

by iodine using potassium iodide in absolute acetone solution. A comparison was made of the effect of these groups with the methylthio, phenoxyl and phenyl groups when similarly situated.

2.  $\beta$ -Chloro-ethyl phenyl sulfide was found to have only a weak vesicant action and the  $\gamma$ -chloropropyl phenyl sulfide was completely non-vesicant.

3. The following substances were isolated and characterized for the first time:  $\beta$ -hydroxyethyl phenyl sulfide,  $\gamma$ -hydroxypropyl phenyl sulfide,  $\gamma$ -hydroxypropyl  $\alpha$ -naphthyl ether,  $\gamma$ -chloropropyl  $\alpha$ -naphthyl ether,  $\gamma$ -chloropropyl  $\beta$ -naphthyl ether.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

### COMPETITIVE HYDROGENATIONS

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The importance of precise information on the relation of the structure of a compound to its reactivity as manifested in the ease of reduction led Vavon and Husson<sup>1</sup> to devise a unique method for the experimental study of the rate of reduction of certain derivatives of cinnamic acid. Their method consisted in adding one mole of hydrogen to a mixture of one mole of *d*- $\alpha$ -pinene and one mole of the compound under consideration, and then calculating the distribution of the hydrogen between the two compounds from the change in optical activity of the mixture. They assumed that the distribution of the hydrogen between the pinene and the unsaturated compounds was a measure of the ease of reduction of the unsaturated compounds. If, for example, cinnamic acid took up 57% of the hydrogen (pinene 43%) and  $\alpha$ -methylcinnamic acid took up 26% (pinene 74%), they concluded that cinnamic acid was reduced much more easily than the substituted acid. This method of comparison has two very considerable advantages over the usual one of noting the rate of absorption of hydrogen by a single compound. The latter method for an accurate comparison demands that the comparisons be made over catalysts of identical activity. This is a condition which it is difficult if not impossible to meet if an extended list of compounds is to be compared. This method also presupposes that there is no impurity in any of the compounds which would lower the activity of the catalyst. An attempt was made to repeat and extend their work because of our interest in simultaneous reactions and because previous work in this Laboratory made it seem probable that the ratio of the distribution would be a func-

<sup>1</sup> Vavon and Husson, *Compt. rend.*, **176**, 989 (1923).

tion of the particular catalyst and the solvent used as well as of the structure of the organic compounds reduced.

Four hundredths of a mole of *d*- $\alpha$ -pinene and 0.04 of a mole of cinnamic acid or other unsaturated compound were mixed in a solvent and the volume made up to 100 cc. A quantity of Adams and Voorhees' platinum oxide was added and followed by 0.04 mole of hydrogen under a pressure of 0.2 of an atmosphere. The bottle containing the reaction mixture was agitated. A polarimetric reading of the mixture was taken before and after the addition of hydrogen. A second solution containing only *d*- $\alpha$ -pinene was fully reduced and the rotation noted. The distribution of the hydrogen between the two compounds may be calculated from the readings on the hydrogenated pinene, the unreduced mixture and the mixture after absorption of one mole of hydrogen. Whenever a new catalyst was prepared, its activity was standardized by a trial run. Allowance was made for the volume of hydrogen absorbed by the platinum oxide on being reduced to platinum black. All of the results given in this paper were checked at least once and most of them several times, using different preparations of catalyst and solvent.

There is no very marked difference in the rate of reduction of a mixture of pinene and cinnamic acid irrespective of whether methyl (33 m.) or ethyl alcohol (37 m.) or acetic acid (40 m.) is used. The rate is much lower in ethyl acetate (70 m.) and the higher alcohols propyl (65 m.) and butyl (85 m.). Ferrous sulfate has no effect upon the rate but 0.001 mole of manganese (55 m.) and especially zinc (180 m.) and nickel acetates (180 m.) very greatly reduce the rate of hydrogenation. There was very little difference in the rate of reduction of mixtures in acetic acid of pinene and cinnamic acid (40 m.),  $\alpha$ -methylcinnamic acid (35 m.), methyl  $\beta$ -methylcinnamate (33 m.) and ethyl  $\beta$ -methylcinnamate (33 m.).

