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The radical anion of naphthalene as promoter of the selective catalytic dehydrogenation of 1,4-cyclohexadiene to benzene and of the isomerization of linear 1,4- to 2,4-hexadienes

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Abstract

Two new examples of the application of the naphthalene radical anion, namely two cases of catalytic C–H bond activation, are described; viz.: (a) selective room temperature dehydrogenation of 1,4-cyclohexadiene to benzene, and (b) partial transformation of 1,4-hexadiene into its internal conjugated isomer. Radical anions derived from other bi- or tricyclic aromatics were tried in the reaction of the cyclic diene, and their behaviour found to depend to some extent on their reduction potentials. The use of a negatively charged electrode in place of the radical anion promoters was investigated, but no transformation of 1,4-cyclohexadiene was observed under the conditions of the electrochemical experiments. Careful GC analysis of the products from the isomerization reaction showed that no dihydronaphthalene was produced, thus excluding pathways initiated by action of the naphthalene radical anion as a base.

Introduction

The polymerization of conjugated dienes in the presence of alkali metals or their organic derivatives has been a widely studied process since its discovery almost eighty years ago, but the behaviour of other dienes under similar conditions has been much less deeply studied. In particular, treatment of linear and cyclic hexadienes with alkali metals [1] or strong bases [2] has been the subject of only occasional studies during the last three decades. Catalytic cyclohexadiene disproportionation to cyclohexene and benzene was reported to be promoted by alkali metals [1a], and by iridium complexes [3] or iron atoms [4]. Disproportionation was also observed in the presence of stoicheiometric amounts of potassium and an excess of triethylamine [1c]. Disproportionation and dehydrogenation were observed as side reactions, together with dominant oligomerization, in the presence of the naphthalene radical anion [1d]. Use of an excess of alkali metal amides was found to promote both disproportionation and dehydrogenation [2c]. More recently, catalytic dehydrogenation of 1,4-cyclohexadiene to benzene and dihydrogen was accomplished by use of reduced species obtained from arene transition-metal complexes by treatment with potassium [5].

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We report here that electron transfer from catalytic amounts of potassium/naphthalene in dimethoxyethane (DME) induces carbon–hydrogen bond activation reactions at room temperature with both 1,4-cyclohexadiene (**1**) and open-chain 1,4-hexadienes (**2**).

Experimental

All operations were carried out under prepurified nitrogen. Reagent-grade DME was refluxed for 2 h over $LiAlH_4$ prior to distillation. The reagent-grade polycyclic aromatics were degassed. A Vibro-Mixer equipped with a perforated plate immersed in the molten metal was employed for the preparation of potassium sand in hot n-heptane and sodium sand in hot xylene, respectively.

Analyses of the organic products were performed with a DANI 8400 GC and a HP 5595A GC/MS, both equipped with a 6 ft 10% diethyleneglycol succinate on chromosorb W HP (100–120 mesh) packed column. For the analysis of products derived from naphthalene the injection syringe was washed many times with the solution prior to sampling, in order to preclude contamination by adsorbed water.

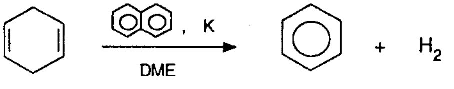
Dihydrogen evolution was monitored at atmospheric pressure by means of a thermostated gas-volumetric apparatus.

Electrochemical experiments were carried out in a cell suitable for Schlenk techniques. Reagent-grade $AgNO_3$, $NaClO_4$ and $(Bu_4N)ClO_4$ were dried over a prolonged time at $> 80\,°C/5 \cdot 10^{-2}$ Torr.

Typical reaction procedure. To the mixture of polycyclic aromatic (0.3 mmol) and alkali metal sand (0.5 mmol), were added DME (25 mL) and the diene (4–5 mmol). In the case of dehydrogenation, the mixtures were then stirred in vacuo to prevent pressure build up, except in the gas-volumetric measurements (see above).

Results and discussion

In the presence of the naphthalene/potassium sand system, 1,4-cyclohexadiene undergoes smooth dehydrogenation to benzene, while in 40–50 mol% of both isomers * of 1,4-hexadiene the terminal double bond shifts to the conjugated position, as revealed by GC and MS analysis. (The remainder of the substrate is converted into less volatile products, probably oligomers.)



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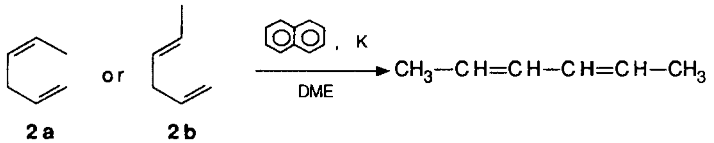

2a **2b**

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* The *cis*-isomer **2a** (Fluka) and a mixture of the *cis*- and *trans*-isomers **2a**/**2b** (Janssen) gave very similar results.

