Hydrogen Transfer. Part VI. Metal-catalysed Transfer-hydrogenation of Ethylenic Compounds.*

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*cyclo*Hexene, and similar hydroaromatic compounds which readily disproportionate at moderate temperatures in the presence of metal catalysts, can be used as hydrogen donors for the reduction of ethylenic and acetylenic bonds in hydrocarbons and carboxylic acids. Thus, stilbene is quantitatively converted into dibenzyl, and maleic acid into succinic acid, on treatment with *cyclo*hexene and palladium in boiling tetrahydrofuran at 65°. The disproportionation of the donors is suppressed by the acceptors to varying extents; in favourable cases, transfer occurs exclusively although it usually proceeds more slowly than does disproportionation in the absence of acceptor. The results can be interpreted in terms of co-adsorption of the donor and acceptor on the catalyst surface.

The first investigation of metal-catalysed hydrogen-transfer under mild conditions was described by Wieland in a classical paper published just over forty years ago (*Ber.*, 1912, **45**, 484). Wieland showed, *inter alia*, that dihydronaphthalene disproportionates rapidly in the presence of colloidal palladium at room temperature to naphthalene and tetralin, and he predicted that dihydrobenzene would undergo an analogous reaction even more readily. This was later confirmed by Zelinski and Pavlov (*Ber.*, 1933, **66**, 1420) who found, moreover, that *cyclo*hexene also disproportionates with ease in the presence of palladium to give *cyclo*hexane and benzene (cf. Corson and Ipatieff, *J. Amer. Chem. Soc.*, 1939, **61**, 1056). By contrast, 9 : 10-dihydroanthracene, the disproportionation of which would involve the loss of benzenoid character in one ring, only undergoes a small amount of dehydrogenation under similar conditions.

Wieland employed equimolar or even larger proportions of palladium in his experiments; he considered the metal to be a reactant rather than a catalyst and represented disproportionation by two distinct steps, dehydrogenation of one molecule with the formation of

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* Part V, preceding paper.

chemisorbed hydrogen, followed by hydrogenation of another molecule. An alternative view is that disproportionation at moderate temperatures is a linked process in which dehydrogenation and hydrogenation take place simultaneously at the catalyst surface, *i.e.*, that disproportionation involves direct hydrogen transfer between identical donors and acceptors. The latter view receives support if the reaction proceeds stoicheiometrically even under conditions favouring the removal of any chemisorbed hydrogen, *e.g.*, when small proportions of metal are used in a boiling solvent. Such is found to be the case in the disproportionation of *cyclo*hexene in tetrahydrofuran, and further evidence on this point is given below. The disproportionation of other hydrobenzenoid compounds under similar conditions normally appears to follow the same course (Linstead, Braude, Mitchell, Wooldridge, and Jackman, *Nature*, 1952, **169**, 100); evolution of hydrogen is observed only at elevated temperatures at which dehydrogenation also takes place with systems which do not disproportionate (cf. Knoevenagel and Bergdolt, *Ber.*, 1903, **36**, 2857; Linstead and his co-workers, *J.*, 1937, 1146; 1940, 1127, 1134, 1139). The postulate of "linked disproportionation" does not exclude the presence of some chemisorbed hydrogen on the catalyst; in fact, unpublished experiments by Dr. K. R. H. Wooldridge and Mr. K. D. E. Whiting on the kinetics of disproportionation of *cyclo*hexene under such conditions have shown that the reaction is accelerated by absorbed hydrogen. Apart from its possible effects on the surface dimensions, the main function of chemisorbed hydrogen may indeed be to act as a link between adsorbed but non-adjacent *cyclo*hexene molecules and to reduce the degree of close approach required for the reaction (Figs. 1 and 2).*

FIG. 1. *Schematic representation of termolecular disproportionation of* cyclo*hexene.*

