The Reduction of Anthraquinone and other Polycyclic Quinones with Aluminium Alkoxides (Meerwein–Pondorff Reagent).

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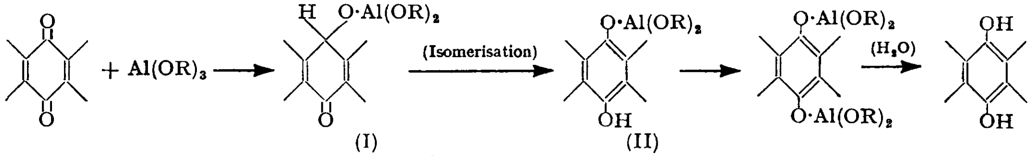
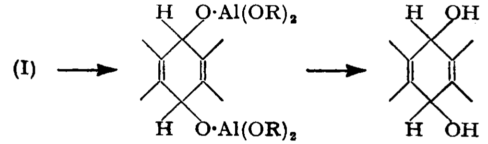
In the reaction between aluminium alkoxides and anthraquinones the corresponding anthracene, 9 : 10-dihydroxyanthracene, or 9 : 10-dihydro-9 : 10-dihydroxyanthracene may be obtained depending on the alkoxide used and the experimental conditions. From nitroanthraquinones, aminoanthraquinones are first formed and these may react further with the products obtained from the oxidation of the alkoxide; 1-amino-2-methylanthraquinone affords 2 : 4-dimethyl-3-azabenzanthrone. 1 : 5-Dichloroanthraquinone cannot be reduced beyond the dihydrodihydroxyanthracene stage. Anthanthrone and flavanthrone are reduced to anthanthrene and flavanthrene respectively.

THE Meerwein–Pondorff reaction for reducing aldehyde and keto-groups to primary and secondary alcoholic groups respectively by treatment with an aluminium alkoxide has been studied for a wide range of compounds (cf. " Organic Reactions," Vol. II, p. 178, John Wiley & Son Inc., New York, 1944), but it has only recently been applied to an aromatic polycyclic ketone. By treating *meso*benzanthrone and anthrone respectively with aluminium *iso*propoxide in *iso*propanol, Campbell and Woodham (*J.*, 1952, 843) obtained benzanthrene in 75% and anthracene in quantitative yield, the reduction proceeding further than the expected alcohol stage and so becoming irreversible. As far as can be ascertained, there is no mention in the literature of the reaction having been studied with polycyclic quinones, although it is recorded that benzoquinone is reduced to quinol. According to Boyland and Manson (*J.*, 1951, 1837) anthraquinone is converted into 9 : 10-dihydro-9 : 10-dihydroxyanthracene and 1 : 4-naphthaquinone into 1 : 2 : 3 : 4-tetrahydro-1 : 4-dihydroxynaphthalene and 1 : 2 : 3 : 4-tetrahydro-4-hydroxy-1-oxonaphthalene by reduction with lithium aluminium hydride, which often gives a similar result to the Meerwein–Pondorff reaction.

The reduction of anthraquinone and a number of its derivatives by a series of aluminium alkoxides has now been studied. From anthraquinone the reaction produces 9 : 10-dihydroxyanthracene, 9 : 10-dihydro-9 : 10-dihydroxyanthracene, or anthracene according to the alkoxide employed. Alkoxides of lower primary alcohols, *e.g.*, the ethoxide and *n*-butoxide, give only 9 : 10-dihydroxyanthracene. In these cases probably only one keto-group in the anthraquinone molecule is involved in the initial reaction which may be represented as :



With aluminium *iso*propoxide, which is a more powerful reducing agent, the second keto-group in (I) also reacts, leading to the formation of the alkoxide of 9 : 10-dihydro-9 : 10-dihydroxyanthracene, as normally expected from a Meerwein–Pondorff reduction :



9 : 10-Dihydroxyanthracene is not reduced to 9 : 10-dihydro-9 : 10-dihydroxyanthracene by this reagent so that, as expected, it is probably the keto-group in (I) which is attacked.

