Anal. Calcd. for $C_{11}H_{13}O_4N$: C, 59.19; H, 5.83. Found: C, 59.17; H, 6.18.

The Phenyl-urethan of Ethyl *p*-Hydroxymethyl-benzoate, *p*-$C_6H_5NHCOOCH_2$-$C_6H_4COOC_2H_5$.—A mixture of 7 g. of ethyl *p*-hydroxymethyl-benzoate and 5 g. (one molecular equivalent) of phenyl isocyanate was heated on the steam-bath for one hour. On cooling, the contents of the flask solidified. The colorless solid was soluble in alcohol and benzene, and insoluble in water. Recrystallized from a mixture of benzene and petroleum ether, it melted at 107°; yield, 10.5 g., or 80%.

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.23; H, 5.69. Found: C, 68.22; H, 6.03.

Pharmacological tests of these substances are now in progress.

Summary

1. A new and convenient synthesis of *p*-hydroxymethyl-benzoic acid is described.

2. A series of esters of this acid of possible value as local anesthetics has been prepared. These consist of (a) simple esters obtained by esterifying the carboxyl group; (b) esters (such as the benzoate derivatives and urethans) derived from the hydroxyl group of the ethyl ester of the acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PLATINUM AND PALLADIUM OXIDES AS CATALYSTS IN THE REDUCTION OF ORGANIC COMPOUNDS. IX. THE REDUCTION OF OLEFINS[1]

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The conversion of ethylene compounds into their corresponding ethane derivatives is not always readily accomplished by chemical reagents. The advantage of hydrogenation by catalysis, since it is general in application and quantitative, has been recognized by numerous investigators[3] and many types of compounds have been successfully hydrogenated by means of nickel, platinum or palladium. Most of these reductions have been made at high temperatures (usually 180° for hydrogenation in the gaseous phase or at the boiling point of some solvent when hydrogenating in solution) and in no case has a careful, complete study of the reduction of different types of ethylenic compounds been made. Frequently the reductions reported in the literature were carried out on small amounts of material with large amounts of catalyst and were, for the most part, time

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[2] This communication is an abstract of theses submitted by J. W. Kern and R. L. Shriner in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] See "Catalysis in Organic Chemistry" by Sabatier, translated by Reid, D. Van Nostrand Co., 1922.

consuming. An historic sketch of the catalytic reduction of olefins, therefore, is of little value, since exact conditions have only rarely been defined, and where they are stated differ so widely that comparisons cannot be made.

Since the oxides of platinum and palladium prepared by the fusion of sodium nitrate with chloroplatinic acid or palladous chloride gave platinum and palladium blacks which were efficient and standard catalysts for the reduction of aldehydes to alcohols,[4] the quantitative study of these catalysts has been extended to the hydrogenation of various types of olefins.

This investigation had several objects in view: (a) to demonstrate the efficiency of platinum and palladium black from the corresponding oxides by comparing their activities in the reduction of olefins with platinum and palladium black made by other methods, (b) to compare platinum black with palladium black in the reduction of various olefins, (c) to study the effect of the character of the groups attached to the carbons holding the ethylene linkage on the speed of reduction, and (d) to determine whether there is any relationship between catalytic reduction and reduction by chemical reagents.

In order that the comparative results on the reduction of various olefins might have significance, a large amount of pure platinum and palladium catalyst was prepared so that the single samples were sufficient in quantity to provide catalyst for all of the reduction experiments described in this communication. The same samples of olefinic compounds were also used throughout. The apparatus and general procedure for reduction were those previously described for the reduction of aldehydes.[4b,4e] Specifically 0.1 mole of reactant in 150 cc. of 95% alcohol was reduced with hydrogen under 2 to 3 atmospheres' pressure at room temperature with 0.1 g. or in a few cases 0.05 g. of platinum or palladium oxide. These standard conditions were modified in only a few instances; for example, the amount of reactant had to be decreased in one instance in order that it might be completely in solution before the reduction started.