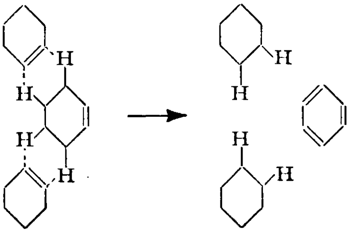
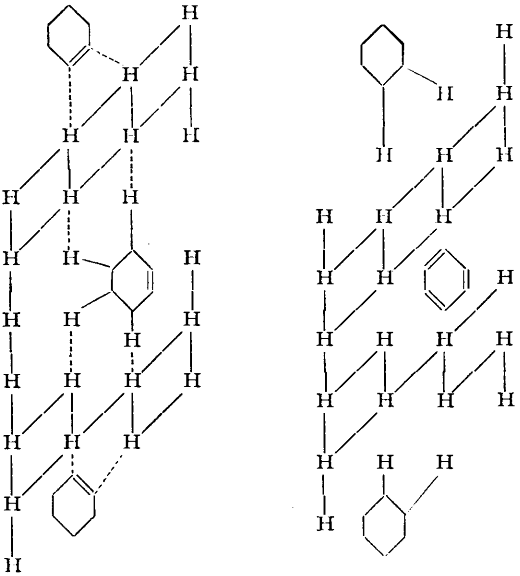


FIG. 2. *Schematic representation of termolecular disproportionation of* cyclo*hexene in presence of chemisorbed hydrogen.*



Another question which arises in the case of *cyclo*hexene is whether disproportionation is bimolecular or termolecular, *i.e.*, whether *cyclo*hexadiene is an intermediate in the formation of benzene or whether four hydrogen atoms are removed simultaneously. Kinetically, there is no objection to a termolecular reaction on a catalyst surface, while energetically it will be favoured owing to the much larger resonance energy of benzene compared with that of *cyclo*hexadiene. The facts that no spectroscopically detectable amount of *cyclo*hexa-1 : 3-diene is formed during the disproportionation of *cyclo*hexene, and that *cyclo*-

* Figures 1, 2, and 3 are only intended to illustrate the topography of the surface reaction, and no account has been taken of the (unknown) conformation of the *cyclo*hexene ring on the catalyst. The stereochemical aspects will be discussed in a later paper, in conjunction with kinetic data.

pentene, *cyclo*heptene, and *cyclo*octene are not disproportionated under similar conditions, are in accord with (though of course they do not prove) the termolecular mechanism for *cyclo*hexene. The simultaneous, rather than stepwise, removal of six hydrogen atoms in the dehydrogenation of *cyclo*hexane has been favoured for similar reasons (Taylor, *J. Amer. Chem. Soc.*, 1938, **60**, 627).

The possibility thus suggests itself of effecting hydrogen transfer between non-identical donors and acceptors without the intervention of molecular hydrogen. Such processes are almost unknown in the field of heterogeneous liquid–solid phase reactions, although they are thought to be of great importance in biological systems. Use has occasionally been made of donors such as tetralin (Akabori and Suzuki, *Proc. Imp. Acad. Japan*, 1929, **5**, 255; Suzuki and Inove, *ibid.*, 1930, **6**, 266; Kinder and Peschke, *Annalen*, 1932, **497**, 193; Orchin, *J. Amer. Chem. Soc.*, 1944, **66**, 535; Ashida, *J. Agric. Chem. Soc. Japan*, 1944, **20**, 621; 1950, **23**, 2311), and *cyclo*hexanol and other alcohols (Armstrong and Hilditch, *Proc. Roy. Soc.*, 1919, *A*, **96**, 322; Belopolski and Maksimov, *Bull. Far East Branch Acad. Sci. U.S.S.R.*, 1936, **17**, 3; *Chem. Abs.*, 1936, **30**, 5939; *Maslovoino Zhirovoe Delo*, 1937, **13**, 13; *Chem. Abs.*, 1937, **31**, 7397; Rush and Dvinyaninkova, *J. Appl. Chem. U.S.S.R.*, 1937, **10**, 702; Puzanov, *ibid.*, 1938, **11**, 670; Dubois, *Compt. rend.*, 1947, **224**, 1234; Kleiderer and Kornfeld, *J. Org. Chem.*, 1948, **13**, 455; Mechelen, *Bull. Soc. chim. Belg.*, 1949, **58**, 247; Akabori and Sataki, *J. Chem. Soc. Japan*, 1949, **70**, 84; Pietra and Traverso, *Gazzetta*, 1951, **81**, 687), for the reduction of various acceptors in the presence of nickel or palladium; and conversely acceptors such as maleic and cinnamic acid (Akabori and Saito, *Proc. Imp. Acad. Japan*, 1930, **6**, 236; *Ber.*, 1930, **63**, 2245; Majima and Marahasi, *Proc. Imp. Acad. Tokyo*, 1934, **10**, 341; Hoshino and Takivra, *Bull. Soc. Chem. Japan*, 1936, **11**, 218; Kotake and Kubota, *Annalen*, 1940, **544**, 253; Elderfield and Maggiolo, *J. Amer. Chem. Soc.*, 1949, **71**, 1906; Culvenor, Goldsworthy, Kirby, and Robinson, *J.*, 1950, 1485; Badcock and Pausacker, *J.*, 1951, 1373; Doering and Rhoads, *J. Amer. Chem. Soc.*, 1953, **75**, 4738), benzene (Adkins and his co-workers, *ibid.*, 1948, **70**, 381; 1949, **71**, 2955; Pines, Olberg and Ipatieff, *ibid.*, p. 533), and acetone (Heer and Miescher, *Helv. Chim. Acta*, 1948, **31**, 1289) have been employed to promote the dehydrogenation of various donors; but most of these reactions undoubtedly take place in two distinct steps since they were generally carried out under conditions under which dehydrogenation of the donors occurs even in the absence of acceptor; the donor merely acts as a convenient source of hydrogen, or the acceptor helps to remove hydrogen from the catalyst. Possible evidence for direct hydrogen transfer was, however, obtained by Wieland (*Ber.*, 1912, **45**,

