chloride (AR). This corresponded to about a 6 to 1 molar ratio of chloride to epoxide. The solution was permitted to remain at 30° for three hours before drowning in water. The precipitate was identical with starting material on comparison of m.p. and infrared spectrum. (b) The *cis* epoxyketone was far less soluble and the reaction had to be carried out at the boiling point of ethanol. However, after three hours of refluxing, the product recovered was very pure *cis* starting material, as shown by m.p. and infrared spectrum.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE NEWARK COLLEGE OF ARTS AND SCIENCES OF RUTGERS UNIVERSITY]

Peroxide Induced Reduction of 9,10-Anthraquinone by Sodium Borohydride in Diglyme[1]

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9,10-anthraquinone is not reduced at room temperature by sodium borohydride in pure diglyme (dimethyl ether of diethylene glycol). In the presence of peroxides, 9,10-anthraquinone is reduced to 9,10-anthradiol in diglyme. A possible mechanism for the peroxide promoted reduction may be the cleavage of the solvent to aldehydes by a peroxide-induced reaction followed by the conversion of the aldehydes so produced to alkoxyborohydrides which are the effective reducing agent.

It has been reported that quinones may be quantitatively reduced to the hydroquinone by aqueous solutions of sodium borohydride at room temperature.[2] It has been found in this laboratory that although such quinones as 1,4-naphthoquinone and 9,10-phenanthrenequinone are readily reduced, 9,10-anthraquinone is not reduced under these conditions.

When 9,10-anthraquinone was treated under an argon atmosphere at room temperature with sodium borohydride in freshly purified diglyme (dimethyl ether of diethylene glycol), no visible evidence of a reaction was observed after 5 hr. Upon acidification of the reaction mixture, the volume of hydrogen evolved was equivalent to the amount of sodium borohydride initially present.

However, when 9,10-anthraquinone was treated with sodium borohydride in diglyme which had been exposed to air for as short a time as one day, a rapid reaction took place. The red color of the 9,10-anthradiol salt appeared within 3 min. A gasometric analysis at the end of 5 hr. showed a loss of borohydride equivalent to 100% reduction of the anthraquinone.

The positive reaction in the aged solvent suggested that peroxides, which form readily in the polyethers, might be involved in the reaction. To determine whether this positive reaction is due to the formation of peroxides in the diglyme, small amounts of various peroxides were added to the solution of anthraquinone and sodium borohydride in freshly purified diglyme under anaerobic conditions. In the case of benzoyl peroxide, lauroyl peroxide and *tert*-butyl hydroperoxide, the anthraquinone was reduced after an induction period of approximately 5 min. In a series of experiments with benzoyl peroxide it was shown that as little as 0.005 mole of the peroxide was sufficient to promote the reduction of a mole of anthraquinone. In a control experiment without added peroxide no reduction took place even after 5 hr. at room temperature.

To determine the role of the benzoyl peroxide in promoting the reduction, combinations of two of the reagents were mixed and allowed to stand for 10 min. before the addition of the other two. In only one case was the induction period for the reaction reduced from the normal value of 5 min. for the quantities used. This was when the benzoyl peroxide and the diglyme were allowed to age together before the addition of the anthraquinone and sodium borohydride. That the reduction was promoted by a product of the reaction between peroxide and the solvent was further proven by experiments with di-*t*-butyl peroxide. This peroxide did not cause a positive reaction under the conditions which were successful with the three mentioned previously. However, when the diglyme was first heated with di-*t*-butyl peroxide, and then cooled to room temperature, the reaction took place upon the addition of the sodium borohydride and anthraquinone.

There remained the possibility that the effect of the peroxide on the diglyme involved the formation of aldehydes by a free radical cleavage of the polyether. Thomas has reported that the peroxide-catalyzed thermal decomposition of a polyether yields aldehydes among other products.[3] While freshly prepared diglyme gave a negative Schiff test, it was found that the addition of a small

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[1] This work was conducted under a research grant provided by Metal Hydrides, Inc., of Beverly, Mass.

[2] B. Lindberg and J. Paju, *Svensk Kem. Tidskr.*, 65, 9–10 (1953).

[3] J. R. Thomas, *J. Am. Chem. Soc.*, 77, 6107–9 (1955).

amount of benzoyl peroxide to the solvent caused the development of a pronounced positive test for aldehyde. Similarly, the aged diglyme preparations gave a positive Schiff test.

Small amounts of a wide variety of freshly distilled aldehydes were added to a solution of anthraquinone and sodium borohydride in diglyme. In each case the reduction of anthraquinone took place. In a series of experiments with isobutyraldehyde it was proved that as little as 0.01 mole of the aldehyde was sufficient to promote the reduction of one mole of anthraquinone. Alcohols were without effect in promoting the reduction even when used in rather large amounts.