The substances studied may be divided into two groups, (A) olefins in which the atoms or groups directly attached to the carbons holding the double bond are alkyl or aryl radicals, (B) olefins in which the carbon-carbon double bond is conjugated with a carbonyl group. Group A was subdivided into (1) allyl and propenyl benzenes, and (2) other olefin hydrocarbons; and Group B was divided into (1) α,β-unsaturated ketones and (2) α,β-unsaturated acids and esters.

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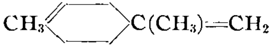
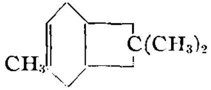
[4] Previous articles in this field: (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers and Adams, *ibid.*, **45**, 1071 (1923). (c) Adams and Shriner, *ibid.*, **45**, 2171 (1923), preparation of catalyst. (d) Kaufmann and Adams, *ibid.*, **45**, 3029 (1923). (e) Carothers and Adams, *ibid.*, **46**, 1675 (1924). (f) Shriner and Adams, *ibid.*, **46**, 1684 (1924). (g) Carothers and Adams, *ibid.*, **47**, 1047 (1925). (h) Pierce and Adams, *ibid.*, **47**, 1098 (1925).

TABLE I

TIME REQUIRED FOR THE ABSORPTION OF ONE MOLECULAR EQUIVALENT OF HYDROGEN AT 2 TO 3 ATMOSPHERES PRESSURE

	Substance	Formula	Wt. reduced in g. (0.1 mole)	Time in min. for absorption of 1 mol. equiv. of H_2 at 2–3 atm. press. and 25° PtO_2H_2O 0.10 g.	PtO_2H_2O 0.05 g.	PdO 0.10 g.	PdO 0.05 g.
1.	Eugenol	$(CH_3O)(HO)C_6H_3CH_2CH=CH_2$	16.4	...	3.5	...	9
2.	Safrol	$CH_2O_2C_6H_3CH_2CH=CH_2$	16.2	...	9	...	9
3.	Iso-eugenol	$(CH_3O)(HO)C_6H_3CH=CHCH_3$	16.4	...	10	...	19
4.	Isosafrol	$CH_2O_2C_6H_3CH=CHCH_3$	16.2	...	11	...	13
5.	Anethol	$CH_3OC_6H_4CH=CHCH_3$	14.8	...	14	...	8
6.	Undecylenic acid	$HO_2C(CH_2)_8CH=CH_2$	18.4	1.5	2.5	17	32
7.	Phenylethylene	$C_6H_5CH=CH_2$	10.4	...	9	...	10
8.	Limonene		13.6 { 1st bond	3	4	42	...
			2nd bond	6	15	240	...
9.	Pinene		13.6	7	...	260	...
10.	Cyclohexene		8.2	3.5	7	13	31
11.	Trimethylethylene	$(CH_3)_2C=CHCH_3$	7.0	6	12.5	30	135
12.	Stilbene	$C_6H_5CH=CHC_6H_5$(*trans*)	18.0	38	...	69	...
13.	Diphenylethylene	$(C_6H_5)_2C=CH_2$	18.0	10	21	14	57
14.	Diphenylmethylethylene	$(C_6H_5)_2C=CHCH_3$	19.4	153	312	...	...
15.	Mesityl oxide	$(CH_3)_2C=CHCOCH_3$	9.8	5.5	10	15	43
16.	Benzal-acetone	$C_6H_5CH=CHCOCH_3$	14.6	11	67	27	87
17.	Benzal-acetophenone	$C_6H_5CH=CHCOC_6H_5$(*trans*) (in ethyl acetate)	20.8	181	...	480	...
18.	Dimethylacrylic acid	$(CH_3)_2C=CHCO_2H$	10.0	7	25	173	...
19.	Maleic acid	$HO_2CCH=CHCO_2H$	11.6	18	95	18	120
20.	Fumaric acid	$HO_2CCH=CHCO_2H$	11.6	10.5 hrs.	...	101	...
21.	Ethyl maleate	$C_2H_5O_2CCH=CHCO_2C_2H_5$	17.2	19.5	41	9	13
22.	Ethyl fumarate	$C_2H_5O_2CCH=CHCO_2C_2H_5$	17.2	31	...	30	...
23.	Cinnamic acid	$C_6H_5CH=CHCO_2H$(*trans*)	14.8	149	...	82	...
24.	Ethyl cinnamate	$C_6H_5CH=CHCO_2C_2H_5$(*trans*)	17.6	172	...	26	...
25.	Sodium cinnamate	$C_6H_5CH=CHCO_2Na$(*trans*)	8.5 (0.05 mole)	82	...	52	...

