genated to $R'CH_2COCH_3$. In no case was there reduction of the carbonyl group. However, in the previous work,[2] the carbonyl groups in $ArCOCH_3$ and $ArCOCH_2CH_2COOCH_3$ were almost completely reduced to methylene groups.

With the primary alcohols RCH_2OH, VI, and RCH_2CH_2OH, VII, not only was the ring smoothly dehydrogenated but the primary alcohol function was degraded by loss of one mole of hydrogen and one of carbon monoxide according to the following equations:

$$C_{10}H_{11}CH_2OH \longrightarrow C_{10}H_8 + 3H_2 + CO$$
$$C_{10}H_{11}CH_2CH_2OH \longrightarrow C_{10}H_7CH_3 + 3H_2 + CO$$

Such degradation of primary alcohols to the next lower hydrocarbon is not new[19] and probably proceeds by dehydrogenation to an aldehyde[20] followed by decarbonylation to a hydrocarbon.[2,21] In these reactions we believe that the removal of the hydrogen from the ring precedes the degradative reaction, because gas analyses showed that the proportion of carbon monoxide increases with time. Furthermore the ease of dehydrogenation would indicate that the ring is being dehydrogenated while oxygen was still attached to the molecule, for we have noted repeatedly that tetralin hydrocarbons dehydrogenate very slowly in our experiments whereas oxygenated derivatives dehydrogenate easily if at all.

The behavior of RCH_2OH stands in marked contrast to that of $ArCH_2OH$ in which the carbinol group was largely hydrogenolyzed to a methyl group.

When the hydroxyl groups in VI and VII were protected by acetylation, however, the carbon-oxygen bonds in VIII and IX were hydrogenolyzed only to the extent of 14 and 28%, respectively.[22] The main reaction with IX was dehydrogenation to the corresponding $R'CH_2CH_2OCOCH_3$, but with VIII, only 26% of ring dehydrogenation to $R'CH_2OCOCH_3$ occurred, VIII being recovered (51%) unchanged.

Thus it is apparent that the relative positions of the hydrogens to be removed and the oxygenated functions are quite important in determining the fate of the oxygenated function in catalytic dehydrogenation. Further experiments are necessary to ascertain how important is the position of the substituent on the aromatic nucleus.

Summary

The liquid phase catalytic dehydrogenation over a palladium-on-charcoal catalyst of nine oxygenated 1-substituted-1,2,3,4-tetrahydronaphthalenes is described.

The methyl esters, $C_{10}H_{11}(CH_2)_nCOOCH_3$, where $n = 0$ and 1, were converted in high yields into the corresponding naphthalene derivatives with the evolution of the theoretical amount of hydrogen.

The ketones $C_{10}H_{11}COCH_3$ and $C_{10}H_{11}CH_2CH_2COCH_3$ were largely recovered unchanged, but $C_{10}H_{11}CH_2COCH_3$ was smoothly dehydrogenated into $C_{10}H_7CH_2COCH_3$.

The alcohols $C_{10}H_{11}CH_2OH$ and $C_{10}H_{11}CH_2CH_2OH$ were smoothly degraded to the next lower hydrocarbon according to the type equation $RCH_2OH \rightarrow (R - 4H)H + 3H_2 + CO$.

Protection of the alcoholic hydroxyls by acetylation prevented the degradative reaction.

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[19] Adkins and Wojcik, THIS JOURNAL, **55**, 1293 (1933); Paul, *Compt. rend.*, **208**, 1319 (1939); Badin, THIS JOURNAL, **65**, 1809 (1943).

[20] See, for example, Adkins and Reeves, *ibid.*, **62**, 2874 (1940).

[21] Hurd, "The Pyrolysis of Carbon Compounds," A. C. S. Monograph No. 50, Chemical Catalog Co., New York, N. Y., 1929, pp. 236–242.

[22] It is possible that the acetates were pyrolyzed into olefins and acetic acid and that the former were then dehydrogenated to the hydrocarbons observed. We prefer the hydrogenolysis mechanism.

[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

The Catalytic Hydrogenolysis of Halogen Compounds[1]

BY RICHARD BALTZLY AND ARTHUR P. PHILLIPS

The removal of halogen during catalytic hydrogenations of organic compounds is a familiar phenomenon and has even been made—under special conditions—the basis of analytical methods. Largely as a result of this, and despite occasional instances to the contrary, most workers have considered loss of halogen inevitable in catalytic hydrogenations.

