## 1138. *Mechanisms of Hydrogenation. Part III.* Geometrical and Electronic Factors and the Role of the Solvent.*

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The influence of substituent groups R and R′ on the hydrogenation of a series of acetylenes RC≡CR′ indicates an absorbed state in which these substituents are projected away from the catalyst surface. The effect on the hydrogenation of butynediol, butenediol, and mesityl oxide of a series of competitors for the catalyst surface implies a close parallel between the bonding in chemisorption and in metal complexes in which these competitor substances act as co-ordinating ligands. The importance of polar forces in the neighbourhood of the catalyst surface is illustrated by the effect of the solvent, and of ions, on the proportions of 5α- and 5β-steroid ketone obtained on hydrogenation of some 3-oxo-$\Delta^{4,5}$-steroids. An ion-exchange resin used as a catalyst support influences the stereoselectivity of the catalyst through the nature of the charged centres of the resin surface.



In catalytic hydrogenation steric hindrance is a well-recognised [1] limiting factor associated with difficulty of absorption of the substance that is reduced. The exact nature of the chemisorptive bond is uncertain. The more important substrates and inhibitors in hydrogenation are, however, of a chemical type, which suggests a parallel between chemisorption and transition-metal complex formation. In metal-olefin complexes such as $(C_2H_4PtCl_2)_2$ the olefinic ligand is considered [2a] to retain the double bond, and consequently its molecular geometry, relatively unaltered. Similarly the acetylenic group is thought to be present with only minor molecular alteration [2b] in complexes such as $(RC{\equiv}CR)PtCl_2(C_5H_5N)$ [R = $Me_2C(OH)$], although in other series, *e.g.*, $(ArC{\equiv}CAr)Pt(PAr_3)_2$, the acetylene is combined as a *cis*-ethylenic group.[3]

A chemisorbed molecule may engage more than one " surface site " or atom. Also many transition-metal complexes are derived from a more highly oxidised state of the metal. Despite the parallels, therefore, a chemisorbed olefin or acetylene may differ in bonding and in molecular geometry from a similar constituent in a metal complex. In pursuing the analogy, we were, however, led to examine the effect on the hydrogenation of a series of acetylenes (I), and *cis*-olefins (II) of substituent groups, R and R′, of increasing size. In particular, if the chemisorbed acetylene were to retain the linear geometry of the unabsorbed molecule, large substituent groups should hinder hydrogenation.

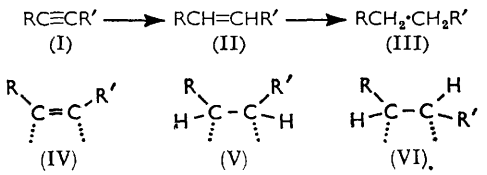



Fig. 1 shows the initial rates of hydrogenation for these substances in standardised conditions [4] at palladised-charcoal in alcohol. The rates depended on the initial acetylene concentration and on the amount of catalyst (Table 1); the results may therefore be taken to refer to processes other than some rate-limiting hydrogen diffusion. By contrast with their marked hindering effect on hydrogenation of the olefins, the relatively slight influence

* Part II, *J.*, 1959, 3169.

[1] Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985; Fieser, *Experientia*, 1950, **6**, 313; Loewenthal, *Tetrahedron*, 1959, **6**, 269.

[2] (*a*) Chatt and Duncanson, *J.*, 1953, 2939; Powell and Sheppard, *J.*, 1960, 2519; Adams and Chatt, *J.*, 1962, 2821; (*b*) Chatt, Guy, and Duncanson, *J.*, 1961, 827.

[3] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.

[4] Cf. McQuillin and Ord, *J.*, 1959, (*a*) 2902, (*b*) 3169.

TABLE 1.

Rates (given in c.c. per min. per mg. of catalyst in the hydrogenations: $RC{\equiv}CR\ (I) \longrightarrow RCH{:}CHR\ (II) \longrightarrow RCH_2{\cdot}CH_2R\ (III)$, in ethyl alcohol.