In Table I are listed the times required for complete absorptions of 1 molecular equivalent of hydrogen under the specific conditions stated above. Although only the results of single experiments have been tabulated, a large number of individual reductions were made and in every case the figures given were checked. In fact, many of the reductions were repeated with another sample of catalyst, and reduced in a different apparatus by a second experimenter. The difference in results, when there was any, never consisted of more than one or two minutes in runs completed within 30 minutes and never more than five minutes in runs requiring a much longer time.

Discussion of Results

In all experiments the time of reduction given does not include the lag that takes place in the reduction of the metal oxides to the black.

Efficiency of Catalysts.—It is necessary merely to scan the table in order to see the remarkable activity of both the platinum and palladium black as catalysts. In order to comprehend the relative efficiencies a few experiments may be cited which have been described in the literature. Fournier[5] reduced 32 g. of eugenol in two hours with 1 g. of ordinary platinum black, while with that from platinum oxide, 50 g. of eugenol could be reduced in eight minutes with 0.05 g. of platinum oxide. Moreover, using four successive portions of 20 g. each and 0.02 g. of catalyst required for the respective successive runs, 13, 11, 17 and 23 minutes. Analogous results were obtained for successive runs of iso-eugenol. Vavon[6] reduced 35 g. of limonene in 120 minutes with 9 g. of platinum black while with platinum-oxide platinum black 13.6 g. of limonene was reduced completely in 9 minutes using 0.1 g. of catalyst. With palladium black as a catalyst Paal[7] reduced 0.3 g. of sodium cinnamate with 0.05 g. of palladium black in 20 minutes, whereas 0.1 g. of catalyst from palladium oxide reduces 8.5 g. in 52 minutes. Willstätter[8] reduced 0.9 g. of limonene with 0.1 g. of palladium black in 30 minutes, whereas 13.6 g. was reduced by 0.1 g. of palladium-oxide palladium black in 34 minutes. These examples are sufficient to show the superiority of these catalysts; moreover, it appears in at least the majority of cases that the colloidal preparations of platinum and palladium are not as active catalysts as the platinum and palladium black obtained by the reduction of the oxides.

It is obvious that the methods employing these catalysts are not purely of theoretical interest but of actual preparative value. In all of the reductions if the amount of catalyst is increased to the proportion usually em-

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[5] Fournier, *Bull. soc. chim.*, [4] **7,** 23 (1910).

[6] Vavon, *Compt. rend.*, **149,** 997 (1909); **152,** 1675 (1911); **158,** 409 (1914); *Bull. soc. chim.*, [4] **15,** 282 (1914); [4] **15,** 287 (1914).

[7] Paal and Gerum, *Ber.*, **41,** 2273 (1908).

[8] Willstätter and Waldschmidt-Leitz, *Ber.*, **54,** 129 (1921).

ployed, the time for completion of the reaction is reduced enormously. As an example may be mentioned the reduction of benzal-acetophenone to benzyl-acetophenone. From the table it appears that the reduction of 20.8 g. required practically three hours for completion. When, however, instead of 0.1 g. of catalyst, 0.2 g. of catalyst is used, 20.8 g. is reduced completely in 24 minutes. An increase in catalyst to 0.5 g. causes the reduction to take place in 3.5 minutes. If merely the preparation of material is in view, an increase in the volume of solvent and quantity of catalyst can advantageously be made. It is to be emphasized, however, that both the substance being reduced and the reduction product must be completely in solution in order that rapid reduction may be secured.

Another advantage of these catalysts lies in the fact that they can be used at ordinary room temperature, and hence decomposition or secondary condensation, caused either by high temperature or chemical reducing agents, does not take place.