Since the aldehyde in the presence of $NaBH_4$ was probably reduced to an alkoxy borohydride very rapidly, it is possible that this is the compound which was active in reducing the 9,10-anthraquinone. Brown, Mead, and Subba Rao[4] have recently found that acetone is reduced in diglyme much more readily by sodium triisopropoxyborohydride than by sodium borohydride. To verify this in the case of the reduction of 9,10-anthraquinone, a sample of the anthraquinone in freshly purified diglyme was treated with sodium trimethoxyborohydride under an argon atmosphere. The reduction was rapid and complete. No induction period was observed.

Amines were found to exert a catalytic effect on the reduction of 9,10-anthraquinone by sodium borohydride in diglyme. This is in agreement with a similar effect noted for the reduction of acetone in diglyme with sodium borohydride.[4] As little as 0.1 mole of *n*-butylamine per mole of 9,10-anthraquinone was found to promote the reduction.

Repeated quantitative experiments in which 9,10-anthraquinone was reduced with sodium borohydride in diglyme and then the excess $NaBH_4$ was determined gasometrically indicated that each mole of 9,10-anthraquinone consumed 2 gram atoms of hydrogen. This would correspond to a reduction to 9,10-anthradiol. The dark red color of the reduced solutions is also characteristic of the salts of 9,10-anthradiol. In order to isolate the product a run was made using larger quantities. The reduction product upon isolation in the acid form was found to be the yellow-green crystalline 9,10-anthradiol. This material dissolved in alkali to give the characteristic red color of the salt. It was soluble in alcohol with a characteristic green fluorescence. However, since it rapidly decomposes in air, no attempt was made to purify it and determine a melting point. Instead a second run was made in which the reduced 9,10-anthraquinone was converted to the diacetate without attempting to isolate the 9,10-anthradiol from the reaction mixture. The diacetate obtained dissolved in glacial acetic acid to give a solution which displayed a blue fluorescence. When the diacetate was vigorously refluxed with aqueous sodium hydroxide it slowly dissolved to give the red color of the leuco sodium salt of anthraquinone.

EXPERIMENTAL

Purification of the solvent. The diglyme as supplied by Ansul Chemical Co. (E-141) was dried by storage over NaOH pellets. It was then refluxed over $NaBH_4$ and distilled. These operations were perfofmed in an atmosphere of deoxygenated nitrogen.

The experiments with peroxides, aldehydes, and amines were conducted on a small scale. In each case the reactions were carried out in an atmosphere of argon. All transfers were made under anaerboic conditions. In a typical experiment 10 mg. of sodium borohydride in diglyme was added to a homogeneous solution of 20 mg. of anthraquinone in diglyme. The peroxide or aldehyde was added to the anthraquinonediglyme solution either directly or as a dilution in diglyme. These reagents were added before the sodium borohydride in all experiments except those used to determine the nature of the peroxide effect.

Preparation of crude 9,10-anthradiol. One gram of 9,10-anthraquinone was dissolved in 20 ml. of diglyme which had been purified as in the preceding paragraph, but then had been allowed to stand exposed to air for several weeks. Upon the addition of 0.25 g. sodium borohydride (98+% pure, as supplied by Metal Hydrides, Inc.) a vigorous exothermic reaction started and the solution turned deep red. The reaction mixture was stirred under argon without heating for 45 min. At the end of this time, the reaction mixture was poured into 500 ml. of cold 1*N* HCl to decompose the excess $NaBH_4$ and precipitate the product. A yellow-green precipitate was obtained. This was filtered and washed with water. The precipitate (0.9 g.) was soluble in alcohol to give a green fluorescence. It dissolved in aqueous NaOH to give the red color of the sodium salt. The melting point of the crude 9,10-anthradiol was 157–180°. An attempt to recrystallize the crude material from alcohol yielded 9,10-anthraquinone (m.p. 285°).

Isolation of 9,10-anthradiol diacetate. The reaction was performed as in the preceding paragraph up to the point where the reaction mixture was added to dilute HCl. Instead of this, 5 cc. of acetic anhydride and 3 g. of fused sodium acetate were added to the dark red reaction mixture. The mixture immediately turned yellow-green. The reaction mixture, still under an atmosphere of argon, was warmed at 70° for 0.5 hr. It was then poured into ice water and the pale yellow precipitate was filtered, washed and dried. The yield was 0.8 gram. Colorless needles (0.6 g.) were obtained upon crystallization from glacial acetic acid. The melting point of the 9,10-anthradiol diacetate was found to be 268–271°, dec. This is in reasonably good agreement with the value reported by Fieser and Putnam[5] of 262–267° for 9,10-anthradiol diacetate prepared by the interaction of $Pb(OAc)_4$ and 9-acetoxyanthracene.

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[4] H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209–13 (1955).

[5] L. F. Fieser and S. T. Putnam, *J. Am. Chem. Soc.*, 69, 1038–41 (1947).