Hydrogen Transfer. Part VII. Metal-catalysed Transfer-hydrogenation of Nitro-compounds.*

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Transfer-hydrogenation, with *cyclo*hexene as a hydrogen donor and palladium as a catalyst, provides a convenient general method for the conversion of aliphatic and aromatic nitro-compounds into primary amines. In the presence of more than one functional group, transfer-hydrogenation is often remarkably selective and affords higher yields than direct catalytic hydrogenation or other methods of reduction. A mechanism is proposed which accounts for the difference in specificity in terms of surface-stereo-chemical effects.

IN Part VI,* the transfer-hydrogenation of ethylenic and acetylenic compounds, with *cyclo*hexene as a donor, was described. The present paper deals with the application of this novel method of reduction to nitro-compounds which, we find, are converted into primary amines, generally in high yields. With this class of acceptor, the method is not merely of theoretical interest, but possesses considerable practical advantages and exhibits certain useful differences in specificity from conventional catalytic hydrogenation and other methods of reduction.

In order to establish optimum experimental conditions, the transfer-hydrogenations of nitrobenzene to aniline and *p*-nitrotoluene to *p*-toluidine were studied in some detail.

(1) *Stoicheiometry.*—Almost quantitative yields could be obtained by using only the theoretical amounts (*i.e.*, 1·5 mols.) of *cyclo*hexene and the rate of transfer shows little increase at higher *cyclo*hexene concentrations, although transfer takes place much more slowly than disproportionation in the absence of foreign acceptor. (Under comparable conditions, in boiling tetrahydrofuran, the half-times are *ca.* 15 hr. and 20 min., respectively.) This shows that the disproportionation of the donor is almost entirely suppressed by the nitro-compound, as it is by some ethylenic acceptors (*e.g.*, maleic acid; Part VI).

(2) *Solvents.*—Although water is formed in the reaction, the use of *cyclo*hexene alone or with other water-immiscible solvents, such as benzene or *cyclo*hexane, is satisfactory in small-scale experiments. For larger-scale experiments, the addition of water-miscible solvents such as methanol, ethanol, or tetrahydrofuran is advantageous; the rate of transfer decreases with increasing dilution, but is of the same order in boiling solvents of similar boiling points (*e.g.*, ethanol, benzene, and *cyclo*hexane, cf. p. 3591). Even in diethyl ether (b. p. 35°) and tetrahydrofuran (b. p. 65°) the rates differ by a factor of less than two, showing that the temperature coefficient is very small and corresponds to an apparent energy of activation of less than 5 kcal./mole. A somewhat reduced rate of transfer is found in acetic acid; this appears to be a specific solvent effect which has also been encountered in the direct catalytic reduction of nitro-compounds (Adams, Cohen, and Rees, *J. Amer. Chem. Soc.*, 1927, **49**, 1093; Line, Wyatt, and Smith, *ibid.*, 1952, **74**, 1808; Iffland and Cassis, *ibid.*, p. 6284; Smith and Bedoit, *J. Phys. Colloid Chem.*, 1951, **55**, 1085). An essential condition, which has a more marked influence than either solvent or temperature variation, is vigorous ebullition. If the reaction mixture, instead of being refluxed, is mechanically stirred at a temperature below the boiling point, the reaction comes to a standstill after 10—20% transfer (Fig. 1); this is not due to preferential disproportionation of the donor under such conditions, since the addition of more *cyclo*hexene is without effect. Somewhat similar observations were made with dehydrogenation reactions by Linstead and Michaelis (*J.*, 1940, 1134) who found that boiling tetralin is dehydrogenated over palladium at 180°, but undergoes little change under tranquil conditions at 200°. It was suggested that the mechanical effect of boiling helps to detach hydrogen from the catalyst surface and thus promotes further reaction, and a similar explanation may be offered in the present case

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* Part VI, preceding paper.

if it is assumed that the amine formed is strongly chemisorbed and that ebullition promotes the transport of reactants and products towards and away from the catalyst surface. A possible alternative explanation is that, in virtue of the greater volatility of *cyclo*hexene than of the nitro-compound, a more favourable adsorption ratio is set up under ebullescent conditions.

(3) *Catalysts.*—Palladium is equally effective in a colloidal form, or deposited chemically on charcoal, calcium carbonate, or alumina, or deposited electrolytically on platinum foil, and the rate of transfer shows only slight dependence on the amount of catalyst, provided the ratio of palladium to reactants is not less than *ca.* 10^{-3}. In practice, a ratio of 10^{-2} was found convenient. Much lower yields are obtained with platinum, and it is of interest that platinum is also reported to be less effective than palladium in the direct hydrogenation of nitro-compounds at atmospheric pressure (Brand and Steiner, *Ber.*, 1922, **55**, 875; Rampino and Nord, *J. Amer. Chem. Soc.*, 1941, **63**, 2745; Streltsova and Zelinski, *Bull. Acad. Sci., U.R.S.S.*, 1941, 401; 1943, 56). As with ethylenic acceptors (Part VI), Raney nickel has only negligible activity under the conditions tried, although it catalyses both the disproportionation of *cyclo*hexene (Corson and Ipatieff, *J. Amer. Chem. Soc.*, 1939, **61**, 1056) and the direct hydrogenation of nitro-compounds (*e.g.*, Lieber *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 384; 1949, **71**, 1515; 1950, **72**, 1190; Johnson and Degering, *ibid.*, 1939, **61**, 3194; Winans, *ibid.*, 1939, **61**, 3564; Samuelsen, Vladimir, Garik, and Smith, *ibid.*, 1950, **72**, 3872; Albert and Ritchie, *J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 74; Allison, Comte, and Fierz-David, *Helv. Chim. Acta*, 1951, **34**, 818).