During a previous research,[2] one of the authors succeeded in isolating methyl-*p*-chlorobenzylamine hydrochloride after the reductive cleavage of methylbenzyl-*p*-chlorobenzylamine hydrochloride and this suggested that aromatic halogens might, on occasion, be fairly resistant to hydrogenolysis. From the practical side, it seemed desirable to study hydrogenolyses under the conditions usually employed for reductions with noble metal catalysts, namely, in acid or neutral solution. This was also indicated by the theoretical consideration that since the analytical procedures call for alkaline or alkaline-buffered media, experiments under conditions less favorable for dehalo-

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[1] Presented in part before the Division of Organic Chemistry, A. C. S., Cleveland, Ohio, April, 1944.

[2] Baltzly and Buck, THIS JOURNAL, **65**, 1984 (1943).

genation might reveal differences in activity of the halogens otherwise not apparent.[3]

Since in the presence of catalysts, such as platinum or nickel,[4] which are effective in the reduction of aromatic systems, a halogen atom might be removed incidentally to the hydrogenation of the ring as well as by an independent process, it seemed best to examine first the effect of a catalyst that is generally inadequate to the reduction of aromatic systems, and subsequently to correlate these results with those obtained using other catalysts. This plan was eventually modified partly because it was found that with the usual Adams catalyst, aromatic reduction was too fast to be differentiated from independent dehalogenation, and partly because this catalyst does not give reproducible control rates after use. We therefore limited ourselves to attempts with members of the classes studied to discover if any independent dehalogenation was actually taking place.

Experimental

Catalysts.—The catalyst chosen for the study of independent dehalogenation was palladized charcoal.[5] Standard batches were prepared by the reduction of 0.6 g. of palladium (as palladium chloride) in the presence of 6 g. of charcoal (Darco G-60) and were employed as units. Such a preparation can be recovered in virtually quantitative fashion and used repeatedly (with frequent calibration against control substances). There is no apparent loss of activity through use, and after as many as twenty or thirty reductions a standard hydrogen absorption can usually be obtained. The control substrates were either benzyl alcohol or cyclohexene. With 5-cc. portions (0.05 mole very nearly) of either of these a maximum absorption rate is found of 19–22 millimoles in the first or second minute (using 2–2.5 atm. of hydrogen over-pressure). A rate of 15 millimoles per minute was felt to call for further examination and a 50% rate was considered to indicate definite inhibition. Such control runs were performed at the close of all experiments and usually by the direct addition of the control substrate to the reduction mixture. In many of the reductions of bromo compounds this direct control showed diminished activity and such was found to be the normal result of the presence of large amounts of bromide ion. In these cases normal controls were obtained after filtration and washing of the catalyst so that there was no question of the presence of an active catalyst poison. It seems likely, in consequence, that our observed reduction rates for the bromo compounds are somewhat too low in comparison with the rates for chloro compounds. There was, however, no apparent way of avoiding this. This condition we define as "inhibition" as distinguished from "poisoning"—as with iodide ion, whose effect is not abolished by washing. Such washing as is convenient with a rather large volume of fairly light catalyst is not likely to achieve quantitative removal, so the distinction is effectively between poisons of greatly different orders of potency.

The behavior of the catalyst in reduction of benzyl alcohol was studied under a variety of conditions. It is particularly sensitive to the presence of alkalies. While halogeno anilines are clearly not strong enough bases to interfere with its action, aniline, pyridine and, of course, sodium hydroxide produced complete inactivation. In each of these cases normal activity was restored when an excess of hydrochloric acid was added to the same solution. Evidently high salt concentration does not interfere unless there is precipitation on the catalyst surface.

Adams catalyst was prepared by the Bruce modification of the older procedure. This catalyst is much less suitable for rate studies since after completing even a successful reduction it no longer gives maximal rates with a control substrate (usually cyclohexene); initially 50-mg. portions with 5 cc. of cyclohexene in methanol give hydrogen absorptions of 10–15 millimoles per minute. It is probable that the loss in activity of the catalyst is a function of a partially irreversible coagulation at the end of a reduction.

A platinized charcoal was prepared in the hope that it would resemble palladized charcoal in permanence and maintain the specific catalytic properties of platinum. By reducing in the presence of 1 g. of Darco G-60 an aqueous solution containing in 100 cc. volume, 0.1 g. of platinum (as chloroplatinic acid) and 0.2 mg. of palladium (as palladium chloride) a catalyst was obtained that gave good reduction (20 millimoles per minute) with cyclohexene and did not affect benzyl alcohol. It is possible that further study may reveal valuable specific properties in this catalyst but unfortunately it proved to be inhibited by a variety of halogen compounds and so was useless for the purpose intended.

