HYDROGENATION OF AROMATIC COMPOUNDS

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Attempt has been made to review the work done on the hydrogenation of aromatic compounds. These compounds are classified according to the catalysts. Some applications of these compounds in industry have also been mentioned.

For a long time organic chemists were interested in methods of hydrogenation of aromatic compounds to obtain alicyclic compounds. This technique was attended by several difficulties. From theoretical considerations[1], addition of hydrogen to an aromatic nucleus is not as simple as is the case with an ethylenic or acetylenic bond since the energy required to hydrogenate an aromatic compound is comparatively very high (in many cases due to resonance stabilisation of the compound), and very active catalysts and special types of equipment like pressure reaction apparatus, are necessary. With the discovery of new hydrogenation catalysts and precision equipment [2], it is now possible to utilise this reaction for synthetic work.

HYDROGENATION CATALYSTS

Adkins and Shriner [3] listed the preparation and properties of a number of catalysts, known since 1902, which were employed by the earlier workers to hydrogenate various aromatic compounds. Skita & Meyer [4], as early as 1912, hydrogenated benzene using colloidal platinum catalyst and obtained cyclohexane. Platinum oxide and platinum black were later introduced by others [5-7]. The hydrogenation of phenol was first accomplished in 1903 by Sabatier & Senderens [8], by passing the vapour of phenol together with hydrogen over reduced nickel catalyst at high temperature. The main product was cyclohexanol, with small quantities of cyclohexane, cyclohexene and benzene. The reductions of cresols and xylenols were also similarly investigated by these workers. Aromatic amines have been reduced in the form of their hydrochlorides using platinum oxide catalyst [9]. Aminophenols are also converted to aminocyclohexanols on similar lines [10].

Hydrogenation catalysts are largely available and can be easily recovered after the process and reused. They possess high activity and fall in the nickel group. They are nickel, nickel on alumina, nickel on kieselguhr, cobalt and iron. Nickel was widely employed by Ipatiev [11] and Adkins [12] for the hydrogenation of phenol at high temperatures in liquid phase. Yukhnovsku *et al.*[13] hydrogenated *o*, *m* and *p*–cresols at 15–20 atmospheric pressure and elevated temperatures over nickel on kieselguhr catalyst mixed with cobalt-nickel-copper catalyst and obtained the corresponding methylcyclohexanols. *m*–cresol was quantitatively hydrogenated to 3-methylcylohexanol under high pressure using a nickel on kieselguhr catalyst by Ebersole [14]. Shuikin *et al.*[15] employed nickel on alumina catalysts for the reduction of *m*–cresol and 3, 4–xylenol at high pressures and obtained 3–methylcyclohexanol (86%), and 3, 4–dimethylcyclohexanol (100%) respectively. They also claimed that the catalyst remained active for a very long time after the process. Nickel, platinum and palladium are recommended in patent literature [16-20] for the hydrogenation of di-*tert*-alkylphenols, which furnish the corresponding alcohols that are of great interest in fine chemicals, plastics, surface coatings, detergents, insecticides and antioxidants for mineral lubricants and petrol.

Outstanding achievements were made by Beletzekovski[21] and Rapoport & Silchenko,[22] who reduced technical phenol using nickel, and nickel–cobalt–aluminium–thorium hydroxide catalysts respectively. Repoport and Silchenko further reported that a supported nickel catalyst previously treated with hydrogen sulphide may be useful for the hydrogenation of phenolic tars. Catalysts based on molybdenum oxides and sulphides proved better by virtue of their resistance to catalyst poisons for the hydrogenation of technical mixtures such as "tricresols" and phenolic oils from the low temperature tar [23,24]. A procedure for the preparation of active molybdenum oxide has been described [25].