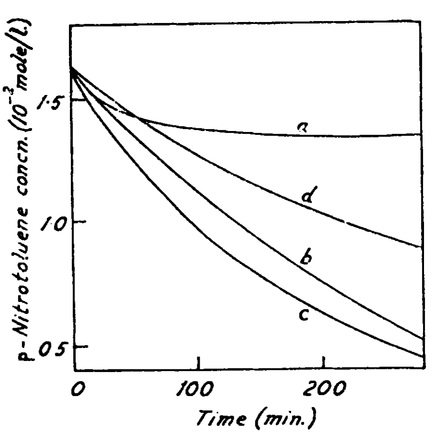


FIG. 1. *Rates of reduction of* p-*nitrotoluene by* cyclo*hexene on palladium.*

(*a*) *In ethanol at* 55·7°.
(*b*) *In methanol at* 64°.
(*c*) *In ethanol at* 78°.
(*d*) *Repeat run in ethanol at* 78°.
(*For details, see Experimental section.*)

TABLE 1. *Transfer-hydrogenation of* p-*nitrotoluene.**

Donor	Solvent	Temp.	Time (hr.)	Transfer (%)
*cyclo*Hexene	Excess of *cyclo*hexene	83°	17	96
,,	Ethanol	78	17	95
,,	Tetrahydrofuran	65	15	85
1-Methyl*cyclo*hexene	Ethanol	78	18	8
4-Methyl*cyclo*hexene	Ethanol	78	18	72
1 : 4-Dihydrophthalic acid	Tetrahydrofuran	65	17	45
Limonene †	None	175	8	15

* For details of conditions, see Experimental section. † With nitrobenzene as acceptor.

A number of other donors were tested against *p*-nitrotoluene, but none was as effective as *cyclo*hexene (Table 1), although disproportionation was again almost completely suppressed in the presence of the acceptor. Thus, 4-methyl*cyclo*hexene gave 72% of *p*-toluidine and 88% of toluene after 17 hours' refluxing in tetrahydrofuran. No transfer took place in boiling ethanol with tetralin, *cyclo*pentene, *cyclo*pent-1-enecarboxylic acid, *cyclo*heptene, *cyclo*octene, or *cyclo*hexanone, and it is significant that none of these compounds undergoes disproportionation under such conditions.

The only examples of catalysed transfer-hydrogenation of nitro-compounds which could be found in the literature involve as donors either hydrazine (Busch and Schulz, *Ber.*, 1929, **62**, 1458; Kuhn, *J. Amer. Chem. Soc.*, 1951, **73**, 1510; Balcolm and Furst, *ibid.*, 1953, **75**, 4334) which gave azoxy-, azo-, and hydrazo-compounds as well as amines, or alcohols and hydrocarbons (Legg and Adam, B.P. 166,283; Castner and Lawson, U.S.P. 2,377,071; *Chem. Abs.*, 1945, **39**, 4093) which have been used only at high temperatures (>250°).

The results of the transfer-hydrogenation of a wide range of nitro-compounds with *cyclo*hexene are summarised in Tables 2 and 3. Mononitro-compounds containing hydroxyl, alkoxyl, keto-, carboxyl, or cyano-substituents give the corresponding amines, these functional groups remaining unchanged. The yields often compare favourably with

TABLE 2. *Transfer-hydrogenation of mononitro-compounds to amines with* cyclo*hexene and palladium.**

No.	Nitro-compound	Solvent	Time (hr.)	Yield (%)
1.	Nitropropane	Ether	72	55
2.	Nitrobenzene	Ethanol	17	93
3.	*o*-Nitrotoluene	,,	17	100
4.	*m*-Nitrotoluene	,,	17	65
5.	*p*-Nitrotoluene	,,	17	95
6.	*p*-*tert.*-Butylnitrobenzene	None	40	54
7.	1-Nitronaphthalene	Ethanol	135	71
8.	*o*-Nitrophenol	Tetrahydrofuran	9	88
9.	*p*-Nitrophenol	,,	9	51
10.	2-Nitroresorcinol	,,	12	17
11.	*p*-Nitroanisole	None	17	83
12.	1 : 4-Diethoxy-2-nitrobenzene	,,	14	96
13—15.	*o*-, *m*-, and *p*-Nitrobenzaldehyde	Ethanol	17	<10
16.	*o*-Nitroacetophenone	,,	24	89
17.	*m*-Nitroacetophenone	,,	48	75
18.	*p*-Nitroacetophenone	None	24	98
19.	1-Nitroanthraquinone	Tetrahydrofuran	17	58
20.	*o*-Nitrobenzoic acid	Ethanol	17	92
21.	*m*-Nitrobenzoic acid	,,	17	58
22.	*p*-Nitrobenzoic acid	,,	17	96
23.	*o*-Nitrobenzonitrile	Tetrahydrofuran	40	59
24.	*m*-Nitrobenzonitrile	,,	40	87
25—27.	*o*-, *m*-, and *p*-Nitroaniline	Ethanol	17	< 2
28.	*o*-Nitroacetanilide	,,	17	100
29.	*m*-Nitroacetanilide	,,	17	81
30.	*p*-Nitroacetanilide	,,	17	27
31.	*NN*-Dimethyl-*m*-nitroaniline	None	20	73
32.	*p*-Bromonitrobenzene	,,	17	< 2
33.	2-Nitrothiophen	,,	90	< 2

* For details see Experimental section.

TABLE 3. *Transfer-hydrogenation of polynitro-compounds.**

No.	Compound	Solvent	Time (hr.)	Product	Yield (%)
34.	*o*-Dinitrobenzene	Ethanol	5	*o*-Nitroaniline	<2
35.	*m*-Dinitrobenzene	Tetrahydrofuran	15	*m*-Nitroaniline	80
36.	*p*-Dinitrobenzene	,,	19	*p*-Nitroaniline	<2
37.	2 : 4-Dinitrotoluene	—	40	2 : 4-Diaminotoluene	75
38.	1-*tert.*-Butyl-2 : 4-dinitrobenzene	—	36	2 : 4-Diamino-1-*tert.*-butylbenzene	95
39.	1 : 8-Dinitronaphthalene	—	17	1 : 8-Diaminonaphthalene	97
40.	2 : 4-Dinitrophenol	Ethanol	48	2 : 4-Diaminophenol	65
41.	3 : 5-Dinitrobenzoic acid	,,	17	3-Amino-5-nitrobenzoic acid	60
42.	1 : 3 : 5-Trinitrobenzene	—	120	3 : 5-Dinitroaniline	9
43.	2 : 4 : 6-Trinitrotoluene	Ethanol	41	4-Amino-2 : 6-dinitrotoluene 2-Amino-4 : 6-dinitrotoluene	11 9
44.	Picric acid	Tetrahydrofuran	14	Picramic acid	28

