two isomeric dinitro-compounds has been separated and the components have been studied.

3. Attempts to prepare diaminodiphenyltetrachlorophthalides by reducing the dinitro-compounds with stannous chloride and hydrochloric acid did not give the desired product. Reduction took place, but the product contained tin, which could not be removed.

4. Phenyltolyltetrachlorophthalide and ditolyltetrachlorophthalide, homologs of diphenyltetrachlorophthalide, have been prepared.

5. Monohydroxydiphenyltetrachlorophthalide and phenylresorcinoltetrachlorophthalein have been prepared and have been found to give yellow and orange solutions, respectively, with alkalies. The acetates of these compounds have also been prepared.

6. The acetate of *o*-benzoyltetrachlorobenzoic acid has been prepared and found to possess the same reactivity towards hydrocarbons and phenols as von Pechmann's "mixed anhydride" of *o*-benzoylbenzoic acid and acetic acid.

ITHACA, N. Y.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN IDENTIFICATION. II. THE IDENTIFICATION OF PHENOLS.

BY E. EMMET REID.

Received December 6, 1916.

Introduction.

As is well known, the usual method for the identification of phenols is by making the benzoates by the Schotten-Baumann reaction. The reaction is not a convenient one to carry out and the yields are uncertain. Sometimes the benzoates prove to be liquids. It is convenient to have several methods of identification since one may apply in a certain case in which another gives poor results and, in important cases, it is desirable to prepare several crystalline derivatives so as to put the identification beyond a doubt.

In a previous paper[1] it has been shown that *p*-nitrobenzyl bromide reacts readily with salts of many acids to form esters, many of which crystallize readily and have convenient melting points. It has also been found that this reagent reacts readily with the sodium or potassium phenolates to form *p*-nitrobenzyl ethers of the phenols and that these ethers frequently crystallize readily and have convenient melting points. The reaction with potassium phenolate is, of course,

$$p\text{-}NO_2C_6H_4CH_2Br + NaOC_6H_5 \longrightarrow p\text{-}NO_2C_6H_4CH_2OC_6H_5 + NaBr.$$

One advantage of this method is that the derivatives obtained are ethers and are not, in general, so liable to be decomposed by saponifica-

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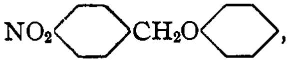
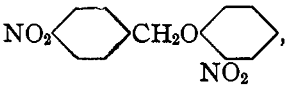
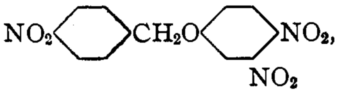
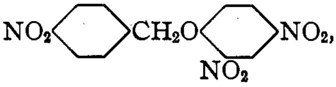
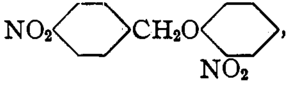
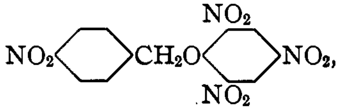
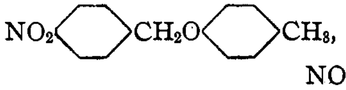
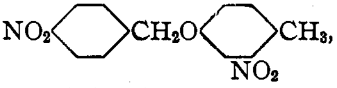
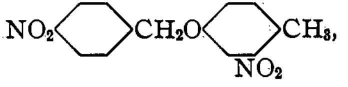
[1] THIS JOURNAL, 39, 124 (1917).

tion or other reactions. Those so far made are very stable and may be recrystallized repeatedly without change. The reaction is a very clean one and, as the results below show, a pure product is obtained directly. For many cases *p*-nitrobenzyl chloride should work nearly as well as the bromide.

Historical.

Three investigators have made phenol ethers of benzyl alcohol, Staedel,[1] Kumpf,[2] and Frische,[3] the last two working under Lothar Meyer at Tübingen. Staedel nitrated benzyl ethers of phenol, *o*- and *p*-cresol and obtained trinitro derivatives in each case, one nitro group entering the benzyl in the para position and the other two entering the phenyl nucleus. He thus obtained *p*-nitrobenzyl ethers of 2,4-dinitrophenol, 3,5-dinitro-*o*-cresol, and 3,5-dinitro-*p*-cresol, melting at 198°, 145°, and 181°, respectively. The numbering is according to Beilstein and appears to be counting the phenolic —OH as 1.