TABLE I

REDUCTION OF PURE COMPOUNDS AND MIXTURES						
Time for reduction in minutes						
Cinnamic acid	Pinene	Mixture	H <sub>2</sub> to pinene, %	Solvent	Catalyst	
31	5	25	35	CH <sub>3</sub> CO <sub>2</sub> H	0.095 g. Pt oxide	
83	124	60	18	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	.095 g. Pt oxide	
..	..	41	15	CH <sub>3</sub> CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	.285 g. Pt oxide	
..	..	19	19	(CH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub>	.285 g. Pt oxide	
59	92	59	14	CH <sub>3</sub> COCH <sub>3</sub>	.095 g. Pt oxide	
..	..	200	20	None	10 g. Ni and kieselguhr	
"Octene,"	6	5	6	CH <sub>3</sub> CO <sub>2</sub> H	0.095 g. Pt oxide	
..	..	200	53	None	10 g. Ni and kieselguhr	
Cyclohexene,	8	5	7	15	CH <sub>3</sub> CO <sub>2</sub> H	0.095 g. Pt oxide
Allyl alcohol,	34	5	6	8	CH <sub>3</sub> CO <sub>2</sub> H	.095 g. Pt oxide
$\alpha$ -Methylcinnamic acid	..	..	93	CH <sub>3</sub> CO <sub>2</sub> H	.10 g. Pt oxide	
Methyl $\beta$ -methylcinnamate	..	..	87	CH <sub>3</sub> CO <sub>2</sub> H	.30 g. Pt oxide	
Ethyl $\beta$ -methylcinnamate	..	..	91	CH <sub>3</sub> CO <sub>2</sub> H	.30 g. Pt oxide	

The data referred to in the last paragraph were obtained at an earlier time and with samples of catalysts which differed somewhat in activity from those referred to in Table I. In Col. 1 of this table is given the time in minutes for the addition of 0.04 mole of hydrogen to 0.04 mole of cinnamic acid or other unsaturated compound. In Col. 2 is given the time required for the similar reduction of pinene and in Col. 3 is given the time required for the addition of 0.04 mole of hydrogen to a mixture of 0.04 mole of pinene and 0.04 mole of the other unsaturated compound under consideration. The percentage of the hydrogen taken up by the pinene is given in Col. 4.

The nature of the solvent and the structure of the cinnamic acid derivatives play a very large role in determining the ratio of distribution of the hydrogen between the compounds of the mixture, as has been pointed out by Vavon and his associates. In an acetic acid solution of cinnamic acid and pinene, 65% of the hydrogen goes to the acid, while in ethyl acetate, acetal or the dimethyl ether of ethylene glycol the acid receives from 81 to 85% of the hydrogen. In an acetic acid solution  $\alpha$ -methylcinnamic acid gets only 7% of the hydrogen, while the esters of  $\beta$ -methylcinnamic acid get only 9 to 13% of the hydrogen.

In acetic acid solution Vavon and Husson found that 57% of the hydrogen went to the cinnamic acid, 26% to the  $\alpha$ -methylcinnamic acid, 45% to the methyl  $\beta$ -methylcinnamate and 31% to the ethyl  $\beta$ -methylcinnamate. Our results are in only fair agreement with those of Vavon and Husson for cinnamic acid and are markedly different for the derivatives of the acid. It is not believed that this is a reflection on the work of either set of investigators, but shows, rather, that the nature of the pinene used affects the distribution of hydrogen. It should be noted that our platinum catalysts were not prepared by the same method as that used by Vavon and his associates.

The salts which have so great an influence on the rate by hydrogenation had no effect upon the distribution of hydrogen between the two unsaturated compounds present in the mixture. The activity of the catalyst is entirely without effect upon ratio of the distribution of the hydrogen.

The most striking results noted in this study have to do with the rates of reduction of pure compounds as compared to the reduction of mixtures. Pinene is much more rapidly reduced in acetic acid solution than is cinnamic acid, yet in a mixture the acid is reduced more rapidly than is pinene. Pinene and octene are reduced at very similar rates, yet in a mixture the octene gets about 75% of the hydrogen. It requires almost seven times as long to reduce a mole of allyl alcohol as it does one of pinene, yet in a mixture allyl alcohol gets 92% of the hydrogen at a rate very similar to that for pinene. These results show that there may be no relationship

between the relative rates of reduction of pure compounds and their rate of reduction in mixtures.

