Hydrogen Transfer. Part VIII. Metal-catalysed Transfer-hydrogenation of Miscellaneous Acceptors.*

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The palladium-catalysed transfer-hydrogenation of miscellaneous acceptors by *cyclo*hexene has been investigated. Not only ethylenic, acetylenic, and nitro-groups (Parts VI and VII), but also azomethine, azo-, and azoxy-groups, and some halogen compounds undergo reduction or hydrogenolysis, whereas cyano- and carbonyl groups (except in quinones and α-diketones) do not react.

IN addition to that of ethylenic, acetylenic and nitro-compounds (Parts VI and VII *), the transfer-hydrogenation of a number of other types of acceptors by *cyclo*hexene in the presence of palladium has been examined.

Benzylideneaniline, azobenzene, and azoxybenzene readily underwent hydrogenolysis to aniline, and 2 : 2′-dimethoxyazoxybenzene similarly gave *o*-anisidine. In the case of azobenzene, the intermediate product, hydrazobenzene, could be isolated if the reaction was interrupted at an early stage. Thus C=N and N=N bonds exhibit a reactivity similar to that of C=C, as in direct catalytic hydrogenation (cf. Adkins and Shriner in Gilman, " Organic Chemistry " Chapter 9, Wiley, New York, 1943). On the other hand, the cyano-group in benzonitrile, as in nitrobenzonitriles, was not reduced. The C≡N bond is also more resistant than C≡C to direct catalytic hydrogenation.

The carbonyl group in aldehydes and ketones, *e.g.*, butyraldehyde, benzaldehyde, *cyclo*hexanone, acetophenone, and benzophenone, was not reduced by *cyclo*hexene and

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* Parts VI and VII, preceding papers.

palladium under the usual conditions, in accord with the observations made with substituted nitro-compounds. Moreover, in αβ-ethylenic aldehydes and ketones, *e.g.*, crotonaldehyde, cinnamaldehyde and mesityl oxide, the ethylenic bond is also unreactive, in contrast to the behaviour of ethylenic acids (Part VI). On the other hand, benzil is slowly converted into benzoin, and benzoquinone into quinol, in conformity with the fact that α-diketones and quinones generally have reduction potentials appreciably different from those of other carbonyl compounds (cf. Cox and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 1151; 1939, **61**, 3364). With benzoquinone, slow uncatalysed hydrogen transfer also takes place (Parts II and III, *J.*, 1954, 3548, 3564) and it is of interest that, whereas transfer from thermally unreactive donors (*e.g.*, *cyclo*hexene, 1 : 2-dihydrobenzene, 1 : 2-dihydronaphthalene) shows appreciable metal catalysis, transfer from thermally reactive donors (*e.g.*, 1 : 4-dihydrobenzene, 1 : 4-dihydronaphthalene, and 1 : 4-dihydrophthalic acid) is only slightly accelerated by palladium. In these cases, the heterogeneously catalysed reaction evidently does not compete effectively with the homogeneous one.

Semiquantitative rate measurements on the effects of potential acceptors on the disproportionation of *cyclo*hexene show that the failure of aldehydes and ketones to undergo transfer is not always due to the same cause (cf. Part VI). Benzaldehyde and *m*-nitrobenzaldehyde almost completely inhibit the disproportionation and are evidently adsorbed strongly, whereas mesityl oxide has little effect on the rate of disproportionation and is presumably adsorbed very weakly.

Benzyl chloride was converted into toluene by boiling *cyclo*hexene and palladium, and cinnamyl chloride similarly underwent hydrogenolysis accompanied by reduction of the double bond to give propylbenzene. Benzoyl chloride reacted slowly to give a low yield of benzaldehyde.

EXPERIMENTAL.

Pd refers to palladium black prepared by the method of Wieland (*Ber.*, 1912, **45**, 484). Pd–C refers to 10% palladised charcoal prepared by the method of Linstead and Thomas (*J.*, 1940, 1130).

Benzylideneaniline and cyclo*Hexene.*—Acceptor (2·5 g.), donor (1·3 ml.), Pd (100 mg.), and tetrahydrofuran (50 ml.) were refluxed for 24 hr. The catalyst was filtered off, the solvent evaporated, and the residue extracted with 2N-hydrochloric acid. The extract was made alkaline with sodium hydroxide and extracted with ether. On passage of anhydrous hydrogen chloride into the dried ethereal solution, aniline hydrochloride (0·74 g., 44%), m. p. 196°, was precipitated.

Azobenzene and cyclo*Hexene.*—(*a*) Acceptor (5 g.), donor (2·8 ml.), Pd (100 mg.), and tetrahydrofuran (50 ml.) were refluxed for 15 hr. The product was worked up by Andrews and Lowry's procedure (*J. Amer. Chem. Soc.*, 1934, **56**, 1411), giving hydrazobenzene (converted into benzidine sulphate, 0·25 g., 3%) and aniline hydrochloride (0·25 g., 7%). (*b*) Acceptor (2·5 g.), donor (10 ml.), Pd–C (200 mg.), and ethanol (50 ml.) were refluxed until the solution was colourless (23 hr.). Working up as above gave only aniline hydrochloride (2·47 g., 97%).