* For details see Experimental section.

those obtained by other methods; thus, *o*-nitroacetophenone gives 95% of *o*-aminoacetophenone, whereas the yields reported for direct catalytic hydrogenation and reduction by tin and hydrochloric acid are 75 and 68%, respectively (Boyd and Leonard, *J. Org. Chem.*, 1946, **11**, 405; Camps, *Arch. Pharm.*, 1902, **240**, 1). On the other hand, hardly any reduction occurs with the three nitroanilines, *p*-bromonitrobenzene, the three nitrobenzaldehydes, and 2-nitrothiophen. Thiophen derivatives are well-known catalyst " poisons " and the nitrobenzaldehydes also resist direct catalytic hydrogenation owing to formation of polymeric products (cf. Phillips and Maggiole, *J. Org. Chem.*, 1950, **15**, 659), but *m*-nitroaniline is smoothly converted into *m*-phenylenediamine, and *p*-bromonitrobenzene into aniline hydrobromide by hydrogen in the presence of palladium, as observed by earlier workers (Rosenmund and Zetsche, *Ber.*, 1918, **51**, 578; Brand and Steiner, *loc. cit.*; Streltsova and Zelinski, *locc. cit.*). The selectivity of transfer-hydrogenation is thus considerably more marked than that of direct catalytic hydrogenation and is further illustrated by the fact that, in contrast to the nitroanilines, the nitroacetanilides and *NN*-dimethyl-*m*-nitroaniline are readily reduced.

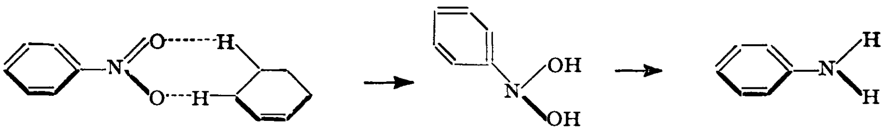
Polynitro-compounds exhibit an even greater specificity. Transfer-hydrogenation of *m*-dinitrobenzene gives exclusively *m*-nitroaniline, as would be expected from the behaviour of the product, but the two alkylated *m*-dinitrobenzenes (Table 3) and 1 : 8-dinitronaphthalene give the diamines in excellent yields. 2 : 4-Dinitrophenol also gives the diamine, whereas only one nitro-group is reduced in 3 : 5-dinitrobenzoic acid and in trinitro-derivatives.

The results summarised in the Tables show that, in addition to cases of complete selectivity, the ease of transfer-hydrogenation of nitro-compounds is very sensitive to structural variations in the acceptor, in contrast to direct reduction with hydrogen on palladium or platinum catalysts where substituents are reported to have relatively little effect on the rate of reaction (Adams *et al.*, *loc. cit.*; Streltsova and Zelinski, *loc. cit.*, 1943; Dunsworth and Nord, *J. Amer. Chem. Soc.*, 1950, **72**, 4197). This lends support to the view (Part VI) that transfer-hydrogenation does not consist of separate donor-dehydrogenation and acceptor-hydrogenation steps, but is a linked process involving specific donor–acceptor relations. It could be suggested that differences observed are primarily due to " poisoning " effects of the acceptors or their reduction products on the disproportionation or dehydrogenation of the donor. That this is not the case is illustrated by the fact that neither *m*-nitroaniline nor *m*-phenylenediamine inhibits the disproportionation of *cyclo*hexene, although they do have a retarding effect. The non-reactivity of *m*-nitroaniline (and presumably of other compounds which undergo direct catalytic hydrogenation) must therefore be due to a lack of acceptor properties, which could conceivably arise from such causes as (i) non-adsorption on the catalyst, (ii) unsuitable orientation on the catalyst surface, and (iii) intrinsically low reduction potential. Since other compounds containing free amino-groups as well as alkylated derivatives of *m*-nitroaniline are readily reduced by transfer-hydrogenation it is difficult to believe that effects of type (i) or (iii) can be primarily responsible. The marked differences in rate produced by various substitutents (Table 1) also cannot be rationalised in terms of usual electronic influences. The most probable cause of the lack of acceptor properties of *m*-nitroaniline is (ii), and the effect of other substituents may also be visualised in terms of the surface-stereochemical requirements of the reaction.

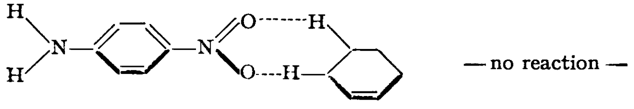
A variety of partly reduced derivatives, particularly hydroxylamines and nitroso-compounds, have been postulated as intermediates in the conversion of nitro-compounds into amines under different conditions (cf. Haber, *Z. physikal. Chem.*, 1900, **32**, 193), and phenylhydroxylamine has been isolated on hydrogenation of nitrobenzene over palladium (Brand and Steiner, *loc. cit.*). Phenylhydroxylamine is also reduced to aniline by *cyclo*hexene and palladium, but nitrosobenzene gave only intractable products. This evidence does not necessarily exclude nitroso-derivatives as intermediates, since they may exert concentration-dependent poisoning effects, but it does render their intervention unlikely in the present case. A plausible reaction course, which does not appear to have been previously considered and does not entail free nitroso-intermediates, involves as a first step the addition of two hydrogen atoms to give either the hydroxylamine *N*-oxide $O \leftarrow NHR{\cdot}OH$