TABLE 1. *Transfer-hydrogenation of ethylenic compounds with* cyclo*hexene in the presence of palladium.**

Acceptor	Product	Donor (mols.)	Time (hr.)	Yield (%)
Allylbenzene	Propylbenzene	2	120	85
Propenylbenzene	„	2	16	85
Indene	Indane	2	16	<10
„	„	6	528	95
trans-Stilbene	Dibenzyl	2	17	100
Tolan	*cis*-Stilbene	2	17	<10
„	„	12 †	1·5	70
„	Dibenzyl	12 †	23	100
Acenaphthylene	Acenaphthene	20 †	15	100
1 : 1-Diphenylethylene	1 : 1-Diphenylethane	2	43	85
But-3-enoic acid	Butyric acid	1·4	73	90
Crotonic acid	„	2	69	89
Oleic acid	Stearic acid	2	68	10
„	„	20 †	17	40
Sorbic acid	Hexenoic acid	2	70	70
„	Hexanoic acid	20 †	17	90
Cinnamic acid	β-Phenylpropionic acid	2	64	90
Maleic acid	Succinic acid	0·5	80	50
„	„	2	15	100
Muconic acid	Adipic acid	20	30	80

* For details, see Experimental section. All reactions in tetrahydrofuran, except those marked † where no solvent was employed.

2606; 1913, **46**, 3327), who found that the dehydrogenation of glucose by palladium black was accelerated by benzoquinone or methylene-blue, and, while the present work was in progress, Bergmann and Eschinazi (*J. Amer. Chem. Soc.*, 1950, **72**, 5651) reported that mesityl oxide can be converted into isobutyl methyl ketone in 88% yield by menth-8-ene in the presence of a palladium–barium sulphate catalyst, whereas in the absence of the ketone rapid disproportionation to menthane and cymene takes place. Even in this case, however, the reaction was carried out at a temperature (140°) at which considerable dehydrogenation of the donor is observed.

In view of its ready disproportionation and availability, *cyclo*hexene is an obvious choice as a donor for metal-catalysed hydrogen-transfer reactions. We find that a wide range of ethylenic hydrocarbons and ethylenic acids undergo transfer-hydrogenation in high yields when heated with *cyclo*hexene at its boiling point or at that of a suitable solvent such as tetrahydrofuran, and a palladium catalyst (Table 1). As would be expected, benzenoid groups are not reduced and no transfer is observed with naphthalene, anthracene, or phenanthrene, whereas acenaphthylene is converted into acenaphthene. One acetylenic acceptor, tolan, has also been examined; as in catalytic hydrogenation with molecular hydrogen (Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77), *cis*-stilbene is the first product. Further reduction gives dibenzyl, the second stage being slower than the first.

