

THE META PHOTOCYCLOADDITION OF ANISOLE AND BENZENE TO 2-METHYL-1,3-DIOXOLE

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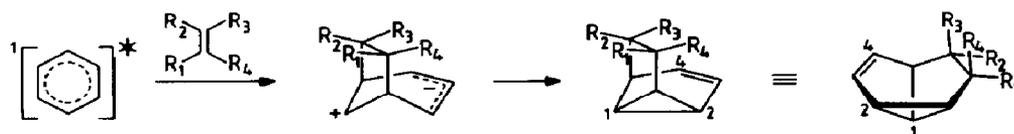
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Summary

In order to investigate some stereochemical aspects of the meta photocycloaddition of arenes to alkenes, anisole and benzene were irradiated at 254 nm in the presence of 2-methyl-1,3-dioxole. The main products formed were those having the least steric hindrance along the proposed pathway.

1. Introduction

Many different mechanisms have been proposed for the meta photocycloaddition of aromatic compounds to alkenes [1 - 3]. One pathway which has recently been advocated and which fits all the experimental evidence involves a dipolar species [3, 4]:



Indications of the existence of such polar species were found in the photoreactions of anisole [5, 6], cyclopropylbenzene [7], α,α,α -trifluorotoluene [8, 9] and benzonitrile [8] with various alkenes: the electron-donating substituents appear on the carbon atom C₁ and the electron-withdrawing substituents appear on carbon atoms C₂ and C₄. In this work we have investigated some stereochemical aspects of this reaction by irradiating benzene and anisole in the presence of 2-methyl-1,3-dioxole.

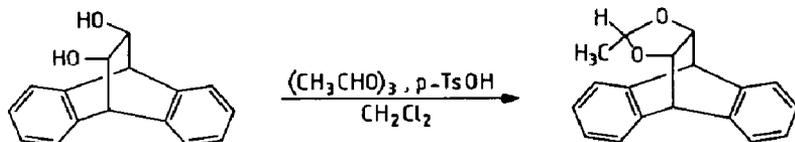
2. Experimental details

2.1. Chemicals and equipment

Benzene, anisole and cyclohexane were purified by distillation. 2-Methyl-1,3-dioxole was synthesized using a general procedure described by Field [10]. For preparative irradiations we used a photoreactor fitted with a quartz immersion well and a low pressure mercury lamp (Hanau TNN 15/32). Small scale irradiations were performed in a merry-go-round (H. Mangels, Bornheim/Reisdorf, Germany; Hanau TNN 15/32). Gas chromatographic analyses of the irradiation mixtures were performed using a Carlo Erba Fractovap 2101 AC (glass column, 5% NPGS and 5% Apiezon L on Chromosorb WAW/DMCS, 80 - 100 mesh) and using an HP5700 capillary gas chromatograph (glass column, OV 101, 30 m, dynamically coated, 403 K). For preparative gas chromatography we used a Varian Aerograph Model 90-P (glass column, 20% SE 30 on Chromosorb WAW, 40 - 60 mesh, 6 m × 8 mm, 408 K, carrier gas: H₂). Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker WM300 at 293 K.

2.2. Preparation of 2-methyl-1,3-dioxole

A mixture of 200 g (0.84 mol) anthracene-vinylenglycol adduct [11], 55 g (1.25 mol) paraldehyde and 2 g *p*-toluenesulphonic acid in 1 l dichloromethane was refluxed using a water separator until no more water was formed. After cooling the solution was washed several times with aqueous potassium carbonate. Drying over potassium carbonate, evaporating to dryness and recrystallizing from *n*-hexane yielded 204 g (92%) anthracene-2-methyl-1,3-dioxole adduct (melting point, 170 - 174 °C; ¹H NMR (CDCl₃, ppm relative to tetramethylsilane (TMS)): δ, 0.68 (d, *J* = 5 Hz, 3H, *endo*-CH₃[†], 4.32 (m, 2H), 4.45 (m, 2H), 4.97 (q, *J* = 5 Hz, 1H, *exo*-H[†]), 7.00 - 7.35 (m, 8H, aromatic H); ¹³C NMR (CDCl₃, ppm relative to TMS): δ, 19.25 (CH₃), 49.15 (CH), 78.81 (CHO), 103.56 (OCHO), 125.23, 125.93, 126.00 and 126.64 (=CH), 139.16 and 140.05 (=C)).



