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A CONVENIENT METHOD FOR INTRODUCING A TERTIARY CARBON CARRYING AN ELECTRONEGATIVE GROUP INTO THE 9-POSITION OF ANTHRACENE

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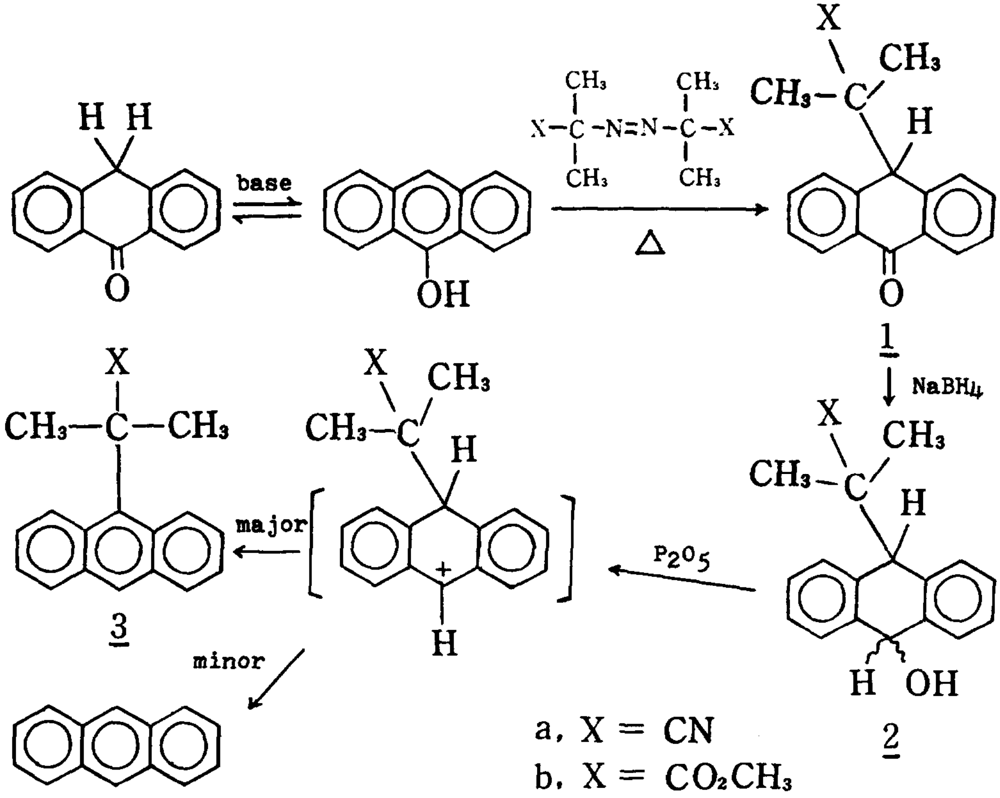
9-tert-Alkylanthracenes are of interest not only because they are congested molecules but also because they lead to triptycene-type compounds in which the stable rotational isomers can be isolated at room temperature.1) These anthracenes are usually prepared by the Grignard reaction of tert-alkylmagnesium halides with anthrone followed by dehydration, whereas the process is not applicable to the compounds carrying a cyano or an alkoxycarbonyl group owing to the reactive nature of the group concerned. Although methyl α-lithioisobutyrate has been reported to exhibit a Grignard-type reactivity,2) the reaction of the lithium salt with anthrone led only to enolization of anthrone. Several attempts to achieve dimethylation of 9-cyanomethylanthracene were unsuccessful, while there was obtained some monomethylated product. The results suggest that any method for the indirect introduction of a tertiary group may not be promising because of the steric effect.

Recently, 9,10-bis-(1-cyano-1-methylethyl)anthracene has been prepared by dehydrobromination of 9-bromo-9,10-bis-(1-cyano-1-methylethyl)-9,10-dihydroanthracene3) which can be obtained from the reaction of 9-bromoanthracene with 1-cyano-1-methylethyl radicals generated from thermal decomposition of azobisisobutyronitrile (AIBN).4) Although the radicals add to anthracene with remarkable ease, the initially formed radical intermediate does not undergo disproportionation to the desired substitution product 3a, but does exclusive combination leading to 9,10-dihydroanthracene derivatives.[5)]

We have found that the action of 1-cyano-1-methylethyl radicals on anthrone, especially under the basic conditions, gave the substitution product 1a in high yield. This finding provides a useful synthetic entry into 3, since it turned out that the sodium borohydride reduction of 1a afforded a mixture of geometrical isomers of the alcohol 2a, which by treatment with phosphorus pentoxide yielded 3a as the major product. In this final step, elimination of a tert-alcohol competes with dehydration because a tert-alkyl cation can be removed instead of a proton from a common cationic intermediate. Nevertheless, due to the electron-withdrawing character of a cyano group the latter process has a distinct advantage over the loss of a destabilized carbocation.