Kumpf prepared *p*-nitrobenzyl ethers of phenol, 2-nitro-, 4-nitro-, 2,4-dinitro, 2,6-dinitro-, and 2,4,6-trinitro-phenols,  m. 91°,  m. 129°,  m. 183°,  m. 201°,  m. 137°,  m. 108°. These were made from *p*-nitrobenzyl chloride or iodide and potassium or silver compounds of the phenols either in solution or suspension in alcohol.

Frische made, in a similar manner, derivatives from *p*-cresol and its nitration products. He also nitrated *p*-cresyl benzyl ether and its lower nitro derivatives. He prepared  m. 91°,  m. 163°,  m. 186.5° (181° according to Staedel).

Method of Work.

Into a 100 cc. flask are measured 25 cc. of 0.2 *N* alkali in 95% alcohol. This is 5 millimols alkali and to this is added a moderate excess, *i. e.*, some-

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[1] *Ann*, **217**, 177 (1883).

[2] *Ibid.*, **224**, 104 (1884).

[3] *Ibid.*, **224**, 137 (1884).

what more than 5 millimols of the phenol. It is usually convenient to use 1.0 g. of the phenol as this is more than 5 millimols for phenols whose molecular weights are under 200. In case the molecular weight is larger, correspondingly more of the phenol is taken.

To this solution is added 1.0 g. *p*-nitrobenzyl bromide. As this has m. w. 216 this is 4.63 millimols. We have in the solution 4.63 millimols of the bromide, 5.00 millimols of the alkali phenolate ROK or RONa and excess of the phenol ROH. The flask is connected with a return condenser and the solution boiled on the steam bath for one hour. The progress of the reaction is shown by the precipitation of sodium or potassium bromide.

At the end of this time water is added, usually 5 to 10 cc. This causes the alkali chloride to dissolve. It is desirable to have most of the compound in solution while the mixture is boiling hot, and more 95% alcohol may be added if the addition of the water causes much precipitation. The solution is cooled quickly while being shaken vigorously to cause the formation of small crystals. The ethers usually separate first as an emulsion and become crystallized on shaking and cooling. During this operation enough powdered caustic alkali is added to make the mixture alkaline to wet litmus paper. The object of this is to prevent the separation of the phenol which might contaminate the *p*-nitrobenzyl ether. The ether is filtered on a disc of paper in a small Büchner funnel. The ether which, for the quantities given, is usually about 1 g. is dissolved in 20 cc. of boiling 95% alcohol and to the boiling solution water is added cautiously till the ether separates on cooling. It is thus brought to crystallization as before.

The amounts used in the present work are regarded as much larger than necessary. Good results should be readily obtained with far smaller quantities.

Results.

Phenol.—The reaction was carried out as described above. The addition of 12.5 cc. of water to the reaction mixture caused the precipitation of the ether as an oil which soon solidified to a mass of nearly white needles. This first crystallization, first crop, abbreviated as 1st 1st, was 1.07 g., calculated yield 1.06 g. It melted at 90.5°. The addition of much water to the filtrate gave a second crop, designated as 1st 2nd, 0.02 g., m. 90.5°. The 1st 1st was dissolved in 70 cc. boiling 81° alcohol, which must have been more than was necessary as the ether did not begin to separate till the solution had cooled to about 30°. This gave 2nd 1st, 0.83 g., m. 91.0°. Dilution with water give 2nd 2nd, 0.20 g., m. 91°.

Kumpf found this compound to melt at 91°.

o-**Cresol.**—The addition of 10 cc. water to the reaction mixture caused the separation of an oil even from the hot solution and 10 cc. of 95° alcohol were added to redissolve it. The hot solution was poured off from a very small drop of the oil. The ether separated as an emulsion which soon became crystalline. The 1st 1st was 0.95 g., m. 86–90°, slightly yellowish. The calculated yield is 1.12 g. The 1st 2nd was 0.13 g., m. 67–71°. The 1st 1st was dissolved in 25 cc. boiling 76% alcohol. This gave 2nd 1st 0.88 g., m. 89.7°, and 2nd 2nd 0.04 g., m. 70–5°.

