenetole was refluxed for 8 1/12 hrs. with 0.1 mol of sodium in ethyl alcohol (run 28). No phenol was formed.

Experiments with Sodium Phenolate.

In runs 16-19, 0.1 mol of ester, 0.1 mol of sodium, and 0.1 mol of phenol in ethyl alcohol were refluxed for 4, 2 1/12, 8 1/12, and 20 hrs. The yields of phenetole ranged from 3 1/2 to 7 g., or 30 to 57%. It will be seen that the yields were considerably larger than in runs 1 - 7, where sodium ethylate was used. Again time had little effect on the yield.

It was not thought that any of the phenetole had been formed from the interaction of sodium phenolate and alcohol, but in order to eliminate this possibility 0.2 mol of sodium and 0.2 mol of phenol were refluxed with 200 cc. of dry alcohol for 8 1/2 hrs. No phenetole was formed.

In all subsequent runs the time of refluxing aimed at was 8 hrs.

In run 20, 25 g. of ester, 0.2 mol of sodium and 0.1 mol of phenol were used. The yield was 41%, the same as in run 18 where the conditions were the same except that 0.1 mol of sodium was used.

In run 21, 0.2 mol of sodium and 0.2 mol of phenol with 0.1 mol of ester gave a yield of 6 1/2 g. of phenetole, or 53%.

In run 22, 0.1 mol of sodium and 0.2 mol of phenol were added. No phenetole was formed. Evidently the presence of free phenol inhibited the formation of phenetole.

In run 24, using 0.1 mol of sodium and 0.3 mol of phenol, 1 1/2 g. or a 12% yield of phenetole was obtained.

In run 25, about 200 cc. of melted dry phenol was used as solvent in place of alcohol. After the heating was finished, the phenol was removed by dissolving in concentrated NaOH solution. No phenyl ether had been formed.

Experiments with Substituted Esters

It was now decided to try some substituted esters. The p-bromphenyl, 2:4-dibromphenyl, and p-nitrophenyl esters of p-toluenesulfonic acid were prepared. The method of preparation was the same for the two brom esters.

40 g. of c,p. NaOH was dissolved in distilled water, and 1 mol of p-bromphenol (or 2:4-dibrom phenol) was dissolved in this solution. 190.5 g. of p-toluenesulfonyl chloride was added gradually with stirring. On diluting with cold water the ester separated out. It was filtered off and dried on a

porous plate. After recrystallization from hot alcohol, the p-bromphenyl ester melted at 94-95°, and the 2:4-dibromphenyl ester melted at 118-119°.

These were new compounds. They were analyzed by the sodium peroxide method.

| | |
|------|------------------------|
| | Calcd. for |
| | $C_{13}H_{11}O_3BrS$ |
| | 24.44 |
| % Br | |
| | $C_{13}H_{10}O_3Br_2S$ |
| | 39.38 |

The method for making the p-nitrophenyl ester was the same, except that the sodium salt of the p-nitrophenol had to be recrystallized from hot water because the p-nitrophenol had contained considerable tarry matter. A large amount of water was necessary to dissolve the sodium p-nitrophenolate. The ester melted at 95-96°. Richter's Lexikon gives the melting point as 97-98°.

0.1 mol of each of the substituted esters was run with 0.1 mol of Na in ethyl alcohol (runs 26, 27, and 29.) The monobrom ester run for 8 1/6 hrs. gave 7 g. of p-bromphenetole boiling at 222-235°, a 35% yield, and 2 g. of p-bromphenol boiling at 215-233°.

The dibrom ester run for 8 1/12 hrs. gave 11 g. of 2:4 dibromphenetole boiling at 286-271°, a 40% yield, and 1/2 g. of 2:4-dibromphenol boiling at 244-249°.

The nitro-ester run for 10 1/4 hrs. gave 1 1/2 g. of p-nitrophenetole boiling at 272-273°, a 10% yield, and a small amount of p-nitrophenol.

