

bromonitro-methane and Schiff bases. The latter are decomposed by bromonitro-methane into benzaldehyde and amine.

The addition compounds of *p*-toluidine and phenylhydrazine may be isolated. They are amphoteric substances, forming salts with both metals and acids.

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THE APPLICATION OF VICTOR MEYER'S ESTERIFICATION LAW TO 2,6-XYLIC ACID AND ITS REDUCED DERIVATIVES.¹

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Historical.

Victor Meyer found that aromatic acids with both *ortho* positions filled are not to be esterified by the usual method. The work of himself and his pupils² led Meyer to formulate the rule which is known as Victor Meyer's Esterification Law. It states, "When in a substituted benzoic acid the two hydrogen atoms adjacent to the carboxyl group are substituted by such groups as Br, NO₂, CH₃, etc., the acid is not esterifiable by alcohol and hydrochloric acid."

Meyer explained this difficulty of esterification by advancing the theory of steric hindrance. He believed that the groups adjacent to the carboxyl covered it up so as to prevent free collision between the alcohol molecule and the carboxyl group. A strong argument in favor of this explanation is the difference in behavior toward esterification of di-*ortho*-substituted benzoic acids and similarly substituted acids with the carboxyl removed from the ring by at least one atom. Symmetrical trimethyl-benzoic acid obeys the law but both mesityl-glyoxylic acid and mesityl-acetic acid esterify readily. In fact, even the *ortho* hydrogen atoms in benzoic acid are credited with some blanketing effect, since it was found that phenylacetic acid is more easily esterified than is benzoic acid itself.

Wegscheider³ advanced some data which are in accordance with Meyer's rule, but he objected to Meyer's steric hindrance explanation and declared that the effect is due to a state of tension within the molecule.

The most antagonistic critic of the steric hindrance idea is M. A. Rosan-

¹ An abstract of a thesis submitted by Ralph W. Hufferd in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

² Meyer, *et. al.*, *Ber.* **27**, 510, 1585, 3146 (1894); **28**, 182, 1254, 2776, 3197, 3219 (1895); **29**, 830, 839, 1397 (1896); *Z. physik. Chem.*, **24**, 219, 221 (1897).

³ Wegscheider, *Monatsch. f. Chem.*, **18**, 643 (1897); *Ber.*, **28**, 2535 (1895).

off.¹ He and his co-workers carried out several esterification experiments in which the acid was heated with ethyl alcohol in a sealed tube without the addition of any mineral acid. Most of the trials were made at the temperature of boiling aniline, and for a much longer time than is ordinarily employed for esterifications. The results of this work led Rosanoff to make the statement, "Di-*ortho* substituted aromatic acids, which are generally assumed to be unesterifiable, can be esterified quantitatively at higher temperatures, or even, by prolonged warming, at the temperature of the water-bath." He restated the Esterification Law to read, "Aromatic acids with one or both positions next to the carboxyl occupied by substituting groups, combine with alcohols more slowly, though to no less extent, than acids otherwise substituted." He further stated, "Our dynamic study proves that Victor Meyer's hypothesis of steric hindrance is untenable and thus, for the present, reduces the Esterification Law to the rank of an empirical rule of no theoretical and limited practical value. The hypothesis that the low rate of esterification is due to the mechanical interference of groups or atoms situated near the carboxyl in the molecule is untenable."

W. L. Prager² followed the methods of Rosanoff and arrived at a similar conclusion.

Theoretical.

From the preceding résumé of the literature it is evident that there are two distinct points of view from which a reaction may be considered. Meyer studied the qualitative aspect to draw his conclusions, which he couched in quantitative terms. Rosanoff, following the belief of Bredig³ that everything chemical must be considered quantitatively from the dynamic side, considers it useless to distinguish between *difficult* and *easy* reactions. According to him, no rule of any great value could be deduced from such a grouping, and no knowledge could be gained as to molecular structure by correlating such reactions.

Although Rosanoff refuses to give any consideration to Meyer's explanation of the hindrance being due to a blanketing effect, he very willingly accepts Wegscheider's idea that it is due to a condition of strain within the molecule induced by the substituting groups.

