to 50 g. of sulfuric acid (sp. gr. 1.84) and heated at 125° for 15 minutes. The reaction product was poured into a mixture of 300 g. of 95% ethyl alcohol and 150 g. of conc. sulfuric acid, cooled to 5°, and then diazotized with 30 g. of sodium nitrite in conc. water soln. Copper powder was added to catalyze the reaction, after which the solution was distilled with steam. The yield of the nitro-xylene was 35 g. The nitro-xylene was recrystallized from alcohol.

To a solution of 150 g. of stannous chloride in 200 g. of hydrochloric acid (sp. gr. 1.19), the nitro compound was added in small portions. Heat was necessary to start the reaction. After the addition of all the nitroxylene, the reaction mixture was heated on the steam bath for an hour, diluted, cooled, made alkaline, and distilled with steam. The yield of *s*-xylidine was 15 g.

The acetyl derivative was prepared and purified as already described for the *s*-acet-xylide from mesitylene. The melting-point was 139.6° to 140.2°. Samples of the 2 preparations and of their mixture were attached to the same thermometer and all 3 softened and melted within 0.1° of one another.

Optical Properties (by Edgar T. Wherry). When studied by the immersion method under the microscope, these preparations have identical properties, as follows.

Habit: plates, rather irregular in outline, and often overlapping. System: apparently monoclinic, with clinopinacoid prominent.

Refractive indices (D): $\alpha = 1.45$, β-indeterminate, $\gamma = 1.69$, $\gamma - \alpha = 0.24$.

As seen in polarized light, nicols crossed: Colors around 2nd order; the overlapping and stepped variation in thickness of the plates producing striking mosaic effects; elongation negative; extinction angle (on edges most frequently present) 12°.

In convergent polarized light, nicols crossed: Shows no definite interference figures, the optic normal being apparently perpendicular to the surfaces of the plates.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

PARA CYMENE AS A SOLVENT.

BY A. S. WHEELER.

Received May 22, 1920.

Until the discovery was made that spruce turpentine, a by-product of the manufacture of spruce pulp by the sulfite process, consisted largely of *p*-cymene this hydrocarbon was not available as an ordinary solvent. The price is now so much lower that it shuold be placed on the regular list of solvents.

Cymene assumes an important position as a solvent because it is a hydrocarbon of high boiling-point and, where possible, is to be preferred to such colored solvents as aniline or nitrobenzene, or an ill-smelling solvent such as pyridine. Cymene boils at 176.5° and in point of availability comes next to xylene in the benzene series. It should be useful as a simple solvent or in mixed solvents and in molecular weight determinations where the elevation of the boiling-point method is employed. The solubilities of a variety of types of compounds in it have been determined and the results are given below. Owing to the method used the first group (Table I) are of moderate accuracy only.

Purification of Cymene.—Considerable work was done in searching for the best method of isolating the cymene from spruce turpentine. A very large yield was readily obtained from spruce turpentine made at Canton, N. C., where a moderate temperature was employed in digesting the spruce wood but this supply gave out and the spruce turpentine obtained from Erie, Pa., was a darker product and contained larger quantities of substances other than cymene.

The removal of sulfur dioxide was the first problem. Several methods were available: (1) extraction with water which is too slow and laborious; (2) the dioxide could be boiled out successfully, but explosions will sometimes occur; (3) shaking with dilute sodium hydroxide removes it, but produces a precipitate difficult to handle; (4) shaking with lime, 150 g. per 3000 cc., also causes a troublesome precipitate, although Andrews[1] has adopted this method; (5) hot air drawn through the turpentine readily removes the dioxide; (6) air of the ordinary temperature drawn through five gallons removes the sulfur dioxide completely in 10 hours. The volume diminishes 5%. This method needs no attention and is the best of any.