Several types of Raney nickel catalysts have been described in literature [26,27]. Since each one has its own specific activity, care should be exercised in their choice. They have been widely employed for the reduction of phenols and aromatic amine hydrochlorides under normal and extraordinary high pressures. Polycyclic phenols, such as 1, 5–dihydroxynaphthalene (I) [28], 1–isopropyl 6–hydroxytetralin (II) [29], 4–isopropyl–6–hydroxytetralone–1 (III) [29], 2–methyoxy–4a–methyl–1, 2, 3, 4, 4a, 9, 10, 10a–octahydro–8–phenanthrol (IV) [30] and 7–ethylendioxy–5, 6, 7, 8, 9, 10, 13, 14 "α"–octahydro–1–hydroxy–13–methyl–phenantherene (V) [31] are conveniently hydrogenated with Raney nickel catalysts to the corresponding hydroaromatic derivatives, which are useful intermediates in terpene and steroid synthesis.

The hydrogenation of highly hindered phenols such as 2, 6–dialkylphenols are accomplished with Raney nickel in presence of traces of alkali which promotes the process. The promoting effect of alkali in these hydrogenations was first observed by Ungnade *et al.*[32], and later by Stork[33]. Stork observed that the hydrogenation of β–naphthol (VI) proceeds in two different ways; in acidic or neutral media giving ar–tetrahydro–β–naphthol (VII) and in basic medium giving ac–tetrahydro–β–naphthol (VIII). From these he concluded that in presence of alkali the reaction proceeds through the tautomeric conjugated ketone (IX). The phenol–ketone tautomerism is a common feature in these hydrogenations. The promoting effect of a base in these processes is thus known as "base effect". The formation of cyclohexanone besides cyclohexanol in the hydrogenation of phenol (in presence of alkali) is explained on the basis of this argument.

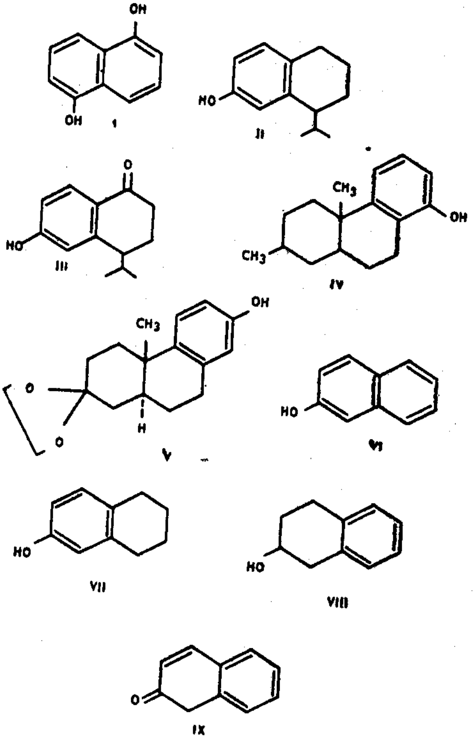

Fig. 1—Aromatic Compounds

Dominguez *et al.* [34] reported very powerful Raney nickel–Ti catalyst, which could hydrogenate phenol, resorcinol, quinol α and β–naphthols, to the corresponding hydroaromatic derivatives under mild conditions (2–6 atmospheres). Since the catalyst retains certain amount of alkali in its preparation and since traces of alkali aid the tautomerism of phenols to the corresponding conjugated ketones, hydrogenation of phenols over this catalyst are rather facile.

Adkins copper chromite catalyst [35] is a rugged one commonly used in hydrogenations of ethylenic bonds, esters amides under high pressures and temperatures, but rarely employed to reduce aromatic compounds. It is less susceptible to poisons. With this catalyst phenanthrene [36] and anthracene [37] are converted to their dihydroderivatives, whereas napthalene [38] was converted to tetralin. In general, copper chromite catalyst is employed in hydrogenations of compounds where reducible groups other than aromatic nucleus are to be hydrogenated in preference, or where a portion of the aromatic ring only has to be hydrogenated.

The noble metals, rhodium and ruthenium alone or on support over materials like alumina or carbon, are potential catalysts [39]. Since they cause the least hydrogenolysis at normal and elevated temperatures and pressures in compounds possessing *C–O* or *C–N* linkages, in which the carbon atom is either part of a ring or not, they find wide application in the reduction of phenols., amines and heterocyclic compounds. A number of examples covering the uses of these catalysts could be found in the current literature [40-44] .