The transfer-hydrogenation of ethylenic and acetylenic compounds thus exhibits the same kind of specificity as catalytic hydrogenation with molecular hydrogen and it offers no important practical advantage with this type of acceptor, except that no special apparatus is required. Palladium black or other forms of palladium catalyst can be used, but Raney nickel is ineffective, although it catalyses the disproportionation of *cyclo*hexene (Corson and Ipatieff, *loc. cit.*). The *cyclo*hexadienes or 1 : 4-dihydronaphthalene can replace *cyclo*hexene as a donor; with maleic acid as the acceptor, the reaction times required are of the same order.

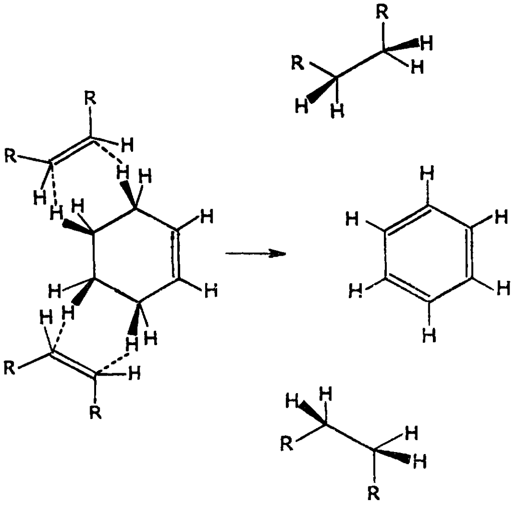


FIG. 3. *Schematic representation of hydrogen transfer between* cyclo*hexene and ethylenic acceptors.*

The stoicheiometry of the above reactions has not been examined in detail, but at least with one acceptor (maleic acid) 4 hydrogen atoms per *cyclo*hexene molecule and 2 hydrogen atoms per *cyclo*hexadiene or dihydronaphthalene molecule are available for transfer. In most cases, 2 molar proportions of *cyclo*hexene were employed, while in a few instances a large excess of *cyclo*hexene was necessary to effect appreciable reduction. These results are in accord with a picture of disproportionation and transfer as competing reactions on the catalyst surface. An important requisite for transfer will be co-adsorption of the donor and the acceptor. In a favourable case, these will be interspersed in the appropriate ratio, so that donor and acceptor molecules, but not two donor molecules, occupy adjacent positions and transfer will be facilitated, while disproportionation will be almost completely suppressed (Fig. 3). In less favourable cases where the acceptor is adsorbed much more strongly than the donor, the acceptor will act as a " poison " and effective co-adsorption only takes place if the donor is present in excess. Rate measurements in which the disappearance of *cyclo*hexene was followed quantitatively confirm (Table 2) that acceptors invariably decrease the rate of disproportionation and that transfer occurs more slowly than disproportionation in the absence of an acceptor. Moreover, of the acceptors listed in Table 1, those (*e.g.*, acenaphthylene) which require a large excess of *cyclo*hexene have a much more marked retarding effect on disproportionation than those (*e.g.*, maleic acid) which undergo stoicheiometric transfer. Although a more detailed analysis must await direct measurement of adsorption, it appears that adsorption decreases in the sequence acenaphthylene>cinnamic acid>maleic acid>fumaric acid.

An interesting observation was made in the case of maleic acid. Although the catalyst, after being washed, was found to retain its activity, and although neither of the major products of the transfer reaction, *i.e.*, succinic acid and benzene, were inhibitors, yet the crude solid product completely inhibited the disproportionation of *cyclo*hexene. This effect was also produced by maleic anhydride, which does not undergo transfer, and the product-poisoning found in the transfer reaction with maleic acid is probably to be ascribed to formation of a small amount of maleic anhydride by dehydration. It is significant that the Diels–Alder adduct of maleic anhydride and *cyclo*hexa-1 : 3-diene, which might be expected to be formed at least in traces if the diene were an intermediate in disproportionation, does not show an inhibiting effect.

TABLE 2. *Effects of acceptors and non-acceptors on disproportionation of* cyclo*hexene. Initial first-order rate constants under comparable conditions.**

Acceptor	k (hr.$^{-1}$)	Acceptor	k (hr.$^{-1}$)	Non-acceptor	k (hr.$^{-1}$)
None	0·85	Cinnamic acid	0·08	None	0·85
Maleic acid	0·35	Acenaphthylene	0·02	Succinic acid	0·85
Fumaric acid	0·50			Maleic anhydride	<0·001
				Benzene	0·7

* See Experimental section.