With the higher-boiling butanols, particularly with butan-2-ol, the 9 : 10-dihydro-9 : 10-dihydroxyanthracene is reduced a stage further to give anthracene, and with aluminium tri(*cyclo*hexyl oxide) in *cyclo*hexanol 9 : 10-dihydroxyanthracene also is reduced to the hydrocarbon. 1-Chloro- and 1 : 5-dichloro-anthraquinone could not be reduced beyond the dihydrodihydroxyanthracene stage.

In nitroanthraquinones the nitro-group appears to be reduced before the keto-group, which is unusual in this type of reaction, and 1-amino-2-methylanthraquinone preferentially undergoes condensation with *iso*propanol (or the acetone formed by oxidation) to form 2 : 4-dimethyl-3-azabenzanthrone.

The polynuclear quinones anthanthrone and flavanthrone are reduced to anthanthrene and flavanthrene respectively. Thus this method of converting quinones into the corresponding hydrocarbons is a reasonable alternative to that of Clar (*Ber.*, 1934, **67**, 1229) using zinc and zinc chloride but, in the cases investigated, shows no marked advantage.

EXPERIMENTAL

Preparation of Various Aluminium Alkoxides.—The alcohol was dried by distillation over calcium oxide or calcium carbide. In most experiments the following procedure was adopted: the alcohol (100 c.c.) and aluminium turnings (5 g.) were boiled under a reflux condenser fitted with a calcium chloride tube. A trace of mercuric chloride and dry carbon tetrachloride (1 c.c.) were added to catalyse the reaction and the mixture refluxed overnight (all the aluminium had then reacted), leaving a slight grey precipitate in a clear solution which was used without further treatment.

Reductions of Anthraquinone.—(*a*) *With aluminium* iso*propoxide.* Aluminium *iso*propoxide solution (100 c.c.), anthraquinone (10 g.), and *iso*propanol (50 c.c.) were refluxed together for 48 hr. The excess of *iso*propanol was distilled off and the residue poured into 3% aqueous sodium hydroxide (500 c.c.). The deep red aqueous alkaline solution of 9 : 10-dihydroxyanthracene was filtered. The residue, consisting of hydrated alumina and organic material, was stirred with a little alkaline dithionite solution to remove any anthraquinone remaining unchanged or re-formed by atmospheric oxidation of 9 : 10-dihydroxyanthracene, and was extracted with benzene.

The aqueous filtrate oxidised rapidly and gave a precipitate of anthraquinone which was taken as a measure of the yield of 9 : 10-dihydroxyanthracene. The benzene extract on evaporation gave colourless needles (4·4 g.), m. p. ~160°. The yield of 9 : 10-dihydroxyanthracene was approximately equal to that of the colourless reduction product. The experiment was repeated using 200 and 400 c.c. of aluminium *iso*propoxide solution, but in each case similar yields were obtained. When less than 100 c.c. of alkoxide solution was used a lower yield of the colourless reduction product and a higher yield of 9 : 10-dihydroxyanthracene were obtained.

The colourless reduction product was 9 : 10-dihydro-9 : 10-dihydroxyanthracene (Found: C, 79·4; H, 6·0. Calc. for $C_{14}H_{12}O_2$: C, 79·3; H, 5·7%); the diacetyl derivative (prepared by treatment with acetic anhydride in pyridine on a water-bath for 6 hr.) had m. p. 175° (from alcohol) (Found: C, 72·7; H, 5·7. Calc. for $C_{18}H_{16}O_4$: C, 73·0; H, 5·4%).

A mixture of the reduction product (0·5 g.), pyridine (5 c.c.), and benzoyl chloride (5 c.c.) was kept at room temperature for 24 hr., then poured into water and extracted with benzene. A brown oil, which solidified on long standing, was obtained, which was dissolved in alcohol and treated with charcoal. The dibenzoyl derivative was obtained as colourless needles, m. p. 145° (Found: C, 80·1; H, 4·7%. Calc. for $C_{28}H_{20}O_4$: C, 80·0; H, 4·8%).