Azoxybenzene and cyclo*Hexene.*—Acceptor (2·5 g.), donor (10 ml.), Pd–C (250 mg.), and ethanol (50 ml.) were refluxed for 46 hr. Working up gave aniline hydrochloride (0·38 g., 8%).

2 : *2′-Dimethoxyazoxybenzene and* cyclo*Hexene.*—Carried out exactly as the preceding experiment, this gave *o*-anisidine (2·0 g., 84%), b. p. 59—60°/1 mm., after 4 hours' refluxing.

Benzonitrile and cyclo*Hexene.*—The nitrile (5 g.), *cyclo*hexene (8 ml.), Pd (100 mg.), and tetrahydrofuran (50 ml.) were refluxed for 28 hr. Working up for benzylamine gave less than 10 mg. of hydrochloride.

Aldehydes and Ketones, and cyclo*Hexene.*—The following were recovered unchanged ($\nless$ 90%) when 0·01 mole was refluxed with Pd (50 mg.), *cyclo*hexene (3·3 g.), and tetrahydrofuran (25 ml.) for the periods stated : butyraldehyde (25 hr.), benzaldehyde (23 hr.), crotonaldehyde (91 hr.), cinnamaldehyde (47 hr.), *cyclo*hexanone (92 hr.), benzophenone (65 hr.) and mesityl oxide (42 hr.).

Benzoquinone and cyclo*Hexene.*—(*a*) The quinone (1·3 g.), Pd (50 mg.), *cyclo*hexene (0·5 g.), and tetrahydrofuran (30 ml.) were refluxed for 40 hr. After removal of the catalyst and solvent, the residue was dissolved in hot benzene (15 ml.). On cooling, quinhydrone (0·35 g.), m. p. 170°, separated. (*b*) A similar experiment in which palladium was omitted gave 0·06 g. of quinhydrone after 5 days' refluxing.

Benzil and cyclo*Hexene.*—Benzil (2·1 g.), Pd (50 mg.), *cyclo*hexene (1·64 g.), and tetrahydrofuran (25 ml.) were refluxed for 40 hr. Removal of the catalyst and solvent gave a product, m. p. 73—91°, 0·5 g. of which gave 0·156 g. of cuprous oxide on boiling with Fehling's solution, corresponding to a benzoin content of 45%. The presence of benzoin was confirmed by the formation of the acetate, m. p. and mixed m. p. 81—83°, and the phenylurethane, m. p. and mixed m. p. 166—168°.

Benzoquinone and 1 : 2-*Dihydrobenzene*.—(*a*) The quinone (1·34 g.), 1 : 2-dihydrobenzene (0·5 g., b. p. 82°/752 mm., n_D^{20} 1·4695; prepared by Crossley's method, *J.*, 1904, **85**, 1416), Pd (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 40 hr. The solvent and catalyst were removed, and the dark-green product was crystallised from benzene, giving quinhydrone (0·95 g.), m. p. 168—170°.

(*b*) The above experiment was repeated but without the palladium. The orange product, which consisted largely of the quinone–diene adduct (cf. Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2364), was extracted with *cyclo*hexane and the residue was dissolved in benzene containing some benzoquinone. On cooling, a small amount of quinhydrone (40 mg.) separated.

Benzoquinone and 1 : 4-*Dihydrobenzene*.—(*a*) The quinone (1·34 g.), 1 : 4-dihydrobenzene (0·5 g.; b. p. 86°, n_D^{15} 1·4795; prepared by Wibaut and Haak's method, *Rec. Trav. chim.*, 1948, **67**, 85), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 40 hr. The solid product obtained on evaporation was dissolved in hot benzene; on cooling, quinhydrone (1·0 g.), m. p. 169°, separated. (*b*) A similar experiment, but without palladium, gave 0·9 g. of quinhydrone.

Benzoquinone and 1 : 2-*Dihydronaphthalene*.—(*a*) The quinone (1·67 g.), 1 : 2-dihydronaphthalene (1·0 g.), Pd (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 168 hr. The solid product was extracted with boiling *cyclo*hexane (20 ml.). The residue was quinhydrone (0·63 g.). The *cyclo*hexane solution on partial evaporation yielded benzoquinone (0·35 g.). The remaining solvent was then distilled off and the residue was treated with picric acid in ethanol, giving naphthalene picrate (0·61 g.), m. p. and mixed m. p. 146—148°. (*b*) A similar experiment, but without palladium, gave only 0·1 g. of quinhydrone and no picrate could be obtained from the *cyclo*hexane-soluble residue.