Materials.—Most of the substrates were purified from commercial products of the best grade available, or were derived from such by simple procedures (esters, acetanilides, etc.). Where possible, compounds were recrystallized until maximum melting point was secured. Liquids were redistilled at least once. In no case was there any indication of the presence of catalyst poisons.

Only one of the substrates, *p*-chlorophenyltrimethylammonium bromide appears to be a new substance. It was obtained as a "by-product" through the classical procedure for making dimethylanilines.[6] Thirty-five grams of *p*-chloroaniline hydrobromide was heated with 30 cc. of methanol in a bomb for eight hours at 155°. On opening, considerable material crystallized as glossy plates. This was the impure quaternary salt, but could not easily be purified at this stage. After partitioning the mixture between ether and sodium carbonate solution, the ethereal layer was evaporated yielding 9.5 g. of weak base. The aqueous layer was acidified with hydrochloric acid, taken down *in vacuo* and redissolved in absolute alcohol. At this point some sodium chloride was filtered off and virtually all the remainder removed by saturating with gaseous hydrogen chloride. The filtrate was again evaporated *in vacuo*. To this residue was added 20 cc. of 48% hydrobromic acid, the material was brought into solution and again evaporated *in vacuo*. Crystallization from absolute alcohol yielded 22 g. of platelets, m. p. 199–200°, and another crystallization raised this to 200.5–201°.

Anal. Calcd. for $C_9H_{13}NBrCl$: C, 43.11; H, 5.21. Found: C, 43.12; H, 5.49.

The corresponding chloride is much more soluble and less suitable for purification.

Methods.—The apparatus used was a modification[7] of the standard Adams type machine manufactured by Burgess–Parr. Reductions were carried out with the full charge of palladized charcoal (6.6 g.) or with the stated amounts (50 mg. or 100 mg.) of Adams catalyst. The quantity of substrate was, unless otherwise stated, 0.05 mole dissolved in 50 cc. of methyl or ethyl alcohol. These solvents showed no significant difference except occasionally in solvent power. Hydrogen chloride, when added to anhydrous solutions was in the form of absolute alcoholic solutions of known weight-per cent.

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(3) The work of Busch and Schmidt [*Ber.*, **62B**, 2612 (1929)] on the formation of diphenyl derivatives during dehalogenations with palladium-calcium carbonate in alkaline conditions, together with our own results, leads one to suspect that catalytic dehalogenation under alkaline conditions is fundamentally a different phenomenon.

(4) Nickel probably is not a very effective dehalogenation catalyst; *cf.* Winans, THIS JOURNAL, **61**, 3564 (1939).

(5) Ott and Schröter, *Ber.*, **60**, 633 (1927); Hartung, THIS JOURNAL, **50**, 3370 (1928).

(6) Typical literature reports on this process reveal rather poor yields of tertiary amine. It is clear that the loss occurs through transformation into quaternary salt.

(7) Buck and Jenkins, THIS JOURNAL, **51**, 2163 (1929).

TABLE I

TYPICAL HYDROGENOLYSES WITH PALLADIZED CHARCOAL

0.05 Mole of Substrate in 50 cc. of Solution

Expt.	Substrate	Solvent	Excess HCl present initially, millimoles	H_2 absorbed in second minute, millimoles	Total H_2 absorption millimoles	Time of reduction, minutes
1	*p*-$ClC_6H_4NH_2$	MeOH	..	4	37	11[a]
2	*p*-$ClC_6H_4NH_3Cl$	Abs. EtOH	50	..	..	[b]
3	*p*-$ClC_6H_4NH_3Cl$	H_2O	70	$^1/_3$	35	186[c]
4	*p*-$ClC_6H_4N(CH_3)_3{\cdot}Br$	60% EtOH	..	..	13	120
5	*p*-$BrC_6H_4NH_2$	MeOH	..	16	50	3[a]
6	*p*-$BrC_6H_4NH_3Cl$	Abs. EtOH	50	2	50	
7	BrC_6H_5	MeOH	..	4	50	290
8	*o*-$ClC_6H_4NHCOCH_3$	95% EtOH	..	..	4	31
9	*o*-$BrC_6H_4NHCOCH_3$	Abs. EtOH	..	4	52	240
10	*p*-ClC_6H_4COOH	95% EtOH	..	..	10	71[a]
11	*m*-BrC_6H_4COOH	95% EtOH	..	3	49	378
12	*p*-BrC_6H_4COOEt	MeOH	..	1	51	490
13	*p*-$BrC_6H_4OCH_3$	MeOH	50 (HBr)	1	47	530
14	$C_6H_5CH_2CH_2Br$	MeOH	..	..	..	[b]
15	$BrCH_2COOEt$	MeOH	..	$^1/_2$	55	485
16	$Cl_2CHCOOEt$	75% EtOH	..	3	60	296
17	Cl_3CCOOH	50% MeOH	..	10	110	370
18	Cl_3CCOOH	MeOH	..	8	73	197
19	C_6H_{10} (cyclohexene)	MeOH	..	19–22	49–55	5
20	$C_6H_5CH_2Cl$	MeOH	..	22	49–55	3
21	$C_6H_5CH_2OH$	MeOH	..	20–22	49–55	3
22	$C_6H_5CH_2OH$	85% MeOH	50 (HBr)	14–16	49–55	8–10