In runs 30-32 the substituted esters were run with 0.1 mol of sodium and 0.1 mol of phenol. The yields of substituted phenetoles were decreased from 35, 40 and 10% to 15, 22, and 0%. It was not to be expected that phenol would have the same effect with the substituted esters as with the unsubstituted, as phenol could not be formed from them during the reaction.

The dinitro ester described in the two articles mentioned at the beginning of this section (1) and (2) was prepared (m.p. 120°) and run with 0.1 mol of sodium in ethyl alcohol (run 44.) 1 1/2 g. of p-nitrophenol was obtained, but no p-nitrophenetole.

Experiments with Sodium Methylate.

In runs 33, 34, 38 and 39, methyl alcohol was used in place of ethyl. With 0.1 mol of sodium, 3/4 g. or a 7% yield of anisole and 1 1/2 g. of phenol were formed. With 0.2 mol of sodium no anisole and 1/2 g. of phenol were formed. 0.1 mol of sodium and 0.1 mol of phenol gave 1/2 g. of anisole, or a 5% yield, while 0.2 mol of Na and 0.2 mol of phenol gave 3 g. or a 28% yield.

Experiments with Sodium Butylate.

In runs 36, 37, 42 and 43, butyl alcohol was substituted for ethyl. 0.1 mol of sodium gave 3 g. of a 20% yield of butyl-phenyl ether and 1/2 g. of phenol. 0.2 mol of Na gave 3 1/2 g. or a 23% yield of the ether and no phenol. 0.1 mol of sodium and 0.1 mol of phenol gave 5 g. or a 33% yield of the ether; and 0.2 mol of sodium and 0.2 mol of phenol gave 5 1/2 g. or a 37% yield.

Experiments with the Ethyl Ester.

In run 40, 0.1 mol of phenyl ester was run with just a trace of sodium, in order to see if any ethyl ester could be isolated at the end of the run when the amount of sodium ethylate was insufficient for the formation of phenetole. The crystals and filtrate were examined, but no ethyl ester could be isolated.

Since it was thought that ethyl ester was formed during the course of the reaction in which phenetole was formed, it was desirable to find out whether the ethyl ester and sodium phenolate would actually give phenetole.

The ethyl ester of p-toluenesulfonic acid was prepared in the following manner (3):

190 g. of p-toluenesulfonyl chloride was placed in a flask under a reflux condenser. 87.4 g. of absolute alcohol was added and refluxed for 4 1/2 hours. The mass was poured into cold water and allowed to stand over night. The ester was too oily to separate from the water by filtration, so it was extracted with ether. The ether extract was dried on CaCl₂ and the ether distilled off. The ester remaining in the flask solidified when the flask was placed in ice water, and melted at 32°. The yield was 39 g.

0.1 mol of the ethyl ester refluxed for 8 1/6 hrs. with 0.1 mol of sodium and 0.1 mol of phenol gave a 30% yield of phenetole: exactly the same yield as was obtained from the phenyl ester and sodium ethylate under the same conditions. This would indicate that in both cases an equilibrium exists between the phenyl ester and sodium ethylate and the ethyl ester and sodium phenylate.

In order to see if the high yields of sodium salt which accompanied low yields of phenetole could be accounted for by a reaction between the ethyl ester and sodium ethylate to form the sodium sulfonate and ethyl ether, a little less than 0.1 mol of ethyl ester was refluxed for 8 hrs. with a corresponding amount of sodium in ethyl alcohol. 12 g. of sodium salt was formed.