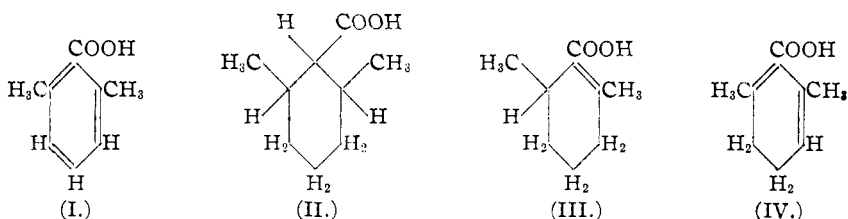
Without accepting entirely either of the above explanations but with a firm conviction that organic structures can be deduced from cumulative evidence of a qualitative nature and cannot be assigned numerical values, the present work was undertaken.

If Meyer's explanation is correct, the following results can be predicted: 2,6-Xylic acid (I) should not esterify.

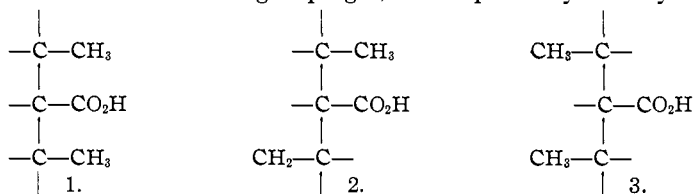
¹ Rosanoff, *THIS JOURNAL*, 30, 1895 (1908).

² Prager, *ibid.*, 30, 1908 (1908).

³ Bredig, *Z. physik. Chem.*, 21, 154 (1896).



Hexahydro-2,6-xylic acid (II), has very much the same grouping as xylic, but is purely aliphatic in nature. Its three isomers would be expected to give different results, which might be predicted as follows: The one with the grouping, 1, should not esterify. The second, with the grouping 2, would be expected to esterify with very poor yields. The third, which would have the grouping 3, would probably esterify easily.



Δ_1 tetrahydro-2,6-xylic acid (III), in which the carboxyl is in the same plane with only one methyl group, would not be expected to esterify with as much difficulty as xylic acid itself.

$\Delta_{1,5}$ dihydro-2,6-xylic acid, IV, of which the linkage of the carboxyl group is the same as in xylic acid, should not esterify easily.

The Δ_3 tetrahydro-2,6-xylic acids from their similarity to the hexahydro acids would be expected to behave in much the same manner as these.

Discussion of Results.

The results obtained in this study of 2,6-xylic acid and its reduction products agree quite well with the predictions based on Victor Meyer's Esterification Law.

Acid.	Predicted esterification.	Found. %.
Benzoic.....	Quantitative	96
Xylic.....	None	3.5
Δ_1 tetrahydro-xylic.....	Fair	41
Δ_3 tetrahydro-xylic.....	Poor to good	75
$\Delta_{1,5}$ dihydro-xylic.....	None	47
Hexahydro-xylic.....	Poor to good	52

From this comparison of the results obtained with those predicted it is evident that the Esterification Law cannot be applied quantitatively. However, the results offer strong evidence combating Rosanoff's statement that the law is of little practical value.

It is clear, as Victor Meyer claimed, that *ortho* substituents interfere with the esterification of aromatic acids, though Rosanoff is also right

in saying that they do not absolutely prevent esterification. Physical chemistry has, as yet, given no satisfactory explanation of why certain reactions take place slowly while others go rapidly. Until it can do this, the idea of steric hindrance seems to be useful as a superficial explanation, at least, for the results which have been found.

It seems possible that the mechanism of the reactions studied by Rosanoff, in which he used only mixtures of an acid with alcohol, is different from that of the reactions in the presence of hydrochloric acid as a catalytic agent. Rosanoff's reaction may be a direct substitution of ethyl for hydrogen. In Victor Meyer's studies and ours there is probably an intermediate addition reaction. A study of velocities in the presence and absence of hydrochloric acid might throw light on this question.

Experimental.

The methods of preparation of the materials used in this work are in general those employed by one of us in previous work.¹

Mesitylene.—In the preparation of mesitylene the same proportions of acetone and sulfuric acid were used, but in each run 2300 g. of acetone were condensed. The yield of carefully purified mesitylene was 16 to 19% of that calculated for the acetone used.