[a] Run not carried to a stop. [b] No significant absorption beyond that of the catalyst. [c] Used only 0.033 mole of amine.

The marked effect on the reduction rate of acid initially present was observed only with halogeno anilines and derivatives of dichloroacetic acid. After this was ascertained, duplicate runs in the presence of excess acid were largely dispensed with.

Temperature was not controlled but can be taken as that of the laboratory (25–30° according to the season) except in very fast reductions when a rise to 40° or even 45° was observed. In such cases thermostating would be difficult and, we believe, unprofitable. We do not attach significance to small differences in reduction rate as these might be dependent on too many other variables.

Reductions were considered at an end when the fall in hydrogen pressure was 1 lb. or less in thirty minutes (in our apparatus this corresponds to 1 millimole of hydrogen if the volume of solution is 50 cc.). Such a rate is about six times the leak-rate of the apparatus and so does not indicate a complete stop but is so slow as to prolong an experiment unduly and is unlikely to have any relevance to practical synthetic procedures. The results (Table I) of the palladized charcoal reductions are expressed as rates (absorption in the second minute of reduction) and as total absorption for the time of the experiment. The catalyst, when free of hydrogen, absorbs about 5 millimoles independent of reduction. When freshly filtered off from a reduction, it may take up only 2–3 millimoles. This absorption is complete in a few seconds. The pressure-drop in the second minute of the reduction is, therefore, a better criterion of rate than that in the first. In slow reductions this rate also is rather illusory and a better standard would appear to be the total absorption and the time therefor. Such results as that with *o*-chloroacetanilide (Table I, No. 8) (4 millimoles) represent effectively zero reduction and in some earlier experiments were so recorded. Similarly, a number of rapid reductions were interrupted after a satisfactory rate had been obtained and were not carried to completion.

A number of aliphatic compounds bearing rather reactive halogens were reduced with palladized charcoal for purposes of comparison.

As Adams catalyst did not give reproducible rates, it was tried only on certain chloro compounds of each class studied, and the reductions were interrupted before completion in an attempt to separate the products. The results are shown in Table II. In all cases unchanged starting material and completely reduced material were isolated. From the reduction of *o*-chloroaniline in the presence of excess hydrogen chloride, a considerable amount (1 g.) of aniline was demonstrated as acetanilide. The products from the reductions of ethyl *m*-chlorobenzoate, *p*-chlorophenol and *p*-chloroanisole contained at most traces of dehalogenated aromatic compound. It is probable that in the last case traces of anisole were present, and the phenolic fraction from the reduction of *p*-chlorophenol contained non-isolable amounts of phenol that could be demonstrated by coupling with diazotized sulfanilic acid.

Results

Table I contains a representative selection of the results of hydrogenolyses with palladized charcoal. The behavior of the various groups of substrates is summarized below:

Halogenoanilines.—The chloroanilines were dehalogenated rapidly, the bromoanilines very rapidly. The hydrogen absorption in the second minute of reduction varied from 4 to 8 millimoles with the chloroanilines and from 15 to 16 millimoles with the bromoanilines. The low value (4 millimoles) for *p*-chloroaniline may have been due to the physical state of the substance—as compared to its isomers which are liquids. In absolute alcoholic solution the presence of excess hydrogen chloride (2 moles to 1 of base) suppressed the hydrogenolysis of the chloro compounds and lowered the rate with the bromo com-