150 g (0.59 mol) anthracene-2-methyl-1,3-dioxole adduct were heated on an open flame in a distillation apparatus under nitrogen as described by Field [10]. All glassware had been treated with a sodium hydroxide solution to prevent acid-catalysed side reactions [12]. The olefin, which was formed by a retro Diels-Alder reaction, was collected in a Schlenk flask cooled by

[†]The *endo* configuration of the recrystallized anthracene-2-methyl-1,3-dioxole adduct was proved using NMR spectroscopy by comparison with the anthracene-2,2-dimethyl-1,3-dioxole and the anthracene-1,3-dioxole adducts.

dry ice. 1 g potassium carbonate and 0.1 g 4-*t*-butylcatechol were added in order to avoid polymerization or acid-catalysed rearrangements [11]. 38 g (75%) 2-methyl-1,3-dioxole were obtained after distillation under nitrogen at 62 °C and 760 Torr (IR (neat): ν (cm⁻¹), 3140 (=CH), 1623 (C=C); ¹H NMR (C₆D₆, ppm relative to TMS): δ , 1.35 (d, J = 5 Hz, 3H, CH₃), 5.75 (q, J = 5 Hz, 1H, OCHO), 6.10 (s, 2H, =CH); ¹³C NMR (C₆D₆, ppm relative to TMS): δ , 19.94 (CH₃), 106.64 (OCHO), 128.11 (=CH)).

2.3. Preparative photoreactions

A solution of 5 g (0.058 mol) 2-methyl-1,3-dioxole and 22 g (0.2 mol) anisole or 18 ml (0.2 mol) benzene in 150 ml cyclohexane was irradiated under nitrogen at 254 nm for 60 h. The solvent was distilled off under reduced pressure at room temperature. In both cases at 70% conversion the yield of 1:1 photoadducts was 50% - 60%. The product ratios are strongly dependent on the irradiation time owing to the formation of photolabile ortho adducts. The presence of ortho adducts was detected from the Diels-Alder reaction of the product mixture with tetracyanoethylene [13]. The meta adducts were isolated by preparative gas chromatography. Product ratios at low conversion (5%, merry-go-round) were determined by irradiating solutions of 0.5 M arene with 1.5 M alkene and analysing them by means of NMR and capillary gas chromatography. The meta photocycloadducts were identified by means of NMR.

3. Results and discussion

2-Methyl-1,3-dioxole can approach the excited arene in four different ways that lead to four different products. If the photoreaction does involve a transition state or an intermediate with a similar stereochemical structure to the one proposed above, the endo and the exo approach with the methyl group directed towards the six-membered ring will be less favourable than the approaches with the methyl group away from the ring, owing to the steric requirements of the methyl group. This effect will of course be more pronounced in the case of the endo approach. One would therefore expect to find a predominance of two products. The products and their ratios are presented in Fig. 1.

The orientation of the methyl group was determined by means of nuclear Overhauser effect (NOE) experiments. NMR data are presented in Tables 1 and 2.

This preference is indeed to be found, both in the case of the exo approach (product 1) and in the case of the endo approach (product 3), indicating the existence of such an intermediate. At first sight it seems surprising that there is also a preferential mode of approach in the case of the exo adducts, especially as the methyl group does not experience any steric hindrance in the exo intermediate. It is likely that the product ratio is determined before the bonds between the six-membered ring and the dioxole have

