On the Mechanism of Dehydrogenation of the 2, 4, 5-Triphenyl-4, 5-dihydroimidazole over Solid Catalysts

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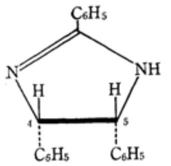
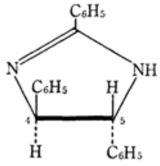
There have been a number of stereochemical studies of the hydrogenation of olefinic double bonds and aromatic rings over metal catalysts.[1,2] The results suggest that, at least in the cases of platinum catalysts used at room temperature, cis-addition predominates both in the hydrogenation of olefinic double bonds[1] and in the hydrogenation of aromatic rings.[2,3]

In contrast with the case of hydrogenation, however, little is known about the mechanism of dehydrogenation over metal catalysts. In order to obtain some information about the mechanism of the dehydrogenation of ring compounds over metal catalysts, the catalytic dehydrogenations of a dihydroimidazole ring over a Raney nickel catalyst and other metal catalysts have been studied. The present paper will report on the results of an investigation with stereoisomers of 2, 4, 5-triphenyl-4, 5-dihydroimidazole.

2, 4, 5 - Triphenyl - 4, 5 - dihydroimidazole is known to give three stereoisomers because of the differences in the conformations of the 4- and 5-hydrogen atoms; the cis isomer, amarine, which is not resolvable into optical antipodes, and the trans isomer, isoamarine, which is resolvable into optical antipodes, *d*- and *l*-isoamarine.



isoamarine



amarine

The dehydrogenations of amarine and *dl*-isoamarine in solutions over such solid catalysts as Raney nickel, platinum black, palladium black and active carbon have been investigated to ascertain the steric course of the dehydrogenation at the adjacent carbon atoms of a planar ring.

Experimental

Amarine and *dl*-isoamarine were prepared by the method of Japp and Moir;[4] amarine, m. p. 130∼131°C, and *dl*-isoamarine, m. p. 200∼201°C.

Raney nickel, platinum black and palladium black were prepared by the ordinary methods. The active carbon used was Norite-A. The reagents and solvents used were special-grade chemicals of Wako Pure Chemical Industries, Ltd.

The investigations of dehydrogenation with solid catalysts were carried out by the following procedure. A solution of 0.1∼0.6 g. of amarine or isoamarine in 5∼25 ml. of a solvent was refluxed with 0.1∼0.5 g. of a catalyst for 3 hr. Then the catalyst was filtered off and washed. The filtrate was evaporated under reduced pressure, and the residue was warmed with 2 N hydrochloric acid. The amarine and isoamarine were dissolved, whereas the 2, 4, 5-triphenylimidazole (lophine) formed by the dehydrogenation was scarcely dissolved at all. The lophine was filtered off, and the weight of the lophine was determined to ascertain the extent of dehydrogenation carried out in the solution with a catalyst.

Results and Discussion

When amarine was heated in a hard glass tube at about 140°C[5] in a boiling xylene bath for 3 hr., amarine[6] was completely dehydrogenated in a molten state, giving lophine (m. p. 271∼272°C), which was identified by no depression of its melting point on mixture with an authentic sample. However, when amarine was heated at 110°C in a boiling toluene bath in which amarine did not melt, dehydrogenation did not take place. The dehydrogenation of isoamarine did not occur at all when it was heated in a hard glass tube at 140°C in a boiling xylene bath in which isoamrine was not in a molten state. The dehydrogenation of isoamarine occurred

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[1] K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 138 (1942); A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 837 (1937).

[2] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942). In this report a number of references about hydrogenation over platinum, palladium and nickel catalysts are cited.

[3] R. B. Woodward and W. E. Doering, ibid., **67**, 864 (1945).

[4] F. R. Japp and J. Moir, *J. Chem. Soc.*, **77**, 781 (1900).

[5] A catalytic action of hard glass in the dehydrogenation of molten amarine was recognized, since the dehydrogenation of amarine did not occur in a quartz tube at 140°C.

[6] H. L. Snape and A. Brook, *J. Chem. Soc.*, **75**, 211 (1881).

in a molten state at 240°C. These facts showed that amarine, the cis isomer, tended to be subjected to dehydrogenation in itself much more easily than *dl*-isoamarine, the trans isomer.[7] When amarine was heated in a solution in xylene, toluene or benzene under reflux for 3 hr., lophine, the product of the dehydrogenaton, was not isolated. As expected, the dehydrogenation of isoamarine did not take place in solutions under the same experimental conditions. Hence, it was confirmed that neither amarine nor isoamarine was subjected to dehydrogenation by refluxing solutions without the addition of a catalyst, at least below 140°C.

Raney nickel was found to exhibit a catalytic action in dehydrogenation of the *cis*-4, 5-dihydroimidazole ring, since the hydrogenation of amarine with Raney nickel in ethanol at room temperature yielded 2, 4, 5-tricyclohexylimidazole, from which the 4- and 5-hydrogen atoms of amarine had been removed, along with *cis*-2, 4, 5-tricyclohexyl-4, 5-dihydroimidazole.[8] The dehydrogenation of amarine and isoamarine over Raney nickel in solutions was first investigated.