TABLE II

HYDROGENOLYSES WITH ADAMS PLATINUM CATALYST

0.05 Mole of substrate in 50 cc. of solution.

Substrate	Solvent	PtO_2 added, mg.	H_2 absorbed in second minute, millimoles	Total H_2 absorption, millimoles	Time of reduction, minutes	Components of reduction mixture demonstrated
p-$ClC_6H_4NH_2$	MeOH	51	1	107	278	*p*-$ClC_6H_4NH_2$ (0.01 mole), $C_6H_5NH_2$ (0.02 mole), $C_6H_{11}NH_2$
p-$ClC_6H_4NHCOCH_3$	MeOH	100	1	106	906	*p*-$ClC_6H_4NHCOCH_3$, (0.015 mole)
o-$ClC_6H_4NH_2$ + 100 millimoles HCl	EtOH	100	1	131	900	*o*-$ClC_6H_4NH_2$, $C_6H_5NH_2$ (0.01 mole), $C_6H_{11}NH_2$ (0.01 mole)
m-$ClC_6H_4COOC_2H_5$	EtOH	51	1	78	420	*m*-$ClC_6H_4COOC_2H_5$, $C_6H_{11}COOC_2H_5$
p-ClC_6H_4OH	MeOH	50	1.5	151	357	*p*-ClC_6H_4OH, 0.03 *M* HCl, C_6H_5OH (trace), C_6H_{12}
p-$ClC_6H_4OCH_3$	MeOH	50	2	153	298	*p*-$ClC_6H_4OCH_3$, 0.029 *M* HCl, anisole?, C_6H_{12}
Cyclohexene (control)	MeOH	100	12–15	49–55	5	(Cyclohexane)

pounds to 2–2.5 millimoles per minute. Hydrogen bromide was equally effective. The inactivation by acid was incomplete when no excess of acid was present or in aqueous solution. The same inactivation was found when a permanent cationic group (No. 6 of Table I) was present.

Bromobenzene and *m*-bromotoluene absorbed hydrogen at moderate rates (2.5–4 millimoles per minute) and this may be taken as the normal rate of hydrogenolysis of aromatically bound bromine. The rate with bromoanilines in the presence of excess acid is not significantly different and we take it that a cationic group neither activates nor inactivates the halogen atom, whereas the free amino group produces a marked labilization.

The corresponding acetylated compounds certainly showed no activation. The hydrogenolysis of *o*-bromoacetanilide proceeded at the same rate as that of bromobenzene. The *m* and *p* isomers appeared somewhat less reactive but this, especially in the case of *p*-bromoacetanilide, may have been due to insolubility.

Halogenophenols and Anisoles.—The three chlorophenols and *p*-chloroanisole resisted hydrogenolysis under our conditions. *o* and *p*-bromophenol were reduced very slowly (19 and 24 millimoles in 290 and 280 minutes, respectively). The corresponding anisoles gave reduction rates approximating that of bromobenzene but generally lower. These substances may exhibit inactivation.

Halogenobenzoic Acids and Their Esters.—The chloro compounds resisted hydrogenolysis. The ethyl bromobenzoates were reduced uniformly at maximal rates of 1 millimole per minute. The *o*- and *m*-bromo acids were dehalogenated at about the same rate, *p*-bromobenzoic acid very slowly, if at all. In view of the behavior of the esters, we are inclined to attribute this result to insolubility. There is no evidence here of labilization of halogen. The dehalogenation of *p*-bromobenzene sulfonamide was found to proceed at a normal rate (3 millimoles per minute).

Aliphatic Halogen Compounds.—Simple aliphatic bromides (isobutyl bromide, *t*-butyl bromide, *t*-amyl bromide and phenethyl bromide) were not reduced under our conditions. Cyclohexyl bromide also was unaffected. Only when the halogen was unusually reactive was it removed; such substances as ethyl *β*-bromopropionate and monochloroacetic acid retained their halogens. The very reactive bromine of ethyl bromoacetate (Table I, No. 15) was removed quantitatively but less rapidly than the bromine of bromobenzene. Phenacyl chloride lost its halogen very fast (absorption in second minute 20 millimoles), being converted to ethylbenzene. Dehalogenation must have preceded reduction and removal of the carbonyl oxygen. Benzyl chloride absorbed hydrogen with unusual speed (22 millimoles per minute); this reduction probably should be classed as a debenzylation. Allyl chloride was hydrogenated at a moderate apparent rate complicated by the release of gaseous material. The chlorine was removed quantitatively, so dehalogenation must have preceded saturation of the ethylenic bond.