or the isomeric dihydroxyamine (nitroso-hydrate) $R{\cdot}N(OH)_2$, followed by hydrogenolysis of the N–O bonds. On this basis, a tentative interpretation of the remarkable difference in specificity observed in transfer-hydrogenation may be given. The first step may be represented as in Fig. 2*a* with the nitro-group initially lying flat on the catalyst surface alongside a donor molecule. As $-NO_2$ is converted into $-N(OH)_2$, the nitrogen atom passes from a planar to a tetrahedral valency-bond configuration, and whereas in the nitro-compound the nitro- and phenyl groups are essentially uniplanar (cf. Hodgkin and Pitt, *Ann. Reports*, 1950, **47**, 455), in the dihydroxy-amine, the benzene ring and the two oxygen atoms can no longer simultaneously retain their positions on the catalyst surface. Normally, the benzene ring will be lifted off the surface, while the $-N(OH)_2$ group will remain preferentially adsorbed, thus allowing the reduction to go to completion by subsequent hydrogenolysis (Fig. 2*a*). If, however, the benzene ring carries another substituent (*e.g.*, NH_2) which also has a strong affinity for the catalyst, the chemisorptive forces acting on the ring may exceed those acting on the nitro-group. In this case, the plane of the benzene ring will remain parallel to the catalyst surface, while one or both N–O links of the nitro-group undergoing reduction will be forced to become directed away from the surface and transfer will be inhibited (Fig. 2*b*). But if now an additional substituent (*e.g.*, *tert.*-butyl) is introduced, sufficiently bulky to prevent the benzene ring from lying flat on the catalyst surface, hydrogen transfer will again be possible, even in the presence of a strongly chemisorbed group such as NH_2 (Fig. 2*c*). This phenomenon may be termed " positive catalyst hindrance " and compared with the " negative catalyst hindrance " encountered in direct catalytic hydrogenation (Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985).

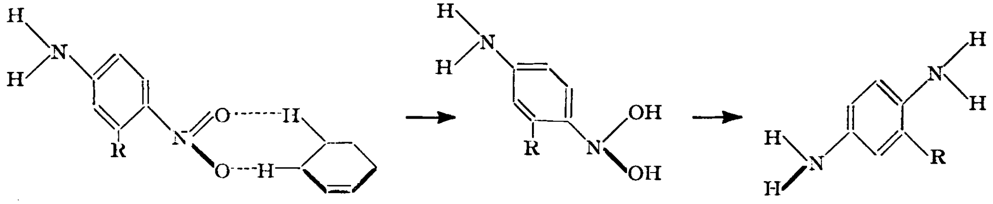
FIG. 2.



(*a*) *Catalytic transfer-hydrogenation of nitrobenzene* (*schematic*).



(*b*) *Inhibition of hydrogen-transfer to* p-*nitroaniline* (*schematic*).



(*c*) *Hydrogen-transfer to* p-*nitroaniline containing a bulky substituent* ortho *to the nitro-group* (*schematic*).

EXPERIMENTAL

Materials.—The nitro-compounds were either purified commercial specimens or prepared by the methods indicated below. *cyclo*Hexene was distilled from sodium and stored in the dark. Tetrahydrofuran was refluxed with potassium hydroxide for several hours and then fractionated. Commercial absolute ethanol was used without purification. Palladium black was prepared by Wieland's method (*Ber.*, 1912, **45**, 484); it is important to add the formic acid immediately after the sodium hydroxide otherwise a dark brown catalyst instead of the more active black form results. Palladised charcoal was prepared by the method of Linstead and Thomas (*J.*, 1940, 1130).

Transfer-hydrogenation of p-*Nitrotoluene.*—(a) *General procedure. p*-Nitrotoluene (2·5 g.), *cyclo*hexene (4·5 g.) and palladium black (20 mg.) were heated under vigorous reflux for 17 hr. At the end of this time, the solution was practically colourless. The catalyst was filtered off and constituents boiling below 100° were removed on the steam-bath. The residue was dissolved in ether (100 ml.), the ether solution was dried ($MgSO_4$) and filtered, and anhydrous hydrogen chloride was passed in. The precipitate was washed with dry ether, giving *p*-toluidine hydrochloride (2·5 g., 96%), m. p. 235°. The base was liberated by aqueous sodium hydroxide and had m. p. 45° undepressed on admixture with an authentic specimen, and gave a benzoyl derivative, m. p. 158°.

(b) *Catalyst variation.* Yields of *p*-toluidine were reproducible within $\pm 5\%$ when the same batch of catalyst was used. The reproducibility of different batches of palladium black is illustrated below. 2·5 g. of nitrotoluene, 15 ml. of *cyclo*hexene and 20 mg. of catalyst were refluxed for 7 hr. in each case :

Batch number	1	2	3	4	5	6	7	8
Yield of *p*-toluidine (%)	90	89	69	86	70	74	60	77

Subsequently, the activity of each batch was checked against *p*-nitrotoluene under these conditions. Results obtained with other catalysts, with the same quantities of *p*-nitrotoluene and *cyclo*hexene, are shown below.

Catalyst	Amount (mg.)	Time (hr.)	Yield (%) of *p*-toluidine	Catalyst	Amount (mg.)	Time (hr.)	Yield (%) of *p*-toluidine
10% Pd–C	190	7	95	Pt black	20	7	18
1% Pd–$CaCO_3$ [a]	100	18	95	10% Pt–C	350	7	13
0·1% Pd–Al_2O_3	1000	18	64	PtO_2	45	17	0
$PdCl_2$	20	17	1	Raney Ni [c]	100	22	2
Pd–Pt [b]	10	13	100	W.7 Raney Ni [d]	100	100	2

[a] The catalyst was heated with boiling *cyclo*hexene for a few minutes before adding nitrotoluene. [b] 10 mg. of Pd deposited electrolytically (cf. Hamer and Acree, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 87) on an 1 × 1″ Pt foil. [c] Mozingo, *Org. Synth.*, 1941, **21**, 15. [d] Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695.

(c) *Solvent and concentration variation.* Except where otherwise indicated, the following experiments were all carried out with 2·5 g. of *p*-nitrotoluene, 4·6 g. (2 mols.) of *cyclo*hexene, 20 mg. of palladium black, and the solvent at the b. p. for 17 hr.