The individual *cis*- and *trans*-9 : 10-dihydro-9 : 10-dihydroxyanthraquinones (it may also exist in polymorphic forms) and its derivatives have not yet been characterised satisfactorily. Boyland (*loc. cit.*) isolated two forms (needles, m. p. 140°, and plates, m. p. 137°) and one dibenzoate (m. p. 127—128°); Prevost (*Compt. rend.*, 1935, **200**, 408) describes the parent compound, prepared from anthracene, as flexible needles, m. p. 150—180° (very indefinite) (benzoate, m. p. 127—128°), and Dufraisse and Houpillart (*Compt. rend.*, 1937, **205**, 740) have described a compound prepared by reducing anthracene photo-oxide having a very indefinite maximum m. p. ~195°.

(*b*) *With aluminium* n*-butoxide.* 9 : 10-Dihydroxyanthracene only was present after anthraquinone (10 g.) had been boiled in aluminium *n*-butoxide solution [aluminium (5 g.) in butanol (150 c.c.)] for 48 hr.

(*c*) *With aluminium* sec.*-butoxide.* When the above experiment was repeated using aluminium *sec.*-butoxide in butan-2-ol, anthracene (4·2 g.) separated as flat platelets, m. p. 218° (Found: C, 94·4; H, 6·1. Calc. for $C_{14}H_{10}$: C, 94·4; H, 5·6%), on evaporation of the benzene extract. Anthraquinone (present as 9 : 10-dihydroxyanthracene) (3·6 g.) was recovered from the aqueous alkaline dithionite liquor.

(*d*) *With aluminium* iso*butoxide*. With aluminium *iso*butoxide in *iso*butanol, anthracene (1 g.) was obtained, the remainder being 9 : 10-dihydroxyanthracene.

(*e*) *With aluminium tri*(cyclo*hexyl oxide*). Anthraquinone (10 g.), aluminium tri(*cyclo*hexyl oxide) solution (100 c.c.), and *cyclo*hexanol (50 c.c.) were refluxed for 48 hr., and poured into water. Sufficient benzene was added to give a clear upper layer. The mixture was filtered and the residue extracted with benzene. The combined benzene extracts on steam-distillation afforded 6·8 g. of anthracene. This appeared to be the sole product, but it was not easy to isolate it quantitatively from the *cyclo*hexanol also present.

(*f*) *With aluminium ethoxide*. The sole product was 9 : 10-dihydroxyanthracene.

Reduction of 9 : 10-*Dihydroxyanthracene*.—When anthraquinone was replaced by 9 : 10-dihydroxyanthracene, no further reduction occurred with aluminium *iso*propoxide over a wide range of concentrations, but by using aluminium tri(*cyclo*hexyl oxide) a quantitative yield of anthracene was obtained from both 9 : 10-dihydroxyanthracene and 9 : 10-dihydro-9 : 10-dihydroxyanthracene.

Reduction of 1 : 5-*Dichloroanthraquinone*.—Aluminium *iso*propoxide solution (100 c.c.), 1 : 5-dichloroanthraquinone (14 g.), and *iso*propanol (50 c.c.) were refluxed for 48 hr., the excess of alcohol was removed, and the product poured into dilute alkali to give a pale red solution and the usual precipitate, which was filtered off. The dried residue was extracted with benzene, 1 : 5-dichloroanthraquinone was removed by treatment with warm, alkaline sodium dithionite solution, and the remaining product, when crystallised from benzene, gave mainly *trans*-1 : 5-dichloro-9 : 10-dihydro-9 : 10-dihydroxyanthracene (4·5 g.), m. p. 220—224° (cf. Barnett, Cook, and Matthews, *Rec. Trav. chim.*, 1925, **44**, 728; *Ber.*, 1925, **58**, 975) (Found : C, 59·1; H, 4·0; Cl, 25·1. Calc. for $C_{14}H_{10}O_2Cl_2$: C, 59·7; H, 3·6; Cl, 25·2%). The diacetyl derivative, m. p. 247—248°, crystallised from benzene (Barnett *et al.*, *loc. cit.*, give 249°) (Found : C, 59·4; H, 4·1; Cl, 19·9. Calc. for $C_{18}H_{14}O_4Cl_2$: C, 59·2; H, 3·8; Cl, 19·5%).