An attempt was made to find a set of conditions under which the distribution of hydrogen between two compounds could be studied over both a platinum and a nickel catalyst. This was unsuccessful, since nickel is not active toward the compounds under consideration at room temperature, nor in the presence of ethyl acetate or acetic acid. Platinum is apparently not active at the higher temperatures at which nickel functions as a catalyst. Mixtures of 0.25 mole of cinnamic acid and 0.25 mole of pinene and of octene and pinene were hydrogenated at 135° in a glass container at a pressure of from one to two atmospheres using 10 g. of Reid and Rather's<sup>2</sup> nickel catalyst reduced for two hours at 450°. The calculated distribution of hydrogen between the competing compounds is given in Table I.

**Reduction of Furfural Acetone.**—Since the solvent apparently plays so large a role in determining the relative rates of reduction of various pairs of unsaturated compounds, some experiments were carried out on a larger scale upon the reduction of furfural acetone, which contains four points of unsaturation in the molecule.

One-half mole of hydrogen was added to 0.5 mole of furfural acetone in 125 cc. of the solvent at from one to three atmospheres' pressure of hydrogen, using 0.2 g. of catalyst in alcohol and ethyl acetate and 0.5 g. of a less active catalyst in petroleum ether. The hydrogenation was complete in three to four hours. The larger amount of catalyst used in the petroleum ether was necessary in order to complete the reduction in the usual time as the hydrocarbon mixture apparently dissolved rubber from the stopper of the hydrogenation bottle and thus the catalyst became poisoned. Six of these reaction products were combined (total 540 g.) and fractionated six times at 3 mm. through a 50-cm. Vigreux column (see Table II). The second fraction boiled at 201–202° at atmospheric pressure and the third melted at 38–39°. The semicarbazones from the second fractions melted at 143°. These values show that the fractions were almost pure 4- $\alpha$ -furfurylbutanone-2 and furfural acetone, respectively. The lower fractions consisted very largely of the butanone and the third fraction was made up largely of furfural acetone.

TABLE II  
HYDROGENATION OF FURFURAL ACETONE IN VARIOUS SOLVENTS

Solvent	% in various fractions			95–97° Furfural acetone	Total distillate, %
	50–77.5°	77.5–78.5° 4- $\alpha$ -Furfuryl butanone-2	78.5–95°		
C <sub>2</sub> H <sub>5</sub> OH	10.6	36.1	9.6	12.2	68.5
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	4.4	25.7	8.5	35.1	73.7
C <sub>n</sub> H <sub>2n+2</sub>	8.6	48.6	14.1	16.0	87.3

<sup>2</sup> Reid and Rather, THIS JOURNAL, 37, 2116 (1915).

A comparison of ethanol, ethyl acetate and petroleum ether as solvents for the reduction of furfural acetone shows that much more furfural acetone was left after the addition of the hydrogen when ethyl acetate was used as a solvent. This means that this solvent facilitated the addition of more than one molecule of hydrogen to a molecule of the ketone, thus causing more complete hydrogenation and poorer yields of 4- $\alpha$ -furfurylbutanone-2. Ethyl alcohol facilitated resinification so that although the yield of the 4- $\alpha$ -furfurylbutanone-2 was higher than with ethyl acetate the recovery of furfural acetone was very low. Petroleum ether did not facilitate the complete hydrogenation noted with ethyl acetate, nor was resinification so high, so that excellent yields of the 4- $\alpha$ -furfurylbutanone-2 were obtained.

### Reagents

*d*- $\alpha$ -Pinene was obtained through the kindness of Professor Floyd E. Rowland of the Oregon Agricultural College and the Western White Cedar Co., Marshfield, Oregon. It came from a source which yields a pinene having the highest specific rotation that has been reported in the literature.<sup>3</sup> Its constants were those given by Dr. Thurber, *i. e.*, b. p. 156–156.5°,  $[\alpha]_D^{20} +53.01$ . The authors were very fortunate to obtain this pure *d*- $\alpha$ -pinene as the pinene separated from ordinary American turpentine has only a small optical activity. Vavon and Husson presumably used pinene from French turpentine, which contains a much larger proportion of the dextro isomer than does ordinary American turpentine.