EXPERIMENTAL

Disproportionations.—cyclo*Hexene.* Commercial *cyclo*hexene was purified by refluxing over sodium, followed by fractionation, and had b. p. 82·5°/755 mm., n_D^{21} 1·4460. When *cyclo*hexene (10 ml.) was warmed with palladium black (100 mg.; prepared by Wieland's method, *Ber.*, 1912, **45**, 484) an exothermic reaction occurred and the liquid boiled vigorously for a few minutes without further heating. After 3 hours' refluxing, less than 0·3% of *cyclo*hexene remained, as shown by titration with bromine, and the liquid had n_D^{20} 1·4462, $\lambda_{max.}$ 2550 Å, $E^{1\%}_{1\,cm.}$ 9·0 (in EtOH), while a synthetic mixture of benzene (1 mol.) and *cyclo*hexane (2 mol.) had n_D^{20} 1·4490, $\lambda_{max.}$ 2550 Å, $E^{1\%}_{1\,cm.}$ 9·0. Treatment with chlorosulphonic acid gave benzenesulphonamide, m. p. 151°, in similar yields (49 and 52%, respectively) from the disproportionation product and the synthetic mixture. The unchanged residue was *cyclo*hexane, b. p. 80·5°/760 mm., n_D^{18} 1·4270. An identical result was obtained on carrying out the disproportionation in tetrahydrofuran.

1 : 4-*Dihydronaphthalene.*—1 : 4-Dihydronaphthalene (5 g.; m. p. 26°; prepared and purified according to Bamberger, *Ber.*, 1887, **20**, 3075, and Sand and Genssler, *Ber.*, 1903, **36**, 3705), palladium (100 mg.), and tetrahydrofuran (25 ml.) were heated under reflux for 40 hr. The solvent was removed through a column, and the residue treated with picric acid in ethanol, giving naphthalene picrate (5·3 g.), which was filtered off. The filtrate was diluted with water and extracted with chloroform. The extract was washed with sodium hydrogen carbonate and water, dried, and evaporated, giving tetralin (1·4 g.), b. p. 102°/20 mm., n_D^{21} 1·5433, identified as the sulphonamide, m. p. and mixed m. p. 135°.

1 : 2-*Dihydronaphthalene.* 1 : 2-Dihydronaphthalene (5 g.; m. p. −11°, n_D^{18} 1·5768; prepared by Strauss and Lemmel's method, *Ber.*, 1921, **54**, 25), palladium (0·1 g.), and tetrahydrofuran (25 ml.) were heated under reflux for 40 hr. Working up as above gave naphthalene picrate (6·7 g.) and tetralin (1·9 g.).

Transfer-hydrogenations with cyclo*Hexene.*—*Maleic acid.* (*a*) The acid (1·16 g.), *cyclo*hexene (1·64 g.), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 15 hr. After being filtered, the solution was evaporated, giving succinic acid (1·1 g.), m. p. and mixed m. p. 185—187°.

(*b*) A similar experiment with reflux for only 1 hr. gave, after oxidation with potassium permanganate in sulphuric acid, 0·5 g. (40%) of succinic acid.

(*c*) A similar experiment with 0·41 g. of *cyclo*hexene gave 0·63 g. (52%) of succinic acid after 80 hours' reflux.

(*d*) A similar experiment in which palladium was replaced by Raney nickel gave 0·05 g. (4%) of succinic acid after 72 hours' refluxing.

Crotonic acid. The acid (1·7 g.), *cyclo*hexene (3·3 g.), palladium black (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 69 hr. The product was an oil (1·7 g.), b. p. 160—170°, n_{D}^{23} 1·4050, which contained 11% of crotonic acid as indicated by titration with potassium permanganate, and gave butyranilide, m. p. and mixed m. p. 95°.

But-3-enoic acid. The acid (3·4 g.), *cyclo*hexene (5 g.), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 73 hr. Fractionation gave butyric acid (3·1 g.), b. p. 61—63°/12 mm., n_{D}^{22} 1·4002 (anilide, m. p. 96°).

