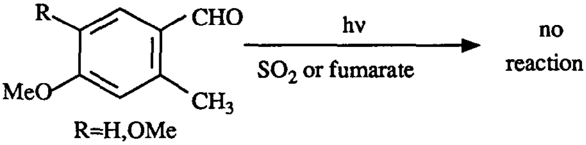
Tetrahedron Letters,Vol.29,No.44,pp 5595-5598,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SUBSTITUENT EFFECTS ON THE PHOTOCHEMISTRY OF o-TOLUALDEHYDES

James L. Charlton* and Kevin Koh
Department of Chemistry, University of Manitoba
Winnipeg, Canada R3T 2N2

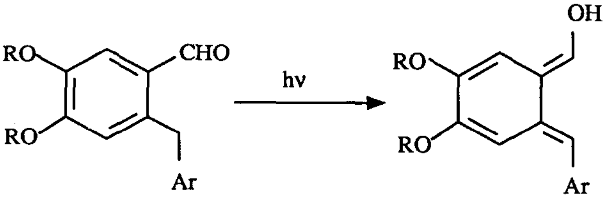
Summary: The effect of 4-oxy and 4,5-dioxy substituents on the photochemical conversion of 2-methylbenzaldehydes to o-quinodimethanes (o-QDMs) has been studied. The presence of a 4-methoxy, or a 4 and 5-methoxy substituent prevented the photochemical formation of the o-QDM whereas 4-acetoxy and 4,5-diacetoxy-2-methylbenzaldehyde and the corresponding mesylates and tosylates were successfully converted to the o-QDMs.

Orthoquinodimethanes have been extensively used as intermediates in organic synthesis and there have been many studies on their preparation and reactions[1]. While photolysis of a 2-methylbenzaldehyde is one of the simplest methods for producing an o-QDM for subsequent Diels-Alder reactions with dienophiles, we have found that a methoxy group at the 4 positon or at both the 4 and 5 position blocks the formation of both SO_2 and dimethyl fumarate adducts.



The failure of these reactions may be due to the unsuccessful formation of the o-QDMs or to the low reactivity of the o-QDMs with dienophiles. Although there is no direct evidence it is possible that the alkoxy substituent(s) affects the reactivity of the excited state of the aldehydes by lowering the ππ* state below that of the more reactive nπ* state thereby blocking the intramolecular hydrogen abstraction and o-QDM formation.

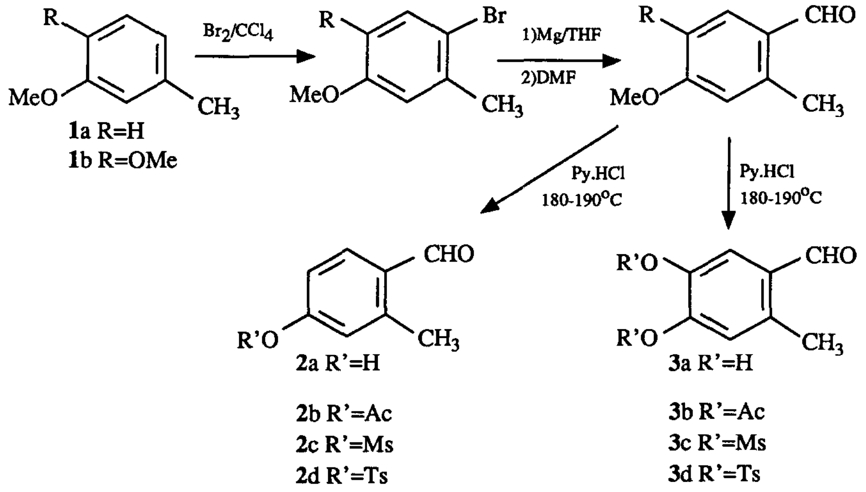
An examination of the literature shows that an alkoxy substituent at the 4 position does not always block photoconversion to the o-QDM. For instance, ortho-(arylmethyl)benzaldehydes with 4-oxy substituents readily form o-QDM on photolysis[2].



In cases such as these the increased stability of the o-QDM due to conjugation with the additional aryl ring apparently favours its formation from the excited state of the aldehyde. In another case, Qinkert describes the conversion of a 4-methoxy-2-methylbenzophenone to its corresponding photoenol although under rather unusual experimental conditions[3].