Comparison of Platinum and Palladium Black.—Palladium, with a very few exceptions, is a less effective catalyst than platinum in the reduction of olefins. A notable difference appears in the reduction of anethol, fumaric acid, ethyl maleate, cinnamic acid and ethyl cinnamate. The difference in activity of platinum and palladium is probably to be explained by a difference in the adsorptive powers of the two metals for the ethylene compound. It cannot be due to a difference in the adsorption of hydrogen, since it is well established that palladium black absorbs more hydrogen than platinum black.[9] In order to confirm this with palladium and platinum black made from the oxides, 0.1g. samples of the two catalysts were allowed to absorb hydrogen under the same conditions. The results showed that the platinum absorbed 32.8 cc. and the palladium 34.0 cc. of hydrogen at 25° and atmospheric pressure. These amounts are far in excess of that necessary for the reduction of the oxide to the metal. The amount necessary for the reduction of $PtO_2.H_2O$ to Pt is 21.0 cc. and for conversion of PdO to Pd 17.5 cc. Consequently the amount of hydrogen absorbed after the catalysts had been converted to the blacks was for platinum 11.8 cc. and for palladium 16.5 cc. Whether the palladium activates as high a proportion of the hydrogen as the platinum, cannot be stated from these preliminary experiments, but when one recalls (a) that the two metals are practically equally active in the reduction of aldehydes and (b) the varying effect of iron salts on the two catalysts,[4f] it appears more logical to attribute the difference of speed in hydrogenation by platinum and palladium to a difference in the specific adsorptive capacities of the two metals for the unsaturated compound. This speci-

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[9] Paal and Gerum, *Ber.*, **41**, 805 (1908). Taylor and Burns, THIS JOURNAL, **43,** 1273 (1921). Mond, Ramsay and Shields, *Phil. Trans. Roy. Soc.*, **186,** 657 (1896); *Proc. Roy. Soc.*, **62**, 50, 290 (1897). Dewar, *Chem. News*, **76,** 274 (1897).

ficity of the catalyst is important, since it is certain from the experiments that adsorption alone is insufficient for chemical reaction. The fact that maleic acid and its ester are more rapidly reduced than fumaric acid and its ester might be attributed to the different space arrangements of the carboxyl group or even possibly to a difference in the diffusion rates of the unsaturated compounds to the catalyst.

Effect of Groups on Speed of Reduction

Unconjugated Olefins.—The compounds in which one of the carbons holding the double bond has two hydrogens attached reduce with remarkable speed. This is illustrated by Compounds 1, 2, 6, 7, 8 and 13. In general the monosubstituted compounds of this group reduce the fastest (1, 2, 6, 7) but even a second substitution when unsymmetrical has very little effect upon the speed (8,13).

With the unconjugated symmetrically disubstituted olefins the speed of reduction depends to a considerable extent on the character of the groups; thus a methyl and phenyl or substituted phenyl (3, 4, 5) have only a slight effect upon the speed, and the two groups attached to the double bond, cyclohexene (10) still less. The slowing up of the reduction is more pronounced when two phenyl groups (12) are present.

Finally the speed of reduction of the trisubstituted olefins varies from great rapidity in trimethylethylene (11) and the second double bond in limonene (8) to comparative slowness with diphenylmethylethylene (14).

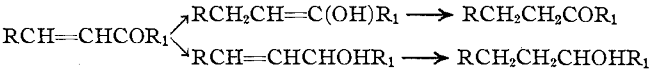
Conjugated Olefins.—It is rather remarkable that the α,β unsaturated ketones (15, 16, 17) are so readily reduced, in view of the fact that the acetyl group might be expected to have a considerable effect, more so especially than a methyl group (compare with 11). It is obvious that in these compounds a phenyl reduces the speed of reduction more than two methyl groups, and the acetyl much less than a phenyl (compare with 12).

The reduction of the α,β unsaturated acids and esters except for dimethylacrylic acid (18) showed a most surprising irregularity. The compounds reduce comparatively slowly, indicating the effect of the carboxyl group in decreasing the speed of reaction especially when a second carboxyl or phenyl group is substituted in ethylene.