The turpentine was then submitted to distillation with super-heated steam, in apparatus arranged so that the vapors passed first through a 30% solution of sodium hydroxide and then into the condenser. As suggested by Professor R. H. McKee in a private communication, 3 fractions were collected : (1) 16%; (2) 50%; (3) 16%. The non-volatile residue made up the remainder of about 18%. In this laboratory we have obtained such an excellent yield of 2-bromocymene from pure cymene that I propose to test the quality of these fractions by brominating them.

To determine the next step in the purification, the following experiments were tried: the distillate was shaken (1) with a solution of sodium plumbate; (2) with a 0.5% solution of potassium permanganate; (3) it was boiled in a stream of hydrogen with copper chloride upon pumice stone; (4) it was boiled with metallic sodium; (5) it was shaken with conc. sulfuric acid. This acid attacks the impurities but also sulfonates the cymene even at ordinary temperature. We have completely sulfonated cymene at room temperature by shaking it for a week with conc. sulfuric acid. Schorger[2] states that pure cymene is not colored by sulfuric acid, but I have not been able to confirm this observation, neither

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[1] U. S. patent 1,314,920, *C. A.*, **13**, 2765 (1919).

[2] THIS JOURNAL, **39**, 2672 (1917).

has Professor McKee, according to a private communication. The distillate was purified by shaking it with a 5% solution of sodium hydroxide and then distilling it over metallic sodium. Young's most complex still head of 5 sections facilitated fractionation. Pure cymene boils at 176–176.5° and has a refractive index of 1.4905 at 12.5°.

These studies were carried out with the aid of Messrs. T. P. Dawson, J. S. Murray and R. H. Sawyer, senior students in Chemistry.

Solubility Determinations.

The following methods were employed to determine the solubilities given in Table I which are of moderate accuracy. For temperatures below 30°, the solid was shaken with the cymene for an hour, then allowed to stand somewhat longer when the solution was filtered into a dish of known weight. The temperatures were room temperatures. For solubilities at 30° the solid and cymene were placed in a tube immersed in a thermostat and stirred mechanically. The solution was drawn into another tube also in the thermostat. For solubilities at 100° a known

Table I.

Substance.	Temp. ° C.	Grams in 100 g. of cymene.	
Acetanilide	30	7.23	Dawson
Anthracene	25	1.57	Murray
	30	1.72	Murray
	100	9.24	Murray
	176	98.60	Murray
Antipyrine	30	2.09	Murray
Caffeine	25	0.76	Dawson
	30	1.10	Dawson
	100	1.74	Dawson
	175	15.58	Dawson
d-Camphoric acid	100	1.53	Dawson
Hexachloro-benzene	23.5	2.93	Sawyer
	100	16.77	Sawyer
	176	106.95	Sawyer
Naphthalene	30	14.22	Dawson
β-Naphthylamine	30	8.63	Dawson
o-Nitro-aniline	30	6.33	Dawson
m-Nitro-aniline	30	1.36	Murray
p-Nitro-aniline	25	0.83	Sawyer
Phloroglucinol	175	0.12	Dawson
Strychnine	30	0.71	Sawyer
	100	0.95	Sawyer
Tartaric acid	27	Insol.	Sawyer
	100	Nearly insol.	Sawyer
Thio-urea	25	Insol.	Sawyer
	100	Nearly insol.	Sawyer
Thymol	25	113.85	Dawson
Urea	27	Insol.	Sawyer
	100	Nearly insol.	Sawyer

weight of substance was placed in a test-tube which was heated by boiling water. Cymene was cautiously added from a buret until complete solution took place. An oil bath was used for higher temperatures. In all cases the solution was placed in a desiccator through which air was drawn. The evaporation was extremely slow and, in view of the danger of sublimation, the results are not as accurate as might be desired.

It was possible to attain greater accuracy in the case of acids since these could be titrated. The temperature adopted was 25°. A saturated solution was first made at 40° and this was placed in a thermostat carefully regulated to within 0.1°. The apparatus of Pawlewski[1] was used for stirring the solution and for transferring it under water. The solution and separated crystals were stirred for half an hour and then drawn over through a filter paper into the weighing tube. The solution was weighed and then transferred to a flask with the aid of a little alcohol. Water was added and the solution was titrated against 0.05 *N* sodium

TABLE II.