Oleic acid. (*a*) The acid (2·8 g.), *cyclo*hexene (1·6 g.), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 68 hr. Removal of the catalyst and solvent gave a product (2·8 g.) of m. p. 39—41°, corresponding to a 9 : 1 mixture of oleic and stearic acid (Smith, *J.*, 1939, 975). This composition was confirmed by titration with bromine in chloroform.

(*b*) The acid (2·8 g.), *cyclo*hexene (25 ml.), and palladium (100 mg.) were refluxed for 17 hr. Removal of catalyst and distillation gave a product, m. p. 50—52°. This corresponds to a 7 : 3 mixture of oleic and stearic acid (Smith, *loc. cit.*), whereas bromine titration indicated a 60% content of oleic acid. Bromine titration of this distillate showed only *ca.* 2% of unchanged *cyclo*hexene.

Cinnamic acid. The acid (1·5 g.), palladium (50 mg.), *cyclo*hexene (1·6 g.), and tetrahydrofuran (25 ml.) were refluxed for 64 hr. Removal of the solvent and catalyst gave 1·4 g. of product, m. p. 43—44°, raised by one crystallisation from light petroleum (b. p. 40—60°) to 48°, the m. p. of pure β-phenylpropionic acid.

Sorbic acid. (*a*) The acid (1·1 g.), *cyclo*hexene (1·6 g.), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 70 hr. The product was an oil, n_{D}^{23} 1·4320, which contained less than 1% of sorbic acid, as shown by its ultra-violet light absorption ($E_{1\,\text{cm.}}^{1\%}$ 4·5 at 2580 Å); it consumed potassium permanganate corresponding to 0·7 ethylenic bond per mol., giving a 10% yield of succinic acid, and evidently consisted of a mixture of hexenoic and hexanoic acids.

(*b*) Sorbic acid (1·65 g.), palladium (100 mg.), and *cyclo*hexene (25 ml.) were refluxed for 17 hr., giving hexanoic acid (1·5 g.), n_{D}^{20} 1·4166 (anilide, m. p. 91—92°).

Muconic acid (with J. F. SMITH). *cis* : *cis*-Muconic acid (0·5 g.), palladium (25 mg.), *cyclo*hexene (10 ml.), and tetrahydrofuran (15 ml.) were refluxed for 30 hr. Removal of the catalyst and solvent, followed by one recrystallisation of the residue from water, gave adipic acid (0·4 g.), m. p. and mixed m. p. 150°.

Allylbenzene. Allylbenzene (3·4 g.), palladium (50 mg.), *cyclo*hexene (3·3 g.), and tetrahydrofuran (25 ml.) were refluxed for 120 hr. Removal of the catalyst and fractionation gave propylbenzene (2·9 g.), b. p. 53—54°/18 mm., n_{D}^{21} 1·4910 (sulphonamide, m. p. 108—109°).

Propenylbenzene. Propenylbenzene (2·4 g.; b. p. 180°/747 mm., $\lambda_{\text{max.}}$ 2480 Å, ε 16,000 in EtOH), palladium (50 mg.), *cyclo*hexene (3·3 g.), and tetrahydrofuran (25 ml.) were refluxed for 16 hr. Removal of the catalyst and fractionation afforded *n*-propylbenzene (2·1 g.), b. p. 81—82°/50 mm., n_{D}^{20} 1·4915, ε 80 at 2480 Å (sulphonamide, m. p. 109—110°).

1 : 1-*Diphenylethylene.* 1 : 1-Diphenylethylene (3·6 g.; b. p. 115—116°/3 mm., n_{D}^{11} 1·6131), palladium (50 mg.), *cyclo*hexene (3·3 g.), and tetrahydrofuran (25 ml.) were refluxed for 43 hr. Removal of the solvent and catalyst, and fractionation, gave 1 : 1-diphenylethane (3·0 g.), b. p. 136—138°/12 mm., n_{D}^{14} 1·5780.

Stilbene. trans-Stilbene (0·9 g.), palladium (50 mg.), *cyclo*hexene (0·8 g.), and tetrahydrofuran (25 ml.) were refluxed for 17 hr. Removal of the catalyst and solvent gave dibenzyl (0·9 g.), m. p. and mixed m. p. 51°.

