

BASE CATALYZED DISPROPORTIONATION  
OF CYCLOHEXADIENE AND RELATED REACTIONS

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In the light of recent interest in hydrocarbon carbanion reactions in polar solvents (1) we wish to report the discovery of a homogeneous base catalyzed trans-hydrogenation reaction. Kinetics of this reaction indicate that hydride transfer is the rate-determining step. Carbon-carbon hydride transfers are well known in acid media (2, 3) and are important in

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- (1) A. Schriesheim, J. E. Hofmann, C. A. Rowe, Jr., J. Am. Chem. Soc., 83, 3731 (1961); A. Schriesheim, R. Muller, C. A. Rowe, Jr., *ibid.* 84, 3164 (1962).
- (2) P. D. Barlett, F. E. Condon and A. Schneider, J. Am. Chem. Soc., 66, 1531 (1944).
- (3) O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, J. Chem. Phys., 17, 418 (1949); J. Am. Chem. Soc., 73, 5741 (1951); 74, 3299 (1952).

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hydrocarbon conversions such as isomerization and alkylations. However, very little work has been done in the area of base catalyzed carbon-carbon hydride transfers. Pines (4) has reported several examples of

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- (4) H. Pines and M. Kolobielski, J. Am. Chem. Soc., 79, 1698 (1957).

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disproportionations involving hydride transfers using various sodium catalysts in which the reaction system is clearly heterogeneous and the nature of the

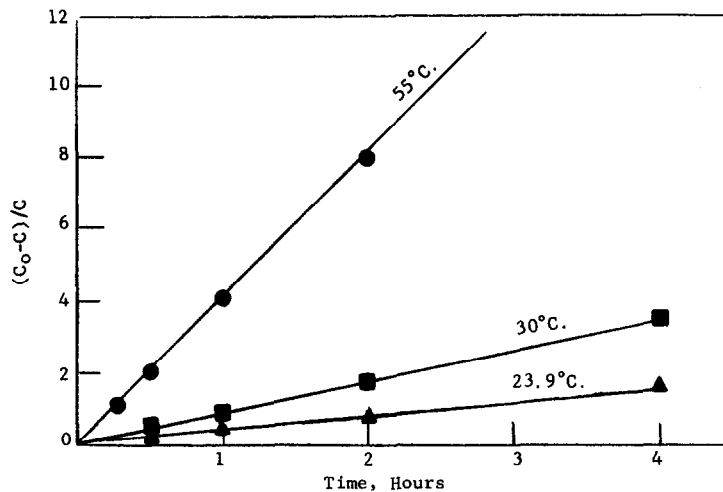
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reactive intermediate dubious. It has now been found that strong bases in dimethylsulfoxide promote the disproportionation of cyclohexadiene to benzene and cyclohexene.

The present work was carried out by treating 3.0 millimoles of 1,3 cyclohexadiene with 7 ml. of a 0.6 molar solution of sublimed potassium tert-butoxide in dimethylsulfoxide. At 55°C., cyclohexadiene was quantitatively converted to benzene and cyclohexene in 24 hours. The activation energy for the disproportionation reaction was found to be 13.5 kcal/mole and the kinetics were clearly second order in cyclohexadiene concentration (Figure 1). The observed kinetics lead to a postulated mechanism where

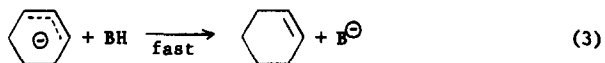
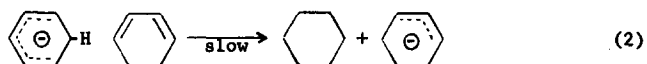
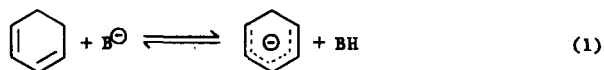
Figure 1

Disproportionation of 1,3 Cyclohexadiene



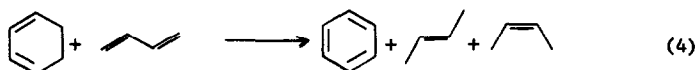
C<sub>0</sub> = Initial conc. of cyclohexadiene  
C = Concentration of cyclohexadiene at time t

hydride transfer is the rate determining step. The isomerization between

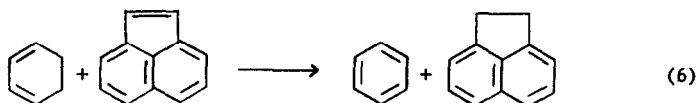
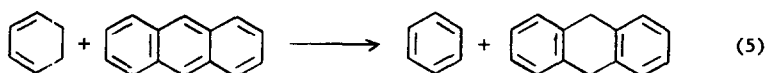


1,3 and 1,4 cyclohexadiene is sufficiently rapid so that either isomer would lead to the same results. In tert-butyl alcohol as a solvent only isomerization is observed with no disproportionation.

When an experiment is carried out in the presence of equimolar quantities of butadiene and cyclohexadiene, cis and trans-2-butene are formed (equation 4). The rate of butene formation is faster than that



of cyclohexene indicating that butadiene is a preferred hydride acceptor as compared to cyclohexadiene. Anthracene and acenaphthalene were also found to be efficient hydride acceptors, resulting in formation of the hydrogenated analogs, 9,10 dihydroanthracene and acenaphthene (equations 5 and 6). In this case the hydrogenated aromatics were produced to



almost the total exclusion of cyclohexene.

Very roughly it is possible to equate the effectiveness of the hydride acceptor with the stability of the anion formed during hydride transfer (equation 2). Thus, butadiene is better than cyclohexadiene because the allylic resonant anion is less strained. Likewise, anthracene and acenaphthalene are extremely effective because the resulting anions are stabilized through the aromatic system.