m-**Cresol.**—The hot reaction mixture remained clear after the addition of 5 cc. water, but, on cooling, the ether came down as an oil which solidified to crystals. The 1st 1st was 0.80 g., m. 50–1° and 1st 2nd 0.31 g., m. 50°, total yield 1.11 g., calculated 1.12 g. The 1st 1st dissolved readily in 20 cc. boiling 95% alcohol and the addition of 5 cc. water caused the separation of only a tiny drop of oil from which the hot solution was quickly poured. The 2nd 1st was 0.68 g., m. 51°, and 2nd 2nd 0.10 g., m. 49°.

p-**Cresol.**—The hot reaction mixture separated only a small amount of oil on the addition of 10 cc. water but the ether crystallized readily on cooling. The 1st 1st was 1.05 g., m. 88° and the 1st 2nd 0.02 g., m. 86°, total 1.07 g., calculated 1.12 g. The 1st 1st dissolved in 25 cc. 76% alcohol and this solution yielded 2nd 1st 0.99 g., m. 88°, and 2nd 2nd 0.02 g., m. 88°. This ether was prepared by Frische who gives the m. p. 91°.

Thymol.—The addition of 12.5 cc. water to the hot reaction mixture precipitated the ether as an oil which soon solidified. The 1st 1st was 1.30 g., m. 85° and 1st 2nd 0.01 g., m. 82°, total 1.31 g., calculated 1.32 g. The 1st 1st dissolved in 35 cc. 81% alcohol and gave 2nd 1st., m. 85.5°, and 2nd 2nd 0.01 g., m. 76°.

Eugenol.—The addition of 10 cc. water to the hot reaction mixture caused the separation of an oil and 10 cc. of 95% alcohol were added to dissolve it. The 1st 1st was 1.23 g., m. 53°, and 1st 2nd 0.04 g., total 1.27 g., calculated 1.39 g. The 1st 1st was dissolved in 50 cc. boiling 76% alcohol and gave 2nd 1st, 1.08 g., m. 53.6° and 2nd 2nd 0.08 g., m. 53.6°.

Vanillin.—The addition of 10 cc. water to the hot reaction mixture caused the precipitation of the ether in crystalline form. The 1st 1st was 1.28 g., m. 125° and 1st 2nd 0.06 g., m. 124°, total 1.34 g., calculated 1.33 g. The 1st 1st was dissolved in 30 cc. hot alcohol and 12.5 cc. water added. This gave 2nd 1st 1.245 g., m. 124.5° and 2nd 2nd 0.025 g., m. 123.7°.

The results are brought together in tabular form. The second and third columns give the weight of the first and second crops of crystals, those obtained directly and those obtained by the addition of water to the mother liquor. The sum of these is given in the third column as total yield. This should equal the calculated yield, which is given in the first. In two cases the yield is slightly in excess of the calculated, which is to be attributed to inaccuracy in the hand scales on which the reagent was weighed. The yields obtained show that the reaction is practically quantitative in each case so far tried. The ethers are precipitated almost completely by diluting the mother liquors with several volumes of water. In the fifth and sixth columns are given the weights of the two crops of crystals obtained by recrystallizing the 1st 1st. The sum of these two are given in the seventh column and, were there no loss, should equal the weight taken which is found in the second column The loss appears to be 0.01 to 0.07 g. and represents the amount not precipitated by the addition of water and the mechanical losses. The eighth and ninth columns give the strength and volume of alcohol used in recrystallizing the 1st 1st. The next two columns give the number of cubic centimeters of hot and cold alcohol, of the strength stated in the eighth, to dissolve 1 g. of the ether. These are only approximate as they are calculated from the data in this table simply. The last two columns give the first and the final melting points of the ethers. The slight differences between these show that the ethers as first obtained are practically pure and have substantially the correct melting points. Of course this would not be the case were the ethers prepared from mixtures of two or more phenols. The melting points were taken with the same simple bulb that was used in the former work. The m. p. of pure benzoic acid was 121.6° with the same apparatus and thermometer.

TABLE I.

Yields and Properties of *p*-Nitrobenzyl Ethers of Various Phenols.