Tolan. (*a*) Tolan (0·9 g.; m. p. 61—62°) was subjected to the conditions of the preceding experiment. Mainly unchanged material (0·7 g.; m. p. 58—63°) was obtained.

(*b*) Tolan (2·0 g.), palladium (50 mg.), and *cyclo*hexene (15 ml.) were refluxed together, the progress of the reaction being followed by evaporating aliquots of the solution. After 23 hr., the products were homogeneous and removal of solvent and catalyst gave pure dibenzyl (2·0 g.), m. p. 51°.

(*c*) The above experiment was repeated, except that the reaction was interrupted after 1½ hr., the products being then completely liquid at room temperature. Distillation gave *cis*-stilbene (1·4 g.) b. p. 101—102°/1 mm., n_{D}^{22} 1·6195, which formed (±)-2 : 3-dibromo-1 : 4-diphenylbutane, m. p. 110—111°, on treatment with bromine in ether (cf. Buckles, *J. Amer. Chem. Soc.*, 1949, **71**, 1157).

Indene. (*a*) Indene (2·3 g.; b. p. 68°/15 mm., n_{D}^{22} 1·5746; freshly generated from the picrate), palladium (50 mg.), *cyclo*hexene (1·6 g.), and tetrahydrofuran (25 ml.) were refluxed for 16 hr. Removal of the catalyst and fractionation gave unchanged indene (2·0 g.).

(*b*) The above experiment was repeated, but with 4·9 g. of *cyclo*hexene and refluxing for 528 hr. The product (2·2 g.), b. p. 59—60°/12 mm., n_D^{18} 1·5312, showed no rapid reaction with bromine in chloroform and was almost pure indane, which formed a sulphonamide, m. p. 134—135°.

Acenaphthylene. Acenaphthylene (1·0 g.; m. p. 85°), palladium (50 mg.), and *cyclo*hexene (15 ml.) were refluxed for 15 hr., after which the solution was colourless. Removal of the catalyst and solvent gave acenaphthene (1·0 g.), m. p. 94—95° (picrate, m. p. and mixed m. p. 161°).

No transfer took place in a similar experiment in which palladium was omitted.

Naphthalene. Naphthalene was recovered unchanged after 1 g. had been refluxed with palladium (50 mg.) and *cyclo*hexene (25 ml.) for 90 hr. No evidence of transfer was also obtained with anthracene, phenanthrene, or fluoranthene under similar conditions.

Transfer-hydrogenations with Other Donors.—Maleic acid and cyclo*hexa*-1 : 3-*diene.* The acid (1 g.), the diene (1 g.), palladium (50 mg.), and tetrahydrofuran (25 ml.) were refluxed for 75 hr. Removal of the catalyst and solvent, and crystallisation of the residue from water, gave fumaric acid, m. p. >280°. The aqueous solution was oxidised with potassium permanganate and sulphuric acid, giving succinic acid (0·6 g.), m. p. and mixed m. p. 185°.

Maleic acid and 1 : 4-*dihydronaphthalene.* The acid (4·5 g.), 1 : 4-dihydronaphthalene (5·0 g.), palladium (0·1 g.), and tetrahydrofuran (25 ml.) were refluxed for 46 hr. The catalyst was filtered off, and the solution was diluted with ether (50 ml.) and extracted with 10% aqueous sodium hydroxide (33 ml.). The alkaline extract was acidified and extracted with ether, the ether was evaporated, and the product (3·5 g.) was oxidised as above, giving succinic acid (1·6 g.), m. p. 185—186°.

Rate Measurements.—General procedure. The solutions of the reactants in tetrahydrofuran were refluxed (b. p. *ca.* 65°) with the palladium-black catalyst in a closed reaction vessel. The rate of disappearance of *cyclo*hexene was determined by withdrawing 1-ml. samples at appropriate intervals, adding excess of bromine in carbon tetrachloride, and back-titrating the solution with aqueous sodium thiosulphate. With any one batch of catalyst, the results, only a selection of which are recorded in detail below, were reasonably consistent, considering the difficulty of exactly reproducing conditions in such a system. A number of runs were also carried out in which the *cyclo*hexene content was estimated by quantitative hydrogenation; the results are in good agreement but the method is less convenient. A third procedure consists of estimating the benzene formed by ultra-violet spectrometry; this will be described later.

