n_D^{20} 1.5685). The infrared spectrum of an authentic sample was identical with that of the electrolysis product.

Diphenylacetic acid in dimethylformamide. The solution was electrolyzed for 17.8 hr. and the voltage was increased from 130 volts to 220 volts during the electrolysis. The reaction mixture was poured into water and extracted three times with ether. Some organic material remained suspended in the ether layer and it was filtered, air dried, and crystallized from chloroform. The ether extract was washed with water, sodium bicarbonate solution, and again with water. The ether was distilled *in vacuo* and the residue was crystallized from chloroform. A further crop of crystals was obtained on concentration of the combined chloroform mother liquors.

A total of 4 g. (24%) of crude product was obtained and was recrystallized from chloroform, m.p. 207–208°. A mixed m.p. with authentic tetraphenylethane⁸ was undepressed at 206–207°.

Hydratropic acid⁹ in methanol. The solution was electrolyzed for 10.7 hr. and the voltage was increased from 80 volts to 120 volts during the electrolysis. The reaction mixture was poured into a liter of salt water and was extracted three times with ether. The ether was washed successively with water, saturated sodium bicarbonate solution, water, 1:1 hydrochloric acid, water, sodium bicarbonate solution, and again with water. After drying over magnesium sulfate the ether was distilled through a Vigreux column and the yellowish residue was distilled at 19 mm. A clear liquid, 3.1 g., b.p. 56–60°, n_D^{28} 1.4950 (reported¹⁰ for methyl α-phenethyl ether n_D^{25} 1.4911) was obtained as the first fraction. Analysis by vapor phase chromatography showed it to consist of 87% of α-phenethyl methyl ether, 3% of styrene (dibromide, m.p. 70–71°, reported¹¹ m.p. 73°) and a third unidentified component.

The residue was a tan oil, 5.9 g., which solidified on cooling. Crystallization from methanol afforded 721 mg. (6.9%) of solid, m.p. 122–123°, mixed m.p. with authentic *meso*-2,3-diphenylbutane, 122–123°.

The methanol mother liquor was distilled at 0.08 mm. through a short path still. Two fractions were collected: (1) 2.262 g., n_D^{28} 1.5408 and (2) 1.042 g., n_D^{28} 1.5523. Analysis by vapor phase chromatography indicated the following total yield: *meso* and DL-2,3-diphenylbutane, 2.2 g. (21%); α-phenethyl methyl ether, 2.7 g. (19.9%); α-phenethyl alcohol, 0.18 g. (1.5%); and acetophenone, traces.

The infrared spectra of fractions (1) and (2) confirm the presence of the identified substances. A pair of bands at 5.88μ and 7.96μ seem to indicate that the unisolated and unidentified substance retained by the column is an ester.

Hydratropic acid in dimethylformamide. The solution was electrolyzed for 10.3 hr. and the voltage was increased from 130 volts to 260 volts during the electrolysis. The reaction mixture was poured into a liter of salt water and extracted four times with 150-ml. portions of ether. The ether extract was washed successively with water, 1:1 hydrochloric acid, water, saturated sodium bicarbonate solution, again with water, and dried over magnesium sulfate. The ether was distilled through a Vigreux column and the residue was taken up in methanol. Cooling afforded 1.32 g. of *meso*-2,3-diphenylbutane, m.p. 116–120°. The methanol mother liquor was distilled *in vacuo* and three fractions were obtained: (1) 0.7 g., b.p. 96–112° at 15 mm., n_D^{25} 1.5170; (2) 0.4 g., b.p. 112–145° at 15 mm., n_D^{25} 1.5238; (3) 2.8 g., b.p. 115–145° at 0.8 mm., n_D^{25} 1.5455; a further 0.1 g. of *meso*-2,3-diphenylbutane was obtained as a solid in the distillation

apparatus. Fractions (1), (2), and (3) were analyzed by vapor phase chromatography.

The total yield of *meso* and *dl*-2,3-diphenylbutane was 4.3 g. (41%) and of α-phenethyl alcohol, 1 g. (8.2%).

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Palladium Catalysts. IX.¹ Kinetic Studies

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Previous papers report that the qualitative character of palladium-on-carbon catalysts may be influenced by such factors as the presence of other metals,⁴ the ratio of metal to carrier,⁵ and by the nature of the anion present when the metal is deposited on the carrier.¹,⁶ There is also evidence that a product formed during the hydrogenation reaction may inhibit the catalytic reaction.⁷ Results of further studies along these lines are now presented.