Benzoquinone and 1 : 4-*Dihydronaphthalene*.—The reactions were carried out exactly as with 1 : 2-dihydronaphthalene, except that the time of reflux was 24 hr. (*a*) In the presence of palladium, the products isolated were quinhydrone (0·44 g.), unchanged benzoquinone (0·50 g.), and naphthalene, as the picrate (0·73 g.). (*b*) In the absence of palladium, there were obtained quinhydrone (0·35 g.), benzoquinone (0·62 g.), and naphthalene picrate (0·60 g.).

Benzoquinone and 1 : 4-*Dihydrophthalic Acid*.—(*a*) Benzoquinone (1·3 g.), the acid (1·0 g.; m. p. 145°; prepared according to Alder and Backendorf, *Ber.*, 1938, **71**, 2199), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 120 hr. The catalyst and solvent were removed and the solid products were extracted with boiling benzene. The residue, on crystallisation from water, gave phthalic acid (0·30 g.), m. p. and mixed m. p. 195° (*p*-nitrobenzyl ester, m. p. 155°). The benzene solution was evaporated and the residue partitioned between ether and aqueous sodium hydrogen carbonate. From the ether layer, quinhydrone (0·68 g.) was obtained, while the aqueous layer, on acidification, gave unchanged dihydrophthalic acid (0·20 g.), m. p. 145°. (*b*) A similar experiment, but without palladium, gave phthalic acid (0·28 g.), quinhydrone (0·53 g.), and unchanged dihydrophthalic acid (0·22 g.).

Benzoquinone and 9 : 10-*Dihydroanthracene*.—(*a*) The quinone (1·2 g.), 9 : 10-dihydroanthracene (1·0 g.), m. p. 108°, palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 120 hr. After removal of the catalyst and solvent, the solid product was extracted with boiling *cyclo*hexane and then with water. Treatment of the aqueous solution with charcoal and evaporation gave quinol (0·45 g.), m. p. and mixed m. p. 172°. The water-insoluble residue was crystallised from benzene–ethanol and gave anthracene–benzoquinone adduct (0·13 g.) (cf. Clar, *Ber.*, 1931, **64**, 1684; Bartlett, Ryan, and Cohen, *J. Amer. Chem. Soc.*, 1942, **64**, 2649) (Found : C, 84·1; H, 5·0. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%). (*b*) A similar experiment, without palladium, gave 0·11 g. of quinol and 0·04 g. of adduct.

Benzyl Chloride and cyclo*Hexene*.—The chloride (5·0 g.), *cyclo*hexene (15 ml.), and Pd (100 mg.) were refluxed for 30 hr. with exclusion of moisture. Hydrogen chloride was steadily evolved. On fractionation, a mixture of benzene and toluene was obtained which was treated with boiling 0·25N-sodium carbonate (100 ml.) and potassium permanganate (12 g.). The solution was decolourised with sodium sulphite, filtered, concentrated, acidified, and cooled, giving benzoic acid (2·35 g., 49%), m. p. 123°.

Cinnamyl Chloride and cyclo*Hexene*.—The chloride (2·7 g.), *cyclo*hexene (15 ml.), and Pd (100 mg.) were refluxed for 40 hr. Fractionation of the product gave *n*-propylbenzene (1·0 g., 50%), b. p. 160°, n_D^{19} 1·4920 (von Auwers and Kolligs, *Ber.*, 1922, **55**, 26, give b. p. 159·5°, n_D^{20} 1·4924).

Benzoyl Chloride and cyclo*Hexene.*—The chloride (2 g.), *cyclo*hexene (15 ml.), and Pd (50 mg.) were refluxed for 16 hr. The catalyst was filtered off and the solution heated with methanol for 1 hr. to remove unchanged chloride. The solvents were then removed on the steam-bath and the residual liquid treated with Brady's reagent, giving benzaldehyde 2 : 4-dinitrophenylhydrazone (0·35 g., 10%), m. p. and mixed m. p. 136°. No benzaldehyde was obtained in a similar experiment in which Pd was omitted.

Rate Measurements.—These were carried out by the procedure described in Part VI. The following runs refer to 1M-solutions of *cyclo*hexene in boiling tetrahydrofuran (25 ml.) containing 50 mg. of Pd. *x* is the volume (ml.) of 0·05M-bromine consumed by 1 ml. after *t* hours.

(i) *cyclo*Hexene alone :

t	0	0·5	1	1·5	3	4·5	10
x	19·7	12·8	8·4	6·4	3·2	1·2	0·3

(ii) With mesityl oxide (0·5M) :

t	0	1	5	12	21	50	74	147
x	29·5	19·6	12·2	10·0	9·5	8·9	9·0	8·9

(iii) With benzaldehyde (0·5M) :

t	0	1	3	20	44	68
x	20·0	18·9	18·4	18·2	17·9	16·8

(iv) With *m*-nitrobenzaldehyde (0·5M) :

t	0	1	4	10	22	82
x	19·5	19·8	19·4	19·7	20·0	20·1

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