Comparison of Reduction by Catalysis and Other Reagents.—Although reduction of olefins of practically all types is possible by catalytic methods this is not always true of the reduction by means of other reagents. Phosphorus and iodine are perhaps the reagents most general in their application, but their use sometimes involves heating to a high temperature and the yields are not always good. Other reducing agents such as chromous chloride, sodium and alcohol, sodium amalgam or aluminum amalgam have their action restricted to those olefins in which conjugation with the ethylene linkage exists,[10] as in propenyl benzenes, α,β unsaturated ketones, acids and esters. These facts have led most naturally to an assumption of 1,4 or 1,6 addition for the mechanism of reduction by means of such reagents. It is of particular interest, therefore, to compare the speed of reduction by catalysis on compounds which can and cannot be reduced by the latter reagents. By catalysis the allyl benzenes are more rapidly reduced than the corresponding propenyl derivatives (1, 2, 3, 4); and in general those compounds without conjugation more rapidly than those with conjugation regardless of the groups present (compare 6 and 18). The relative ease with which the α,β-unsaturated ketones are reduced catalytically does not absolutely exclude the assumption of 1,4 addition, but this seems unlikely.

During the past year two papers have appeared which discuss the mechanism of catalytic hydrogenation, giving especial consideration to the question of 1,4 addition. Conant[11] has discussed the difference between reversible and irreversible reduction and from a consideration of comparative reduction potentials and the kinetics of enolization in certain compounds where 1,4 addition is possible states that "the catalyst activates the gaseous hydrogen and adds hydrogen atoms *directly* to the ethylene linkage in contrast to chromous chloride which adds hydrogen only to the oxygen atoms at the end of a conjugated system."

On the other hand, Straus and Grindel[12] as a result of their study of the catalytic reduction of α,β-unsaturated ketones give the following series of equations,



$$\mathrm{RCH{=}CHCOR_1}\begin{array}{l}\nearrow \mathrm{RCH_2CH{=}C(OH)R_1} \longrightarrow \mathrm{RCH_2CH_2COR_1}\\ \searrow \mathrm{RCH{=}CHCHOHR_1} \longrightarrow \mathrm{RCH_2CH_2CHOHR_1}\end{array}$$

That is, the above-mentioned authors assume 1,4 addition in order to get the saturated ketone, and 1,2 addition in order to get the alcohol. The reasons assigned were (a) some unsaturated ketone is always present after one equivalent of hydrogen has been absorbed, and (b) it was found impossible to reduce the saturated ketone to the alcohol, but when unsaturated ketone was the starting material some alcohol was always present.

It has also been found during the course of this work that when benzalacetone has absorbed one equivalent of hydrogen, the reduced products contain about 3% of unsaturated compounds, as shown by bromine titration;

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[10] Weyl, "Die Methoden der Organischen Chemie," Georg Thieme, **1922,** vol. 2, p. 213 and those following.

[11] Conant and Cutter, *J. Phys. Chem.*, **28,** 1105 (1924). See also Skita, *Ber.*, **43,** 3393 (1910); **45,** 3312 (1912). Boeseken, Van der Weide and Mom, *Rec. trav. chim.*, **35,** 260 (1916). Vavon, *Compt. rend.*, **176,** 989 (1923); **177,** 401 (1923). Fokin, *Z. angew. Chem.*, **22,** 1492 (1909).

[12] Straus and Grindel, *Ann.*, **439,** 276 (1924).

but when the reduction is carried out in the presence of 0.0001 mole of iron salt which it will be remembered retards the reduction of the ethylenic linkage but not the carbonyl group, 5% of unsaturated compounds was found. Moreover, the saturated ketone benzyl-acetone was further reduced to the alcohol and then to the cyclohexyl-1-butanol-3, a fact which has also been noted by other investigators.[13] Benzyl-acetophenone could also be reduced to the alcohol in a similar manner. Therefore, since the saturated ketones are further reducible it seems more logical to assume that the formation of the alcohol occurs through the saturated ketone instead of by the mechanism suggested above. The fact that a higher percentage of unsaturated compounds was found when iron was present indicates that the saturated ketone was formed by 1,2 addition and not 1,4 addition. In general, the data in this paper confirm Conant's conclusion that catalytic hydrogenation is by 1,2 addition.