We wished to prepare tetralins from the 4-oxy and 4,5-dioxy substitued 2-methylbenzaldehydes via Diels-Alder reactions of the corresponding o-QDMs. Since the alkoxy derivatives could not be converted to the o-QDMs we attempted the reaction on the corresponding acetoxy, mesyloxy and tosyloxy compounds. Acyloxy and sulfonyloxy substituents were chosen as they should reduce the electron donor characteristic of the oxy substituent and less affect the excited state of the aldehyde. In addition, these substituents should be relatively amenable to functional group interconversion in later reactions.

4-Hydroxy and 4,5-dihydroxy-2-methylbenzaldehyde **2a** and **3a**, were synthesized as shown below in ca 40% overall yield following published procedures[4-6].

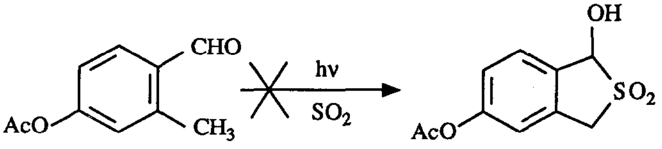


1a R=H
1b R=OMe

2a R'=H
2b R'=Ac
2c R'=Ms
2d R'=Ts

3a R'=H
3b R'=Ac
3c R'=Ms
3d R'=Ts

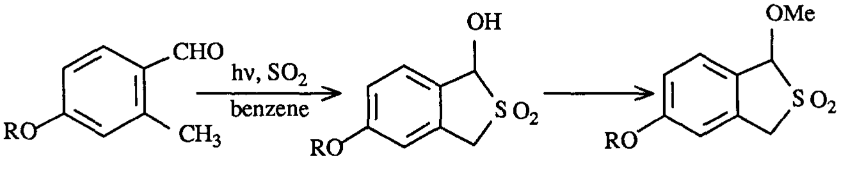
The irradiation of the acetate 2b (from 2a, Ac_2O/NaOAc, r. temp, under N_2, 96%) in benzene/SO_2(10% SO_2 by weight, medium pressure mercury lamp through 1 mm pyrex) gave a slow decomposition of the starting material but we were unable to isolate the sulfone adduct 4b.



2b

4b

Previous work has shown that o-QDMs are very readily trapped by SO_2 to form hydroxysulfones such as 4[7]. The mesylate **2c** (CH_3SO_2Cl, $N(Et)_3$, CH_2Cl_2, r. temp, 90%) , in contrast to the acetate, was cleanly converted to the hydroxysulfone **4c**, in good yield (70%). Unfortunately the product was very insoluble in most organic solvents. It was converted to the more soluble methoxy derivative **5** (methanol/methylene chloride/toluenesulfonic acid at reflux[7]) which gave satisfactory spectral and analytical data. The tosylate **2d** (toluenesulfonyl chloride, $N(Et)_3$, CH_2Cl_2, r. temp, 80%), also readily formed the hydroxy sulfone **4d** (67%) which could be characterized despite the fact that it was thermally unstable, decomposing back to the aldehyde over a few days at room temperature.

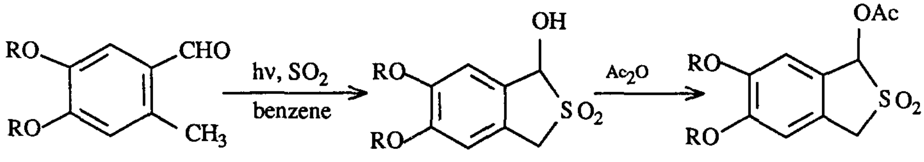


2c R = $-SO_2Me$
2d R = $-SO_2Tol$

4c R = $-SO_2Me$
4d R = $-SO_2Tol$

5 R = SO_2Me

In a similar manner the dimesylate **3c**, and ditosylate **3d** (prepared as described above for the mono mesylate and tosylate) gave the corresponding hydroxysulfones **6c** and **6d** on irradiation in benzene in the presence of SO_2. The dimesylate hydroxysulfone **6c** was formed in 70% yield and was also quite insoluble in organic solvents. It was converted to the acetoxy compound **12** (Ac_2O, NaOAc, r. temp, 30%) for purification and determination of spectral properties. The ditosylate sulfone **6d** was thermally unstable and decomposed to the aldehyde and other products at room temperature. It could be characterized by nmr only.