Aceto-mesitylene.—Aceto-mesitylene was prepared, starting with 255 g. quantities of mesitylene. Half an hour after adding the aluminum chloride the whole mixture was poured into a large flask of cracked ice. The carbon disulfide layer was separated and the residue extracted with 500 cc. of carbon disulfide. The disulfide was distilled off from the combined extracts and the residue distilled through a Skinner column.² In order to obtain a product which does not darken on standing, it was found necessary to redistil under diminished pressure. The yield, boiling at 122–122.5° at 19 mm., was 300 g.

Oxidation of Aceto-mesitylene.—By using a mechanical stirrer it was found possible to oxidize 90 g. of aceto-mesitylene at a time in a 5-liter balloon-flask. The flask was cooled with tap water so as to keep the temperature below 40°. To the aceto-mesitylene were added 27 g. of sodium hydroxide and 1000 cc. of water; 180 g. of potassium permanganate was added in portions of 10 to 15 g. After about half of the permanganate had been added, 900 cc. of water was poured in and the remainder of the permanganate added as before. This process took about 3 hours.

The solution was then stirred for another hour and the flask transferred to the steam-bath and heated with occasional shaking until all of the permanganate was destroyed. To the hot solution was carefully added 225 cc. of 50% sulfuric acid, and the mixture returned to the steam-bath for half an hour. This oxidized the mesityl-glyoxylic acid present, $C_6H_2(CH_3)_3COCO_2H$, to trimethyl-benzoic acid. It was then cooled under the tap and 145 g. of sodium hydroxide added. When the hydroxide was all in solution the flask was returned to the stirrer and 500 cc. of water added. 230.5 g. of permanganate was added in four portions at half-hour intervals. Stirring was continued for 3 hours. The flask was transferred to the steam-bath and heated until all of the permanganate was destroyed. To the hot solution were added 700 cc. of 50% sulfuric acid and enough sodium hydrogen sulfite to destroy the oxides of manganese. The hot solution was quickly filtered by suction and the filtrate discarded. The precipitate was

¹ Noyes, *Am. Chem. J.*, **20**, 789 (1896); **22**, 1 (1898).

² Skinner, *THIS JOURNAL*, **39**, 2718 (1917).

dissolved in strong ammonium hydroxide, the solution cooled and shaken out with ether, and then filtered by suction. The acid was thrown out by adding sulfuric acid. It was filtered hot and washed with hot water.

The yield of dry acid varied from 70 to 95 g. in a great number of runs in which there was no apparent difference in procedure. It is very slightly soluble in hot or cold ether and insoluble in hot chloroform.

Esterification of Dimethyl Terephthalic Acid.—The yield of the acid ester was consistently over 97%, thus indicating quantitative prevention of esterification of the protected carboxyl.

Preparation of the Amido Acid.—The ester was dissolved in about twice its weight of strong ammonium hydroxide, the solution cooled under the tap, and ammonia gas passed in for 3 or 4 days. The temperature was held at about 45° during this time. The crystalline ammonium salt was then filtered off, sucked dry, washed with cold, strong ammonium hydroxide and then allowed to stand covered with ether for several hours. The ether was sucked off and the powdered salt partially dissolved in hot water. Hydrochloric acid was added with stirring and the mixture cooled under the tap for 2 hours. The amide was filtered off, washed with cold water, sucked dry, and then suspended in ether and let stand overnight. The ether was sucked off and the amide washed on the filter with ether. The ammoniacal mother liquors were aerated and then acidified. The precipitated dimethyl terephthalic acid was dried, esterified, and again treated with ammonium hydroxide. The total yield of amide was about 75% of the calculated amount for the acid used. It is insoluble in ether, benzene, and chloroform, and soluble in hot water, from which it crystallizes on cooling.

Preparation of *p*-Iodo-2,6-Xylic Acid.—The amide was carried through to the iodo acid without isolating any intermediate product. 15.5 g. of the finely powdered amide was ground into 60 cc. of 10% sodium hydroxide solution which had been cooled to zero in an ice-salt mixture; 120 cc. more of the cold hydroxide solution was slowly added with constant grinding. A cold solution of 5 cc. of bromine in 100 cc. of 10% sodium hydroxide solution was slowly added with grinding. A clear solution was obtained. It was transferred to a flask, 20 cc. of 50% sodium hydroxide solution added, and immersed in a boiling water-bath for 25 minutes. It was then cooled under the tap to about 50°, transferred to a large beaker standing in tap water, and 50% sulfuric acid added until the precipitate which formed had redissolved; 50 cc. more of the acid were added and the solution filtered to remove a small quantity of dark-colored solid matter.