Quite recently Nishimura [45] introduced a new rhodium-platinum catalyst, prepared in the same manner as Adam's platinum oxide catalyst [6], by choosing the proportion of the two metals in 3 : 1 ratio. This was found to be four to six times as active as the platinum oxide catalyst and was capable of reducing unsaturated compounds containing oxygen with minimum hydrogenolysis, thus exhibiting simultaneously the high activity of platinum and low tendency towards hydrogenolysis of rhodium. Phenol, hydroquinone, α—and β–naphthols, anisole, cinnamyl alcohol, pyridine and quinoline were conveniently hydrogenated with this catalyst to the corresponding saturated compounds with least hydrogenolysis [46]. In the course of work carried out by the author on the preparation of hydroaromatic compounds as intermediates in the synthesis of terpenoids and steroids, hydrogenation of 4–isopropyl–6–hydroxytetralone–1 (III) was carried out with rhodium–platinum oxide, rhodium on carbon and ruthenium oxide as catalysts. In the case of all these three catalysts it was observed that hydrogenolysis could be controlled and the reaction proceeds with minimum hydrogenolysis. This confirms the observations of the earlier workers (*loc cit*). Such catalysts, therefore, appear to be very useful for hydrogenation of polycyclic aromatic ring systems containing *C—O* or *C–N* linkages in which hydrogenolysis has to be suppressed or prevented.

STEREOCHEMISTRY OF CATALYTIC HYDROGENATION

Linstead and associates [47] published a series of papers concerning the stereochemistry of catalytic hydrogenation of aromatic compounds. According to them the hydrogenation of an aromatic compound is governed by three hypothesis :

(*i*) in a compound possessing one or more aromatic rings the attack of hydrogen is always from one side of the molecule, during a single period of hydrogenation (one sided addition);

(*ii*) the orientation of the absorption of the aromatic molecule on the catalyst surface is affected by hindrance between the catalyst and substrate ("catalyst hindrance"), and

(*iii*) the derivatives of open chain acids such as diphenic acid are hydrogenated in the coiled phase ("coiling").

The primary factor which determines the formation of the product is the adsorption of the aromatic molecule on a suitable part of the catalyst followed by the addition of hydrogen from underside. The variations in the seats of adsorption of the aromatic molecule and its flatness on the catalyst surface are probably responsible for the formation of different products of hydrogenation (*e.g.*, *cis*-or-*trans*; *syn*-or-*anti* type). It is thus, the orientation of the metallic atoms in the lattice of the catalyst which exert its capacity to adsorb an aromatic molecule, causes stereo-specific hydrogenation. The stereospecificity of various catalysts also depends on environmental factors *e.g.*, pH of the substrate, polarity of the solvent, temperature, pressure and period of hydrogenation. Linstead *et al.* observed *cis-syn-cis* configuration in the products of the catalytic hydrogenation of nine derivatives comprising diphenic acid and phenanthrene over a platinum catalyst in acetic acid (in some cases alcohol as solvent). Thus one can expect the formation of a *cis*-ring annelation rather than a *trans*-ring one in the hydrogenation of an unhindered aromatic molecule. The hydrogenation of phenols present more complicated problems. The stereochemistry of the alcoholic hydroxyl group arising out of the hydrogenation of phenols is often assessed by physical and chemical data [48,49] (infra-red absorption bands in the region 1000—1100 cm^{-1}, elution in chromatography on column and ease of esterification with p-nitro or 3, 5-dinitrobenzoic acids or acid chlorides).

APPLICATIONS IN INDUSTRY

Hydrogenation of aromatic compounds often yield intermediates of considerable importance in basic organic chemical industry. Cyclohexane, cyclohexanol, methylcyclohexane, methylcyclohexanol, methylcyclohexanyl adipate, tetralin and decalin are excellent industrial solvents. Cyclohexanone and cyclohexanol are the starting materials for the production of adipic acid, which is an intermediate in the manufacture of Nylon—66. Di-*tert*-alkylcyclohexanols are valuable starting materials in plastic industry. Cyclohexylamine is a potential intermediate in synthetic drugs. Salts of dicyclohexylamine are vapour phase corrosion inhibitors and dicyclohexylamine is a constituent of insecticidal paints.

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