The 9-Anthroxy-group as a Protecting Group for Hydroxy-functions: Mild, Low-temperature Removal by Singlet-oxygen Oxidation

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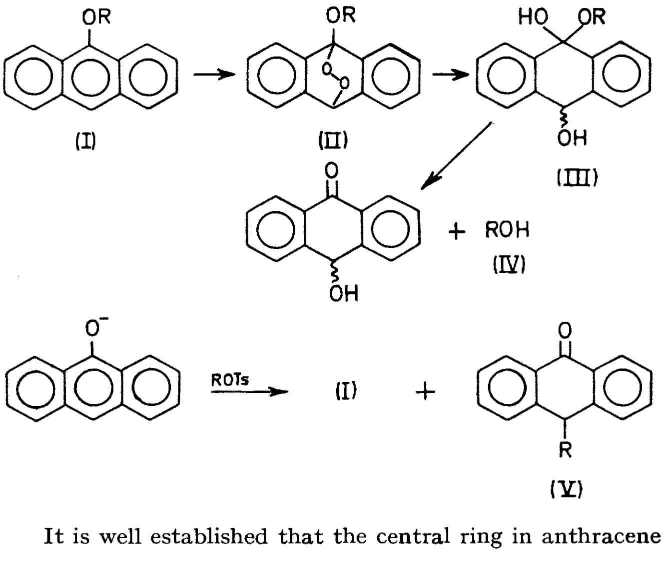
Summary A new kind of protecting group, the 9-anthroxy-group, is readily cleaved by a novel reaction sequence utilizing singlet oxygen.

An important operation in organic synthesis is the protection of a sensitive functional group while other groups are being transformed. The sensitive group is changed chemically into an unreactive unit by attaching a protecting group.[1] A variety of such protecting groups is available for the OH function. For reactions under non-acidic conditions, the OH group may be conveniently protected as an acid-sensitive tetrahydropyranyl,[2] benzyl,[3] diphenylmethyl,[4] trityl,[5] or tritylone ether[6] or ester. In principle, aromatic ethers might have certain advantages over these acid-sensitive ether groups, but in practice, aromatic ethers have seldom been used. It seems that the extra stability of aromatic ethers as compared with normal ethers is not only an advantage resulting in a more stable protecting group, but it is also a disadvantage in that the aromatic carbon–oxygen bond is difficult to cleave.[7]



It is well established that the central ring in anthracene undergoes a series of reactions of the kind not usually associated with aromatic behaviour.[8] Thus it was felt that the 9-anthroxy-group might be a good protecting group even when it was part of an ether function. We now report an efficient and highly selective method for cleaving the aromatic carbon–oxygen bond in 9-anthroxy-ethers. The method is very mild and should allow the 9-anthroxy-group to be a useful protecting group in a wide variety of problems. The scheme involves low-temperature (approximately $-30°$) singlet oxygen oxidation[9] to the anthracenyl peroxide,[10] (II) followed by mild catalytic reduction[11] of the O–O bond. The initial reduction product is presumably a hemiacetal (III) which spontaneously decomposes to 10-hydroxyanthrone and the alcohol (IV) which was protected. The efficiency of this sequence was demonstrated by an n.m.r. analysis† of the crude oxidation–reduction product from 9-(1-hexadecyloxy)anthracene. There was essentially no $\cdot O \cdot CH_2 \cdot$ absorption at δ 4·0—4·1 due to starting ether, and in the region δ 3—4·5, only the triplet for hexadecanol was observed at δ 3·6. The conversion was almost quantitative.

As might be expected, the 9-anthroxy-group may be conveniently attached to an alcohol by a two-step sequence involving conversion of the alcohol into its tosylate, followed by a displacement with the phenolate ion derived from anthrone.[12] For ordinary tosylates this is satisfactory, but we have not tested more reactive tosylates such as benzyl tosylate. The method may not be applicable to these, because it has been known for some time that very reactive alkylating agents[13] undergo a competitive carbon alkylation to give products of the type (V).

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† N.m.r. spectra were recorded on a Varian HA-100 instrument; chemical shifts are standardized to $Me_4Si = \delta$ 0·00.

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