The filtrates from three such runs were combined in a 3-liter flask and cooled to --2°. A solution of 60 g. of potassium nitrite in 75 cc. of water was added in 4 portions at 5-minute intervals. This was allowed to stand for 15 minutes during which time a heavy yellow precipitate formed. The mixture was then poured into a 5-liter flask containing 150 g. of potassium iodide and 250 cc. of 25% sulfuric acid, and heated on the steam-bath with occasional shaking until effervescence ceased. The flask was then cooled under the tap and sodium hydrogen sulfite added until the free iodine was destroyed. The iodo acid was filtered off and thoroughly washed.

Preparation of 2,6-Xylic Acid.—The iodo acid was dissolved in 50 cc. of strong ammonium hydroxide, care being taken to prevent the solution from becoming hot. A few grams of zinc dust was added and the flask shaken under the tap for a few minutes. After about half an hour more zinc and ammonium hydroxide were added and the flask placed on the steam-bath in such a position that a temperature of about 70° would be maintained, and let stand overnight. The zinc was filtered off by suction and the acid thrown out by adding hydrochloric acid. The xylic acid was filtered off and the filtrate twice extracted with ether. The residue from evaporating off the ether was

combined with the acid on the filter and the whole distilled at 17 mm. It distilled between 155° and 160° and melted at 114°. When crystallized from hot water it melted sharply at 116°. The yield in several runs was consistently over 65% of that calculated for the amide used.

The acid does not distil well with steam.

Reduction of 2,6-Xylic Acid.—Six g. of xylic acid was dissolved in 150 cc. of dry *iso*-amyl alcohol in a 1-liter round-bottom flask specially constructed to carry a large reflux condenser, a mercury-seal motor-driven stirrer, and a tube for admitting pieces of sodium. The solution was heated to boiling with a free flame, the stirrer started, and 30 g. of sodium added from time to time in pieces of about a gram each. More alcohol was added as needed to prevent crust formation. When all of the sodium was used up the flame was removed and the hot solution poured with stirring into a large beaker containing a liter of water.

A second batch of 6 g. was treated with alcohol and sodium in the same manner and poured into the beaker with the first. The procedure was repeated with two more 6-g. lots of the acid. The alcohol layer from the whole lot was placed in a large distilling flask with a piece of porous plate, a liter of water added, and the mixture boiled until about 500 cc. remained in the flask. The aqueous layer was then poured in and the distillation continued. More water was added as needed to distil out the amyl alcohol. Frothing marked the removal of the last of the alcohol.

The alkaline solution was cooled and poured into a large beaker cooled with ice-water. Hydrochloric acid was added to excess and the solution twice extracted with ether. The strong smelling oil obtained by evaporating off the ether was dissolved in warm ligroin to get rid of water, the water being sucked off through a pipet drawn to a fine tip. The ligroin was evaporated off and the residue placed in a vacuum desiccator over phosphoric anhydride. After 3 hours the residue was dissolved in amyl alcohol and divided into 3 portions, each of which was treated as before with 30 g. of sodium. The acid was recovered as after the first reduction and again reduced in 3 portions. After the alcohol was removed following the third reduction, the alkaline solution was extracted with ether before acidifying. The residue, after extracting and evaporating off the ether, was distilled at 23 mm. Almost all of it came over at 154–6°. The distillate weighed 19 g.

It was dissolved in carbonate solution and extracted with ether. The acid was divided into 5 portions by means of partial precipitation with hydrochloric acid and shaking out with ether.

Δ_3 Tetrahydro-2,6-Xylic Acid.—When the third and fourth fractions from above were let stand for 3 weeks a heavy growth of crystals formed. These were separated from the liquid acids and washed several times with low-boiling petroleum ether. They were then dissolved in carbonate solution, the solution extracted once with ether and twice with petroleum ether, the last traces of the petroleum ether aerated out, and the solution cooled in ice and acidified with dil. sulfuric acid. The unsaturated acid came out as an oil which immediately solidified. When pressed out on filter paper, it melted at 85–7°. It was then distilled at 28 mm., coming over at 158° to 160°. After solution in carbonate solution and reprecipitation, a product was obtained which melted at 93.4°.