In order to control external variables during the hydrogenation reaction the apparatus shown schematically in Fig. 1 was designed. With it one may maintain a constant pressure of hydrogen within the vicinity of one atmosphere throughout the entire course of the reaction; the rate of agitation is constant; the temperature may be controlled to within 0.2°. Results obtained with this apparatus permit the observation of the kinetic order of the reaction and allow for more valid comparison of one reaction with another and, it is hoped, contribute to a better understanding of the catalytic mechanisms.

In Fig. 2 are shown graphically the effects of temperature variation on the reduction of nitrobenzene. In all instances the rate of hydrogen absorption with respect to substrate is zero order as was previously observed by Rampino and Nord.⁸

The phenylcarbonyl compounds with one molecule of hydrogen form the corresponding carbinols, and with two molecules of hydrogen undergo

(1) For number VIII see W. D. Cash, F. T. Semeniuk, and W. H. Hartung, *J. Org. Chem.*, **21**, 999 (1956).

(2) Sharp and Dohme Fellow 1952–1955. Present address: Polychemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Del.

(3) Experimental work performed at the University of North Carolina.

(4) W. H. Hartung and Y.-T. Chang, *J. Am. Chem. Soc.*, **74**, 5927 (1952).

(5) J. G. Young and W. H. Hartung, *J. Org. Chem.*, **18**, 1659 (1953).

(6) E. W. Reeve and W. H. Hartung, unpublished. See note in ref. (4).

(7) K. L. Waters and W. H. Hartung, *J. Org. Chem.*, **10**, 524 (1945).

(8) L. D. Rampino and F. F. Nord, *J. Am. Chem. Soc.*, **65**, 429 (1943).

(8) F. J. Norris, R. Thomas, and B. M. Brown, *Ber.*, **43**, 2959 (1910).

(9) E. L. Eliel and J. P. Freeman, *J. Am. Chem. Soc.*, **74**, 923 (1952).

(10) S. I. Miller, *J. Org. Chem.*, **21**, 247 (1956).

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 315.

Fig. 1. Scheme of hydrogenation
apparatus. The upper phthalate reser-
voir may be adjusted up or down, de-
pending on the barometric reading and
the vapor pressure of the solvent at the
temperature of the reaction. Di-n-butyl
phthalate, because of its negligible
vapor pressure, is used to displace the
hydrogen in the gas buret. The air in
the apparatus may be swept out and
displaced by hydrogen through stop-
cock 3 and out at stopcock 6. The pres-
sure is measured by attaching a man-
ometer at stopcock 3. Constant rate of
stirring is maintained by a constant
voltage regulator and the speed is meas-
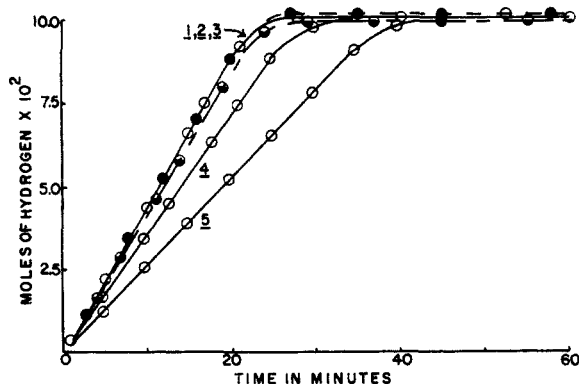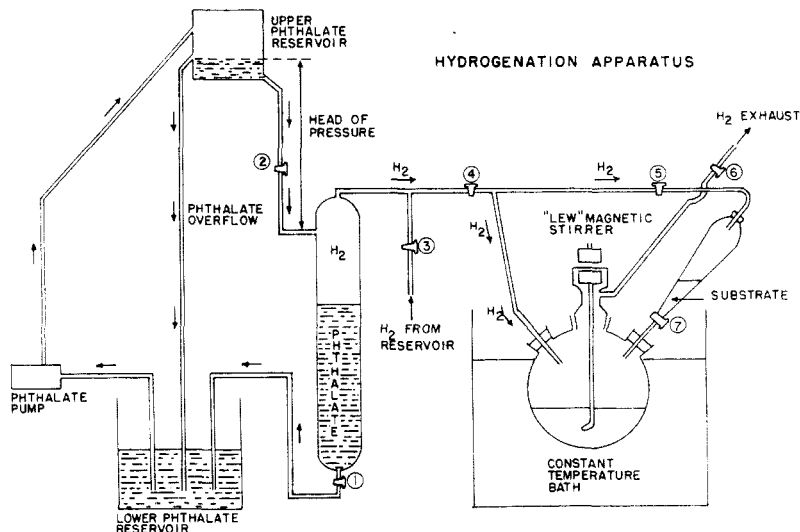ured with a hand tachometer

