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Catecholborane Reductions of Ditosylhydrazones to the Corresponding Methylene Derivatives

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ABSTRACT

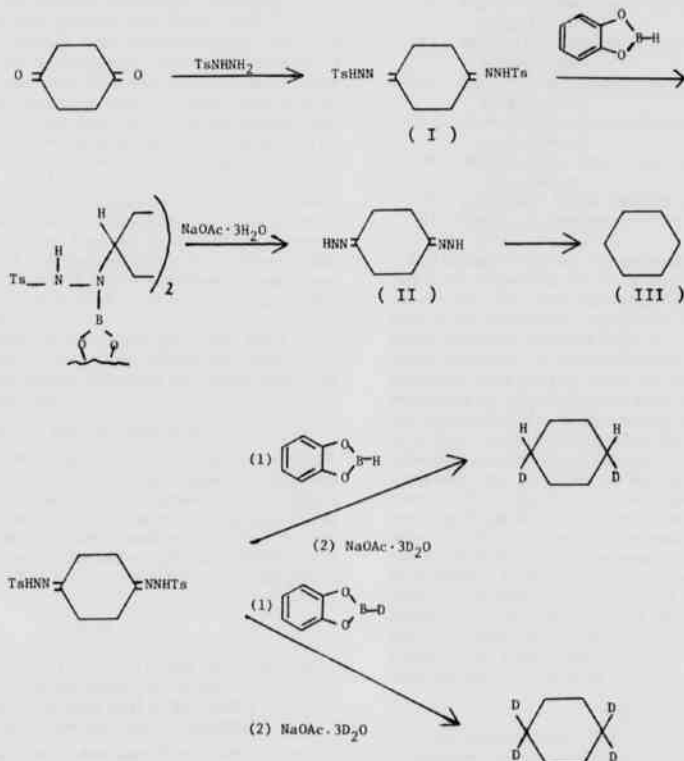
The smooth deoxygenation of diketones via the Catecholborane reduction of the corresponding ditosylhydrazones is described. The reductions occur under mild conditions and are suitable for sensitive compounds.

The reduction of tosylhydrazones by boron hydride reagents provides a convenient and mild alternative to the Wolff-Kishner and Clemmensen reductions (Hutchins, et al. 1975; Kabalka and Baker, 1975; Kabalka et al. 1976). Using Catecholborane (1,3,2-benzodioxaborole), reductions can be carried out in near quantitative yield in any of the common, aprotic, organic solvents (Kabalka et al. *in press*). Furthermore, tosylhydrazones are selectively reduced in the presence of nearly all organic functional groups (Kabalka et al. 1976, 1977).

We wish to report the extension of the general procedure to ditosylhydrazones in respectable yields. The marked decrease in solubility of ditosylhydrazone (I) as compared to that of monotosylhydrazone in chloroform necessitated longer reaction time in the formation of diazene (II). The subsequent decomposition of compound II using sodium acetate trihydrate to cyclohexane (III) with the evolution of nitrogen presented no problem.

We are currently investigating the regiospecific deuterium labeling by using NaOAc·3D₂O and Catecholborane-d (Yang and Kabalka, *in press*).

FIGURE 1



EXPERIMENTAL SECTION

The ditosylhydrazones of 1,4-cyclohexanedione (m.p. 166-167°) and 2,5-hexanedione (m.p. 208-211°) were prepared according to a published procedure (Hutchins, et al. 1975). Catecholborane was purchased from Aldrich Chemical Company and was also prepared via Brown's procedure (Brown, 1975). GLC were performed on a Varian Aerograph (model 1700) using a 6 ft., 15% SE-30 on Chromosorb W. Proton NMR spectra were recorded on Varian T-60 and HA-100 spectrometers.

Reduction of 2,5-Hexanedione Ditosylhydrazone

To a slurry of 2,5-hexanedione ditosylhydrazone, 2.5 mmol (1.18g) in 10 ml of chloroform at room temperature, were added n-heptane, 2.5 mmol (0.365 ml, internal standard), and catecholborane, 12.5 mmol (1.5 ml), in a round-bottomed flask fitted with a septum inlet. The reaction was allowed to proceed overnight. Sodium acetate trihydrate, 15 mmol (2.04 g), was added and the reaction mixture was brought to a gentle reflux for one hour. GLC analysis of the filtrate indicated a 57% yield of n-hexane.

Reduction of 1,3-Cyclohexanedione Ditosylhydrazone

The reduction was carried out as described above except that NMR analysis indicated a 65% yield using anisole as the internal standard.

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LITERATURE CITED

- BROWN, H.C. 1975. Organic syntheses via boranes. Wiley-Interscience, New York. pp. 63-65.
- HUTCHINS, R.O., M. KACHER and L. RUA. 1975. The synthetic utility and mechanism of the reductive deoxygenation of β -unsaturated p-tosylhydrazones with sodium cyanoborohydride. *J. Org. Chem.* 40:923-929.
- KABALKA, G.W. and J.D. BAKER. 1975. A new mild conversion of ketones to the corresponding methylene derivatives. *J. Org. Chem.* 40:1834-1835.
- KABALKA, G.W., J.D. BAKER and G.W. NEAL. 1977. Catecholborane (1,3,2-benzodioxaborane) - a versatile reducing agent. *J. Org. Chem.* 42:512-517.
- KABALKA, G.W., J.D. BAKER and D.T.C. YANG. 1976. Catecholborane - a versatile reagent. Abst. 172 ACS National Meetings, San Francisco, California. *ORGN.* p. 171.
- KABALKA, G.W., D.T.C. YANG and J.D. BAKER. 1976. Deoxygenation of β unsaturated aldehydes and ketones via the catecholborane reduction of the corresponding tosylhydrazones. *J. Org. Chem.* 41:574-575.
- KABALKA, G.W., D.T.C. YANG and J.D. BAKER. In press. Regiospecific deuterium incorporation via the reduction of tosylhydrazones to the corresponding methylene derivatives. *Synthesis*.
- YANG, D.T.C. and G.W. KABALKA. In press. An improved synthesis of 5 α -cholest-3-ene. *Org. Prep. Proc., International*.