Influence of Purity of Compounds.—In previous communications[4b] the importance of the purity of the catalyst and the marked influence of the presence of small amounts of metallic salts have been pointed out. The present work has shown that the degree of purity of the compound being reduced has a very great influence on the speed of reduction. The effect of impurities was especially noticeable in the reduction of the allyl benzenes. For example, the reduction with 0.05 g. of platinum black of 20 g. of eugenol purified by simple fractionation required 14 minutes, whereas the product obtained by solution in alkali, extraction with ether and then precipitation by acid and distillation required only five minutes. Similarly, the reduction of 0.1 mole of anethol, purified by distillation only, required 114 minutes with 0.05 g. of platinum black, while the product obtained by washing with sodium bisulfite and distillation in carbon dioxide to prevent oxidation and then immediately used, required only 14 minutes. Moreover, the addition of ferrous sulfate accelerated the reduction of impure anethol from 114 minutes to 22 minutes. Since previous work[4b] has shown that aldehydes were only slowly reduced by pure platinum but rapidly so in the presence of iron salts, and since it has been found that iron inhibited the reduction of olefins, it seemed clear that the impurity in ordinary anethol must be its oxidation product—anisaldehyde. In order to prove this point the series of reductions shown in Table II were performed. This table also shows the effect of 1 cc. of 0.1 *M* ferrous sulfate on the reduction of other olefins.

The data in Table II and other reductions of impure and purified samples of the allyl benzenes may be summed up as follows: (a) the slowness of the reduction by platinum of impure samples of the allyl benzenes is due to presence of aldehyde which is presumably formed by air oxidation; (b) the addition of ferrous salt inhibits the reduction of all types of

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[13] Vavon, *Compt. rend.*, **154**, 1705 (1912).

TABLE II

EFFECT OF FERROUS SULFATE ON REDUCTION OF OLEFINS

0.1 Mole of compound dissolved in 150 cc. of alcohol and 0.05 g. of catalyst were used in each reduction.

	Compound	Time in min. for absorption of 0.1 mole of H_2 Pt	Pd
1.	Anethol, pure	14	8
2.	Anethol, pure + $FeSO_4$	31	13
3.	Anethol, pure + 1% anisaldehyde	28	8
4.	Anethol, pure + 1% anisaldehyde + $FeSO_4$	17.5	11
5.	Anethol, impure	114	..
6.	Anethol, impure + $FeSO_4$	22	..
7.	Ethyl maleate	41	13
8.	Ethyl maleate + $FeSO_4$	181	20
9.	Mesityl oxide	10	43
10.	Mesityl oxide + $FeSO_4$	50% red. in 9 hrs.	50

olefins with both platinum and palladium, provided that the compounds *are pure:* if they are not pure, then when platinum is used the reduction will be accelerated. No such action occurs with palladium, since it has been shown that iron is not essential for the reduction of aldehydes by a palladium catalyst. In the case of limonene, the impurities present greatly influenced the reduction of the second double bond. The reduction of 16.4 g. of limonene purified by fractionation only with 0.03 g. of platinum oxide required five minutes for the first double bond and 138 minutes for the second. Purification through sodium bisulfite, sodium, etc., gave a product in which the times required were four and fifteen minutes for the first and second double bonds, respectively. The nature of this impurity could not be determined. It was not an aldehyde, since washing with sodium bisulfite alone did not remove it.

The careful purification of all the olefins was, of course, of great importance in this work and it is possible in spite of the precautions observed that some of the results may vary from the correct values because of this factor.

The activating influence of iron salts on the reduction of aldehydes led to similar experiments in the reduction of olefins. The results showed in general that the presence of iron salt retarded the catalytic reduction of the ethylene bond.

The effect of oxygen as a reactivator in the reduction of aldehydes was important when the preparation of any considerable amount of material was to be considered. No such effect of oxygen is observed in the reduction of olefins; at any rate, such a reactivating effect is by no means general and more frequently it seems to retard further reduction rather than accelerate it.

