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A NEW PHOTOCHEMICALLY BASED SYNTHESIS OF PHENANTHRENE-9,10-QUINONES

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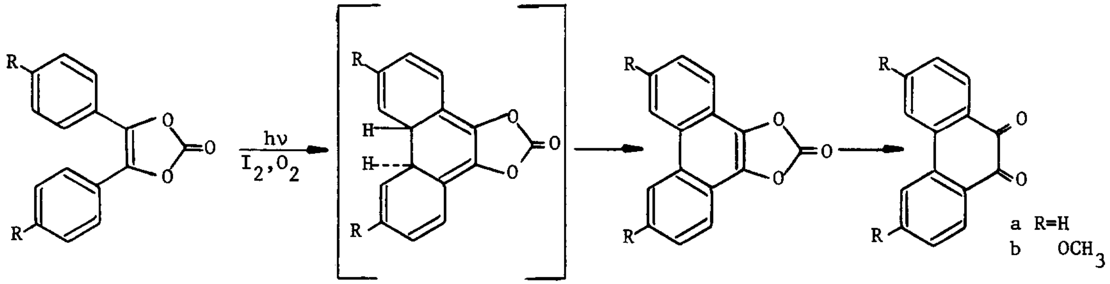
Phenanthrene-9,10-quinones are an important class of intermediates whose utility in the syntheses of fused phenanthro-heterocycles[1] and in the more recent synthesis of the schizandrin type lignans has been amply demonstrated. In spite of these applications methods for their efficient synthesis are still lacking. The best currently available approach entails the photochemical generation of suitably substituted phenanthrenes and an oxidative transformation, employing either a CrO_3 process, often of unpredictable nature, or a two step but higher yield sequence[2] which lacks practical application for large scale synthesis. We would like to present in this report a simple three step synthesis of a substituted phenanthrene-9,10-quinone from a readily available benzoin precursor, which involves a high yield air oxidation for the final conversion.



1a,b 2a,b 3a,b 4b

Our sequence is based on the photochemical closure of 1,2-diarylvinylidene-carbonates, e.g. 1a or 1b, available from benzoins by treatment with phosgene[3].

Irradiation and conversion of 1a to 3a has been demonstrated by Nozaki et. al.[4]; similar transformation of 1b, however, has been reported unsuccessful[5]. We have reinvestigated the photochemical behavior of the latter compound and found that while room temperature irradiations (benzene, chloroform, benzene/cyclohexane solvents) produces multicomponent mixtures, the desired closure could be carried out effectively in refluxing cyclohexane. Operationally, 4-5 g. quantities of 1b and .4-.5 g. of iodine were irradiated in 4 l. solvent in a 5 liter three-neck flask fitted with a condenser and a quartz well accomodating a 275 watt mercury arc. Stirring was maintained by a slow stream of air, and the radiant energy supplied the heat for the reflux. Reaction times of 6-7 hr. were sufficient to obtain 60-70% conversions, affording crystalline 3b (from $CHCl_3$, mp. 222-224°[6]) in a 50% yield. Based on the results of the analogous room temperature reaction, we feel that the elevated temperature not only increases the solubility of 1b in the solvent but also accelerates the rate of dehydrogenation of the primary anti-dihydro photointermediate 2b[7] to the isolated product 3b.

The final transformation of 3b to 3,6-dimethoxyphenanthrene-9,10-quinone (4b)[6] was readily accomplished in 85% yield by bubbling air through its refluxing aqueous 80% acetic acid solution. The structure of 4b was fully supported by the spectroscopic properties and by having an identical mp. (229-232°) with the previously reported compound prepared by an independent sequence[8].

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