Platinum oxide was prepared as by Adams, Voorhees and Shriner.<sup>4</sup> The platinum black after use was converted to platinic chloride either by the method described in their papers, using hydrobromic acid or by dissolving in aqua regia. After several such recoveries the platinum was purified as by Wichers.<sup>5</sup>

Allyl alcohol was purified according to the method of "Organic Syntheses."<sup>6</sup> It absorbed the theoretical quantity of hydrogen and distilled at 95.5–96.5°. The petroleum ether was an Eastman Kodak Company product purified by permanganate and boiling at 35–60°. Furfural acetone was prepared as indicated in "Organic Syntheses,"<sup>7</sup> and showed a melting point of 38°. The octene used was that isomer known as di-*iso*-butylene and was prepared from tertiary butyl alcohol by Walter Arthur, using a method similar to that described by Edgar.<sup>8</sup> It boiled at 101° at 742 mm. and absorbed the theoretical amount of hydrogen. The cyclohexene was fractionated so that the sample used had a boiling-point range from 81.9 to 82.1°. It absorbed 96% of the theoretical quantity of hydrogen.

The cinnamic acid was purified from a commercial product by repeated recrystallization from a mixture of 60% alcohol and 40% water. The melting point was 133°. The  $\alpha$ -methylcinnamic acid (m. p. 74–76°) was made by a standard laboratory method for cinnamic acid by substituting sodium propionate and propionic anhydride for the

<sup>3</sup> Thurber, *Ind. Eng. Chem.*, **19**, 739 (1927).

<sup>4</sup> Voorhees and Adams, *THIS JOURNAL*, **44**, 1397 (1922); Adams and Shriner, *ibid.*, **45**, 2171 (1923).

<sup>5</sup> Wichers, *ibid.*, **43**, 1268 (1921).

<sup>6</sup> "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. II, p. 15.

<sup>7</sup> "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 42.

<sup>8</sup> Edgar, *Ind. Eng. Chem.*, **19**, 146 (1927).

corresponding acetates. The methyl (b. p. 152° (26 mm.)) and ethyl (b. p. 162–163° (26 mm.)) esters of  $\beta$ -methylcinnamic acid were made as described by Lindenbaum.<sup>9</sup>

### Summary and Conclusions

It appears that the factors determining the distribution of hydrogen by platinum between two competing reactants, like the factors determining the proportion of dehydration and dehydrogenation of an alcohol over zinc oxide, for example,<sup>10</sup> bear little relationship to those factors which determine the amount of material reacting in unit time. The addition of zinc and nickel acetates, for example, retarded the rate of reduction but did not modify the distribution of hydrogen. The use of acetic acid, ethyl acetate and various alcohols as solvents modified the rate of reaction of hydrogen and in addition determined in part the ratio of its distribution between the two reactants. It seems that the salts poison the catalyst for the reaction of the two unsaturated compounds to an equal extent,<sup>11</sup> presumably through adsorption in certain areas of the catalyst. It may be suspected that in addition to this the solvent plays a part in the rate of formation and the stability of an intermediate compound of platinum–hydrogen–reactant–solvent.

The relative ease of reduction of two substances in a mixture may not be certainly determined even qualitatively by determining the rates of reduction of the two substances separately.

In the reduction of furfural acetone there are three competing reactions: (1) simple hydrogenation of the alkene linkage in the open chain, (2) the addition of more than one molecule of hydrogen to a molecule of the ketone and (3) "resinification." The ratio of these reactions may be markedly changed by varying the solvent.

The esterification of cinnamic acid or the substitution of a methyl group for a hydrogen on the  $\alpha$ - or  $\beta$ -carbon atom very greatly reduced the proportion of hydrogen going to the alkene linkage when the compounds in a mixture with *d*- $\alpha$ -pinene were treated with hydrogen. No considerable difference was observed between the adsorption of hydrogen by the methyl and ethyl esters of  $\beta$ -methylcinnamic acid.

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<sup>9</sup> Lindenbaum, *Ber.*, **50**, 1270 (1917).

<sup>10</sup> Adkins and Lazier, *THIS JOURNAL*, **48**, 1671 (1926).

<sup>11</sup> Cf. Tuley and Adams, *ibid.*, **47**, 3061 (1925).