If the compounds are impure and contain traces of aldehydes, oxygen activation should shorten the time. The disagreement among various workers on the question of the necessity for oxygen has undoubtedly been influenced by the purity of the compound being reduced.

Experimental Part

Preparation of Catalysts.—The oxides of platinum and palladium were prepared from spectroscopically pure chloroplatinic acid and palladous chloride by fusion with an excess of sodium nitrate as described in previous papers.[4e,4f]

Purification of Compounds.—*Eugenol* was purified by treating commercial material with 5% potassium hydroxide solution in the proportion of 3 parts of eugenol to 20 parts of alkaline solution. Any undissolved material was extracted with ether and the eugenol precipitated with hydrochloric acid, washed with water and distilled under diminished pressure. The fraction boiling at 128–130° (15 mm.) was used for reduction.

Iso-eugenol was purified by fractionation of the commercial product under highly diminished pressure; it boiled at 120–123° (1.5 mm.).

Safrol was purified by washing the commercial product with concd. sodium bisulfite solution, then with sodium hydroxide solution and finally with distilled water. It was then fractionated under diminished pressure and the portion boiling at 114–115° (15 mm.) collected.

Isosafrol was purified by fractionation under diminished pressure; the product boiling at 125–127° (16 mm.) was collected.

Anethol, owing to its ease of oxidation in air to anisaldehyde, was washed with sodium bisulfite solution, then with dil. sodium hydroxide solution and finally with water. It was distilled under diminished pressure in an atmosphere of carbon dioxide and kept in sealed bottles under carbon dioxide until used. It boiled at 112–114° (15 mm.).

Undecylenic acid was purified by fractionation of a technical product. The portion boiling at 165–167° (15 mm.) was collected.

Phenylethylene which had been preserved by the addition of a trace of hydroquinone was distilled and a fraction collected that boiled at 142–144° at atmospheric pressure. Owing to its tendency to polymerize, it was used immediately after distillation.

Limonene was purified from technical material by fractionation and collection of the portion boiling at 176–180° at atmospheric pressure. This was washed with sodium bisulfite solution, then with 20% sodium carbonate solution, followed by 10% hydrochloric acid and dried with calcium chloride. It was then allowed to stand over sodium for nearly ten days. It was finally distilled over sodium at diminished pressure and a fraction collected that boiled at 72–73° (20 mm.).

Pinene was obtained by fractionating commercial oil of turpentine. The fraction boiling 155–160° (750 mm.) was washed with sodium bisulfite solution, dil. hydrochloric acid and dil. sodium carbonate solution, dried and distilled over sodium; 156–158°.

Cyclohexene was made by the dehydration of cyclohexanol and then fractionation with the collection of the portion boiling at 82–85° at atmospheric pressure.

Trimethylethylene was produced by dehydration of trimethylethyl carbinol, the product was dried over sodium and distilled, and the fraction collected that boiled at 37–38° at atmospheric pressure.

Stilbene (*trans*) was made by dehydration of benzylphenyl carbinol and melted after crystallization at 124°.

α,α-Diphenylethylene was prepared by dehydration of the product obtained from the reaction of methylmagnesium iodide and benzophenone. It was merely necessary to vacuum—distil the material in order to cause the dehydration to take place. The olefin was finally distilled over sodium and that portion collected which boiled at 162–163° (25 mm.).

α,α-Diphenyl-β-methylethylene was prepared in a similar manner by dehydration of the product from ethylmagnesium iodide and benzophenone. It was finally crystallized thrice from alcohol and then melted at 45°.

Benzal-acetone was first distilled under diminished pressure and the product then crystallized from a mixture of ether and petroleum ether; m. p., 41°.

Mesityl oxide was distilled and the portion boiling at 130° (748 mm.) collected.

Benzal-acetophenone was crystallized twice from alcohol just before being used, and melted at 56°. Owing to its comparatively slight solubility in alcohol, ethyl acetate was the solvent used during the reduction.

Dimethylacrylic acid was purified by crystallization from hot water; m. p., 70°.

Maleic acid obtained by the commercial oxidation of benzene was recrystallized with bone black several times from water and then melted at 132°.

Fumaric acid, also a commercial product from the oxidation of benzene, was purified by crystallization from water and melted at 200°.