A solution of 0.5 g. of amarine in 20 ml. of xylene was refluxed at 140°C in an oil bath for 3 hr. with Raney nickel, prepared from 0.7 g. of Raney nickel alloy powder. The xylene was then evaporated in vacuo, the residue being extracted with ethanol. The ethanolic solution was poured into water to yield a precipitate. The filtered precipitate was treated with 2 N hydrochloric acid to separate lophine. An almost theoretical amount of lophine was obtained. This result showed that amarine was completely dehydrogenated at 140°C in xylene with Raney nickel. Under the same conditions, no dehydrogenation of isoamarine occurred. Without the presence of oxygen, amarine was dehydrogenated with Raney nickel by refluxing a solution in xylene in an atmosphere of hydrogen or nitrogen. Hence, the dehydrogenation of amarine with Raney nickel in xylene was not due to oxidation, but was directly concerned with the catalyst. The dehydrogenation of amarine with Raney nickel was also completely effected by refluxing solutions in toluene, benzene, ethyl methyl ketone or acetone and partly occurred in cyclohexane, carbon tetrachloride or ethanol[9]. No dehydrogenation of amarine was effected by refluxing solutions in ethyl acetate, hexane, chloroform, acetic acid or pyridine with Raney nickel. In each of these solvents, no dehydrogenation of isoamarine took place either. These results indicate that, in the presence of solid catalysts, amarine in solutions is dehydrogenated in the absence of oxygen, even at rather low temperatures, such as the boiling points of benzene and acetone, and that the nature of solvents, as well as the temperature of reflux, is a strongly effective factor in dehydrogenation, although the polar nature of the solvents appears to play no part in the dehydrogenation, its mechanism being consequently considered to be non-ionic.

As in the experiments with Raney nickel, platinum black and palladium black, the dehydrogenation of amarine was carried out by refluxing solutions in xylene, toluene or benzene respectively. No dehydrogenation of isoamarine took place with these catalysts either.

With active carbon, which usually shows no catalytic action in hydrogenation, amarine was dehydrogenated by refluxing solutions in xylene, toluene, benzene or acetone without the presence of oxygen, whereas no dehydrogenation of isoamarine was effected under the same conditions.

Since the dehydrogenation of amarine over active carbon suggested that adsorption on solid catalysts might be strongly effective in the dehydrogenation of amarine, adsorptions of amarine and isoamarine on active carbon from solution in benzene were measured at room temperature. Amarine 0.14 g. was adsorbed on 0.58 g. of active carbon from a solution of 0.30 g. of amarine in 35.0 ml. of benzene at 22.5°C, whereas hardly any isoamarine was adsorbed on active carbon under the same conditions. As was expected from the conformational structures of these stereoisomers, the difference in the adsorptions was very marked of these isomers.

From the experimental results mentioned above, the steric course of the dehydrogenation of amarine was considered to be as follows; an amarine molecule is adsorbed on a solid catalyst with the side of plane of the imidazole ring, from which two cis hydrogen atoms at the 4- and 5-carbon atoms project. These two hydrogen atoms lie very close to the surface of the solid catalyst in such an adsorbed state. (Isoamarine is not adsorbed, since there exists no molecular side such as

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[7] When amarine and isoamarine were each heated at 300°C in a hard glass tube, both compounds, which were in molten states at this temperature, were dehydrogenated to yield lophine with a small amount of *trans*-stilbene.

[8] T. Hayashi and M. Kuyama, *Natural Science Reports of Ochanomizu University*, **6**, 99 (1955).

[9] Although no dehydrogenation of amarine occurred when solutions were refluxed in ethanol or methanol without solid catalysts, the dehydrogenation of amarine did take place in butanol or pentanol without solid catalysts. In the latter cases oxygen was found to be necessary. This fact shows that the mechanism of dehydrogenation by reflusing solutions in alcohols is different from that in the other solvents mentioned above.

that of amarine mentioned above.) Both hydrogen atoms, which originally tend to move from the imidazole ring, as has been mentioned above, are eliminated from the 4- and 5-carbon atoms under the effect of the solid catalyst. Isoamarine is not dehydrogenated with a solid catalyst, since isoamarine is not be adsorbed on a solid catalyst.

This mechanism was supported by the following experiment with sulfur. When a solution of amarine in xylene was refluxed with fine powders of sulfur, amarine was dehydrogenated and hydrogen sulfide was evolve. The dehydrogenation of amarine is likely to follow the reverse couse to the *cis*-hydrogenation of aromatic rings over a platinum catalyst.[5]

Summary

1) Amarine has been completely dehydrogenated, without the presence of oxygen, by refluxing solutions in xylene, toluene, benzene or acetone with Raney nickel, whereas no dehydrogenation of isoamarine occurred at all under the same conditions. Amarine was also dehydrogenated without the presence of oxygen by refluxing solutions with platinum black, palladium black or active carbon. The dehydrogenation of amarine, carried out by refluxing a solution in benzene with sulfur powder, was accompanied by the evolution of hydrogen sulfide.

2) Amarine was adsorbed with active carbon from a solution in benzene at room temperature, whereas hardly any isoamarine was adsorbed under the same conditions, the difference in the dehydrogenation behavior of these cis- and trans-isomers being very marked.

3) Considering the results obtained, the dehydrogenation of amarine by refluxing solutions with solid catalysts may reasonably be considered *cis*-dehydrogenation, the mechanism being as follows; an amarine molecule is adsorbed on solid catalysts with the side of the plane of an imidazole ring, to which cis 4- and 5-hydrogen atoms are attached, and these hydrogen atoms, which tend to move from the imidazole ring, are eliminated under the effect of solid catalysts. Isoamarine, which has a trans-conformation unfavorable to adsorption, is not subjected to dehydrogenation with solid catalysts.

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