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An Efficient Reduction of Anthrones to Anthracenes

Donald J. Marquardt* and Frankie A. McCormick
Department of Chemistry, Tulane University, New Orleans, LA 70118

An efficient and general means of reducing anthrones to anthracenes has been developed. The procedure, which uses $NaBH_4$ as the reducing agent in a mixed solvent system of diglyme/methanol, produced anthracenes in essentially quantitative yield from a variety of anthrones.

In connection with recent efforts[1] to synthesize nonplanar "cyclic" polyacenes via an iterative anthracene DA/homologation sequence, we required an efficient and general means of reducing anthrones to anthracenes. The reduction had to be compatible with a wide range of arenes and polyacene DA adducts which contained alkyl, methoxy, halogen, and/or carboxy groups. Surprisingly, there are very few methods known for anthrone reduction, none of which appears to be generally applicable. Zinc reductions, which are fairly useful for the reduction of anthraquinones,[2] lead mainly to coupled products (pinacols and/or bianthranyls) when applied to anthrones under either acidic (Clemmensen)[3] or alkaline[4] conditions. In addition, zinc reductions would be incompatible with halogenated anthrones.

Reductions by HI in acetic acid have been utilized[5] for anthraquinones and other oxygenated arenes. This reduction appears well suited for anthrones although limited by its incompatibility with halo and oxygen functionality. In our attempts to reduce anthrones with HI, however, we were unable to avoid overreduction to the 9,10-dihydroanthracene (which appeared before the anthrone was consumed). The amount of dihydroanthracene varied considerably.

Anthrone has been reduced in high yield by $NaBH_4$ in trifluoroacetic acid (TFA)[6] and by BH_3·pyridine in TFA,[7] but the product is mainly (or exclusively) 9,10-dihydroanthracene. In addition, the generality of these methods, which may be somewhat limited by the use of TFA as solvent or cosolvent, has not been demonstrated. More recently, $NaBH_4$ in alcoholic solvents has been examined[8] as a means of reducing both anthrones and anthraquinones. While this procedure avoids overreduction, the yields of anthracenes vary widely and do not appear to be correlated with the structure of the anthrone.

Despite the unpredictability of previous $NaBH_4$ reductions,[8] we decided to investigate its use because of its compatibility with a wide variety of functional groups. We now wish to report that anthrones can be effectively reduced with $NaBH_4$ in a mixed solvent system of diglyme/MeOH.[9] The new procedure gave essentially quantitative yields with a variety of alkyl- and hetero-substituted anthrones (see table). Anthrones are easily prepared from readily available benzylbenzoic acids.[11] The reduction of anthrones via the described procedure should make the benzylbenzoic acid route a general means of synthesizing anthracenes. Similar

Table: Reduction of Anthrones With $NaBH_4$ in Diglyme/MeOH

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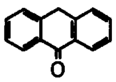
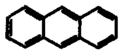
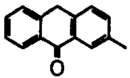
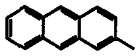
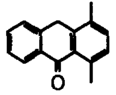
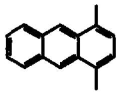
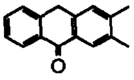
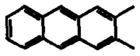
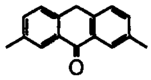
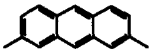
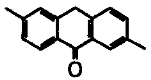
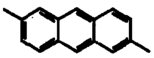
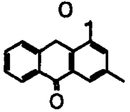
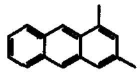
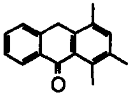
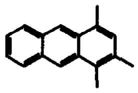
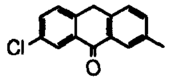
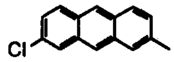
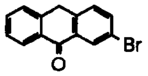
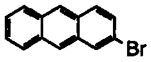
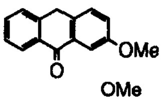
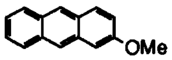
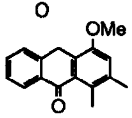
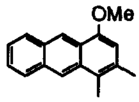
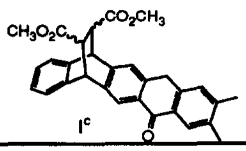
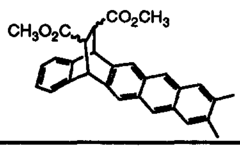
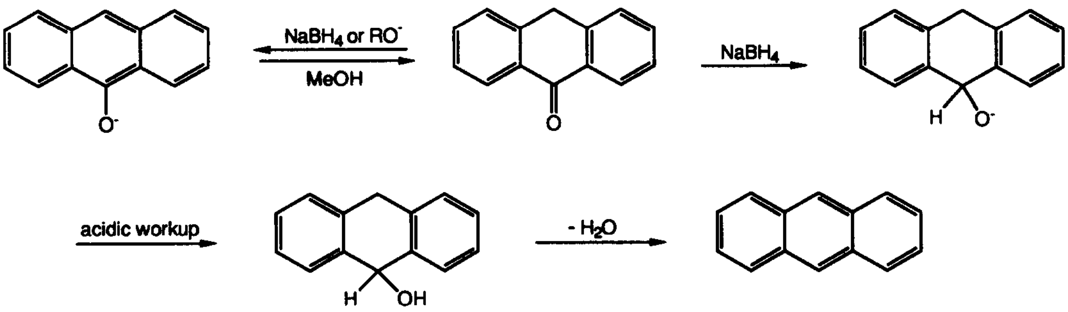
1			100%
2			100%
3			98%
4			94%
5			100%
6			100%
7			94%
8			96%
9			94%
10			92%
11			94%
12			98%
13	 I^c		85%

