The Selective Reduction of Benzene to Cyclohexene

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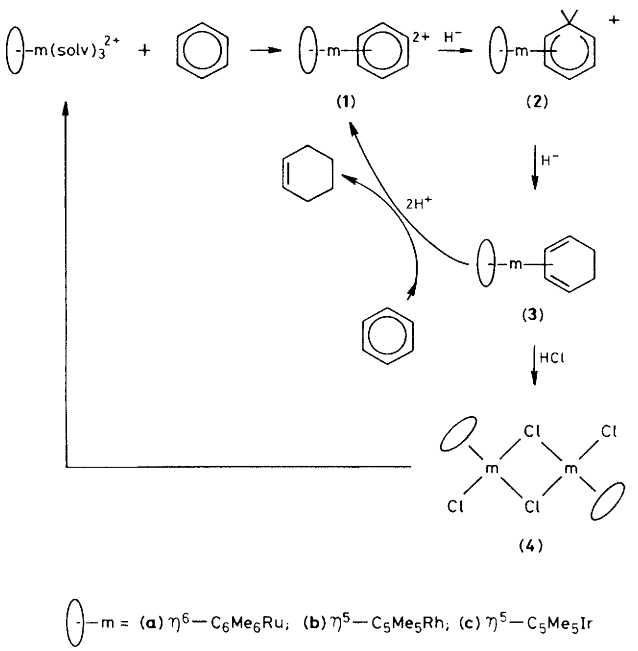
Hydride attack on a dicationic η^6-benzene complex gives the η^4-cyclohexadiene, which with acid yields cyclohexene; in the presence of benzene the initial η^6-benzene complex can be regenerated and a cycle established.

There are now a number of catalyst systems, heterogeneous,[1] homogeneous,[2] and mixed,[3] for the complete hydrogenation of benzene to cyclohexane. Synthetically and industrially, however, it would be of much greater interest to reduce partially benzene to cyclohexene. Unfortunately ΔG° (298 K) for benzene to cyclohexene (-23 kJ mol^{-1})[4] is substantially smaller than for the through reaction, benzene to cyclohexane (-98 kJ mol^{-1}).[4] Hence there is a strong tendency for



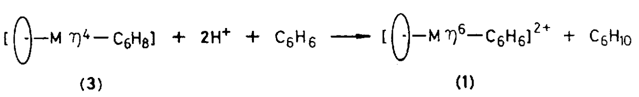
Scheme 1

the reaction, once it is initiated, to proceed all the way to cyclohexane. Nevertheless, heterogeneous catalysts promoting the hydrogenation to cyclohexene have been reported,[5] but the selectivity achieved was low ($<20\%$).[6]

We describe here an alternative approach which yields cyclohexene with high selectivity and uses the strategy outlined in Scheme 1.

The formation of the η^6-benzene complexes (**1a**—**c**) and their reduction to the η^5-cyclohexadienyl complexes (**2a**—**c**) are well documented.[7] For example, (**2a**) is obtained in 86% yield by $NaBH_4$ reduction of (**1a**) (in H_2O at 0 °C), and (**2c**) is obtained similarly (76% yield).

We now find that a further hydride can be added to (**2**) under more forcing conditions[8] {*e.g.* $Na[AlH_2(OCH_2CH_2OMe)_2]$ in toluene} to give the cyclohexadiene complexes (**3**) in good yield [*e.g.* 70% for (**3a**), 56% for (**3b**),[9] and 83% for (**3c**)]. Reaction of the cyclohexadiene complexes (**3**) with HCl



Scheme 2

liberates cyclohexene ($\geqslant 92\%$ yield) with 100% selectivity. The other product is (**4**), which can be easily reconverted into (**1**).[7]

Alternatively, the cyclohexadiene complex (**3**) can be treated with $BF_3.2H_2O$ in benzene; this again gives only cyclohexene and directly regenerates the η^6-benzene dicationic complex (**1**), for example, (**1a**), 60%; (**1c**), 94% (Scheme 2). This reaction therefore completes the cycle where first two hydrides and then two protons are added to η^6-complexed benzene to give cyclohexene; this can be further developed into a process catalytic in the platinum metal complex.

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References

1 P. N. Rylander, 'Catalytic Hydrogenation over Platinum Metals,' Academic Press, New York, 1967, p. 309; R. B. Moyes and P. B. Wells, *Adv. Catal.*, 1973, **23**, 121.
2 E. L. Muetterties and J. R. Bleeke, *Acc. Chem. Res.*, 1979, **12**, 234.
3 M. J. H. Russell, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1977, 427; A. Millan and P. M. Maitlis, unpublished data, see also P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.
4 R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, 'Properties of Gases and Liquids,' McGraw-Hill, New York, 1977.
5 W. C. Drinkard (du Pont), U.S.P., 3,767,720.
6 C. U. I. Odenbrand and S. T. Lundin, *J. Chem. Tech. Biotech.*, 1980, **30**, 677.
7 C. White and P. M. Maitlis, *J. Chem. Soc. A*, 1971, 3322; C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 1654; M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, 1979, **175**, 87.
8 See also D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458; W. Lamanna and M. Brookhart, *J. Am. Chem. Soc.*, 1981, **103**, 989.
9 K. Moseley and P. M. Maitlis, *J. Chem. Soc. A*, 1970, 2884.