Solvent	Vol. (ml.)	Yield (%)	Solvent	Vol. (ml.)	Yield (%)
Ethanol	20	93	Acetone	50	90
„	50	77	Acetic acid [1]	10	55
„	125	73	*cyclo*Hexane	50	75
Ether	50	55	Benzene [2]	50	16
Tetrahydrofuran	50	85	Benzene [3]	50	73

[1] 14 g. of *cyclo*hexene. [2] " AnalaR." [3] Purified by treatment with Raney nickel and distillation.

With ethanol (125 ml.) as a solvent, the yield of *p*-toluidine was increased by less than 10% on increasing the amount of *cyclo*hexene from 1·5 to 6 mols., or the amount of catalyst from 20 to 80 mg.

When *p*-nitrotoluene (0·289 g.), *cyclo*hexene (0·390 g.), ethanol (50 ml.), and palladium black (20 mg.) were mechanically shaken at 30°, the extent of reduction, determined spectrometrically by the decrease in the intensity of the 2690-Å band (ε 9700), was 7% after 30 min. and 15% after 90 min. No further reduction was observed during 6 hr.

(d) *Donor variation. p*-Nitrotoluene (3·57 g.), 4-methyl*cyclo*hexene (2·60 g.; b. p. 102—104°, n_D^{20} 1·4443), ethanol (52 ml.), and palladium black (30 mg.) were heated under reflux for 18 hr. The catalyst was filtered off and the mixture distilled on the steam-bath. The distillate (50 ml.) had $\lambda_{max.}$ 2620 Å, $E_{1\,cm.}^{1\%}$ 1·00 corresponding to a toluene content of 4·6% (2·3 g., 88%). (Toluene in ethanol exhibits $\lambda_{max.}$ 2620 Å, $E_{1\,cm.}^{1\%}$ 22·0.) The residue was dissolved in ether, dried ($MgSO_4$), and treated with anhydrous hydrogen chloride, giving *p*-toluidine hydrochloride (1·82 g., 72%).

A similar experiment with 1-methyl*cyclo*hexene (b. p. 108—110°/756 mm., n_D^{15} 1·4541; cf. Vogel, *J.*, 1938, 1322) gave a distillate containing toluene (0·42 g., 18%) and furnished only 8% of *p*-toluidine hydrochloride.

p-Nitrotoluene (2·5 g.), 3 : 6-dihydrophthalic acid (0·81 g.), tetrahydrofuran (35 ml.), and palladium black (50 mg.) were heated under reflux for 17 hr. The catalyst and solvent were removed and the residue was dissolved in ether. The ethereal solution was extracted with 10% sodium hydroxide solution. The aqueous layer, on acidification with hydrochloric acid, gave phthalic acid (0·41 g., 50%), m. p. and mixed m. p. 206°. The ethereal layer was dried ($MgSO_4$) and anhydrous hydrogen chloride was passed in, giving *p*-toluidine hydrochloride (0·159 g., 45%), m. p. 235°.

No *p*-toluidine could be detected from the attempted reduction of *p*-nitrotoluene with the following (solvent and time in parentheses, palladium-black catalyst in all cases) : *cyclo*pentene (ether, 25 hr.), *cyclo*pentene-1-carboxylic acid (tetrahydrofuran, 27 hr.), *cyclo*heptene (tetrahydrofuran, 27 hr.), *cyclo*octene (ethanol, 68 hr.), limonene (tetrahydrofuran, 10 hr.), tetralin (ethanol, 7 hr.), *cyclo*hexanol (tetrahydrofuran, 12 hr.).

Transfer-hydrogenation of Other Nitro-compounds.—(CH = *cyclo*hexene, Pd = palladium black. For % yields, see Tables 2 and 3, unless stated. Some of the lower yields are based on the results of single experiments and could undoubtedly be increased by prolonging the reaction time. Examples 34, 36, 42, and 43 were carried out by R. CHAYEN.)

1. Nitropropane (2·84 g.), CH (8 g.), ether (50 ml.), and Pd (50 mg.) after 72 hr. gave *n*-propylamine hydrochloride (1·63 g.) (derived picrate, m. p. 134°).

2. Nitrobenzene (61·5 g.), CH (90 ml.), and Pd (0·53 g.) were heated for 24 hr. under vigorous reflux. After being filtered from the catalyst, the solution was dried ($MgSO_4$) and fractionated through a short column, giving two main fractions : (i) (55 ml.), b. p. 77—79°/760 mm., n_D^{14} 1·4950, $\lambda_{\text{max.}}$ 2550 Å ($E^{1\%}_{1\,\text{cm.}}$ 26) in ethanol, which consisted largely of benzene ($\lambda_{\text{max.}}$ 2550 Å, $E^{1\%}_{1\,\text{cm.}}$ 27); (ii) (43 g.), b. p. 71—72°/14 mm., completely soluble in dilute hydrochloric acid, consisting entirely of aniline (93% yield). It was identified as the hydrochloride, m. p. 195°, and benzanilide, m. p. 160°.

3. *o*-Nitrotoluene (1·81 g.), CH (3·25 g.), ethanol (36 ml.), and Pd (15 mg.) were refluxed for 17 hr. The products were worked up as described above for *p*-nitrotoluene, giving *o*-toluidine hydrochloride (1·92 g.), m. p. 212° (benzoyl derivative, m. p. 144°).

4. *m*-Nitrotoluene (2·46 g.), CH (4·63 g.), ethanol (49 ml.), and Pd (49 mg.) after 17 hr. gave *m*-toluidine as the hydrochloride (1·70 g.) (benzoyl derivative, m. p. 124°).

6. *p-tert.*-Butylnitrobenzene (2 g.; Craig, *J. Amer. Chem. Soc.*, 1935, **57**, 195), CH (15 ml.), and Pd (24 mg.) after 40 hr. gave *p*-amino-*tert.*-butylbenzene as the hydrochloride (1·10 g.) (benzoyl derivative, m. p. 140°; Malherbe, *Ber.*, 1919, **52**, 322, gives m. p. 134—136°).

7. 1-Nitronaphthalene (2·10 g.), CH (3·5 g.), ethanol (44 ml.), and Pd (15 mg.) after 17 hr. gave 1-naphthylamine as the hydrochloride (0·51 g., 24%) (benzoyl derivative, m. p. 158°). After 135 hr., the yield was 1·58 g. (75%).