Fig. 2. Reduction of nitrobenzene. Solvent: ethanol.
Total volume: 100 ml. 0.033 mol. nitrobenzene. 2 g. of cata-
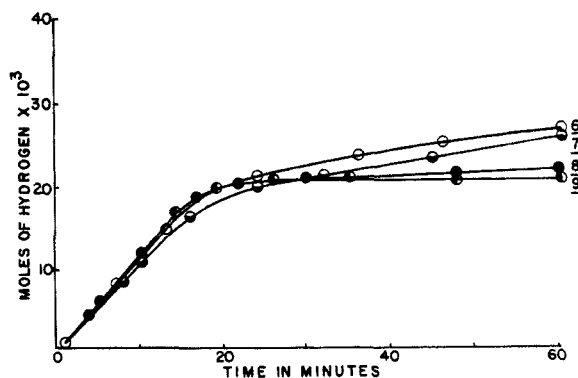lyst, 20 mg. PdCl₂ per gram. Curves 1, 2, and 3 at 35°; curve
4 at 30°; curve 5 at 25°

Fig. 3. Reduction of propiophenone. Solvent: ethanol.
Total volume: 100 ml. 0.02 mol. propiophenone. 2.0 g. of
catalyst, 50 mg. PdCl₂ per gram. Curve 6: no propylben-
zene; curve 7: 0.040 mol. propylbenzene; curve 8: 0.060 mol.
propylbenzene; curve 9: 0.10 mol. propylbenzene

hydrogenolysis to form the hydrocarbon. Hartung
and Crossley,[9] reported that propiophenone was
reduced to propylbenzene without evidence of
forming the intermediate carbinol; presumably
during a single contact of the substrate with the
catalyst two molecules of hydrogen were trans-
ferred.[10] The palladium then employed regret-
tably is no longer available.[11] Subsequent studies
have been carried out with catalysts prepared

from pure palladium.[12] The results now point to a
reduction in two steps, first to the carbinol and then
hydrogenolysis to the hydrocarbon. Typical results
are shown graphically for propiophenone in Fig. 3.
The first half of the reaction is zero order; the second
half is indeterminate, the hydrogenolysis of the
carbinol being progressively inhibited by the hy-
drocarbon as it forms in increasing amounts. Thus
curve 6 of Fig. 3, for example, had the reaction
been continued (as observed in other experiments)
would have approached with decreasing slope the
value of hydrogen uptake calculated for complete
conversion to propylbenzene. Curve 7, showing the
reduction of 20 millimoles of propiophenone in the
presence of 40 millimoles of propylbenzene, slopes
off much earlier; and curves 8 and 9, with 60 and
100 millimoles, respectively, of propylbenzene,
become substantially parallel with the time
axis when the ketone is reduced to carbinol.

(9) W. H. Hartung and F. S. Crossley, J. Am. Chem.
Soc., 56, 158 (1934).

(10) E. W. Reeve (unpublished) later repeated these
experiments and was able to detect, by interrupting the
reaction, traces of carbinol in the mixture comprised
principally of unreduced propiophenone and propylbenzene.
This is felt to establish only that with the catalyst then
available only a small amount of product was desorbed
after the transfer of one molecule of hydrogen into the
ketone.

(11) W. H. Hartung and Y.-T. Chang, J. Am. Chem. Soc.,
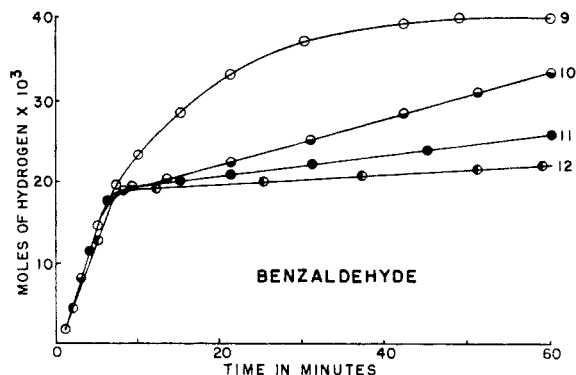74, 5927 (1952).

(12) Cf. footnote 8 in ref. (11).