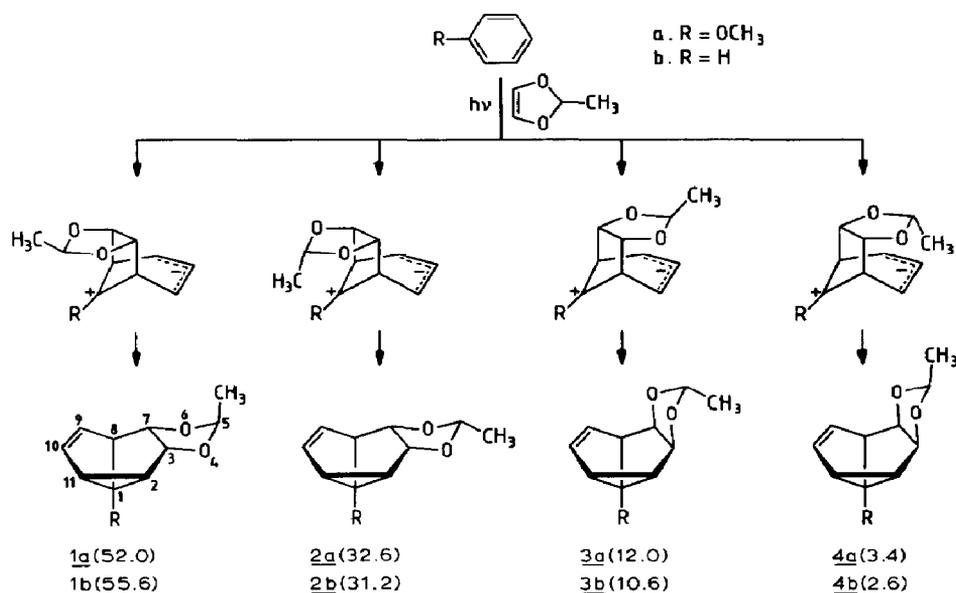


Fig. 1. Meta photocycloaddition of 2-methyl-1,3-dioxole to the excited arene.

TABLE 1

Proton chemical shifts (in ppm relative to TMS) of compounds 1a - 4a and 1b - 4b in CDCl₃ (300 MHz) at 293 K

Protons	1a	2a	3a	4a	1b	2b	3b	4b
1					2.60	2.62	2.68	2.77
2	2.15	2.21	2.22	2.12	1.75	1.85	1.78	1.65
3	4.39	4.16	5.05	4.98	4.57	4.27	5.07	5.03
5	5.58	4.96	5.40	5.12	5.56	4.94	5.48	5.22
7	4.18	4.10	5.15	4.98	4.14	4.13	5.07	4.89
8	3.47	3.54	3.46	3.44	3.34	3.43	3.26	3.21
9	5.51	5.48	5.80	5.71	5.39	5.36	5.72	5.63
10	5.67	5.67	5.84	5.83	5.63	5.66	5.83	5.84
11	2.30	2.31	2.30	2.31	1.96	1.99	2.01	2.07
CH ₃	1.35	1.46	1.20	1.33	1.34	1.42	1.20	1.36
OCH ₃	3.37	3.42	3.35	3.37				

been formed and before the six-membered ring has become puckered. Calculations indicate that some degree of charge transfer between the two parts of the six-membered ring is probable when the two molecules are 2.5 Å apart [14] and at this distance (with a nearly flat benzene ring) the steric hindrance of the methyl group is noticeable, resulting in a preference for product 1.

As in the case of anisole with 1,3-dioxoles [15] and of benzene with 1,3-dioxoles [4] the strong preference for the exo orientation indicates that by the time the orientation is determined, the dipolar character of the six-membered ring is already developed. The electronic repulsion between the

TABLE 2

Coupling constants (in hertz) of compounds 1a - 4a and 1b - 4b in CDCl₃ at 293 K

<i>J</i>	<i>1a</i>	<i>2a</i>	<i>3a</i>	<i>4a</i>	<i>1b</i>	<i>2b</i>	<i>3b</i>	<i>4b</i>
1,2					7.1	7.1	6.4	6.4
2,3	a	a	5.6	6.1	a	a	6.6	6.0
3,7	4.1	4.6	7.5		3.9	4.7		6.3
7,8	a	a	7.5	7.1	a	a	5.7	8.1
8,9	2.7	2.7	3.2	2.7	2.3	2.2	2.5	2.3
9,10	5.7	5.6	5.7	5.7	5.4	5.4	5.4	5.5
10,11	2.4	2.4	2.3	2.4	2.1	2.1	2.2	2.2
1,11					7.3	7.1	6.4	5.0
1,8					5.4	5.4	6.4	6.4
2,11	9.1	9.0	8.6	8.6	7.1	6.9	5.6	5.0
3,8	a	a	1.7	1.4	a	a	b	1.6
9,11	a	a	1.1	a	a	a	a	a
5,CH ₃	4.8	4.8	4.9	4.9	4.8	4.8	4.9	4.9

^aToo small to be detected.

^bCoupling has been shown to be present by using decoupling techniques but cannot be determined owing to the high multiplicity of the signals.

negatively charged p orbitals of the allylic moiety and the orbitals of the oxygen causes the endo approach to be less favourable. In the case of anisole with 2,2-dimethyl-1,3-dioxole [15] and in the case of the formation of products 4a and 4b in the irradiations we investigated there is also the added steric hindrance due to the methyl group, rendering this approach even less favourable. The fact that these products are formed at all can be taken as an indication that an approach of the alkene in which the oxygen atoms are tilted away from the six-membered ring can also lead to a sufficient degree of interaction.

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