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Chemistry

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reaction scheme: compound (I) is converted by pathway A to compound (III) and then to compound (II), or by pathway B to an enolic diol intermediate and then to compound (II)

Figure 1: reaction scheme: compound (I) is converted by pathway A to compound (III) and then to compound (II), or by pathway B to an enolic diol intermediate and then to compound (II)

Abstract

Full Text

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ON THE STEREOCHEMISTRY OF CATALYTICALLY ACTIVE COMPLEXES

As was shown earlier (1), in the catalytic hydrogenation of 2,3-dihydro-(2,3; 5′, 6′) (5,6; 5″, 6″) (7,8; 5‴, 6‴)-tribenzobicyclo-(2,2,2)-octadiene-5,7-dione-1′,4′ (I), which is a derivative of triptycene, in the presence of a skeletal nickel catalyst at atmospheric pressure in dioxane medium at 45°, three moles of hydrogen are absorbed and the corresponding hexahydroaromatic diol is formed: 1′, 2′, 3′, 4′, 5′, 6′-hexahydro-(2,3; 5′, 6′) (5,6; 5″, 6″) (7,8; 5‴, 6‴)-tribenzobicyclo-(2,2,2)-octadiene-5,7-diol-1′,4′ (II). The kinetic curve of hydrogen absorption in this process undergoes a sharp break after the absorption of one mole of hydrogen (33.3% conversion), which indicates the selective character of the hydrogenation. However, it had not yet been experimentally established through which stages the reaction proceeds, since two possible reaction pathways can be envisaged: according to scheme A or B.

According to the multiplet theory (2), in consecutive reactions on a nickel catalyst the olefinic bond should be hydrogenated first and only then the carbonyl bond, since the height of the energy barrier of the reaction ($-E$) for the first of these ($-E = 2.9$ kcal) is lower than for the second ($-E = 10.1$ kcal).

In accordance with these theoretical considerations, supported by numerous experimental data (3), it should be expected that in compound (I) the double bond $C = C$ will first undergo hydrogenation with formation of the corresponding hexahydroaromatic diketone (III), and then the two ketone groups $C = O$ will be hydrogenated, which will lead to the hexahydroaromatic diol (II).

To elucidate the mechanism of the reaction, we carried out the hydrogenation of compound (I), obtained according to (4); m.p. 207° (decomp.).

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Fig. 1

Figure 2: Fig. 1

Found, %:	C 83.90; 84.01;	H 4.95; 4.94
$C_{20}H_{14}O_2$. Calculated, %:	C 83.91;	H 4.89

The hydrogenation was carried out in a thermostated duck-shaped vessel (TS-17 thermostat) at 45° and atmospheric pressure over a skeletal nickel catalyst (0.35 g) in freshly distilled dioxane (absence of peroxides). The experimental procedure and preparation of the catalyst are described in (^{1}).

After the absorption of one mole of hydrogen, which in a parallel experiment corresponded to the bend in the kinetic curve in the coordinates: rate

(ml of H_2, etc., per min.)—the depth of reaction in % (see the arrow in Fig. 1), the product was filtered off from the catalyst and recrystallized from a mixture of dioxane and toluene (1 : 1). The investigation showed that the substance obtained is product III, 1′,2′,3′,4′,5′,6′-hexahydro-(2,3; 5′,6′) (5,6; 5″,6″) (7,8; 5″,6″)-tribenzobicyclo-(2,2,2)-octadiene-5,7-dione-1′,4′—a compound not described in the literature. In pure form it consists of yellowish crystals with m.p. 182–3° (decomp.).

Found, %: C 83.10; 82.90; H 5.47; 5.53
$C_{20}H_{16}O_2$. Calculated, %: C 83.33; H 5.55

Product III did not give a reaction for a quinoid structure (the starting compound (I) showed coloration under the action of $KJ + J_2 + KOH$), gave no reaction for an olefinic bond, did not form a phenylurethane, and did not react with maleic anhydride. In reaction with 2,4-dinitrophenylhydrazine, III gives a mono-2,4-dinitrophenylhydrazone, crystallizing well from an ethanol-chloroform mixture (1 : 2), with m.p. 186–8°.

Found, %: N 12.28; 12.41
$C_{20}H_{20}N_4O_5$. Calculated, %: N 11.69

From the literature there are known cases of formation of monophenylhydrazones of 1,4-diketones (^{5}).

Fig. 1

The data obtained confirm the prediction of multiplet theory that hydrogenation of compound I proceeds in direction A of the scheme shown above. At the same time, the results found serve as another example of the sequence of hydrogenolysis of bonds under catalysis over a nickel catalyst, broadly confirmed by experiment and derived from multiplet theory (^{2}, ^{3}).

Multiplet theory makes it possible to construct stereochemical models of the active complexes of the reactions considered above.

diagram

Figure 3: diagram

structural reaction scheme

Figure 4: structural reaction scheme

According to this theory, owing to the small radius of action of valence-chemical forces, molecules come into contact with the catalyst by their reacting atoms, which determines the orientation of molecules during catalysis. On this basis, models of the hydrogenation of various triptycene derivatives are shown to scale below. The molecules have a complex configuration: the six-membered rings adjacent to the central bicyclic system are arranged at an angle of 120° to one another, which in projection is represented as follows:

Therefore the molecule cannot be situated entirely on a plane surface. In the models of Fig. 2, the molecules of triptycene derivatives are oriented toward the catalyst surface according to the above-mentioned requirements of multiplet theory. Here model **a** corresponds to the hydrogenation of triptycenehydroquinone, which was discussed in work (1). This model is based on the sextet mechanism of hydrogenation. In Fig. 2 **b** is shown the model of hydrogenation of compound (III), and the model of this doublet reaction

constructed in accordance with the model considered earlier (6). The existence of the reaction III → II and of the corresponding model in Fig. 2 necessarily follows from the fact that the reaction I → III occurs, the existence of which is demonstrated in the present communication, and from the reaction I → II observed in (1).

In Fig. 2 a model is constructed for the hydrogenation of compound I. This model corresponds to the edgewise arrangement of the six-membered ring on the surface of the catalyst (2). From Fig. 2 it is seen that in cases and the molecule does not fit on the plane because of steric hindrance, and hydrogenation must occur at protrusions of the catalyst, whereas in case hydrogenation can also proceed on a flat surface of the catalyst.

In the case of hydrogenation of triptycenequinone, described in the article (1), the considerable interatomic distance O–O in the quinone indicates that hydrogenation is carried out not by molecular hydrogen, but by atoms of the latter, in accordance with the requirement of the theory (6). Apparently, hydrogenation proceeds through a semihydrogenated form, which is attached to nickel through only one oxygen, just as in the hydrogenation of ketones (7). The radical corresponding to the semihydrogenated form in the present case is the semiquinhydrone of the structure:

It is known that under certain conditions similar radicals are very stable: their solutions are usually intensely colored.

semiquinhydrone structure

Figure 5: semiquinhydrone structure

However, during the hydrogenation of triptycenequinone the yellow solution of the latter gradually became decolorized, which indicates that if such a radical is formed, it is not desorbed into the solution, but undergoes further chemical transformations here, on the surface of the catalyst. The results obtained are important for understanding the nature of catalytically active centers.

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