Disproportionation of cyclo*hexene.* Under the conditions used, the order of the reaction with respect to *cyclo*hexene varied between 1 and 2, but for convenient comparison the results are expressed as first-order rate constants. The rate constants were approximately proportional to the amount of catalyst. The following runs refer to M-solutions of *cyclo*hexene in boiling tetrahydrofuran (25 ml.) at *ca.* 65° with (i) 10 mg., (ii) 25 mg., (iii) 40 mg., and (iv) 50 mg. of palladium. x is the volume (ml.) of 0·232M-bromine consumed by 1 ml. after t min.

(i) t	0	12	23	29	35	41	49	58	100	1400
x	4·20	3·74	3·32	3·08	2·90	2·71	2·57	2·36	1·88	0·66
10^2k_1 (min.$^{-1}$)	—	0·9	1·0	1·0	1·0	1·0	1·0	1·0	1·8	—

(ii) t	0	11	19	26	36	45	58	73	196
x	3·90	3·13	2·52	2·06	1·64	1·38	1·15	0·94	0·38
10^2k_1 (min.$^{-1}$)	—	1·9	2·2	2·4	2·4	2·3	2·1	1·9	—

(iii) t	0	8	16	22	28	35	41	53	360
x	4·20	3·07	2·21	1·73	1·39	1·17	1·00	0·80	0·29
10^2k_1 (min.$^{-1}$)	—	4·0	4·1	4·0	3·9	3·7	3·5	3·1	—

(iv) t	0	10	17	23	30	37	44	56	156
x	4·30	2·54	1·88	1·51	1·21	0·98	0·82	0·60	0·16
10^2k_1 (min.$^{-1}$)	—	5·3	4·9	4·7	4·3	4·0	3·8	3·5	—

Effects of acceptors. The following runs were carried out with solutions M with respect to *cyclo*hexene and 0·5M with respect to acceptor in boiling tetrahydrofuran (25 ml.) containing 50 mg. of palladium. x is the volume (ml.) of 0·05M-bromine consumed by 1 ml. after t hours.

(i) No acceptor:

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
k_1 (hr.$^{-1}$)	—	0·87	0·85	0·76	0·61	0·62	—

(ii) With maleic acid :

t	0	0·5	1	3	6	23
x	20·0	16·7	14·1	13·1	12·7	11·4
k_1 (hr.$^{-1}$)	—	0·35	0·35	0·14	0·075	0·023

The catalyst from this run, after being washed with tetrahydrofuran, still caused disproportionation of *cyclo*hexene, at about one-third of the rate of (i). The solid product obtained from (ii) by evaporation of the solvent almost completely arrested the disproportionation of a fresh solution of *cyclo*hexene in the presence of fresh catalyst.

(iii) With fumaric acid :

t	0	1	2	3	17	40
x	20·0	12·5	6·8	4·2	0·5	0·1
k_1 (hr.$^{-1}$)	—	0·47	0·54	0·52	0·20	—

(iv) With cinnamic acid :

t	0	0·5	5	10	28
x	19·7	19·0	14·3	10·1	0·6
k_1 (hr.$^{-1}$)	—	0·078	0·062	0·067	—

(v) With acenaphthylene :

t	0	2	4	20	45	69	117
x	29·5	28·5	28·3	28·0	26·5	24·4	20·8
k_1 (hr.$^{-1}$)	—	0·024	0·017	0·0042	0·0037	0·0043	0·0049

Effects of non-acceptors. The following runs were carried out under the same conditions as the foregoing series.

(i) With succinic acid :

t	0	0·5	1	3	21
x	20·1	13·2	8·5	3·2	0·3
k_1 (hr.$^{-1}$)	—	0·85	0·86	0·61	—

(ii) With benzene :

t	0	1	2	3	5	16
x	19·9	10·0	5·8	4·1	2·0	0·4
k_1 (hr.$^{-1}$)	—	0·69	0·62	0·72	0·46	—

(iii) With maleic anhydride :

t	0	1	2	6	10	19
x	19·9	19·8	19·9	19·8	19·8	19·8
k_1 (hr.$^{-1}$)	—	$<$0·001				—

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