(a) *Effect of concn.*

| R | Concn. ($10^{-2}$M) | Reaction (I) ⟶ (II) | Reaction (II) ⟶ (III) | Concn. ($10^{-2}$M) | Reaction (I) ⟶ (II) | Reaction (II) ⟶ (III) |
|---|---|---|---|---|---|---|
| $CH_2{\cdot}OH$ ... | 4·3 | 0·42 | 0·48 | 17·2 | 0·34 | 0·67 |
| $CHMe{\cdot}OH$ | 3·7 | 0·40 | 0·28 | 14·1 | 0·64 | 0·43 |
| $CMe_2{\cdot}OH$... | 3·1 | 0·45 | 0·12 | 13·6 | 0·62 | 0·22 |

(*b*) R = $CMe_2{\cdot}OH$. Effect of amount of catalyst (in alcohol, 30 c.c.) (concn. 0·03M).

| Catalyst (mg.) ..... | 4 | 8·4 | 14·9 | 21·0 | 37·8 |
|---|---|---|---|---|---|
| Reaction (I) ⟶ (II) ..... | 0·4 | 0·4 | 0·35 | 0·35 | 0·4 |
| Reaction (II) ⟶ (III) ..... | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 |

of larger substituents R and R′ in the case of the acetylenes offers *prima facie* evidence that in the chemisorbed state of the acetylenes the groups R and R′ project away from the catalyst surface.[1]

Some " bending back " of the substituents attached to the acetylenic ligand has been envisaged in alkyne–$Pt^{II}$ complexes.[2b,5] Deformation of a chemisorbed acetylene towards

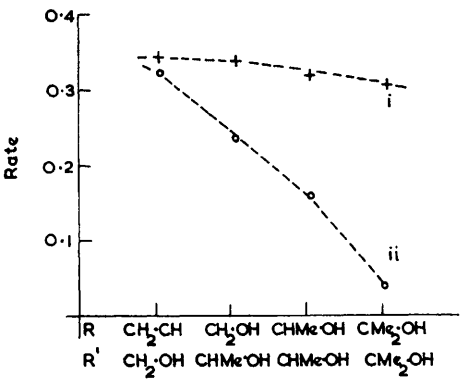



FIG. 1. Rates of hydrogenation (c.c. per min. per mg. of palladised charcoal) of $RC{:}CR'$ (i) ⟶ $RCH{:}CHR'$ (ii) ⟶ $RCH_2{\cdot}CH_2R'$ ($5{\cdot}9 \times 10^{-2}$M) in alcohol.

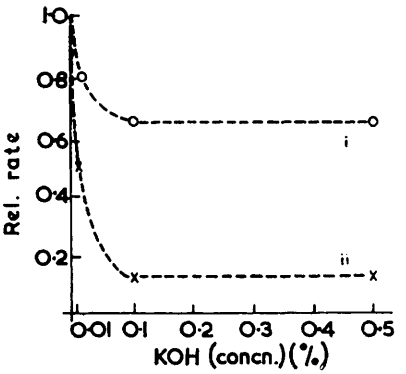



FIG. 2. Rates of hydrogenation of (i) mesityl oxide ($4{\cdot}3 \times 10^{-2}$M) and (ii) butyne-1,4-diol ($5{\cdot}7 \times 10^{-2}$M) in alcoholic potassium hydroxide at palladised charcoal, relative to the rate in alcohol.

the geometry of a *cis*-olefinic residue, as in (IV), will reduce the compression between the substituent groups and the catalyst " surface," but will at the same time greatly increase the mutual compression between these substituents. For a *cis*- or *trans*-olefin, however, absorbed as in (V) or (VI), the substituent groups remain close to the catalyst surface. If interaction of substituent groups with the " surface " may be associated with kinetic difficulty in absorption, and increased mutual compression between the substituents with reduced heat of absorption, the results of Fig. 1 are understandable. In the case of an acetylene, kinetic difficulty to absorption arising from the bulk of the substituents will be compensated by an increased reactivity owing to the consequent reduced heat of absorption. A closely similar effect of substituents is noted [6] for $Ag^+$–olefin and –acetylene complexes.

The olefinic intermediates formed in these experiments were the *cis*-isomers; the results do not, therefore, appear to be due to any large change in isomeric composition of the olefin as R and R′ are varied.

[5] Orgel, " An Introduction to Transition Metal Chemistry," Methuen, London, 1960, p. 153.
[6] Muhs and Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697.