Analyses. Calc. for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 69.77; H, 9.07.

Bromine was added and the resulting compound analyzed.

Calc. for $C_9H_{14}O_2Br_2$: Br, 50.88. Found: 50.43.

Treatment with 1:1 sulfuric acid destroyed the acid.

Heating for 24 hours with 50% potassium hydroxide did not change either the melting point or the refractive index of the acid.

Since the Δ_1 acid is known and is different from this acid, the above data were considered as sufficient to place the new acid as the Δ_3 tetrahydro-2,6-xylic acid, n_D^{25} , 1.4462; d^{25} , 0.9553.

Employing the Lorentz-Lorenz formula, the molecular refractivity is $M_D = 43.06$.

Hexahydro-2,6-Xylic Acid.—The remaining fractions from the reduction of the xylic acid together with the washings from the tetrahydro acid were freed from ether and ligroin and stirred into 20 cc. of hydrobromic acid, saturated at 0. The mixture was covered and set away in the ice box for 24 hours. It was then let stand at room temperature for 12 hours. Crushed ice and 20 cc. of ice-water were added and the solid acid separated from the solution. It was washed with cold water and suspended in sodium hydrogen carbonate solution in a flask fitted with a stirrer and surrounded with ice. A kilogram of 3% sodium amalgam was added, and carbon dioxide was passed in for 12 hours. Enough water was added from time to time to keep the bicarbonate in solution. The mercury was removed and the reduced acid thrown out with sulfuric acid. It was extracted with ether and the ether aerated off. It was then treated as before with hydrobromic acid, followed by amalgam. The sodium hydrogen carbonate solution was cooled with a freezing mixture and treated with permanganate solution until the addition of a little 2% permanganate solution gave a color which held for one minute. Some sodium hydrogen sulfite was added and the reduced acid thrown out with sulfuric acid. More sodium hydrogen sulfite was stirred in until all color was destroyed. The acid was filtered off and redissolved in sodium carbonate solution, the solution cooled and permanganate added until a permanent pink was obtained. The acid was precipitated, filtered off, and washed thoroughly. It melted at 74.5–75.3°.

The acid was distilled with steam with conductivity water and collected in 3 fractions. In order to ascertain the degree of purity of the material, the melting point and refractive index of each fraction were determined.

Fraction.	Melting point, °C.	n_D^{25}
Original	74.5–75.3	1.4372
1	75.6	1.4371
2	75.5–75.8	1.4369
3	75.5–75.8	1.4366
Residue	74.5–75	1.4370

Fractions 2 and 3 were used for conductivity and density work; n_D^{25} , 1.4371; d^{25} , 0.9454; M_D , 43.28 (Lorentz-Lorenz).

Preparation of Δ_1 -Tetrahydro-2,6-Xylic Acid.—Two g. of the hexahydro acid was cautiously treated in an open-bomb tube with 3 g. of phosphorus pentachloride, and then warmed for a few minutes in the steam-bath. It was cooled, 0.657 cc. of bromine was added, and the tube sealed. It was heated in the steam-bath for 3 hours, cooled, the tube opened and the contents poured into ice-water.¹ After stirring for 15 minutes, the bromo-acid chloride was taken out with ether, the ether solution dried with sodium sulfate, the ether aerated off, and the residue dissolved in glacial formic acid and refluxed for an hour. It was allowed to stand overnight, during which time the bromo acid crystallized in its characteristic flakes. The crystals were filtered off and the filtrate diluted and extracted with ether. The ether was removed and the residue and crystals refluxed for 10 hours with alcoholic potash. Most of the alcohol was distilled off, sulfuric acid was added, and the unsaturated acid taken out with ether. The ether was

¹ It is interesting to note that this bromo acid chloride is very stable, not being affected by stirring overnight with 0.1 *N* alkali, and resisting heating to boiling in 25% potassium hydroxide solution, thus agreeing well with the findings of Sudborough, *J. Chem. Soc.*, 67, 601 (1895).

removed and the residue distilled with steam. After several hours cooling under the tap most of the acid crystallized from the distillate. It was extracted with ether and again steam-distilled, using conductivity water. The part coming over in the middle of the distillation crystallized when cooled overnight. The yield was 2 g. from 6 g. of the hexahydro acid. It melted at 91–91.5°; d_4^{25} , 0.8625; n_D^{25} 1.4700; M_D , 49.87 (Lorentz-Lorenz). It is slowly soluble in petroleum ether.

