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o-Nitroaryldioxolanes for protection of pheromones. Study of the photodelivery of carbonyl compounds

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o-Nitrophenyldioxolanes **1** to **12** have been prepared and the rate of their photocleavage determined. Steric congestion in the molecule causes a decrease of the reaction rate. The decrease in the rate is especially important in the presence of a nitro group in a second phenyl ring.

Keywords: *o*-nitrophenyldioxolanes, pheromones, photodelivery

The reaction of aldehydes and ketones with 1 2-diols to afford 1,3-dioxolanes constitutes a well known protection method for carbonyl groups. Deprotection is commonly achieved hydrolytically, but photocleavage occurs when the starting diols are *o*-nitrophenyl substituted; aldehydes and ketones may then be recovered efficiently by UV irradiation of the dioxolanes (Scheme 1).[1]

This protection-photorecovery may provide a system for the controlled release of volatile aldehydes, and could be useful in the design of dispensers for the slow release of semiochemical aldehydes as, for instance, the mixture of aldehydes which constitute the pheromone of the rice borer *Chilo suppressalis*, a world-wide pest of rice crops. In order to meet the requirements of this technological application, a steady slow delivery of the carbonyl compound must be attained for about four months in the field; a slow cleavage is then sought instead of the fast reaction usually desirable for preparative procedures. In this context, some *o*-nitrophenyldioxolanes derived from decanal have been attached by some of us to polystyrene resins and the resulting resins have been found to release the aldehyde to the air when irradiated with an ultraviolet lamp. However, this was too fast for the aforementioned purpose.[2] We wanted to know now whether structural modification of the *o*-nitrophenyldioxolanes would lead to a slower release of the aldehydes. Some substituted dioxolanes have been thus prepared and the rates of their cleavage by UV irradiation found to vary by a factor up to 20. A short account of part of these findings has been reported.[3]

The main aspects of the mechanism of this photocleavage was established by Gravel (Scheme 2), [1] and parallel Corrie's recent findings on the photolysis of 1-acyl-7-nitroindoles in aqueous medium.[4] Gravel's mechanism suggests that steric congestion and changes of the chromophoric system may modify the rate of photocleavage.

The progress of the reaction has been studied through the changes of the chromophoric systems which occur on irradiation of nitrophenyl 2,3-dimethyldioxolanes in solution. Some *p*-dimethylaminophenyl dioxolanes have been studied as well, since they reveal the release of a carbonyl compound whose absorption (λ_{max} 320 nm) does not overlap with the bands of either the starting nitrodioxolanes or the final nitroso compounds.

Dioxolanes **1** to **6** (Fig. 1) should provide some information on the influence of electronic effects on the rates of the photocleavage, whereas compounds **7** to **12** would give information on the influence of steric effects and of other structural features. Dioxolanes **1** to **3** were prepared by acid catalysed acetalisation of the aryl diols **13** to **15,** which are either commercial products or were prepared previously by some of us (Scheme 3).[2] Dioxolanes **4**, **6**, **7** and **8** were obtained from *o*-nitrobenzaldehyde **16** by Wittig olefination followed by dihydroxylation of the olefins **17** and ketalisation of the diols **18** (Scheme 4). The dioxolane **7** was obtained as a 6/4 *cis/trans* diasteroisomeric mixture which was resolved chromatographically, whereas only the *trans* diasteroisomers of the diaryl dioxolanes **4b** and **6** were isolated.

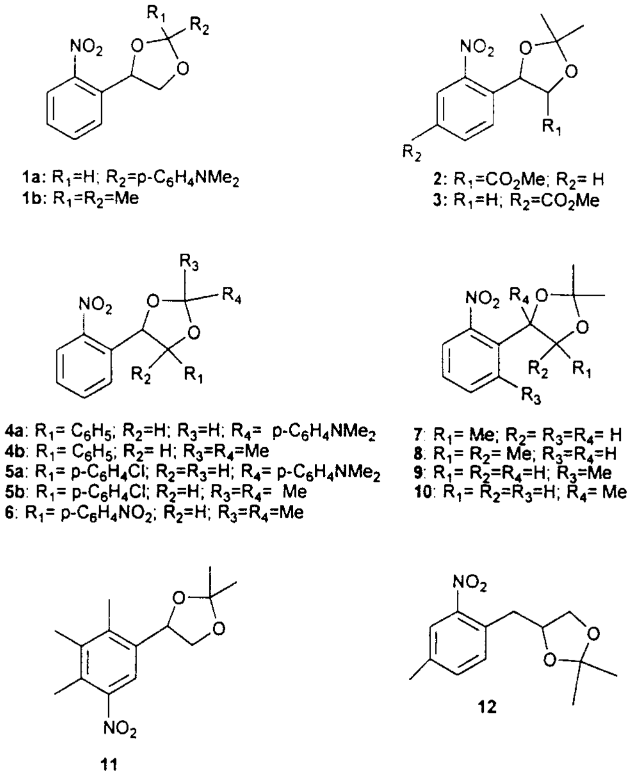

Figure 1

The chloro-nitro-diphenyl dioxolanes **5a** and **5b** were prepared by a different approach, based on the directed benzoin condensation[5] (Scheme 5). Thus, the trimethylsilylated cyanohydrin of *p*-chlorobenzaldehyde **19** and *o*-nitrobenzaldehyde **16** gave the *p*-chloro *o*-nitrobenzoin **20**. Reduction of this gave a diastereoisomeric mixture of diols **18e**, which was resolved chromatographically. Reaction of the *cis* diol with *p*-dimethylaminobenzaldehyde gave the corresponding acetal **5a** as a diastereoisomeric mixture, whereas ketalisation of each single *cis*-and *trans*-diol **18e** led to the corresponding *cis*- and *trans*- 2,2-dimethyldioxolanes **5b**.This directed benzoin condensation failed for benzaldehydes with more than one electron-withdrawing group in the ring. The dihydroxylation of stilbenes substituted by more than two electron-withdrawing groups also failed.