In a number of examples,[7] an olefinic group $>C{:}C{\cdot}CH_2-$ in a molecular environment which renders it sterically resistant to hydrogenation becomes reducible when converted into the conjugated ketone derivative $>C{:}C{\cdot}CO$. The keto-group appears, therefore, to assist absorption or to provide an alternative route of reaction. Certain platinum(II) complexes of styrene [8] and phenylacetylene [3] are reported to be stabilised by electron-withdrawing substituent groups in the aromatic ring. Experimental evidence, however, indicates that mesityl oxide, for example, is less strongly absorbed than an olefin such as cyclohexene.[9] To determine how far hydrogenation may be influenced by electronic factors and to obtain more direct evidence regarding the behaviour of the groups, $-C{\equiv}C-$, $>C{=}C<$, $>C{=}C{\cdot}CO$, we examined hydrogenation of these groups in the presence of competitors. In Table 2 these results are set out as initial rates of hydrogenation in the presence of the competitor substances, expressed as a fraction of the normal rate, *i.e.*, in the absence of the competitor, the concentration and the amount of catalyst being the same. The competitors were chosen to include typical metal-complex-forming ligands.

Certain of the results in Table 2 are supported by the literature. Hydrogenation in presence of nitrogenous bases was formerly a recognised means of semihydrogenation of acetylenes.[10] Pyridine and 2,2′-bipyridyl have been observed to retard hydrogenation of crotonic acid at nickel.[11] Hydrogenation of $\Delta^{5,6}$-steroids, towards which acids generally act catalytically, is apparently not assisted by hydriodic acid.[12] The relatively greater retardation, by alkali, of hydrogenation of an olefinic bond in comparison with a carbonyl-conjugated olefin is paralleled for a variety of instances, and at nickel,[13] platinum,[14] and palladium catalysts.[15] For our examples we have examined also the influence of alkali concentration (cf. Fig. 2).

The order of effectiveness of the competitors in Table 2, *viz.*, $Ph_3P$, $(PhO)_3P$ > amines, and $I^- > Br^- > Cl^-$, is significant as being also the relative order of affinities of these as

TABLE 2.

Fractional rates of hydrogenation at palladised charcoal in alcohol in presence of competitors.

| Competitor ($10^{-2}$M) | Substrate ($5 \times 10^{-2}$M) Butynediol * | Butenediol * | Mesityl oxide * | Competitor ($10^{-2}$M) | Substrate ($5 \times 10^{-2}$M) Butynediol * | Butenediol * | Mesityl oxide * |
|---|---|---|---|---|---|---|---|
| Diphenylamine ..... | 1·0 | 0·8 | 0·36 | Calcium chloride ..... | 0·95 | 0·97 | 1·0 |
| Ethanolamine ..... | 1·1 | 0·4 | 0·33 | Lithium bromide ..... | 0·7 | 0·8 | 0·6 |
| Pyridine ..... | 1·2 | 0·36 | 0·36 | Sodium iodide ..... | 0·12 | 0·04 | 0·02 |
| Ethylenediamine ..... | 0·9 | 0·25 | 0·35 | Potassium cyanide †... | (0·08) | (0·14) | (0·04) |
| 8-Hydroxyquinoline ... | 1·06 | 0·23 | 0·03 | Potassium acetate ... | 0·75 | 0·48 | 0·8 |
| 2,2′-Bipyridyl..... | 1·1 | 0·13 | 0·015 | Potassium hydroxide | 0·15 | 0·13 | 0·65 |
| Triphenyl phosphite ... | 0·2 | 0·03 | Nil | Sodium salicylate ..... | 1·0 | 0·97 | 0·8 |
| Triphenylphosphine ... | 0·1 | 0·04 | Nil | | | | |

* Standard rates: butynediol 0·33, butenediol 0·33, mesityl oxide 0·22 c.c. per min. per mg. of catalyst. The rate of hydrogenation of mesityl oxide increased with increasing concentration, *viz.*, $5 \times 10^{-2}$M 0·22, $15 \times 10^{-2}$M 0·24. † $2 \times 10^{-3}$M.

[7] Doree, McGhie, and Kurzer, *J.*, 1948, 988; Djerassi, Fricke, Rosenkranz, and Sondheimer, *J. Amer. Chem. Soc.*, 1953, **75**, 3496; Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921.

[8] Joy and Orchin, *J. Amer. Chem. Soc.*, 1959, **81**, 305.

[9] Braude, Linstead, Mitchell, and Wooldridge, *J.*, 1954, 3595.

[10] Ruzicka and Muller, *Helv. Chim. Acta*, 1939, **22**, 755; Isler, Huber, Ronco, and Kofler, *ibid.*, 1947, **30**, 1911; Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 2028; Oroshnik, Karmas, and Mebane, *J. Amer. Chem. Soc.*, 1952, **74**, 295.

[11] Badger, Jackson, and Sasse, *J.*, 1960, 4438.