Normality of NaOH, 0.0486.

No.	Weight of sample. G.	NaOH. Cc.	Grams in 100 g. of cymene.
Benzoic acid.			
1	3.8445	39.9	6.545
2	4.1514	42.9	6.532
3	2.8170	28.97	6.500
Succinic acid.			
1	6.5898	0.475	0.020
2	4.8862	0.375	0.022
3	6.1368	0.425	0.020
Anthranilic acid.			
	Normality of NaOH, 0.04676.		
1	4.7168	5.45	0.746
2	6.3264	7.25	0.740
3	9.3118	10.775	0.747
Citric acid.			
1	9.5310	1.05	0.036
2	10.9468	1.10	0.032
3	11.4490	1.50	0.034
Picric acid.			
1	4.6383	11.05	2.536
2	4.7848	11.40	2.618
3	5.6180	13.35	2.611
Phthalic acid.			
1	11.7587	0.80	0.026
2	12.1394	0.90	0.028
3	11.9753	0.75	0.024
Salicylic acid.			
1	5.5047	8.35	0.989
2	5.5831	8.45	0.986
3	6.9183	10.35	0.975

[1] *Ber.*, 32, 1040 (1899).

hydroxide solution which had been standardized against benzoic acid.[1] Each acid was carefully purified. Benzoic acid was recrystallized from alcohol and then sublimed. Anthranilic, citric, picric, salicylic and succinic acids were recrystallized from hot water. Phthalic acid was recrystallized from hot water and also reprecipitated from its sodium salt.

These solubility experiments with the acids were carried out by H. M. Taylor, Senior student in Chemistry.

A Color Reaction.—In working with certain samples of cymene, it was observed that they turned red rather quickly when they contained *p*-anisidine in solution. The amount of *p*-anisidine used was small, about one part in 500. A study of this phenomenon developed the fact that a perfectly pure cymene does not change color, at least within 2 hours, if exposed to a moderate light. Impure cymene will turn pale yellow, deep yellow, pale red or deep red according to the degree of impurity or to the time of action. A strong light, especially sunshine, facilitates the development of the color. Coloration also occurs in the dark. It may be added that solutions of *p*-anisidine in other solvents also develop a color.

CHAPEL HILL, N. C.

[CONTRIBUTIONS FROM BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

CRYSTALLINE CHLOROTETRACETYL FRUCTOSE AND RELATED DERIVATIVES.[2]

BY D. H. BRAUNS.

Received May 28, 1920.

The acetates of fructose have been obtained crystalline only by applying a principle which differs materially from the ordinary methods of acetylation. This principle consists in the action of acetylating agents on *finely powdered fructose at a low temperature* (*below* 0°).[3] The present communication deals with the use of these stable crystalline *acetates* as starting material for the preparation in the crystalline state of other derivatives of fructose.

Crystalline β-penta-acetyl or tetra-acetyl fructose in chloroform solution gives with phosphorus pentachloride and aluminum chloride a crystalline substance which has proved to be one of the isomeric forms (probably α-) of chloro-tetra-acetyl fructose. With phosphorus pentachloride alone it gives a good yield of another crystalline substance, supposed to be the β-isomer. It is to be regretted that the necessity of postponing further investigations has prevented the securing of definite proof of the

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[1] Bur. Standards *Bull.* 8, 643 (1912).

[2] The work described in this paper was done in the Carbohydrate Laboratory of the Bureau of Chemistry at the time when Dr. C. S. Hudson was Chemist in charge of that laboratory.

[3] "On a Crystallized *d*-Fructose-tetracetate," *Proc. Roy. Acad. Amsterdam*, 10, 563 (1907–1908).