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Congested systems became difficult to obtain, and only the methyl substituted dioxolane **9** could be successfully prepared (Scheme 6). The alcohol **21** was easily converted either to the aldehyde **22** or to the bromide **23,** but only the second led conveniently to the styrene **24,** which was easily converted to the diol **25** and to the dioxolane **9**. The 4-methyl-4-aryldioxolane **10** was prepared from *o*-nitroacetophenone **26**, through styrene **27** and diol **28** by the olefination dihydroxylation sequence (Scheme 7).

We had previously prepared aryl glycols by Friedel Craft's acylation with chloroacetyl chloride, followed by reduction of the resulting chloroacetophenone and aqueous alkaline substitution of the chlorine atom by a hydroxyl group.[6] We attempted to use this procedure for the synthesis of more congested *o*-nitrophenyldioxolanes starting from 1,2,3-trimethylbenzene (Scheme 8). However, the nitration of the chloroacetophenones **29** or **30**, of their corresponding intermediate chlorohydrins, the diols or of the dioxolanes by several conventional general methods, or by the Kyodai[7] procedure failed to afford the desired *o*-nitroaryl compounds. Significant amounts of products derived from *ipso*-substitution were encountered. Reduction of **29** and alkaline substitution gave the diol **32** and ketalisation of this led to the dioxolane **33**, but nitration of the latter gave nitroaryldioxolane **11**, but isomer **34**, was not found in the reaction mixture.

In the search for slow release derivatives, the *o*-nitrobenzyldioxolane **12** was prepared by nitration of the diacetate of the *p*-tolylmethyldihydroxypropane **37** (Scheme 9).

Irradiations were carried out with a 160 W medium pressure UV lamp located 30 cm from the sample, for 10^{-5} to 10^{-6} solutions of the dioxolane in methylcyclohexane at 25°C in a 1 cm quartz cell immersed in a Pyrex glass well cooled with water at 20°C. The progress of the reaction has been followed by periodically recording the UV spectra of the reacting solution contained in the cell after convenient irradiation intervals (usually 0.5 h or 1 h). The reaction was studied for short reaction times (within 4 h) and usually by the decrease of the absorption of the band around λ_{max} 250–265 nm. For longer irradiation periods further conversions seemed to occur, which were not studied. Apparently clean photolyses were shown by isosbestic points for all dioxolanes, a feature generally indicative of simple conversions. The photoconversions were first order, and the good linear ratios between absorbance and concentration gave the rate constants as the absolute value of the slope obtained on plotting the natural logarithms of the absorbances against times. Reaction rates are given in the Tables 1 and 2.

As expected from to the accepted mechanism the results gathered in Tables 1 and 2, show that the nitro group must be *ortho* to the dioxolane (compound **11),** the dioxolane must be directly bound to the *o*-nitroaryl ring (compound **12)** and a hydrogen atom is required at C-4 of the dioxolane (compound **10**).

Small effects are associated with the presence of carboxylic groups either at C-5 of the dioxolane or in the aromatic ring, whereas substitution by a phenyl group at C-5 is significant only when the phenyl is substituted by chlorine and, especially by a nitro group. The origin of these latter effects is presently uncertain, although halogen atoms are usually found to reduce quantum yields[4,8] and the *p*-nitrophenyl substituent might be thought to compete with the *o*-nitroaryl unity in the absorption of the irradiation.

The small difference between the rate constants of 2,2-dimethyl and 2-*p*-N,N-dimethylaminophenyl-dioxolanes shows that ketones and aldehydes become free at very similar rates.

In connection with steric effects, only the methyl-substituted *o*-nitrophenyldioxolane **9** has been obtained and this delivers the ketone at a significant slower rate when compared to the simpler nitrodioxolane **1a**. This effect might be associated with the mechanism of the photocleavage; in particular, with the flat structure of the likely intermediate which follows the hydrogen atom transfer.

Table 1 UV absorption maxima, photocleavage first order rates of nitrophenyldioxolanes; electronic effects.

Dioxolane	λ_{max}/nm (ε)	kx10^5 s^{-1}
1a	262 (8912)	13.0
1b	257 (5100)	11.3
2	254 (6000)	5
3	261 (6120)	6
4a	263 (7285)	10.1
4b	242 (5100)	8.4
5a	263 (9710)	4.5
***cis*-5b**	260 (7205)	3.1
***trans*-5b**	250 (6383)	2.7
6	261 (12500)	0.5

Table 2 UV absorption maxima, photocleavage first order rates of nitrophenyldioxolanes: striv and constitutional effects

Dioxolane	λ_{max}/nm (ε)	kx10^5 s^{-1}
1b	257 (5100)	11.3
***cis*-7**	256 (7100)	10.7
***trans*-7**	250 (6400)	7.7
8	254 (3950)	9.5
9	250 (2600)	3.8
10	252 (3700)	0
11	263 (3850)	0
12	257 (3100)	0

The present results show the difficulties in achieving a slow release of a carbonyl compound by irradiation of *o*-nitrophenyldioxolanes. However, the slow reaction in the presence of a second nitro group in the molecule suggests that nitro groups in either a polymeric support of the dioxolanes or in a solvent might provide a system for an adequate release of volatile aldehydes.

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Figure: 1

Schemes: 9

Tables: 2

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