[12] Lewis and Shoppee, *J.*, 1955, 1365.

[13] Butenandt and Schmidt-Thome, *Ber.*, 1938, **71**, 1487; 1939, **72**, 182.

[14] Anliker, Heusser, and Jeger, *Helv. Chim. Acta*, 1952, **35**, 838.

[15] Wieland, Ueberwasser, Anner, and Miescher, *Helv. Chim. Acta*, 1953, **36**, 1231; Zalkow, Markley, and Djerassi, *J. Amer. Chem. Soc.*, 1959, **81**, 2914.

ligands for the group of transition metals known as class (b) acceptors,[16] to which palladium belongs. Metals of this group generally form olefin complexes and are characterised by *d*-orbital electrons available for dative π-bonding The observed parallel offers *prima facie* grounds for regarding the bonding in chemisorption and in metal-complex formation in the same light. The marked competitor influence of cyanide ion, and the effectiveness of the chelating agents, 2,2′-bipyridyl and 8-hydroxyquinoline, by contrast with sodium salicylate, accord with this conclusion.

The effect of the competitor substances on the rate of hydrogenation may be derived by competitive displacement from the catalyst of absorbed molecules of the substance under hydrogenation, and of the solvent, or perhaps from alteration of the surface potential, *e.g.*, by establishment of a surface layer of different polarity.

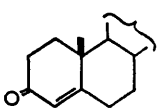
The order of increasing inhibitions by competitors, *e.g.*, butynediol < butenediol < mesityl oxide, is the reverse of the probable order of strengths of absorption, *i.e.*, is consistent with competitive displacement. The relative effectiveness of the competitors, however, is somewhat different for the different substances being hydrogenated, *e.g.*, for butynediol: amines < bipyridyl < $Br^-$ < $HO^-$; for butenediol: $Br^-$ < amines < $HO^-$, < bipyridyl; for mesityl oxide: $Br^-$ < $HO^-$ < amines < bipyridyl. These differences which point to the operation of factors other than simple competition for " surface sites " led us to consider the general role of ions or polar molecules, and of the solvent which, by setting up a surface layer, may influence the polarity of the medium within which absorption and hydrogenation take place.

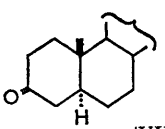
TABLE 3.

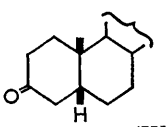
Influence of the solvent on the proportions of 5α- and 5β-product in the hydrogenation of 3-oxo-$\Delta^{4,5}$-steroids.

| Solvent | Ratio 5β/5α-product from cholestenone | Ratio 5β/5α-product from testosterone | Solvent | Ratio 5β/5α-product from cholestenone | Ratio 5β/5α-product from testosterone |
|---|---|---|---|---|---|
| Methanolic KOH, 1% | 10 | 3·1 | 1-Methylpyrrolidone... | 4·2 | 1·0 |
| Methanol..... | 8 | 1·7 | Dioxan ..... | 2·9 | 1·0 |
| Acetic acid ..... | 5·7 | 1·2 | Acetone ..... | 2·6 | — |
| Formic acid ..... | 5 | — | Hexane ..... | 2·4 | 0·7 |
| Methanolic $H_2SO_4$, 1% | 3·8 | 1·5 | | | |

Table 3 summarises the proportions of 5α-steroid (as VIII) and 5β-steroid (as IX) from hydrogenation in different solvents of the 3-oxo-$\Delta^{4,5}$-steroids (as VII), cholestenone and testosterone. Other work [17] indicates that cholestenone is hydrogenated to give very largely the 5β-product, whilst testosterone gives a mixed product containing a high proportion of the 5α-steroid ketone.[18] As indicated in Table 3, the isomeric composition of the product


(VII)


(VIII)

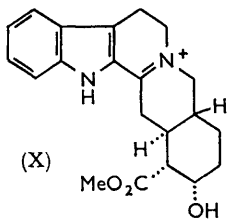

(IX)

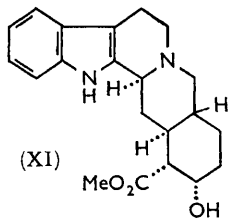
appears, in fact, to be appreciably influenced by the solvent used. We include in Table 3 the results of hydrogenation in alkaline and acidified methanol since alkaline conditions favour [19] hydrogenation in the steric sense (VII) ⟶ (IX), whilst acid [20] has been used to promote formation of the alternative product (as VIII).