(24)

| Run No. | Hours | O.1 mol ester | Solvent | Mols Na | Mols phenol | g. Na Salt | g. ether | g. phenol | % yield ether |
|---------|---------|---------------|--------------|---------|-------------|----------------|----------|-----------|---------------|
| 1 | 2 | phenyl | Et OH | 0.1 | 0 | 16 | 2 1/2 | little | 20 |
| 2 | 5 | " | " " | 0.1 | 0 | 15 1/2 | 4 | 1 | 33 |
| 3 | 6 | " | " " | 0.1 | 0 | 14 1/2 | 2 1/2 | 1 | 20 |
| 4 | 8 | " | " " | 0.1 | 0 | 17 | 3 1/2 | 1 | 30 |
| 5 | 10 | " | " " | 0.1 | 0 | 13 1/2 | 3 | 1/2 | 25 |
| 6 | 12 | " | " " | 0.1 | 0 | 17 | 3 1/2 | 1 1/2 | 30 |
| 7 | 20 | " | " " | 0.1 | 0 | 18 | 2 1/2 | 1 1/2 | 20 |
| 8 | 2 | " | " " | 0.2 | 0 | 19 1/2 | 1 1/2 | 0 | 12 |
| 9 | 4 | " | " " | 0.2 | 0 | 18 1/2 | 1/2 | 0 | 4 |
| 10 | 6 1/6 | " | " " | 0.2 | 0 | 19 1/2 | 1 1/2 | 0 | 12 |
| 11 | 9 1/3 | " | " " | 0.2 | 0 | 18 | 1 | 0 | 8 |
| 12 | 10 | " | " " | 0.2 | 0 | 18 | 1 | 0 | 8 |
| 13 | 12 | " | " " | 0.2 | 0 | 17 1/2 | 1 | 0 | 8 |
| 14 | 20 | " | " " | 0.2 | 0 | 17 | 1/2 | 0 | 4 |
| 15 | 4 1/12 | " | " " | trace | 0 | 1/2 | 0 | 0 | 0 |
| 16 | 4 | " | " " | 0.1 | 0.1 | 9 1/2 | 3 1/2 | - | 30 |
| 17 | 2 1/12 | " | " " | 0.1 | 0.1 | 14 1/2 | 5 | - | 41 |
| 18 | 8 1/12 | " | " " | 0.1 | 0.1 | 12 | 5 | - | 41 |
| 19 | 20 | " | " " | 0.1 | 0.1 | 18 | 7 | - | 57 |
| 20 | 8 | " | " " | 0.2 | 0.1 | 15 | 5 | - | 41 |
| 21 | 8 | " | " " | 0.2 | 0.2 | 15 | 6 1/2 | - | 53 |
| 22 | 8 | " | " " | 0.1 | 0.2 | 1/2 | 0 | - | 0 |
| 23 | no good | | | | | | | | |
| 24 | 8 | " | Ph OH | 0.1 | 0.3 | 1 | 1 1/2 | - | 12 |
| 25 | 8 | " | Ph OH | 0.1 | -- | 0 | 0 | - | 0 |
| 26 | 8 1/6 | p-brom | phenyl Et OH | 0.1 | 0 | 15 | 7 | 2 | 35 |
| 27 | 8 1/12 | 2:4-Dibrom | phenyl Et OH | 0.1 | 0 | 11 | 11 | 1/2 | 40 |
| 28 | 8 1/12 | Phene- | tole Et OH | 0.1 | 0 | 0 | -- | 0 | -- |
| 29 | 10 1/4 | p-nitro | phenyl Et OH | 0.1 | 0 | 13 | 1 1/2 | little | 10 |
| 30 | 8 | p-brom | phenyl Et OH | 0.1 | 0.1 | 4 1/2 | 3? | -- | 15? |
| 31 | 8 1/12 | 2:4-Dibrom | phenyl Et OH | 0.1 | 0.1 | 9 | 6 | -- | 22 |
| 32 | 8 | p-nitro | phenyl Et OH | 0.1 | 0.1 | 1 1/2 | 0 | -- | 0 |
| 33 | 8 | phenyl | Me OH | 0.1 | 0 | 4 | 3/4 | 1 1/2 | 7 |
| 34 | 8 | phenyl | Me OH | 0.2 | 0 | 13 | 0 | 1/2 | 0 |
| 35 | 8 1/12 | none | Et OH | 0.2 | 0.2 | 0 | 0 | -- | 0 |
| 36 | 8 | phenyl | Bu OH | 0.1 | 0 | 4 | 3 | 1/2 | 20 |
| 37 | 8 | phenyl | Bu OH | 0.2 | 0 | 13 | 3 1/2 | 0 | 23 |
| 38 | 8 | phenyl | Me OH | 0.1 | 0.1 | 7 | 1/2 | -- | 5 |
| 39 | 8 1/12 | phenyl | Me OH | 0.2 | 0.2 | 4 | 3 | -- | 28 |
| 40 | 8 | phenyl | Et OH | trace | 0 | no ethyl ester | | | |
| 41 | no good | | | | | | | | |
| 42 | 8 | phenyl | Bu OH | 0.1 | 0.1 | 3 1/2 | 5 | -- | 33 |
| 43 | 8 1/12 | phenyl | Bu OH | 0.2 | 0.2 | 7 | 5 1/2 | -- | 37 |
| 44 | 8 | nitrated | Et OH | 0.1 | 0 | 17 1/2 | 0 | 1 1/2 | 0 |
| 45 | 8 1/6 | ethyl | Et OH | 0.1 | 0.1 | 8 | 3 1/2 | -- | 30 |
| 46 | 8 | ethyl | Et OH | 0.1 | 0 | 12 | -- | -- | -- |

