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THE CATALYTIC HOMOGENOUS HYDROGENATION OF SOME 1,4-DIHYDROAROMATIC COMPOUNDS

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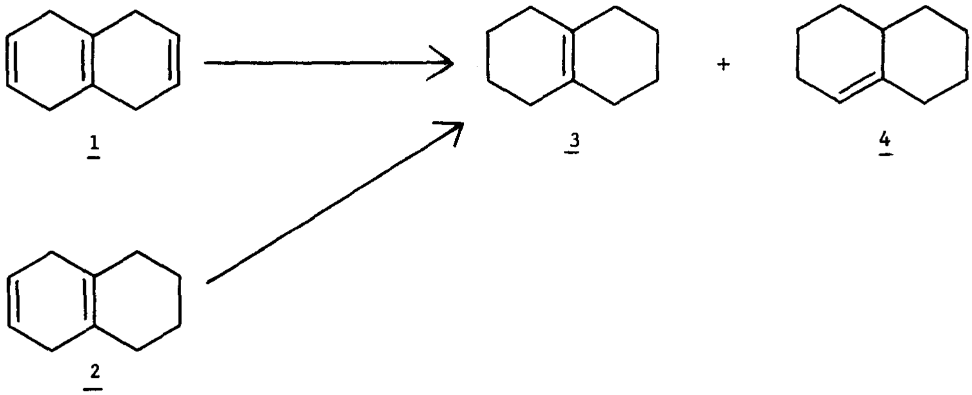
The recent development of a homogenous hydrogenation catalyst, tris-(triphenylphosphine)-chlororodium(I), by Wilkinson and coworkers (1) is especially interesting to organic chemists because of its promise as a highly selective catalyst. Some difficulties of heterogeneous hydrogenation such as allylic rearrangement, double bond migration and lack of stereospecificity may be eliminated by the use of homogenous catalysis (2,3). The rate of hydrogenation of olefinic bonds with Wilkinson's catalyst (2) appears to be inversely proportional to the number of substitutents on the double bond. We were interested in this specificity in connection with other work and have been able to selectively reduce some 1,4-dihydroaromatic compounds with little or no disproportionation.

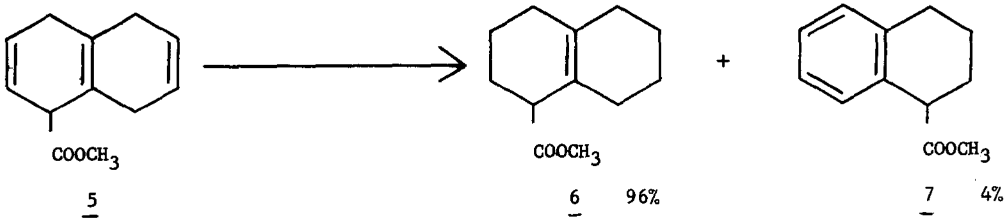
Either isotetralin, 1, or 1,4-dihydrotetralin, 2, was reduced in benzene-ethanol in the presence of the homogeneous catalyst to an identical 80:20 mixture (4) of 9,10-octalin, 3, and 1,9-octalin, 4. There was no trace of any aromatic compound formed by disproportionation when the product was analyzed by vapor phase chromatography. Treatment of 2 with the catalyst in solution, without hydrogen, for several days did not cause any isomerization. When 1 or 2 was reduced with PtO_2 in ether or with 5% $Pd/BaSO_4$ (5) a complex mixture was formed containing aromatic compounds as evidenced by n.m.r. and ultraviolet spectra.

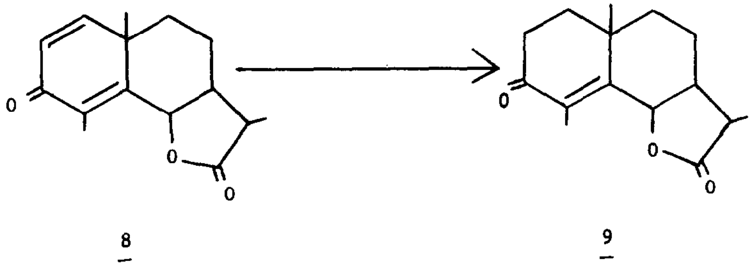
Hydrogenation of methyl 1,4,5,8-tetrahydro-1-naphthoate, 5, with the soluble catalyst yielded the 9,10-octalin ester, 6, in excellent yield along with 4% of the tetralin derivative, 7. In contrast, reduction of 5 with PtO_2/ether gave 6 (56%), 7, (26%) plus two unidentified products. Similarly, the use of 5% $Pd/BaSO_4$ yielded 6 (49%), 7 (26%) plus three unidentified products.

In addition to the above reactions, we also have reduced santonin, 8, to dihydrosantonin A, 9, in 90% yield (6). Only one equivalent of hydrogen is taken up even after several days, leaving the tetrasubstituted double bond intact.

In summary, homogeneous hydrogenation is selective enough to reduce two disubstituted double


1
2
3
+
4


COOCH$_3$
5
COOCH$_3$
6 96%
+
COOCH$_3$
7 4%


O
O
O
8
O
O
O
9

bonds in the presence of a tetrasubstituted one. However, there can be interaction of the catalyst with a tetrasubstituted double bond, which may be seen by the surprising production of 4 by reduction of 1 or 2. Evidence of this interaction is absent in the reduction of 5; possibly the carbomethoxy group can interfere with the coordination of the catalyst with the double bond. Tris(triphenylphosphine)chlororhodium(I) is useful for reduction of 1,4-dihydroaromatic compounds because of the lack of disproportionation encountered with the use of normal heterogeneous catalysts(7).

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REFERENCES

1. J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, Chem. Comm., 131 (1965); F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, Chem. Ind. (London), 560 (1965); J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. (A), 1711 (1966).
2. A. J. Birch and K. A. M. Walker, J. Chem. Soc. (C), 1894 (1966).
3. C. Djerassi and J. Gutzwiller, J. Am. Chem. Soc. **88**, 4538 (1966); M. Brown and L. W. Piszkiewicz, J. Org. Chem. **32**, 2013 (1967).
4. R. A. Benkeser and E. M. Kaiser, J. Org. Chem., **29**, 954 (1964).
5. H. O. House and W. M. Bryant, J. Org. Chem., **31**, 3482 (1966). These workers report hydrogenation of a 1,4-dihydrobenzene derivative without disproportionation using 5% Pd/$BaSO_4$.
6. J. B. Hendrickson and T. L. Bogard, J. Chem. Soc., 1678 (1962). A 30-40% yield of 9 was obtained in this work.
7. All new compounds had correct elemental analyses and consistent spectral properties (i.r., n.m.r., u.v.).