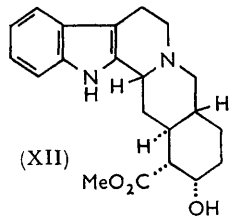
The steroid ketones were chosen to test the influence of solvent since both the starting materials and the products are polar. Results indicating a similar solvent influence in a

[16] Aberland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.
[17] Cf. Mazur and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5220.
[18] Butenandt, Tscherning, and Hanisch, *Ber.*, 1935, **68**, 2097.
[19] Slomp, Shealey, Johnson, Donia, Johnson, Holysz, Pederson, Jensen, and Ott, *J. Amer. Chem. Soc.*, 1955, **77**, 1216.
[20] Wenkert and Jackson, *J. Amer. Chem. Soc.*, 1959, **81**, 5601.

rather different series are on record [21] for the hydrogenation of the dehydroyohimbine salt (X) to the isomeric products (XI) and (XII).




From Table 3, in which the formation of the 5β-steroid is associated with a hydroxylic medium and with the presence of alkali, and of the 5α-isomer with an aprotic, less polar medium, we infer a difference in polarity between the absorbed intermediates leading to these isomeric products. In order to assess how far the solvent effect may be attributed to polar forces at the catalyst surface we have made use of ion-exchange resins as the catalyst support. Palladium, absorbed on to the resin from a solution of the chloride, was reduced as for the preparation of the palladised charcoal [22] catalyst used above. The results in Table 4 indicate an important influence on the steric result of hydrogenation of the $\Delta^{4,5}$-steroid ketones, both of the nature of the catalyst support and of the nature of the ionic centres present. It seems, therefore, reasonable to attribute the effect of solvents, noted

TABLE 4.

Hydrogenation, in methanol, at palladium on ion-exchange resin supports.

| Resin | Type | 5β/5α-steroid from cholestenone | 5β/5α-steroid from testosterone |
|---|---|---|---|
| Dowex 1 | $N^+OH^-$ | 3·8 | 1·5 |
| Dowex 50 | $SO_3H$ | 0·8 | 0·6 |

in Table 3, in part to a similar influence on the polarity at the catalyst surface. The effectiveness of a change of solvent must, however, be limited by the extent to which the pre-existing absorbed ions or water molecules are displaced. Solvent polarity has been noted [23] to influence the rate of hydrogenation. For gases chemisorbed on a metal there is also experimental evidence [24] of interaction between proximate species in the absorbed surface layer.

The sequence of solvents found in Table 3, and the position in the series of acid and of alkali, correspond better with the order of electron-donor capacity rather than with that of dielectric strength. In the group $>C{:}C{\cdot}\underset{|\ \ |}{C}O$, nucleophilic character resides in the carbonyl-oxygen atom which may be concerned in absorption along with the olefinic bond. Absorption through the carbonyl group in this way is, however, likely to be influenced by the solvent medium. A good donor solvent may be competitively absorbed; a polar and especially a protic solvent will solvate the oxo-group.[25] In a less polar, less readily absorbed solvent, on the other hand, absorption through the oxo-group may become relatively more important. In acting as a surface ligand the carbonyl group will be polarised: $>C{:}C{\cdot}\overset{\curvearrowright}{C{=}O}$, and the catalyst, as the acceptor, may be regarded as acting as a Lewis acid. The influence of added mineral acid, noted in Table 3, is in agreement with a similar polarising effect of protonation: $>C{:}\overset{\curvearrowright}{C{=}OH^+}$.

[21] Godtfredsen and Vangedal, *Acta Chem. Scand.*, 1956, **10**, 1414.
[22] Linstead and Thomas, *J.*, 1940, 1127.
[23] Emmett and Yao, *J. Amer. Chem. Soc.*, 1959, **81**, 4125.
[24] Campbell and Thomson, *Trans. Faraday Soc.*, 1961, **57**, 279; Quin and Roberts, *ibid.*, 1962, **58**, 569.
[25] Cf. Djerassi, " Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, p. 61.

5α-Cholestanone, hydrogenated further (at platinum), gave 5α-cholestan-3β- and -3α-ol in the ratio 2 : 1 in methyl alcohol, but 1 : 4 in acetic acid. In hexane and in dioxan, which are aprotic solvents, we found no reduction of cholestanone.