The course of cyclohexadiene dehydrogenation is similar to that observed in the presence of the bis(benzene)chromium(0)/potassium system [5]: at 25 °C, the rate of dihydrogen evolution at atmospheric pressure increased during the first hour of reaction, reaching a value corresponding to a turnover of 5.2 mol of dehydrogenated substrate per mol of naphthalene per hour, and then remained constant as long as the substrate was present.

While the isomerization of the linear dienes in the presence of strong bases [2b,c] is believed to be initiated by an allylic proton abstraction [6], no dihydronaphthalene was found by GLC of samples collected with careful exclusion of moisture. Since 1,4-dihydronaphthalene was reported to be the product of the reaction between the naphthalene radical anion and protic reagents [7], we infer that hydrogen transfer from the substrate to $C_{10}H_8^{\cdot -}$ is not a major pathway in our system.

The alternative view assumes that the radical anion transfers one electron to the diene, thus starting the observed transformations. Some experiments were carried out in order to clarify the reaction mechanism. With potassium as the source of electrons, various radical anion precursors (biphenyl, phenanthrene and anthracene) were tried, and in cases where the reduction potentials were less than 0.1 V within that of naphthalene [8], dehydrogenation of 1,4-cyclohexadiene occurred, though not selectively, owing to concurrent disproportionation to benzene and cyclohexene (biphenyl, 41% disproportionation; phenanthrene, 48%). When the precursor was anthracene, which is reduced at about 0.6 V above naphthalene [8], no dehydrogenation occurred, while 60% of 1,4-cyclohexadiene was transformed into its 1,3-isomer. This result clearly suggests that different electron transfer mechanisms may operate in this type of reaction depending on the reducing properties of the radical anions.

Electrochemical experiments were carried out in DME in the absence of naphthalene and potassium. With 0.1 *M* sodium perchlorate as supporting electrolyte no reduction was observed down to -2.3 V (vs. Ag/saturated $AgNO_3$ in DME) either in the absence or in the presence of 1,4-cyclohexadiene. Prolonged electrolysis of the same mixture at -3.62 V did not result in transformation of the diene. With 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte, no reduction was observed down to -3.5 V in the absence of the diene, while in its presence a low reduction current appeared at about -3 V. Nevertheless, during prolonged electrolysis at -3.5 V the diene remained unchanged.

In our opinion some kinetic aspects related to the heterogeneity of the reducing systems (mercury drop or pool electrodes in polarographic and preparative electrolytic experiments, respectively) could have hampered the reactions in these cases.

In the presence of anthracene, no reaction occurred in the absence of potassium or with sodium (as either sand or mirror) instead of potassium. As also the naphthalene radical anion, if generated by sodium instead of potassium, is inactive towards 1,4-cyclohexadiene, we believe that the alkali metal cation plays a significant role in stabilizing the organic intermediates after electron transfer from the promoter.

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References

1 See, e.g.: (a) Fr. 1,364,405; Jpn. Appl., (1962); Chem. Abstr., 62 (1965) 459h; (b) H. Yasuda, T. Narita and H. Tani, Tetrahedron Lett., 27 (1973) 2443; (c) H. Yasuda, Y. Ohnuna, M. Yamauchi, H. Tani and A. Nakamura, Bull. Chem. Soc. Jpn., 52 (1979) 2036; (d) Z. Sharaby, J. Jagur-Grodzinski, M. Martan and D. Vofsi, J. Polym. Sci., Polym. Chem. Ed., 20 (1982) 901.

2 See, e.g.: (a) J.E. Hofmann, P.E. Argabright and A. Schriesheim, Tetrahedron Lett., 17 (1964) 1005; (b) Jpn. Pat., 45/14047 (1966); Chem. Abstr., 73 (1970) 44866y; (c) E.N. Kropacheva, B.A. Dolgoplosk, I.I. Ermakova, I.G. Zhuchikhina, I.N. Selimanova and I.Yu. Tseretelli, Dokl. Akad. Nauk SSSR, 186 (1969) 637; Chem. Abs., 71 (1969) 60568s; (d) P.W. Rabideau and D.L. Huser, J. Org. Chem., 48 (1983) 4266; (e) C.I. Kowalski and G.S. Lal, J. Am. Chem. Soc., 108 (1986) 5356.

3 R.H. Crabtree and C.P. Parnell, Organometallics, 4 (1985) 519.

4 S.D. Ittel, F.A. Van Catledge and J.P. Jesson, J. Am. Chem. Soc., 101 (1979) 3874.

5 G. Fochi, Organometallics, 7 (1988) 2255.

6 J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 2nd ed., McGraw-Hill, New York, 1977, p. 533.

7 H.F. Ebel, in Houben-Weyl Methoden der organischen Chemie, Vol. 13/1, Georg Thieme Verlag, Stuttgart, 1970, p. 379.

8 G.J. Hoijtink, E. De Boer, P.H. Van der Meij and W.P. Weijland, Recl. Trav. Chim. Pays Bas, 75 (1956) 487.