1,2-Dibromo-hexahydro-2,6-Xylic Acid.—A weighed amount of the Δ_1 tetrahydro acid was dissolved in chloroform and treated with less than the theoretical quantity of bromine. It was decolorized in 3 hours. More bromine was added and the solution let stand overnight. The chloroform and excess bromine were aerated off with dried air, leaving a white solid which dissolved with difficulty in ligroin. This substance had no sharp melting point but melted with decomposition at 128–32° when heated quickly.

0.165 g. of the dibromo acid when titrated with 0.1 *N* alkali used 15.3 cc.; that calculated for neutralizing the carboxyl is 5.2 cc. This result indicated that not only was the carboxyl neutralized but both bromine atoms were removed in the titration.

The solution from the titration was acidified with sulfuric acid and extracted with ether. A very little nitric acid was added and the solution titrated with 0.1 *N* silver nitrate solution; 9.9 cc. was required, whereas the calculated amount was 10.4 cc.

$\Delta_{1,5}$ -Dihydro-2,6-Xylic Acid.—The dibromo acid was heated for half an hour on the steam-bath with a slight excess of 0.1 *N* alkali. The solution was cooled and extracted with ether. An excess of sulfuric acid was added and the solution again extracted. The ether was removed *in vacuo*, leaving a syrupy acid which was almost entirely soluble in a cold sodium carbonate solution. It did not give a test for halogen. The carbonate solution was extracted, acidified, and again extracted. The ether was removed as before and the residue titrated with 0.0161 *N* alkali. There was some insoluble residue. This was removed with ether and the acid recovered by acidifying and extracting. The extract was dissolved in ligroin by warming with a fairly large volume. On evaporating the ligroin *in vacuo* a white solid was obtained. It melted slowly before the beaker had reached room temperature. The acid was titrated and again gave an appreciable quantity of residue even though the alkaline solution was boiled.

These facts together with a changing refractive index showed plainly that either the method did not yield a pure dihydro acid or that the acid was continually going over into another substance by the action of the alkaline solution or the air.

The acid was distilled in an all-glass apparatus. It came over at 155–60° at 28 mm. The distillate was a liquid which on standing *in vacuo* became of the consistency of vaseline. It dissolved completely in sodium hydrogen carbonate solution, reduced permanganate very rapidly, decolorized bromine in chloroform, and was very slightly soluble in petroleum ether even when warmed for some time.

Analysis. Calc. for $C_8H_{12}O_2$: C, 71.01; H, 7.95. Found: C, 70.70; H, 8.11.

Esterification of 2,6-Xylic Acid.

The method employed for the esterification of all of the acids was to dissolve the acid in a large excess of dry methyl alcohol containing 3 or 4% of hydrochloric acid, and reflux for 4 hours after boiling became vigorous. The larger part of the alcohol was then boiled off through a Skinner column. No free acid could be detected in the distillate from any run. The residue in the flask was cooled and diluted. Sodium carbonate solution was added to strongly alkaline reaction and the solution twice

extracted with ether, the ether solution being washed twice with water and the water returned to the solution. The solution was then shaken out twice with ligroin, acidified with sulfuric acid and extracted twice with ether. The ether was washed as before with water, evaporated off in a beaker which was then placed in a vacuum desiccator over phosphorus pentoxide and allowed to stand overnight. It was weighed, the contents taken out with absolute ether and again weighed. The difference between the loss in weight and the weight of the sample was recorded as the amount esterified.

	1 G.	2 G.
Xylic acid	1.000	1.000
Alcohol.....	65	50
HCl.....	2.6	1.8
Xylic acid recovered.....	0.972	0.963
Per cent. esterified.....	2.8	3.5

Questioning Rosanoff's view but hoping to get some of the *iso*-amy ester by direct esterification, we made the following run: xylic acid, 3.6 g.; *iso*-amyl alcohol, b. p. 131°, 100 cc.; sulfuric acid, c. p., 96%, 2.5 cc.; time refluxed, 64 hours; xylic acid recovered, 3.4 g.; esterification, 5.5%.