		First crystallization.			Second crystallization.					Vol. for 1 g.			
	Calc. yield, g.	1st 1st, g.	1st 2nd, g.	Total, g.	2nd 1st, g.	2nd 2nd, g.	Sum, g.	EtOH, %.	Vol., cc.	Hot, cc.	Cold, cc.	First m. p., degrees.	Final m. p., degrees.
Phenol......	1.06	1.07	0.02	1.09	0.83	0.20	1.03	81	70	65	325	90.5	91.0
o-Cresol.....	1.12	0.95	0.13	1.08	0.88	0.04	0.92	76	25	26	650	86–90	89.7
m-Cresol....	1.12	0.80	0.31	1.11	0.68	0.10	0.78	76	25	30	300	50–1	51.0
p-Cresol.....	1.12	1.05	0.02	1.07	0.99	0.02	1.01	76	25	24	1200	88	88.0
Thymol.....	1.32	1.30	0.01	1.31	...[1]	0.01	..	81	35	27	2700	85	85.5
Eugenol.....	1.39	1.23	0.04	1.27	1.08	0.08	1.16	76	50	41	510	53	53.6
Vanillin.....	1.33	1.28	0.06	1.34	1.245	0.025	1.27	67	43	33	1320	125	124.5

A mixture of the phenyl and *o*-cresyl *p*-nitrobenzyl ethers melted at 69–70°, one of the phenyl and *p*-cresyl ethers, at 64°, and one of *o*- and *p*-cresyl ethers, at 66°.

Summary.

p-Nitrobenzyl bromide has been found to react readily and quantitatively with alkali phenolates. The ethers, so far as they have been made, crystallize readily from dilute alcohol, melt sharply and are suitable derivatives for identification. The following ethers have been made:

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[1] Part lost by accident, 0.93 g. saved.

Phenyl *p*-nitrobenzyl ether, $C_6H_5OCH_2C_6H_4NO_2$, m. 91°, *o*-Cresyl *p*-nitrobenzyl ether, *o*-$CH_3C_6H_4OCH_2C_6H_4NO_2$, m. 89.7°, *m*-Cresyl *p*-nitrobenzyl ether, *m*-$CH_3C_6H_4OCH_2C_6H_4NO_2$, m. 51°, *p*-Cresyl *p*-nitrobenzyl ether, *p*-$CH_3C_6H_4OCH_2C_6H_4NO_2$, m. 88°, Thymyl *p*-nitrobenzyl ether, $CH_3(C_3H_7)C_6H_3OCH_2C_6H_4NO_2$, m. 85.5°, Eugenyl *p*-nitrobenzyl ether, $C_3H_5(OCH_3)C_6H_3OCH_2C_6H_4NO_2$, m. 53.6°, and vanillyl *p*-nitrobenzyl ether, $CH_3O(CHO)C_6H_3OCH_2C_6H_4NO_2$, m. 124.5°.

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[CONTRIBUTION FROM THE FOOD INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE VOLATILE REDUCING SUBSTANCE IN CIDER VINEGAR.

BY R. W. BALCOM.

Received November 27, 1916.

The presence of a volatile reducing substance in vinegar appears to have been first noted by Farnsteiner.[1] In following the changes which occurred when some wines were allowed to undergo acetic fermentation he observed a progressive increase in the apparent sugar content, which could not be accounted for by any increase in concentration due to evaporation during the fermentation process. Further investigation showed that the distillate obtained by distilling some of the partially fermented vinegar, as well as that obtained by distilling some of the finished vinegar, reduced Fehling's solution strongly, even at room temperature, and separated silver from an alkaline silver solution. The distillates from some wine vinegars which had been kept for four years exhibited this same reducing power. Since distillates from wines which had not undergone acetic fermentation showed no such reducing properties, Farnsteiner concluded that a volatile aldehyde-like substance was formed during the acetic fermentation of wines. The presence of this substance was found to account in large part for the apparent increase in sugar mentioned above.

Farnsteiner found that in the distillates which he prepared, furfural was either absent or present only in traces, and that formaldehyde was present in very small amounts only. In spite of the fact that this volatile reducing substance appeared to be oxidized to acetic acid by silver oxide, the assumption that it was acetaldehyde was found to be untenable, because dilute solutions of acetaldehyde did not react in the same way as the distillates, with Fehling's solution, Schiff's reagent or with sulfurous acid.

In a second paper[2] Farnsteiner records the result of further attempts

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[1] K. Farnsteiner, *Z. Nahr.-Genussm.*, 2, 198–209 (1899).

[2] *Ibid.*, 15, 321–6 (1908).