8. *o*-Nitrophenol (2·5 g.), CH (4·5 g.), tetrahydrofuran (25 ml.), and Pd (50 mg.) after 9 hr. gave *o*-aminophenol as the hydrochloride (2·3 g.) m. p. 201—203° (free base, m. p. 173°).

9. *p*-Nitrophenol (2·5 g.), CH (4·6 g.), tetrahydrofuran (25 ml.), and Pd (50 mg.) after 9 hr. gave *p*-aminophenol as the hydrochloride (1·27 g.) (free base, m. p. 184°).

10. 2-Nitroresorcinol (2 g.; Kaufmann and de Pay, *Ber.*, 1904, **37**, 725), CH (3·2 g.), tetrahydrofuran (25 ml.), and Pd (50 mg.) after 12 hr. gave unchanged nitroresorcinol (1·66 g., 83%) and 2-aminoresorcinol as the hydrochloride (0·35 g.).

11. *p*-Nitroanisole (2·5 g.), CH (5 g.), and Pd (17 mg.) after 17 hr. gave *p*-anisidine as the hydrochloride (2·17 g.) (free base, m. p. 57—58°; benzoyl derivative, m. p. 159°).

12. 1 : 4-Diethoxy-2-nitrobenzene (25 g.; m. p. 48°; supplied by Whiffen and Co. Ltd., through the courtesy of Dr. J. T. W. Mann), *cyclo*hexene (50 ml.), and 10% palladium–charcoal (1 g.) were heated under vigorous reflux until the solution was colourless (14 hr.). The catalyst was filtered off and the solution evaporated on the steam-bath. The colourless solid residue, m. p. 82—83°, was crystallised from dilute ethanol, giving 2 : 5-*diethoxyaniline* (20·5 g., 96%) m. p. 84° (Found : C, 66·3; H, 8·3; N, 7·8. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3; N, 7·7%).

13—15. Each of the nitrobenzaldehydes (2·5 g.), *cyclo*hexene (2·1 g.), and Pd (18 mg.) were refluxed for 65 hr. Unchanged aldehyde (>90%) was recovered in each case. A solution of *p*-nitrobenzaldehyde (2·5 g.) in ethanol (50 ml.) absorbed less than 5% of the calculated volume of hydrogen on shaking in the presence of Pd (20 mg.).

16. *o*-Nitroacetophenone (0·54 g.), CH (5 ml.), tetrahydrofuran (25 ml.), and Pd (50 mg.) after 17 hr. gave *o*-aminoacetophenone as the hydrochloride (0·50 g.), m. p. 167° (benzoyl

derivative, m. p. 98°; Bogert and Nabenhauer, *J. Amer. Chem. Soc.*, 1924, **46**, 1703, give 98°). A larger-scale run (0·5 mole) in ethanol gave a 95% yield.

17. *m*-Nitroacetophenone (2·5 g.), CH (3·7 g.), ethanol (50 ml.), and Pd (16 mg.) after 48 hr. gave *m*-aminoacetophenone as the hydrochloride (1·95 g.) (free base, m. p. 97°; Leonard and Boyd, *J. Org. Chem.*, 1946, **11**, 405, give m. p. 98—99°).

18. *p*-Nitroacetophenone (5 g.), CH (20 ml.), ethanol (20 ml.), and Pd (250 mg.) after 24 hr. gave *p*-aminoacetophenone (4 g.), m. p. 105°, unchanged on crystallisation from water [Derick and Bornmann (*J. Amer. Chem. Soc.*, 1925, **35**, 1286) give m. p. 110° (corr.)] (benzoyl derivative, m. p. 203°; Chattaway, *J.*, 1904, 386, gives m. p. 205°).

19. 1-Nitroanthraquinone (2·5 g.), CH (15 g.), tetrahydrofuran (30 ml.), and Pd (50 mg.) after 17 hr. gave 1-aminoanthraquinone (1·35 g.), m. p. 244°.

20. *o*-Nitrobenzoic acid (2·5 g.), CH (3·7 g.), ethanol (50 ml.), and Pd (60 mg.) after 17 hr. gave anthranilic acid as the hydrochloride (2·4 g.) (free base, m. p. 146°).

21. *m*-Nitrobenzoic acid (2·5 g.), CH (3·7 g.), ethanol (20 ml.), and Pd (29 mg.) after 17 hr. gave *m*-aminobenzoic acid as the hydrochloride (1·5 g.) (free base, m. p. 173°).

22. *p*-Nitrobenzoic acid (2·5 g.), CH (3·7 g.), ethanol (50 ml.), and Pd (60 mg.) after 17 hr. gave *p*-aminobenzoic acid as the hydrochloride (2·45 g.) (free base, m. p. 187°).

23. *o*-Nitrobenzonitrile (3 g.; Bogert and Hand, *J. Amer. Chem. Soc.*, 1902, **24**, 1035), CH (14 g.), tetrahydrofuran (15 ml.), and Pd (30 mg.) after 40 hr. gave *o*-aminobenzonitrile as the hydrochloride (1·85 g.) (free base, m. p. 45°; acetyl derivative, m. p. 128°; Bogert and Hand, *loc. cit.*, give m. p. 132°).

24. *m*-Nitrobenzonitrile (4 g.), CH (18 g.), tetrahydrofuran (20 ml.), and Pd (40 mg.) after 40 hr. gave *m*-aminobenzonitrile as the hydrochloride (3·61 g.) [free base, m. p. 52°; benzoyl derivative, m. p. 141° (Bogert and Beans, *J. Amer. Chem. Soc.*, 1904, **26**, 464, give m. p. 141°)].

25. *o*-Nitroaniline (2·5 g.), CH (14 g.), and Pd (21 mg.) after 17 hr. gave only unchanged nitroaniline; no *o*-phenylenediamine could be detected by the quinoxaline test.