Fig. 4. Reduction of benzaldehyde. Solvent: ethanol. Total volume: 100 ml. 0.020 mol. benzaldehyde. 2 g. of A-50 catalyst.[1] Curve 9: no toluene; curve 10: 0.05 mol. toluene; curve 11: 0.1 mol. toluene; curve 12: 0.30 mol. toluene

[1] For explanation see ref. (1)

Fig. 6. Reduction of benzyl acetate. Solvent: ethanol. Total volume: 100 ml. 0.005 mol. benzyl acetate. Curve 17: 2 g. of A-100 catalyst; curve 18: 1 g. of A-100 catalyst; curve 19: 0.5 g. of A-100 catalyst; curve 20: 0.25 g. of A-100 catalyst

A similar phenomenon is seen with benzaldehyde, Fig. 4. The reduction to benzyl alcohol proceeds at zero order, and even large amounts of toluene in the solvent have no significant effect on this rate. However, the presence of increasing amounts of toluene have increasing inhibitory effect on the hydrogenolysis of benzyl alcohol.

Other phenylcarbonyl compounds show similar behavior. Desoxybenzoin is rapidly reduced to the carbinol, and the hydrogenolysis of the carbinol then proceeds at a progressively decreasing rate; if diphenylethane is added at the start of the reaction, it has no observable effect on the rate at which the ketone reduces, but has a marked retarding effect on the hydrogenolysis of the carbinol. Acetophenone behaves in an analogous manner.

The hydrogenolysis of benzyl acetate yields interesting results, Figs. 5 and 6. In ethyl acetate solvent the inhibitory effect of the toluene formed during the reaction is sufficiently pronounced to modify the initial zero order to a progressively slowing and indeterminate rate. The addition of
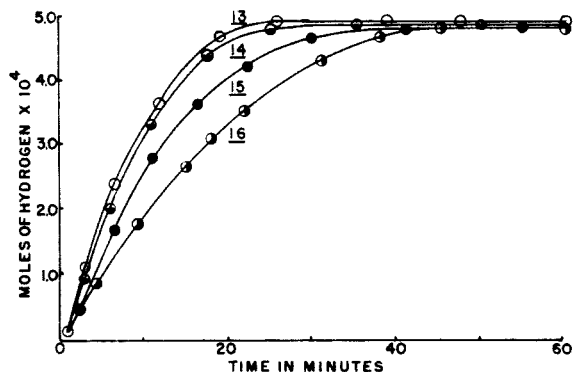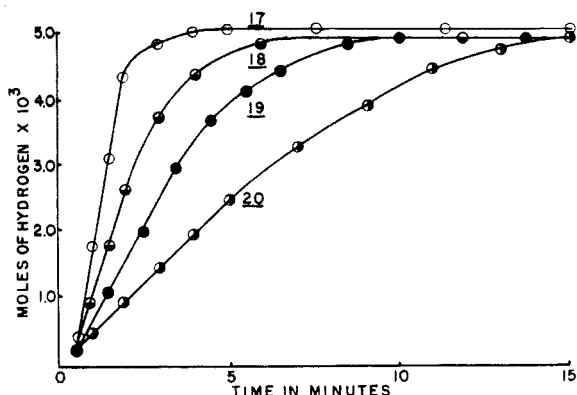

Fig. 5. Reduction of benzyl acetate. Solvent: ethyl acetate. Total volume: 100 ml. 0.005 mol. benzyl acetate. 2 g. of A-100 catalyst.[1] Curve 13: no toluene; curve 14: 0.01 mol. toluene; curve 15: 0.02 mol. toluene; curve 16: 0.04 mol. toluene

[1] For explanation see ref. (1).

toluene at the beginning of the reaction causes earlier deviation. In ethanol solvent the inhibitory effect of the toluene is less pronounced and is absent if adequate catalyst is employed; as the amount of catalyst is decreased, the inhibitory effect becomes correspondingly more pronounced.

A mechanism for the inhibitory effect of propylbenzene in the reduction of the corresponding carbinol is proposed in Fig. 7.

It is not suggested, however, that all deviations from zero order reaction rates are to be attributed to inhibition such as here observed. Another factor that is expected to show similar kinetic results is the erosion or inactivation of the catalyst. A discussion of such phenomena will be delayed until more data become available.

The two-stage hydrogenation as observed with the conversion of phenylcarbonyl compounds to the corresponding hydrocarbon poses an interesting question as to the character of the active sites in the palladium-on-carbon catalysts, especially in view of the observation by Beamer and co-workers[13] that these catalysts have centers which appear to be substrate-specific. It will be observed from Fig. 3 that propylbenzene does not compete with propiophenone for the active sites but does compete with the carbinol; and toluene does not compete with benzaldehyde but does inhibit benzyl alcohol. Does this signify that in the catalyst there are different sites for the carbonyl compound than for the carbinol? This question is all the more interesting since once there was available a catalyst[9] with quite different properties. Further studies are projected.