The behavior of di- and trichloroacetic acids and their esters was most peculiar. In aqueous or aqueous alcoholic solutions reduction proceeded to the mono-chloroacetic acid stage, the first chlorine of trichloroacetic acid or its ester being removed very fast. In absolute alcohol trichloroacetic acid and its ester lost only a little over one mole of halogen and the reduction of the dichloro compounds was also incomplete. In agreement with the above, the hydrogenation of ethyl dichloroacetate was suppressed by excess hydrogen chloride.

Discussion

Since it is now recognized that the departures from parallelism in the behavior of halogen derivatives toward different reagents is due to the existence of different reaction mechanisms, the fact that halogens in aromatic compounds are more labile than in aliphatic substances when subjected to catalytic hydrogenation should not occasion surprise, though it was not anticipated. There was no reason to expect a metathetical mechanism. The observation that the relative position of the substituents of an aromatic system has little or no effect on the liability of the halogen substituent[8] also indicates that the process at work here is not ordinary metathesis. The actual mechanism of activation, however, is obscure. Clearly it is not a function of the various influences by which it is customary to explain aromatic chemistry.

Since the present classical theories do not account for the situation, an explanation based on a different mechanism must be sought. While palladium catalysts do not readily reduce aromatic systems, and the catalyst of our choice does not do so at all at room temperature, it is possible that it does adsorb and reduce certain substituted systems. It is usually expected that the hydrogenation of a benzene ring proceeds to completion as a result of one adsorption; nevertheless, it is unlikely that the six hydrogen atoms should be added simultaneously, and a reaction of an intermediate might predominate if very rapid. The first expected intermediate in the reduction of a halogeno benzene would be a dihydrobenzene and this type, known in general to be unstable, might well split off hydrogen halide so rapidly that this process would take precedence over further reduction. The assumption of such a process can also account for the stripping of hydroxyl and alkoxyl groups that frequently accompanies complete reduction of aromatic systems.

This mechanism actually involves two postulates: (a) that the activating amino group facilitates aromatic reduction, and (b) that elimination of the elements of hydrogen halide, water or alcohol from a dihydro aromatic compound capable of such elimination may proceed more rapidly than further reduction of the substance. It is not possible to test this directly since the required dihydro compounds are not known at present. If they should, in fact, be incapable of existence, that would support the hypothesis but would not prove it.

The interrupted reductions with platinum recorded in Table II were undertaken in the hope that some definite indications on the above points would be obtained. The catalyst used was capable of, and achieved, aromatic reduction. Most of the compounds used were not affected by palladized charcoal under the same conditions. It was hoped to obtain evidence that dehalogenation took place only incidentally to reduction of the aromatic ring. Unfortunately, the results were indecisive. The reductions of *o*- and *p*-chloroanilines yielded considerable amounts of aniline, and the product from the reduction of *p*-chlorophenol contained a demonstrable trace of phenol. With the other reduction products minute amounts of dehalogenated aromatic material probably could not have been detected. If a reduction mixture which had absorbed 2–3 mols of hydrogen had contained no starting material, such would have been a pretty strong indication that dehalogenation was an independent process proceeding at a swifter rate than reduction of the aromatic ring. After all of these reductions, starting material was isolated. If, on the other hand, the mixture from *p*-chlorophenol had contained no phenol at all, there would be reason to believe the two processes were intimately connected, and that the dehalogenation did not proceed apart from reduction of the ring. As it is, the results can be interpreted in either way.

The first of our postulates, however, shows a possibility of being tested separately by a different procedure, and, fortunately, through a series of experiments of independent interest. If the amino group or the halogens do facilitate aromatic reduction, this ought to be revealed by the reduction of compounds containing two different aromatic rings suitably substituted. We hope to be able to report on this project in the near future.

Summary

1. The hydrogenolysis of a variety of aromatic and aliphatic halogen compounds has been studied using as catalysts palladized charcoal and Adams catalyst.
2. Aliphatically bound halogens are quite resistant to hydrogenolysis in acid or neutral conditions unless under the influence of adjacent unsaturation.
3. Unless activated by other substituents aromatically bound chlorine appears to be rather stable under conditions that do not reduce the aromatic ring. Bromine similarly bound is removed at a moderate rate.
4. Amino substitution in the aromatic system labilizes the halogens, regardless of position. This effect disappears when the amino group becomes cationic.

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(8) *Cf.* Mladenovic, *Bull. soc. chim. roy. Yougoslav.*, **4**, 187 (1933). Mladenovic, operating in somewhat different fashion and apparently without controls found no significant difference in the reduction rates of *o*-, *m*- and *p*-bromonitrobenzenes.