26. *m*-Nitroaniline (2·5 g.), *cyclo*hexene (14 g.), and Pd (100 mg.) after 52 hr. gave unchanged *m*-nitroaniline, m. p. 111°, which did not give a brown colour with dilute hydrochloric acid and potassium nitrite at 0°, whereas 2 mg. of *m*-phenylenediamine could be readily detected by this test under the same conditions. A solution of the same sample of *m*-nitroaniline (2·5 g.) in ethanol (50 ml.) when shaken with Pd in hydrogen absorbed the theoretical amount of gas in 150 min.

27. *p*-Nitroaniline under the same conditions as the *o*-isomer gave only unchanged material.

28. *o*-Nitroacetanilide (2·5 g.), CH (14 g.), ethanol (10 ml.), and Pd (15 mg.) after 17 hr. gave *o*-aminoacetanilide (2·05 g.), m. p. 132—133° (Bell and Kenyon, *J.*, 1926, 954 give m. p. 132°).

29. *m*-Nitroacetanilide (2·5 g.), CH (14 ml.), and Pd (15 mg.) after 17 hr. gave *m*-aminoacetanilide as the hydrochloride (2·08 g.), m. p. 246° (free base m. p. 86°; Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1917, **39**, 1448, give m. p. 87°).

30. *p*-Nitroacetanilide (2·5 g.), CH (14 g.), ethanol (10 ml.), and Pd (15 mg.) after 48 hr. yielded unchanged nitro-compound (1·75 g., 70% recovery) and *p*-aminoacetanilide, m. p. 161°.

31. *NN*-Dimethyl-*m*-nitroaniline (2·07 g.; Groll, *Ber.*, 1886, **19**, 198), CH (14 g.), and Pd (20 mg.) after 17 hr. gave *NN*-dimethyl-*m*-phenylenediamine (1·10 g., 73%), b. p. 152—154°/44 mm. (benzoyl derivative, m. p. 163°; Jaubert, *Bull. Soc. chim.*, 1899, **21**, 20, gives m. p. 163—164°).

32. *p*-Bromonitrobenzene (2·5 g.), CH (14 g.), and Pd (26 mg.) after 17 hr. gave no precipitate with hydrogen chloride in anhydrous ether. A solution of the same sample of *p*-bromonitrobenzene (2·5 g.) in ethanol (50 ml.) when shaken with Pd (26 mg.) in hydrogen absorbed the theoretical amount of gas in 195 min., giving aniline hydrobromide, m. p. 283°.

33. 2-Nitrothiophen (1·2 g.), CH (14 g.), and Pd (20 mg.) after 90 hr. gave no precipitate with hydrogen chloride in ether.

34. *o*-Dinitrobenzene (2 g.; Hodgson, Heyworth, and Ward, *J.*, 1948, 1512), CH (9 g.), ethanol (20 ml.), and Pd (50 mg.) after 5 hr. gave an unidentified hydrochloride (0·85 g.), m. p. 130° (Found: C, 44·6; H, 4·4; N, 17·3; Cl, 15·75%).

35. *m*-Dinitrobenzene (2·5 g.), CH (7·3 g.), palladium black (50 mg.), and tetrahydrofuran (25 ml.) after refluxing for 17 hr. gave *m*-nitroaniline as the hydrochloride (2·1 g., 82%). The base was liberated and had m. p. and mixed m. p. 112°.

36. *p*-Dinitrobenzene (2·1 g.; Hodgson *et al.*, *loc. cit.*), CH (9 g.), tetrahydrofuran (20 ml.), and Pd (20 mg.) after 19 hr. gave only unchanged dinitrobenzene.

37. 2 : 4-Dinitrotoluene (2·5 g.), CH (14 g.), and Pd (15 mg.) after refluxing for 40 hr. gave a hydrochloride (2·55 g.) from which an impure base, m. p. 68—72°, was liberted by ammonia. This was converted into 2 : 4-diaminotoluene dibenzenesulphonate (2·2 g., 75%), m. p. 195°.

38. 1-*tert.*-Butyl-2 : 4-dinitrobenzene (5 g.; Du Toit and Malherbe, *Ber.*, 1919, **52**, 321), CH (23 g.), and Pd (100 mg.) after 36 hr. gave 1-*tert.*-butyl-2 : 4-diaminobenzene as the *dihydrochloride* (4·95 g.) (Found: Cl, 30·65. $C_{10}H_{18}N_2Cl_2$ requires Cl, 30·8%). The *dibenzoyl* derivative crystallised from aqueous ethanol in plates, m. p. 259° (Found: C, 77·2; H, 6·5; N, 7·7. $C_{24}H_{24}O_2N_2$ requires C, 77·4; H, 6·5; N, 7·5%).

39. 1 : 8-Dinitronaphthalene (2·5 g.), CH (14 g.), and 10% palladised charcoal (120 mg.) after 17 hr. gave 1 : 8-diaminonaphthalene as the dihydrochloride (2·55 g.) (free base, m. p. 64°; Krollpfeiffer, *Annalen*, 1923, **430**, 199, gives m. p. 66·5°).

40. 2 : 4-Dinitrophenol (2·5 g.), CH (10 g.), ethanol (20 ml.), and 5% palladised charcoal (250 mg.) after 40 hr. gave 2 : 4-diaminophenol as the dihydrochloride (1·71 g.), m. p. 205° (tribenzoyl derivative, m. p. 230°; Meldola and Hollely, *J.*, 1912, 912, give m. p. 240°), and an ether-insoluble product (0·20 g.) (Found: C, 61·8; H, 5·6; N, 11·05%).

41. 3 : 5-Dinitrobenzoic acid (2·5 g.), CH (14 g.), ethanol (20 mg.), and Pd (12 mg.) after 17 hr. gave 3-amino-5-nitrobenzoic acid as the hydrochloride (1·48 g.) (free base, m. p. 208°; Hüber, *Annalen*, 1883, **222**, 81, gives m. p. 208°).

42. 1 : 3 : 5-Trinitrobenzene (4·26 g.), CH (14 g.), and Pd (21 mg.) after 120 hr. gave unchanged material (3·4 g., 80%) and 3 : 5-dinitroaniline (0·34 g.), m. p. 157°.