SUMMARY

1. When the phenyl ester of p-toluenesulfonic acid was refluxed with sodium ethylate in absolute alcohol, with sodium methylate in dry methyl alcohol, and with sodium butylate in dry butyl alcohol, there were formed respectively phenetole, anisole, and butyl-phenyl ether, together with the sodium salt of p-toluenesulfonic acid.

2. The p-bromophenyl- and 2:4-dibromophenyl-esters of p-toluenesulfonic acid were prepared. With sodium ethylate in absolute alcohol they gave the corresponding bromophenetoles in slightly higher yields than the yield of phenetole obtained under the same conditions. The p-nitrophenyl ester gave a very small yield of p-nitrophenetole.

3. When the phenyl ester of p-toluenesulfonic acid was refluxed with sodium phenolate in absolute ethyl alcohol, phenetole and not diphenyl ether was formed. The yield of phenetole was greater in this case than when sodium ethylate was used. Corresponding results were obtained when sodium phenolate was refluxed with the phenyl ester in methyl and butyl alcohols.

4. The mechanism of the preparation of phenetole from phenyl p-toluenesulfonate and sodium ethylate appears to be: first, an exchange of phenyl and ethyl groups between the phenyl ester and the sodium ethylate to form the ethyl ester and sodium phenolate; second, ethylation of the sodium phenolate by the ethyl ester.

The following facts lead to this conclusion:

- a. During the reaction phenol or the corresponding substituted phenol was formed along with the ether.
- b. In general, excess of sodium ethylate decreased the yield of ether, and excess of sodium phenolate increased it.

- c. When the phenyl ester was refluxed with sodium phenolate in phenol as a solvent, no phenyl ether was formed.
- d. The ethyl ester with sodium phenolate in absolute alcohol gave the same yield of phenetole as the phenyl ester with sodium ethylate under the same conditions.
- e. In many cases the yield of sodium salt obtained was higher than the accompanying yield of phenetole. The ethyl ester with sodium ethylate in ethyl alcohol was found to give a good yield of sodium salt. Evidently some of the ethyl ester formed by exchange of groups reacted with sodium ethylate to give sodium p-toluene-sulfonate and ethyl ether.