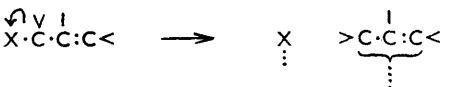
When hydrogenated in various alcohol solvents, cholestenone gave the following 5β/5α ratios in the product: in MeOH 8, EtOH 4·3, $Pr^{i}OH$ 2·6, $Bu^{t}OH$ 2·1. This influence on product ratio is clearly associated with the hydroxyl function which, in this series, is progressively masked by the bulk of the alkyl substituent.

These results imply that the solvent influences the product through the degree of polarisation of the carbonyl group during absorption. For a molecule of the type (VII), a process $>C{=}C{\cdot}C{=}O$, by aiding "uncoupling" of the double bond, will assist deformation in the sense that permits the absorbed molecule to take up the preferred *trans*-decalin-type of configuration. In this way a less polar solvent, or the presence of acid, will result in formation of the 5α-hydrogenated ketone product. Without this assistance, however, the molecule (VII) may be absorbed on either the α- or the β-side in proportion to the relative degree of hindrance presented by substituent groups. Cholestenone with alkaline hydrogen peroxide gives mainly [26] the 4,5β-oxide; under acid catalysis the 4,5α-oxide may be obtained in small yield.[26b] These findings point to an interesting parallel between the factors influencing homogeneous and heterogeneous reactions, and indicate that for cholestenone the β-face of the molecule is the less hindered. In absence of polarisation of the molecule, therefore, 5β-cholestanone would be expected to form the principal product of hydrogenation, as is observed.

(i) 

(ii) 

The alternative absorption processes, represented for, *e.g.*, cholestenone as in (i) and (ii), are relevant to other observations. Hydrogenation of an otherwise sterically resistant double bond may be assisted by absorption through the oxo-group (cf. ref. 7). Conversely the resistance [27] to hydrogenation of the group $\cdot O\cdot C{:}C\cdot CO$ may be attributed to neutralisation of the carbonyl polarisation of the olefinic bond. In (i), which we associate with 5β-hydrogen addition to cholestenone, the substituent R is displaced towards an axial environment. In four cases where R = Me, namely, α-santonin,[28a] α-cyperone,[28b] 4-methylcholestenone,[17] and a similar molecule,[27c] hydrogenation gives largely the 5αH-derivative and none of the highly hindered 4αMe,5βH-isomer.[28b,17] A process similar to (ii) may also represent hydrogenolysis of allyl compounds [29,28b,4b] generalised as in (iii), X = H, OH, OAc, halogen, etc.

(iii) 

The influence of polar substituents, *e.g.*, the >CO group in (ii), or the substituent X in

[26] (*a*) Plattner, Heusser, and Kulkarni, *Helv. Chim. Acta*, 1948, **31**, 1822; (*b*) Oliveto, Gerold, and Hershberg, *J. Amer. Chem. Soc.*, 1957, **79**, 3596.

[27] (*a*) Janot and Goutarel, *Bull. Soc. chim. France*, 1951, 588; (*b*) Bader, *Helv. Chim. Acta*, 1953, **36**, 215; (*c*) Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223; (*d*) Seaton and Marion, *Canad. J. Chem.*, 1957, **35**, 1102; Seaton, Tondeur, and Marion, *ibid.*, 1958, **36**, 1031.

[28] (*a*) Cocker and McMurry, *J.*, 1956, 4549; Banerji, Barton, and Cookson, *J.*, 1957, 5041; (*b*) Howe and McQuillin, *J.*, 1958, 1194.

[29] Bream, Eaton, and Henbest, *J.*, 1957, 1974.

(iii), and the polarised state of many absorbed molecules, suggest that hydrogenation may not necessarily occur solely by homolytic processes.

*trans*-Dibenzoylethylene, when hydrogenated [30] under various conditions, gave 1,2-dibenzoylethane and (±)- and *meso*-1,2,3,4-tetrabenzoylbutane as noted in Table 5. *meso*-

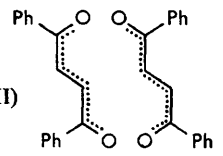
TABLE 5.