43. 2 : 4 : 6-Trinitrotoluene (3 g.), CH (10 ml.), ethanol (20 ml.), and Pd (20 mg.) after 41 hr. gave a mixture which was extracted with 6M-hydrochloric acid (15 ml.). On dilution with water, 4-amino-2 : 6-dinitrotoluene (0·33 g.), m. p. 168° (Brady, Day, and Reynolds, *J.*, 1929, 2264, give m. p. 171°), was precipitated. On addition of ammonia to the filtrate until the pH was 9, 2-amino-4 : 6-dinitrotoluene (0·27 g.), m. p. 155° (McGookin, Swift, and Tittensor, *J. Soc. Chem. Ind.*, 1940, **59**, 92, give m. p. 155°), was precipitated.

44. Picric acid (2·5 g.), CH (8 g.), tetrahydrofuran (25 ml.), and Pd (50 mg.) after 13 hr. gave picramic acid as the hydrochloride (0·67 g.) [free base m. p. 169°; *N*-acetyl derivative, m. p. 204° (Pear and Dehn, *J. Amer. Chem. Soc.*, 1938, **60**, 925 give 204—205°)].

Transfer-hydrogenation of Nitrosobenzene and Phenylhydroxylamine.—(*a*) Nitrosobenzene (2·5 g.), *cyclo*hexene (15 ml.), and Pd (25 mg.) were heated under reflux. The colour of the solution changed from green to dark-brown within a few minutes. After 7 hr., the catalyst was filtered off and the lower-boiling constituents were removed by distillation on the steam-bath. The dark, tarry residue was dissolved in ether and anhydrous hydrogen chloride was passed in. No aniline hydrochloride was obtained. (*b*) Phenylhydroxylamine (1·5 g.), *cyclo*hexene (20 ml.), and Pd (15 mg.) were heated under reflux for 7 hr. Working up as above gave aniline hydrochloride (0·30 g., 17%), m. p. 196°. A similar experiment in which reflux was continued for 17 hr. gave a 30% yield (0·34 g.) of aniline hydrochloride.

Effects of m-*Nitroaniline and* m-*Phenylenediamine on Disproportionation and Transfer.*—(a) *cyclo*Hexene (0·6 g.), ethanol (75 ml.), and 10% palladised charcoal (100 mg.) were heated under reflux. After 1 hr., the catalyst was filtered off and the solution distilled. The distillate had $\lambda_{\text{max.}}$ 2550, $E^{1\%}_{1\,\text{cm.}}$ 0·0375, corresponding to $1{\cdot}33 \times 10^{-3}$ mole of benzene. In a parallel experiment, in which *m*-nitroaniline (50 mg.) was added and the solution was distilled through a short column before spectrometric assay, $0{\cdot}45 \times 10^{-3}$ mole of benzene was formed. (b) *cyclo*Hexene (0·6 g.), ethanol (50 ml.), and 10% palladised charcoal (150 mg.) were heated under reflux. After 1 hr., the distillate exhibited $\lambda_{\text{max.}}$ 2550, $E^{1\%}_{1\,\text{cm.}}$ 0·071, corresponding to $1{\cdot}67 \times 10^{-3}$ mole of benzene. In a similar experiment in which freshly distilled *m*-phenylenediamine (50 mg.) was added, $0{\cdot}47 \times 10^{-3}$ mole of benzene was formed.

Rate Measurements.—Preliminary rate-measurements on the transfer hydrogenation of *p*-nitrotoluene by *cyclo*hexene were carried out by the following technique which will be described in more detail later. A catalyst foil, consisting of a platinum foil (1″ × 1″) coated electrolytically with a thin film of palladium (cf. Nylen, *Z. Elektrochem.*, 1937, **43**, 921; Hamer and Acree, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 87), was mounted on the end of a glass stirrer and placed inside the bulb of a reaction vessel of the type described by Braude, Jones, and Stern (*J.*, 1946, 396); it was provided with a small, glass-stoppered side-arm. The glass stirrer passed through the central neck of the flask by means of a liquid seal filled with solvent and was attached to a synchronous motor. A solution of *p*-nitrotoluene (0·25 g.) and *cyclo*hexene (1 g.) in ethanol or methanol (50 ml.) was placed in the flask contained in a thermostatted bath. As soon as thermal equilibrium was attained, the stirrer carrying the catalyst foil was introduced and rotated at 470 r.p.m. At suitable intervals, 1-ml. samples of the solution were withdrawn through the stoppered side-arm by means of a long-stem, graduated pipette and immediately diluted with 9 ml. of ethanol. The concentration (*c*) of *p*-nitrotoluene was then determined by measuring the extinction at 3650 Å in a 1-cm. cell. *p*-Nitrotoluene and *p*-toluidine exhibit

$E^{1\%}_{1\,\text{cm.}}$ 10·4 and 0·04, respectively, at this wave-length. Details of four typical runs carried out with the same foil are given below (cf. Fig. 1).

(*a*) In ethanol at 55·7° :

Time, min.	0	30	60	90	160	215
E	0·465	0·415	0·398	0·395	0·383	0·384
c, mole/l.	1·63	1·46	1·40	1·39	1·34	1·35

(*b*) In methanol at 64° :

Time, min.	0	270	1080
E	0·462	0·165	0·012
c, mole/l.	1·63	0·58	0·04

(*c*) In ethanol at 78° :

Time, min.	0	10	20	30	40	55	85	115	265
E	0·469	0·435	0·411	0·392	0·365	0·354	0·293	0·258	0·138
c, mole/l.	1·64	1·52	1·44	1·38	1·24	1·20	1·03	0·905	0·484

(*d*) In ethanol at 78° :

Time, min.	0	15	30	45	90	135	180	240	360
E	0·467	0·450	0·432	0·407	0·370	0·310	0·290	0·247	0·233
c, mole/l.	1·64	1·58	1·52	1·43	1·30	1·09	1·02	0·868	0·782

These results clearly illustrate the pronounced influence of ebullition [runs (*a*) and (*b*)], the low temperature-coefficient of the reaction [runs (*b*) and (*c*)], and the slow "ageing" of the catalyst [runs (*c*) and (*d*)].

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