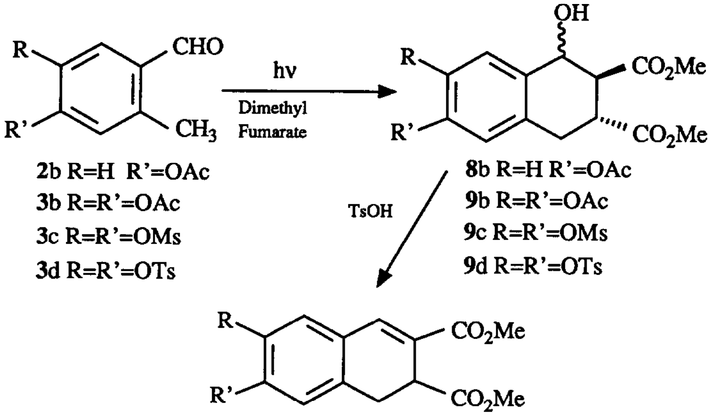


3c R=SO_2Me
3d R=SO_2Tol

6c R=SO_2Me
6d R=SO_2Tol

12 R=SO_2Me

In view of the thermal instability of the sulfones **4d** and **6d** it was possible that the acetoxy aldehyde **2b** did photochemically form an o-QDM but that the sulfone product **4b** was too unstable to isolate. Thus the aldehydes **2b**, **3b**, **3c** and **3d** were irradiated in the presence of dimethyl fumarate, which is known to irreversibly trap o-QDMs[7] to give the results shown below. The cycloadducts **8b** (85%), **9b** (90%), **9c** (54%) and **9d** (65%) were formed as mixtures of diastereomers which were not individually characterized. **8b** and **9b** were dehydrated with deacetylation (toluene sulfonic acid, methanol, r. temp) to give **10b** (99%) and **11b** (98%). **9c** and **9d** were dehydrated (toluene sulfonic acid, toluene, reflux) to the elimination products **11c** (74%) and **11d** (90%). All of the elimination products were fully characterized.



2b R=H R'=OAc
3b R=R'=OAc
3c R=R'=OMs
3d R=R'=OTs

8b R=H R'=OAc
9b R=R'=OAc
9c R=R'=OMs
9d R=R'=OTs

10b R=H R'=OH
11b R=R'=OH
11c R=R'=OMs
11d R=R'=OTs

The formation of sulfur dioxide and fumarate adducts from 4- and 4,5-di acetoxy, mesyloxy and tosyloxy-2-methylbenzaldehydes shows that such oxy substituted aldehydes can be photochemically converted to the o-QDMs. We are currently studying the use of these o-QDMs in cycloaddition reactions with chiral acrylates as an asymmetric route to 2-substituted tetralins.

ACKNOWLEDGMENTS

We would like to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

REFERENCES

1. J. L. Charlton and M. M. Alauddin, *Tetrahedron*, **43**, 2873 (1987) and references cited.
2. J. L. Charlton and M. M. Alauddin, *J. Org. Chem.*, **51**, 3490 (1986); M. B. Glinski and T. Durst, *Can. J. Chem.*, **61**, 573 (1983); B. J. Arnold, S. M. Mellows and P. G. Sammes, *J. Chem. Soc. Perkin I*, 1266 (1973).
3. G. Quinkert and H. Stark, *Angew. Chem. Int. Ed. Engl.*, **22**, 637 (1983).
4. J. R. Falck, L. L. Miller and F. R. Stermitz, *J. Am. Chem. Soc.*, **96**, 2981 (1974).
5. G. Quinkert, W-D. Weber, U. Schwartz, H. Stark, H. Baier and G. Durner, *Liebigs Ann. Chem.*, 2335 (1981).
6. T. Greene in "Protective Groups in Organic Synthesis", John Wiley and Sons, New York, 1981, pg 91.
7. T. Durst, E. C. Kozma and J. L. Charlton, *J. Org. Chem.*, **50**, 4829 (1985).

(Received in USA 6 July 1988)