EXPERIMENTAL

All reagents were carefully purified, and all substrates were "detoxified" by standing in contact for 24 hr. or more with unused Pd-C catalyst.

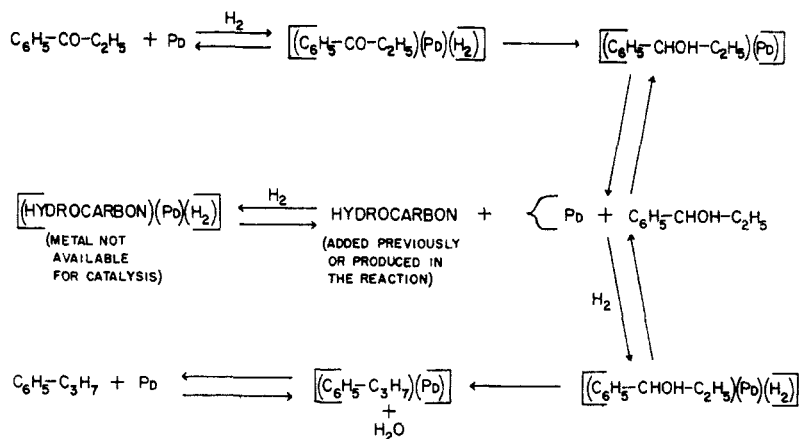(13) R. L. Beamer, J. D. Smith, J. Andrako, and W. H. Hartung, in press.

Fig. 7. Mechanism of inhibition

The catalysts were prepared as described in earlier papers of this series.

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o-Hydroxyphenylphosphonic Acid

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Although a number of hydroxy-substituted arylphosphonic acids are known,[1] the preparation of o-hydroxyphenylphosphonic acid, the phosphorus analog of salicylic acid, has not previously been accomplished. Kennedy, Lane, and Willans[2] have investigated two possible methods for the synthesis of this phosphonic acid. They found that attempts to demethylate o-methoxyphenylphosphonic acid caused cleavage of the carbon-phosphorus bond; and they reported that the diazo reaction could not be used to convert o-benzyloxyaniline to o-benzyloxyphenylphosphonic acid (which they planned to debenzylate by hydrogenation). The present study was undertaken in the hope of developing a satisfactory method for the preparation of o-hydroxyphenylphosphonic acid and related compounds.

As noted by Kennedy, Lane, and Willans,[2] the demethylation of o-methoxyphenylphosphonic

acid is not a promising route to the synthesis of the corresponding hydroxy compound. In this laboratory we found that after the o-methoxy compound was refluxed with 42% hydrobromic acid for 24 hr., over 90% of the phosphorus had been converted to inorganic phosphate. Attempts to replace the bromine in o-bromophenylphosphonic acid with the hydroxyl group were also unsuccessful. Thus, heating the o-bromo compound with $4N$ sodium hydroxide in an autoclave at 120° resulted in splitting little or no bromine from the ring. In the presence of cuprous oxide the bromine could be replaced by the hydroxyl group. In the process, however, a certain amount of phosphorus was also cleaved from the ring, and we were never able to isolate any o-hydroxyphenylphosphonic acid from the reaction mixture. In brief, the results we obtained in trying to convert o-methoxy- or o-bromophenylphosphonic acid into the hydroxy compound were similar to those reported[3] for the corresponding para-substituted acids.

We were successful, however, in obtaining o-hydroxyphenylphosphonic acid by the catalytic hydrogenolysis of o-benzyloxyphenylphosphonic acid. Several methods for preparing the latter compound were examined. We first investigated the preparation of the acid from the corresponding diazonium fluoborate. Although the diazonium compound could not be prepared by diazotizing o-benzyloxyaniline in fluoboric acid, the amine was readily diazotized in hydrochloric acid and the diazonium fluoborate precipitated by the addition of sodium fluoborate. The diazonium salt was then suspended in ethyl acetate and treated with phosphorus trichloride and cuprous bromide under the usual conditions.[4] Steam distillation of the reaction mixture in the customary manner, however, resulted in cleavage of the ether linkage. Accordingly, the conditions were modified to avoid debenzylation; details of the procedure used for iso-

(1) (a) G. B. Arnold and C. S. Hamilton, *J. Am. Chem. Soc.*, **63**, 2637 (1941); (b) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 753 (1952); (c) R. W. Bost and L. D. Quin, *J. Org. Chem.*, **18**, 358 (1953); (d) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **75**, 6307 (1953).

(2) J. Kennedy, E. S. Lane, and J. L. Willans, *J. Chem. Soc.*, 4670 (1956).

(3) V. L. Bell, Jr., and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 4901 (1953).

(4) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).