When the experiment was repeated using aluminium tri(*cyclo*hexyl oxide) solution the dichlorodihydroxyanthracene (6 g.; m. p. 205·9°) consisted mainly of the *cis*-compound as judged from its m. p.

Reduction of 1-*Chloroanthraquinone*.—This reaction in aluminium *iso*propoxide solution afforded 1-*chloro*-9 : 10-*dihydro*-9 : 10-*dihydroxyanthracene* as colourless needles (5·6 g.), m. p. 178° (Found: C, 69·2; H, 4·6; Cl, 14·8. $C_{14}H_{11}O_2Cl$ requires C, 68·1; H, 4·5; Cl, 14·4%). The *diacetyl* derivative, colourless needles from ethanol, had m. p. 160° (Found: C, 64·8; H, 4·5; Cl, 11·1. $C_{18}H_{15}O_4Cl$ requires C, 65·4; H, 4·5; Cl, 10·8%). A similar result was obtained with aluminium tri(*cyclo*hexyl oxide) in *cyclo*hexanol.

Reduction of 1-*Amino*-2-*methylanthraquinone*.—*Preparation of* 2 : 4-*dimethyl*-3-*azabenzanthrone*. 1-Amino-2-methylanthraquinone (10 g.), aluminium *iso*propoxide solution (100 c.c.), and *iso*propanol (50 c.c.) were refluxed for 48 hr., the excess of alcohol was removed, and the residue poured into water. The dried precipitate when extracted with benzene gave red-brown needles (7·6 g.), m. p. 248°. Traces of unchanged 1-amino-2-methylanthraquinone were removed by treatment with alkaline sodium dithionite solution and the product was recrystallised from ethyl acetate as almost colourless crystals, m. p. 254°, of 2 : 4-*dimethyl*-3-*azabenzanthrone*, m. p. 254° (Found : C, 82·8; H, 5·2; N, 5·6. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0; N, 5·4%). The product could not be acetylated.

The same compound was obtained by refluxing 1-amino-2-methylanthraquinone (5 g.), *iso*propanol (100 c.c.), acetone (10 c.c.), and aqueous sodium hydroxide (3·3 g. of NaOH in 6·7 c.c. of water) overnight.

Reduction of 2-*Methyl*-1-*nitroanthraquinone*.—2-Methyl-1-nitroanthraquinone (10 g.), aluminium *iso*propoxide solution (100 c.c.), and *iso*propanol (50 c.c.) yielded 1-amino-2-methylanthraquinone, the nitro-group being reduced preferentially. When three times as much *iso*propoxide solution was used, 2 : 4-dimethyl-3-azabenzanthrone was formed. Reductions of 1-nitro- and 1-amino-anthraquinones gave very complex mixtures.

Reductions of Higher Polycyclic Quinones.—Aluminium tri(*cyclo*hexyl oxide) solution (100 c.c.) and anthanthrone (6 g.) were refluxed for 48 hr., and worked up as usual. Extraction with benzene gave 1·5 g. of anthanthrene as yellow-green leaflets, m. p. 258° (Found : C, 94·8; H, 4·8. Calc. for $C_{22}H_{12}$: C, 95·5; H, 4·5%), identified by comparison with an authentic specimen. Similar reduction of flavanthrone gave flavanthrene (Found : C, 89; H, 3·7; N, 7·1. Calc. for $C_{28}H_{12}N_2$: C, 88·4; H, 4·2; N, 7·4%), also identified by comparison with an authentic specimen.

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