Ethyl maleate was fractionated and the portion boiling at 221° (748 mm.) collected.

Ethyl fumarate was fractionated under diminished pressure and the portion boiling at 100° (14 mm.) was collected.

Cinnamic acid was purified by crystallization from dil. alcohol; m. p., 133°.

Ethyl cinnamate was fractionated under diminished pressure and the portion boiling at 141–144° (15 mm.) collected.

Sodium cinnamate was purified by crystallization from hot water.

It may be stated that in the reduction of all of the compounds listed above, the dihydro product was isolated with practically a quantitative yield and in a very pure state.

On account of the question of the mechanism of the reduction of α,β unsaturated ketones a few experiments were made on the three ketones described in Table I.

More hydrogen than 1 mole was allowed to be absorbed. It was found for example that after the first mole had reacted the second mole of hydrogen was taken up more slowly, and frequently when the amount of catalyst was small, absorption stopped before 2 moles had been absorbed. The presence of iron salt, however, accelerates the speed of the absorption of the second mole. For example, 14.6 g. of benzal-acetone in 150 cc. of 90% alcohol was reduced in the presence of 0.1 g. of catalyst and 1 cc. of 0.1 *M* ferrous sulfate in 15 minutes for 1 mole and 921 minutes for the second mole. The reduction product proved to be practically pure phenyl-1-butanol-3 and boiled at 120–122° (17 mm.); n_{D}^{17}, 1.513. A second experiment similar to the one just described except that 0.2 g. of catalyst was used, required about 236 minutes for the absorption of 2 moles of hydrogen, showing a marked increase in speed with the increase in the amount of catalyst. It has been stated in the literature[12] that it is possible to reduce benzal-acetone only as far as the saturated ketone. This is obviously incorrect, as saturated ketone obtained in a number of the reduction experiments was purified by the bisulfite method, distilled, and the portion collected which boiled at 117–118° (18 mm.) then reduced with platinum. With 0.5 g. of catalyst, 14.8 g. of benzyl-acetone in 150 cc. of 95% alcohol was reduced to the corresponding alcohol in 99 minutes. The hydrogen continued to be absorbed, although much more slowly, and when reactivation with oxygen was occasionally made, it was possible to continue the reduction until practically 4 moles of hydrogen had been absorbed. The reaction yielded practically pure cyclohexyl-1-butanol-3 boiling at 115–116° (18 mm.); n_{D}^{17}, 1.466. In a similar manner with 0.5 g. of catalyst, 20.8 g. of benzal-acetophenone in 150 cc. of C. P. ethyl acetate was reduced in about 1300 minutes, with the absorption of practically 4 moles of hydrogen.

Summary

1. The catalysts obtained by the fusion of chloroplatinic acid or palladous chloride with sodium nitrate have been shown to be very efficient in the hydrogenation of four types of olefins. Their value in preparative experiments has been indicated.
2. A comparison of the relative activities of platinum and palladium in the reduction of olefins shows that the former is, in general, more efficient.
3. The effect of groups on the speed of reduction of olefins has been discussed.
4. The importance of purity of the compound being reduced has been shown.
5. The addition of ferrous salt does not accelerate the reduction of *pure* olefins.
6. The catalytic hydrogenation of all types of olefins probably occurs by 1,2 addition.

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THE NITRATION OF PARA-CARBOXY-PHENOXYACETIC ACID

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When *p*-carboxy-phenoxyacetic acid is treated with one molecular equivalent of nitric acid in the presence of sulfuric acid, 2-nitro-4-carboxyphenoxyacetic acid is formed practically quantitatively. The position of the nitro group is determined by conversion of the nitro acid into 3-nitro-4-hydroxybenzoic acid by hydrolysis with alkali; the hydrolysis product does not lower the melting point of a known specimen of 3-nitro-4-hydroxybenzoic acid prepared from *p*-hydroxybenzoic acid. When, however, two equivalents of nitric acid are used or when the mononitro compound is treated with one equivalent of nitric acid, the reaction proceeds in a rather unexpected direction, and carbon dioxide is evolved from the re-