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B. S. Cum laude, University of Washington, 1916

Teaching Fellow in Chemistry, University of Washington,
1916-17

M. S., University of Washington, 1917

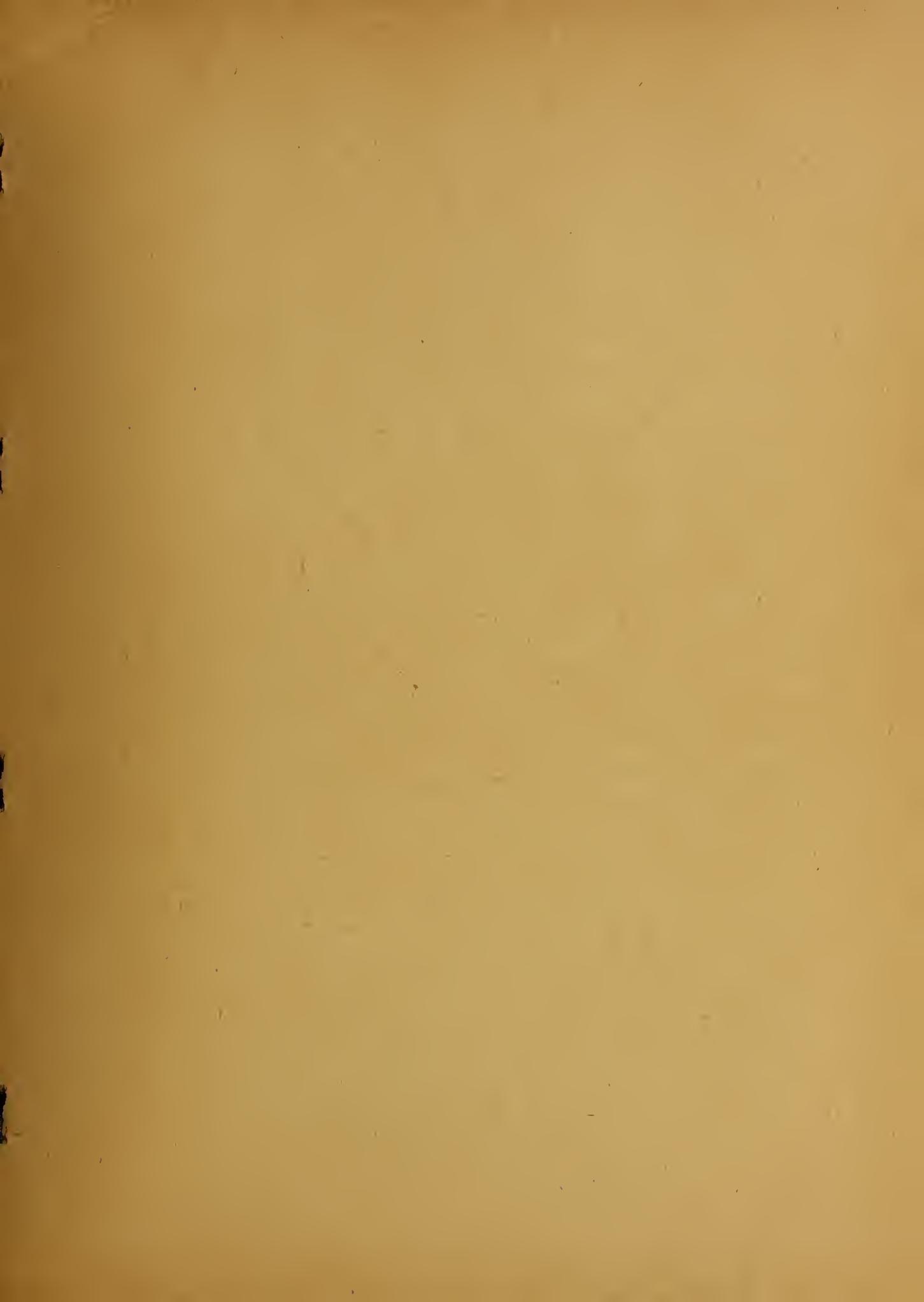
Assistant in Chemistry, University of Illinois, 1917-19

Fellow in Chemistry, University of Illinois, 1919-20.

Publication

Organic Additive Compounds of Potassium Hydroxide

William M. Dehn and Ruth E. Merling. J. Am. Chem. Soc. 39,
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