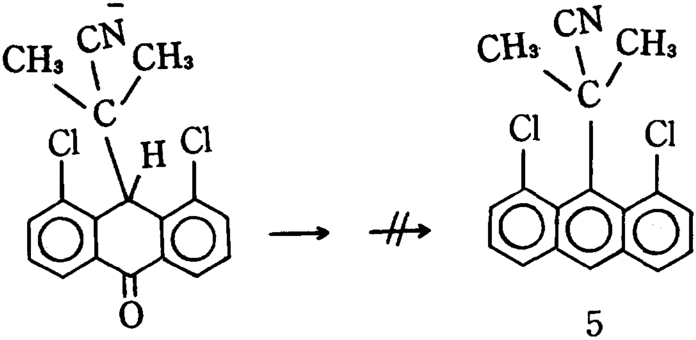


TYPICAL PROCEDURE A solution of 3.07 g (15.8 mmol) of anthrone and 6.0 g

(37 mmol) of AIBN in 30 ml of a 2:1 mixture of pyridine-piperidine was heated at 90°C with stirring under nitrogen for 6 hr. After cooling, the reaction mixture was poured into a large volume of ice-cooled dilute hydrochloric acid. The resulting precipitate was collected and subjected to steam distillation to remove tetramethylsuccinonitrile. The residue was extracted with dichloromethane and the organic layer was dried (Na_2SO_4). Evaporation of the solvent left a pale yellow solid, which was warmed in vacuo until no sublimate appeared and then chromatographed on alumina. Elution with benzene-dichloromethane gave 3.63 g (88% yield) of 1a:[6)] mp 152°C (colorless crystals from benzene-hexane); IR (KBr) 2235 and 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (6H,s), 4.27 (1H,s), 7.3-7.7 (6H,m), and 8.1-8.4 (2H,m). A solution of 0.9 g (24 mmol) of sodium borohydride in 10 ml of 90% ethanol was added dropwise during 10 min to a solution of 0.807 g (3.1 mmol) of 1a in 15 ml of ethanol at reflux. Reflux was maintained for 2 hr and then the mixture was diluted with water and dichloromethane. The organic layer was separated and dried. Removal of the solvent gave 0.77 g (94% yield) of an almost equimolar mixture of geometrical isomers of 2a. To the mixture was added 20 ml of carbon tetrachloride and 5 g of phosphorus pentoxide and heated under reflux for 1 hr. The reaction mixture was filtered, concentrated, and chromatographed on alumina (hexane-benzene). The first fraction contained 0.022 g (4% yield) of anthracene, and the second afforded 0.46 g (64% yield) of 3a: mp 138°C (pale yellow crystals from ethanol); IR 2230 cm^{-1}; NMR 2.37 (6H,s), 7.3-7.6 (4H,m), 7.8-8.1 (2H,m), 8.40 (1H,s), and 8.4-8.7 (2H,m). When treated with dimethyl acetylenedicarboxylate in refluxing toluene, 3a gave the Diels-Alder adduct as a mixture of stable rotational isomers (dl:meso = 44:56). These isomers were separated by TLC (silica gel) and were purified by recrystallization from methanol: the meso form; mp 170°; NMR 2.18 (6H,s), 3.71 (3H,s), 3.77 (3H,s), 5.58 (1H,s), 6.9-7.2 (4H,m), 7.2-7.6 (2H,m), and 7.7-8.0 (2H,m): the dl form; mp 204°C; NMR 2.27 (3H,s), 2.33 (3H,s), 3.76 (3H,s), 3.79 (3H,s), 5.59 (1H,s), 6.9-7.2 (4H,m), 7.2-7.6 (2H,m), and 7.8-8.1 (2H,m).

This procedure may be qualified to be a general method for introducing a sterically hindered functional group into the 9-position of anthracene as well as the 10-position of anthrone, since there are a number of thermally sensitive azo compounds available. Thus, the above procedure using dimethyl azobisisobutyrate gave **1b** (62% yield, mp 90°C), which led to **3b** (41% yield based on **1b**, mp 125°C) and anthracene (13% yield). Similarly, reaction with azobiscyclohexanenitrile afforded 10-(1-cyanocyclohexyl)anthrone (81% yield, mp 205°C), from which 9-(1-cyanocyclohexyl)anthracene (67% yield, mp 152°C) was obtained together with a small amount of anthracene (5% yield).

Under the conditions using a large excess of AIBN in piperidine, 4,5-dichloroanthrone gave **4** (mp 182°C) in good yields (70-80%). The alcohol derived from **4**, however, has not so far operated as a precursor to the highly strained anthracene **5**.



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6) Satisfactory elemental analyses were obtained for all new anthrones and anthracenes quoted.