[a] All compounds gave satisfactory NMR and GC/MS spectra (>98% purity) as well as m.p. for compounds which had previously reported values. [b] Isolated yields. [c] two *trans* isomers

reductions should be useful in preparing other polyacenes as well. Attesting to the generality of the reduction procedure, anthrone I[10] (entry 13) was successfully reduced to the corresponding anthracene, formally a DA adduct of pentacene, without interference from the bicyclo or carbomethoxy moieties.

The mixed solvent system is crucial to the success of the reduction. We propose that the protic solvent is needed to allow equilibration of the anthracenolate anion with the anthrone (Scheme I). Anthracenolate anion is apparently formed via deprotonation of the anthrone or its anthracenol tautomer by either $NaBH_4$ or the alkoxide formed upon reduction of the anthrone. This is supported by the fact that when the reduction is carried out in the absence of MeOH, the diglyme solution rapidly becomes bright yellow or orange in color. We take this color as evidence of the anthracenolate anion. In fact, more electron deficient anthrones become very dark orange while electron rich anthrones only light yellow. If quenched without addition of MeOH, there is obtained a mixture of anthracene and anthrone. This would be expected if anthracenolate were formed since this anion would be unreactive toward $NaBH_4$ and would produce the starting anthrone upon quenching. If MeOH is added after the reaction has proceeded in diglyme, the orange color fades and the reaction goes to completion.

Scheme I



The use of diglyme is also crucial since less satisfactory results are obtained in alcoholic solvents alone. We reason that this is due to a much greater rate of reduction of the anthrone carbonyl in diglyme than in alcoholic solvents. It is likely that the equilibrium between anthracenolate/MeOH and anthrone/methoxide is unfavorable. A rapid and efficient reduction of the anthrone is necessary to drive the reaction to completion. This would be increasingly important as the reaction proceeds and the system becomes more basic.

The initial reduction product is a dihydroanthracenol, which is the main species present in the reaction mixture before quenching (TLC shows little or no anthracene). Careful addition of acetic acid quenches the reaction and causes elimination to the anthracene. The halo anthrones require more acidic conditions to cause elimination. When quenched with acetic acid alone, entries 9 and 10 produced only the corresponding dihydroanthracenols, which could be isolated. Addition of HCl caused elimination to the anthracene in these cases.

We note that oxygen seems to have an adverse effect on the reaction in that it causes discoloration of both the reaction mixture (usually green) and the final product (orange). This lends support to the presence of anthracenolate in the reaction mixture since this anion would be expected to be highly reactive toward oxygen. The discoloration in the reaction could then be due to anthradiol(ate?) or other oxidation products. These oxidation products are apparently also reduced (or formed in small amount) since the final product is still obtained in excellent yield and purity in spite of the discoloration. Nonetheless, we find it desirable to flush the solution with nitrogen before adding the reducing agent. This expedient minimizes discoloration of the final product which is generally still light yellow in color but very pure by TLC, GC, and NMR.

General Procedure

The reductions have been carried out on 100 mg to multigram scales. In a typical reaction, the anthrone (1g) was dissolved or suspended in diglyme (20 mL). The mixture was stirred and flushed with nitrogen for 10-15 m and 0.5g $NaBH_4$ was added. Hydrogen evolution was immediately evident and the mixture turned from almost colorless to a bright yellow or orange solution. After 15-30 m (the anthrone should all be dissolved at this time) MeOH (10mL) was carefully added followed by an additional portion (0.25g) of $NaBH_4$. *Caution:* the addition of MeOH causes rapid hydrogen evolution and an exothermic reaction. The use of a RT water bath to prevent any significant rise in temperature is recommended. The solution was then stirred at RT overnight (it is not practical to try and follow the reaction by TLC). Acetic acid was added until the pH was between 3 and 4. For the haloanthrones, conc. HCl was added after the acetic acid quench until pH<2. The solution then was stirred for an hour to eliminate water from the dihydroanthracenol intermediate. Water (twice the solution volume) was slowly added with rapid stirring to precipitate the resulting anthracene which was subsequently filtered, washed with water and dried under vacuum. The precipitated anthracenes were generally slightly yellow in color but sufficiently pure (>98% by GC/MS and NMR) for further use.

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