ESTERIFICATION OF 2,6-XYLIC ACIDS.
20 g. of Methyl Alcohol Used in Each Case.

	Acid. G.	HCl. G.	Acid recovered. G.	Esterified. %
Hexahydro.....	0.901	0.66	0.433	51.9
	0.433	0.7	0.225	48.0
Δ_1 Tetrahydro.....	0.620	0.7	0.391	36.9
	0.421	0.7	0.250	40.6
Δ_3 Tetrahydro.....	0.309	0.7	0.075	75.0
$\Delta_{1,5}$ Dihydro ^a	0.277	0.7	0.148	47.0

^a The recovered dihydro acid was again esterified and gave 30% esterification. The acid was recovered a second time and esterified to the extent of 23%. In every case both the ester and the recovered acid gave good strong tests for unsaturation. After the third esterification there was evidence of xylic acid in the recovered acid. To determine if the acid is easily oxidized to xylic acid it was heated to near boiling in distilled water for about an hour. On cooling, xylic acid crystallized out and the test for unsaturation was very weak.

Conductivities of 2,6-Xylic Acids.

In all of the conductivity work the solutions were made up by weight at 25°. All measurements were made at 25°. The cell had bright electrodes and was standardized against potassium chloride and checked against pure benzoic acid, giving the values of White and Jones.¹ Λ_{∞} values were calculated by Ostwald's rule. No correction was made for the water used. Conductivity water: 7.0×10^{-7} .

¹ White and Jones, *Am. Chem. J.*, 44, 183 (1910).

	V.	Δ .	α .	k .
2,6-Xylic Acid.....	128	92.53	0.2461	6.28×10^{-4}
	512	160.5	0.4268	6.21×10^{-4}
	1024	199.8	0.5314	5.88×10^{-4}
	∞	376
Hexahydro-2,6-Xylic Acid.....	768	35.70	0.0952	1.30×10^{-5}
	1024	41.07	0.1095	1.31×10^{-5}
	∞	375
Δ_1 Tetrahydro-2,6-Xylic Acid.....	768	62.59	0.1669	4.35×10^{-5}
	1024	71.03	0.1894	4.32×10^{-5}
	∞	375
Δ_3 Tetrahydro-2,6-Xylic Acid.....	768	61.15	0.1631	4.14×10^{-5}
	1024	69.92	0.1864	4.17×10^{-5}
	∞	375

Summary.

1. The method of preparation of 2,6-xylic acid has been improved, and its degree of esterification and its ionization constant have been determined.

2. The method of preparation of hexahydro-2,6-xylic acid has been improved, and its degree of esterification, molecular refractivity, and ionization constant have been determined.

3. A new compound, Δ_3 tetrahydro-2,6-xylic acid, has been prepared, and its degree of esterification, molecular refractivity, and ionization constant have been determined.

4. A new compound, $\Delta_{1,5}$ dihydro-2,6-xylic acid, has been prepared, and its degree of esterification determined.

5. Δ_1 Tetrahydro-2,6-xylic acid has been prepared, and its degree of esterification, molecular refractivity, and ionization constant have been determined.

6. The constants of the acids mentioned and the percentages of esterification on boiling for 4 hours with methyl alcohol containing 4% of hydrochloric acid were as follows:

Acid.	Esterified. %	Mol. refractivity. $L-L$.	k . $V=1024$.
2,6-Xylic.....	3.5	...	5.88×10^{-4}
Hexahydro Xylic.....	52	43.276	1.31×10^{-5}
Δ_1 Tetrahydro Xylic.....	41	49.870	4.32×10^{-5}
Δ_3 Tetrahydro Xylic.....	75	43.057	4.17×10^{-5}
$\Delta_{1,5}$ Dihydro Xylic.....	47

7. The esterification of 2,6-xylic acid on boiling with methyl alcohol containing hydrochloric acid conforms qualitatively to Victor Meyer's law. Esterification proceeds very slowly.

8. The esterification of the hexahydro-2,6-xylic acid indicates far less steric hindrance than occurs with the corresponding xylic acid.

9. There is more hindrance to the esterification of the Δ_1 than to that