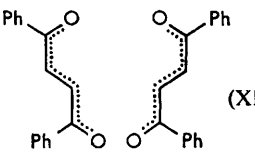
Hydrogenation of *trans*-dibenzoylethylene ($2{\cdot}9 \times 10^{-2}$M) in alcohol–dioxan (1 : 2) (30 c.c.) in presence of catalyst (40 mg.).

| Catalyst | Rel. rate | $(Bz{\cdot}CH_2)_2$ (%) | $(Bz{\cdot}CH_2{\cdot}CHBz)_2$ *meso* (%) | $(Bz{\cdot}CH_2{\cdot}CHBz)_2$ (±) (%) |
|---|---|---|---|---|
| Pd–C | 1 | 58 | 32 | 4 |
| ,, (*a*) | 0·6 | 0 | 5 | 45 |
| ,, (*b*) | 3·1 | 67 | — | — |
| Pd–$SrCO_3$ (*c*) | 2·3 | 97 | 1 | — |
| ,, (*d*) | 0·4 | 90 | — | — |

(*a*) KOH (0·1%) added. (*b*) $HClO_4$ (0·1%) added. (*c*) Prepared as described in ref. 27*c*. (*d*) Catalyst as in (*c*), treated with lead acetate as described by Lindlar (*Helv. Chim. Acta*, 1952, **35**, 446).

(XIII)




(XIV)

Tetrabenzoylbutane may arise by condensation of dibenzoylethylene and dibenzoylethane in solution (cf. ref. 30 and Experimental section). Formation of the (±)-isomer noted in Table 5 must, however, be ascribed to dimerisation on the catalyst between adjacent molecules, as in (XIII); formation of the *meso*-dimer in this way would require reaction in the highly hindered arrangement (XIV). The adjacent absorbed species in (XIII) might be a pair of equivalent half-hydrogenated radicals. The influence of acidity noted in Table 5 is, however, more easily rationalised if the half-hydrogenated intermediate is an enol, which in acid is protonated rapidly to dibenzoylethane, and in alkali condenses, on the surface, with absorbed dibenzoylethylene to give the (±)-dimer, as in (XIII).

The result of hydrogenation of benzylidene acetones was previously found [4a] to depend upon the catalyst, *viz.*:

$$Ar{\cdot}CH_2{\cdot}CH_2{\cdot}COMe \xleftarrow{(i)} Ar{\cdot}CH{:}CH{\cdot}COMe \xrightarrow{(ii)} Ar{\cdot}CH{:}CH{\cdot}CHMe{\cdot}OH$$

Catalyst: (i) Pd–$SrCO_3$; (ii) Pd–C.

Hydrogenation of dibenzoylethylene at palladised strontium carbonate to give dibenzoylethane in high yield (cf. Table 5), *i.e.*, by rapid reaction at the olefinic bond, is a parallel instance. Since this result is the same when the " more active sites " of the catalyst have been deactivated by a lead salt (cf. Table 5) we infer that the catalyst support is responsible.

Taken generally, the present results indicate that in the hydrogenation of the " heteroenoid " group $\gtrless C{:}\underset{|}{C}{\cdot}\underset{|}{C}O$ the modes of absorption and reaction are influenced by the polarisation of the molecule by the solvent, and by the polar nature of absorbed ions and of the catalyst support.

## EXPERIMENTAL

The methods and apparatus were as previously described.[4] Palladised charcoal was made as described by Linstead and Thomas.[22] Comparative experiments were carried out with the same batch of catalyst.

The acetylenic diols were purified commercial samples. The products of semihydrogenation gave the expected physical properties for the *cis*-olefinic diols, *viz.*: butene-1,4-diol, $n_D^{20}$ 1·4710

[30] Cf. Lutz and Palmer, *J. Amer. Chem. Soc.*, 1935, **57**, 1957; Weygand and Meusel, *Chem. Ber.*, 1943, **76**, 498.

(lit.,[31] 1·4716); pent-2-ene-1,4-diol, $n_D^{20}$ 1·4650 (lit.,[32] 1·4633); hex-3-ene-2,5-diol, $n_D^{20}$ 1·4680 (lit.,[33] 1·4680); 1,4-dimethylhex-3-ene-2,5-diol, m. p. 69° (lit.,[34] m. p. 69°).

*Hydrogenation in the Presence of Competitors.*—The catalyst was equilibrated with hydrogen in the presence of the competitor before addition of the substance to be hydrogenated. The same procedure was used in the experiments with different solvents.

*Hydrogenation of Cholestenone, etc.*—The composition of the products of hydrogenation of cholest-4-en-3-one and of testosterone was obtained by thin-layer chromatography on silica gel, and spectrophotometric estimation of the isomeric ketones as their 2,4-dinitrophenylhydrazones.

For cholestenone the hydrogenation product (10 mg.) in alcohol (0·1 c.c.) was treated with 2,4-dinitrophenylhydrazine in alcoholic sulphuric acid (0·1 c.c. of a 20% solution). The precipitated 2,4-dinitrophenylhydrazones were dissolved by addition of chloroform (0·5 c.c.), and the solutions (4 mm.[3]) were applied to the silica-gel plate. Development in benzene separated the 2,4-dinitrophenylhydrazones of 5β- ($R_F$ 0·62) and 5α-cholestanone ($R_F$ 0·54) and the excess of reagent. The dinitrophenylhydrazones were separately extracted into chloroform and estimated from the absorption of the solution at 368 mμ. Tested on artificial mixtures the method had an estimated error of ±2%. 5α-Cholestanone 2,4-dinitrophenylhydrazone, m. p. 229°, had ε 25,000 at 368 mμ, and the 5β-isomer had ε 24,200 at the same wavelength. *5β-Cholestanone 2,4-dinitrophenylhydrazone* has m. p. 167° (from ether–light petroleum) (Found: C, 70·2; H, 8·7; N, 10·2. $C_{33}H_{50}N_4O_4$ requires C, 70·0; H, 8·8; N, 9·9%).

In the case of testosterone, the products were separated before conversion into the 2,4-dinitrophenylhydrazones. The product (10 mg.) in alcohol (1 c.c.) was separated by applying 4 mm.[3] to silica gel on a plate and developing by benzene–ethyl acetate (5 : 1) ($R_F$ of 5α- 0·51 and of 5β-product 0·44). The isomeric ketones were detected by spraying with a solution of 2,4-dinitrophenylhydrazine in alcoholic hydrochloric acid. The resulting dinitrophenylhydrazones were extracted into chloroform and estimated from the absorption at 368 mμ.

*Palladium on Ion-exchange Resins.*—(i) Dowex 1 resin (5 g.) in the chloride form was shaken with sodium hydroxide solution, filtered, washed, and shaken with a solution of palladium chloride (0·5 g.) in hydrochloric acid (0·5 c.c.) and water (35 c.c.). After filtration and washing, the resin, now red-brown, was stirred in 10% sodium hydroxide solution (5 c.c.) and 40% formaldehyde solution (2 c.c.) for 0·5 hr. at 0°. After filtration, the resin, now black, was washed with dilute sodium hydroxide solution and then with water until free from strong alkali; the washings gave finally a pH of 8. The material was finally washed with alcohol and roughly dried.

(ii) Dowex 50 sulphonic acid resin (5 g.) was shaken with a solution of palladium chloride (0·5 g) in hydrochloric acid (0·5 c.c.) and water (35 c.c.) for 15 min. and, after filtration, the resin was reduced in alkaline formaldehyde as in (i). The resin product was acidified by shaking it with 10% hydrochloric acid (25 c.c.) and was washed, first with water until the pH of the washings reached 6, and finally with alcohol.

*Hydrogenation of 5α-Cholestan-3-one.*—The products of reduction at platinum were separated by digitonin precipitation.

*Hydrogenation of* trans-*Dibenzoylethylene.*—Dibenzoylethylene (0·205 g.) in 2 : 1 dioxan–alcohol (30 c.c.) was hydrogenated as indicated in Table 5. The hydrogen uptake was almost 1 mol., except in the hydrogenation in presence of alkali when absorption ceased at *ca.* 0·58 mole. The products, separated by chromatography on alumina, gave 1,2-dibenzoylethane,[35] m. p. 144°, by elution with 1 : 9 benzene–light petroleum, (±)-1,2,3,4-tetrabenzoylbutane,[30] m. p. 168, with 2 : 3 benzene–light petroleum, and *meso*-1,2,3,4-tetrabenzoyl butane,[30] m. p. 202°, with 3 : 2 benzene–light petroleum.

(±)-Tetrabenzoylbutane, when kept in 1% alcoholic potassium hydroxide under nitrogen for some hours, gave the *meso*-isomer, m. p. 201°, quantitatively, without the aid of chromatographic separation. The *meso*-isomer was also prepared from dibenzoylethane and dibenzoylethylene in 1% alcoholic potassium hydroxide solution.

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[31] Johnson, *J.*, 1946, 1014.
[32] Prevost, *Compt. rend.*, 1926, **182**, 1475.
[33] Bourguel, *Bull. Soc. chim. France*, 1929, **45**, 1067.
[34] Prevost, *Ann. Chim.* (*France*), 1928, **10**, 390.
[35] Kapf and Paal, *Ber.*, 1888, **21**, 3053.